# BRITISH CHEMICAL ABSTRACTS

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## A.-PURE CHEMISTRY and a series of a series of the series o

# AUGUST, 1935.

### General, Physical, and Inorganic Chemistry.

Intensity measurements in the fine structure of the Balmer line  $H_{\alpha}$ . L. S. ORNSTEIN, H. LINDE-MAN, and J. A. VREESWIJK, jun. (Physica, 1935, 2, 541-550). M. S. B.

(A) After-effect of a glow discharge in lowering the striking potential in nitrogen, hydrogen, and air. (B) Cause of lowering of striking potential at low pressures. G. MACIUC (Bul. Fac. Stiinte Cernauti, 1933, 7, 59-75, 250-294; Chem. Zentr., 1935, i, 527).-(A) The lowering observed by Badareu in N<sub>2</sub> is due to charging of the glass walls by the first discharge.

(B) Data for the effect of wall charges in lowering the striking potential are recorded. The effect disappears when the walls are rendered conducting and earthed. H. J. E.

New nitrogen afterglow spectrum. J. KAPLAN (Nature, 1935, 135, 1034—1035; cf. A., 1934, 1051).— A new afterglow spectrum obtained by passing a current of low density through  $N_2$  is reproduced. The relative intensity of the Vegard-Kaplan bands, emitted by the  $A^{3\Sigma}$  metastable mol., is markedly enhanced. The new spectrum supports the view that radiations from the night sky agree closely with these bands. L. S. T.

Excitation and emission in the nitrogen band spectrum. G. O. LANGSTROTH (Proc. Roy. Soc., 1935, A, 150, 371-381).—The results of measurements of the intensities of 9 additional second positive N bands for various exciting electron energies between 14 and 160 e.v. are discussed (cf. A., 1934, 1150). No dependence of the relative intensities on the energy of the exciting electrons was found except at low energies, and it is concluded that interaction between the exciting electron and the vibrating nuclei is improbable. The agreement of the observed intensities with those calc. from the excitation and emission probabilities is only approx. The discrepancies are ascribed to neglect of anharmonicity in the theoretical model.

L. L. B.

Oxygen afterglow. (LORD) RAYLEIGH (Proc. Roy. Soc., 1935, A, 150, 34–36).—Stoddart's failure to obtain the afterglow in moist  $O_2$  is ascribed to the use of an unstable type of discharge. The electrodeless ring discharge should be employed.

L. L. B.

Intensity distribution and half-value width of neon lines. I. W. SCHÜTZ. II. W. SCHÜTZ, H. SCHILLBACH, and K. KRÄMER (Physikal. Z., 1935, 36, 403-406, 406-409).—I. The intensity distribution of the Ne lines for different vals. of the ratio of the dispersion width to Doppler width, and the relationship between the total width and both these, are calc. A. J. M.

Absolute output of the Na D line by excitation by electron collision. W. CHRISTOPH (Ann. Physik, 1935, [v], 23, 51-60).—A photo-electric process, using the opposing-field method of Haft (A., 1933, 439) with lowest possible pressure to avoid absorption losses, was employed. The val. obtained is > that of Ornstein. A. J. M.

Emission spectro-photographic determinations of aluminium in the ash of biological material. R. LINDEMANN (Z. Physik, 1935, 95, 6-29).—A low-voltage arc was used to determine the Al content of organs, bones, and gall-stones.

A. B. D. C.

Spectrum of CuIII. L. BLOCH and E. BLOCH (Compt. rend., 1935, 200, 2017—2019).—Data are classified. H. J. E.

Emission bands of selenium. R. K. ASUNDI and Y. P. PARTI (Current Sci., 1935, 3, 548). A. B. D. C.

Multiplets and terms in the first two spectra of niobium. W. F. MEGGERS and B. F. SCRIBNER (J. Res. Nat. Bur. Stand., 1935, 14, 629-647).--Results are reported for the principal multiplets in the Nb I and Nb II spectra. Sextet and quadruplet terms occur in the Nb I and quintet and triplet terms in the Nb II spectra. The normal states of neutral and singly ionised Nb atoms are  $(4d^45s)^6D$  and  $(4d^4)^5D$ , respectively. J. W. S.

Higher terms in the spectrum of Ag II. W. P. GILBERT (Physical Rev., 1935, [ii], 47, 847—850).— Complete measurements and classifications, extending available data, are tabulated for the range 500— 11,000 Å. The ionisation potential is 21.4 volts. N. M. B.

Atomic energy states of tellurium, Te III. S. G. KRISHNAMURTI (Current Sci., 1935, 3, 547). A. B. D. C.

Emission spectrum of Te<sub>2</sub>. E. OLSSON (Z. Physik, 1935, 95, 215-220).—Isotope displacements are used to improve the vibration level formula. A. B. D. C.

Absorption of light in cæsium vapour in the presence of helium. H. J. J. BRADDICK and R. W. DITCHBURN (Proc. Roy. Soc., 1935, A, 150, 478-486). —The absorption of light in Cs vapour is progressively reduced by the addition of He, for He pressures up to 20 cm. About 3 cm. of He reduces it to half-val. at 3150 Å., and about 2 cm. to half-val. at 2250 Å. The mol. absorption of Cs in the region 3430-3530 Å. is completely suppressed by the addition of a small amount of He. L. L. B.

Broadening and displacement of end lines of cæsium series by krypton. C. FÜCHTBAUER and H. J. REIMERS (Z. Physik, 1935, 95, 1-5).—Displacement is towards the red, and from its limit the cross-section of Kr for slow electrons is calculated.

A. B. D. C.

Stark effect for mercury. R. N. H. HASLAM (Proc. Roy. Soc., 1935, A, 150, 338-347).—The Stark effect for Hg has been examined over the range 2200—3000 Å., using a modified form of the Lo Surdo source. The displacements are in agreement with a simplified theory. L. L. B.

Spectral characteristics of electrically exploded mercury. H. P. KNAUSS and A. L. BRYAN (Physical Rev., 1935, [ii], 47, 842-844).—The spectrum of the region 2537—1950 Å., obtained by sending 300 amp. from a 150-volt generator through a small stream of Hg, gave continuous emission strong and clear enough for use in absorption experiments, and showed great broadening of many lines, due to strong electric fields of ions near the emitting atom, and a strong continuous background due to recombinations in which the kinetic energy plays a part. N. M. B.

Hyperfine structure of the mercury hydride bands. S. MROZOWSKI (Bull. Acad. Polonaise, 1935, A, 24—29; cf. A., 1932, 104).—Observations on various HgH bands show each to have a no. of components. The intensity relations are different from those attributable to an isotope effect. A type of hyperfine structure occurs, analogous to that in line spectra. H. J. E. (

Extreme infra-red spectrum of the sun. V. G. VAFIADI, S. S. KRIVICH, and G. V. POKROVSKI (Nature, 1935, 135, 1035).—No radiation in the extreme infra-red has been detected from the sun. L. S. T.

Stark effect of hydrogen in first type stellar spectra. A. PANNEKOEK and S. VERWEY (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 479-489).—Mathematical. N. M. B.

Stark intensities in a canal-ray source at different pressures. R. L. THORNTON (Proc. Roy. Soc., 1935, A, 150, 259-266).—A new canal-ray tube is applied to the measurement of the relative intensities of the Stark components of  $H_{\beta}$  and of the He group 2P-4Q. It is shown that the differences between Stark intensities observed by the canal-ray and Lo Surdo methods are mainly due to the great differences in gas pressures commonly selected.

L. L. B.

Long and short spectral lines. S. DATTA and K. CHATTERJEE (Indian J. Physics, 1935, 9, 357— 368).—The long and short lines obtained in the arc spectrum when an image of the arc in the transverse position is thrown on the slit of a spectroscope have been examined for a Cu arc working at pressures >1 atm. A. J. M. Magnetic and electric spectra in high frequency. V. K. ARKADIEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 204–208). W. R. A.

Quantum theory of metallic reflexion. L. I. SCHIFF and L. H. THOMAS (Physical Rev., 1935, [ii], 47, 860—869).—The classical Drude theory, with Kronig's modifications, gives the electromagnetic field except within a transition layer over a few electron wave-lengths from the surface. In this layer the electric intensity perpendicular to the surface shows considerable fluctuations depending on the nature of the surface potential barrier. This fluctuating field can be used to correct the calc. surface photo-electric effect. N. M. B.

Electromagnetic fields due to variable electric charges and the intensities of spectrum lines according to the quantum theory. H. R. HULME (Proc. Roy. Soc., 1935, A, 150, 416-421).—Schott's treatment of the radiation emitted by an atom (A., 1933, 206) is equiv. to the strict quantummechanical treatment, but the latter affords a simpler method of calculating the intensities. L. L. B.

Photometric measurements of X-ray reflexion. III. Atomic factors of sulphur and lead. P. DE LA CIERVA and J. PALACIOS (Anal. Fis. Quím., 1934, 32, 391-395).—The diagram for the scattering power of S exhibits undulations at vals. of  $\sin \theta/\lambda$ between 0.2 and 0.4 which correspond with those predicted by Hartree but are more pronounced. The Pb diagram contains a horizontal portion at about 0.3, whereas the curve of Pauling and Sherman is continuous. The mean error of the measurements is  $\geq 6\%$ . H. F. G.

Effect of temperature on the scattering of X-rays by solids according to quantum mechanics. H. OTT (Ann. Physik, 1935, [v], 23, 169– 196).—Theoretical. A. J. M.

Deviations from the Sommerfeld formula for the K levels. M. I. KORSUNSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 114—117).—A modification of Sommerfeld's equation yielding better vals. of the electronic charge is discussed. W. R. A.

K-Absorption edges of cobalt and its compounds. K. KOJIMA (Mem. Coll. Sci. Kyoto, 1935, A, 17, 189–190).—Data for Co, Co(OH)<sub>2</sub>, CoS, CoSiO<sub>3</sub>, CoF<sub>2</sub>, CoSO<sub>4</sub>, CoCO<sub>3</sub>, and Co<sub>2</sub>O<sub>3</sub> are recorded. The bivalent compounds show a displacement in the direction of shorter  $\lambda$ . E. S. H.

Secondary cathode rays expelled from metals by molybdenum  $K\alpha$  radiations. H. R. ROBINSON and C. J. B. CLEWS (Proc. Roy. Soc., 1935, A, 149, 587—595).—The energies of the electrons expelled by Mo  $K\alpha_1$  rays from Au, Pt, Ag, and Cu targets, using the magnetic spectrometer, are slightly > those obtained by Kretschmar for the same elements. The results are discussed in relation to the abs. vals. of X-ray  $\lambda\lambda$  and the principal at. consts. L. L. B.

Influence of chemical combination on the  $K\alpha_{1,2}$  doublet of silicon. N. G. JOHNSON (Z. Physik, 1935, 95, 93-96).—O compounds show displacement of approx. 2.4 X, and  $K_2SiF_6$  shows 3.8 X. A. B. D. C.

Spectroscopy of ultra-soft X-rays. IV. M. SIEGBAHN and T. MAGNUSSON (Z. Physik, 1935, 95, 133—157; cf. A., 1934, 232).—Measurements are given for the L series of elements between 27, Co, and 17, Cl. Displacement with chemical combination is recorded for NaCl, AlCl<sub>3</sub>, KCl, RbCl, CsCl, and BaCl<sub>2</sub>. A. B. D. C.

Electronic energy bands of solid copper, nickel, cobalt, and iron. F. C. CHALKIN (Nature, 1935, 135, 998).—Measurements of the intensity of soft X-rays from Cu, Ni, Co, and Fe and the deduced distribution of electronic energy indicate that the electrons in these metals are not completely free and cannot normally occupy the whole of the space lattice of the crystal. L. S. T.

Photo-effect with alkali metal films of atomic thickness on platinum. H. MAYER (Physikal. Z., 1935, 36, 463—464).—With K on Pt, a max. photoeffect is obtained when the K film is unimol., but this is probably due to the presence of  $O_2$ . The secondary emission due to primary electrons of 50—1500 volts was also determined as a function of the thickness of the film. The curve was almost identical with that obtained for the photo-effect in its earlier stages, and showed no max. A. J. M.

Mobility of sodium on tungsten. R. C. L. by a photo-electric method. A clean strip absorbs Na, but a portion of this reappears on the surface and evaporates when the strip is heated above 1300° abs. The capacity of the strip to absorb Na is limited, but when that limit has been attained, any excess of Na is stable on the surface, and if deposited as an active patch migrates over the surface at such a rate that the strip is approx. uniformly active after 1-2 hr. at  $300^{\circ}$  abs. or 5-10 sec. at 800° abs. The migration has an active energy of 0.25 volt, and the same energy is associated with the absorption process, from which it is concluded that the latter consists of migration into slip planes and intercryst. cracks. L. L. B.

Influence of impurities in the core-metal on the thermionic emission from oxide-coated nickel. M. BENJAMIN (Phil. Mag., 1935, [vii], 20, 1-24).—The effect of metallic impurities in Ni on the emission of BaO- and SrO-coated Ni filaments and on the crit. temp. of their emission is attributed to variation in the Ba metal content in the coating with the reducing power of the impurities. The phenomena are discussed with reference to modern theories of the mechanism of emission. J. W. S.

Variation of the mobility of gaseous ions with temperature. I. Positive ions in their own gas. A. M. TYNDALL and A. F. PEARCE (Proc. Roy. Soc., 1935, A, 149, 426-434).—The variation of mobility with temp. of the positive ions of He in He and of N in N<sub>2</sub> has been measured, over the range  $20-480^{\circ}$  abs. in He and  $65-590^{\circ}$  abs. in N<sub>2</sub>. Expressing the results at normal density instead of at normal pressure, the mobility in He is found to be practically independent of temp. from  $480^{\circ}$  abs. to room temp., below which there is a marked decrease. In  $N_2$  the decrease of mobility with fall of temp. is continuous. L. L. B.

Velocities of positive ions in the corona discharge. H. F. BOULIND (Phil. Mag., 1935, [vii], 20, 68—75).—The velocities of positive ions in gases at low pressure can be measured accurately by the corona discharge method provided that X/p is < a certain val. The velocities are > anticipated from mobility measurements at higher pressures, indicating that the positive ions in the corona discharge are single particles and not clusters. Above the crit. val. of X/p the method is inaccurate, but results show that the velocity increases rapidly with X/p, this being attributed to increase in the mean free path of the ions. These observations confirm that positive ions may produce appreciable nos. of new ion pairs by collision with gas mols. (X=electric field strength.) J. W. S.

Fifth Report of the Atomic Weights commission of the International Union for Chemistry. G. P. BAXTER, O. HÖNIGSCHMID, P. LEBEAU, and R. J. MEYER (Ber., 1935, 68, [A], 73—84).—The only alteration is the substitution of 93·3 for 92·91 as at. wt. of Nb. H. W.

Isotope regularities. A. CARRELLI (Nuovo Cim., 1934, [ii], 11, 542—546; Chem. Zentr., 1935, i, 657).— A discussion of nuclear structure. H. J. E.

Volumetric determination of the at. wt. of terbium. J. K. MARSH (J.C.S., 1935, 772-773).— The ratio  $Tb_2O_3: 3C_2O_3$  in the Tb material previously reported (cf. this vol., 180), determined by ignition of the oxalate and by titration with standard KMnO<sub>4</sub>, gave the val. 158.9 for the at. wt. of Tb. N. M. B.

Relative frequency of isotopes of potassium and rubidium. H. BONDY, G. JOHANNSEN, and K. POPPER (Z. Physik, 1935, 95, 46–52).—Massspectrographic measurements give the relative abundance of  $K^{39}$ :  $K^{41}$  as 16.2:1, and of  $Rb^{85}$ :  $Rb^{87}$  as 2.68:1. A. B. D. C.

Isotope effect with copper hydride (CuH/CuD). T. HEIMER (Naturwiss., 1935, 23, 372).—The band spectrum of CuD has been investigated and the nuclear vibration consts. have been calc. The isotope effect is considerable. A. J. M.

Isotopes of platinum. B. FUCHS and H. KOP-FERMANN (Naturwiss., 1935, 23, 372).—Examination of the hyperfine structure of the Pt I lines shows that all lines arising from the lowest state have a definite isotope displacement. Three isotopes, of masses 194, 195, and 196, occur, the abundance ratio being 5:8:8. The mechanical moment of Pt<sup>195</sup> is 1/2. A. J. M.

Isotopic constitution of platinum and rhodium. A. J. DEMPSTER (Nature, 1935, 135, 993).—The analysis of Pt ions from a high-frequency spark (this vol., 677) shows isotopes 192, 194, 195, 196, and 198. The middle three form a triplet of approx. equal strength, whilst the heaviest is weaker and the lightest faint. Using as electrode an alloy of Pt containing 10% Rh direct comparison of the doublycharged Pt ions with Rh<sup>103</sup> gave an at. wt. of  $102.92 \pm$ 0-03 for Rh. L. S. T. Isotopes of the radioactive elements and their disintegration. H. J. WALKE (Phil. Mag., 1935, [vii], 20, 25—32).—The absence of certain isotopes which would be expected for some elements is attributed to the  $\beta$ -radioactivity of these isotopes, leading to their disintegration. This theory is supported by the observed disintegration of the spontaneously radioactive elements. J. W. S.

The actinium problem. V. G. ELSEN (Chem. Weekblad, 1935, 32, 343-344).—A review. The probable at. wt. is  $231\pm0.5$ . S. C.

Tracks of  $\alpha$ -particles and protons in photographic emulsions. H. J. TAYLOR (Proc. Roy. Soc., 1935, A, 150, 382-394).—A study has been made of the tracks of  $\alpha$ -particles and protons in specially prepared photographic emulsions. Exposure of a plate to a neutron source gives rise to well-defined tracks due to the protons ejected by the neutrons in their passage through the gelatin of the emulsion. The experimental errors are discussed, and it is concluded that the method is unsuitable for determining the detailed distribution of neutron energies. L. B.

Specific ionisation of single  $\alpha$ -particles. G. STETTER and W. JENTSCHKE (Physikal. Z., 1935, 36, 441-445).—A double ionisation chamber is used to determine the ionisation curve of single  $\alpha$ -particles. The max. ionisation at n.t.p. occurs at a distance of  $4.4\pm0.3$  mm. from the commencement of the curve. A. J. M.

Energies of  $\alpha$ - and  $\beta$ -rays. H. A. WILSON (Proc. Roy. Soc., 1935, A, 150, 1—8).—Theoretical. Reasons are given for believing that  $\alpha$ - and  $\gamma$ -ray energies, contrary to Gamow's view (A., 1930, 1339), involve electronic energies. The proposed modification in Gamow's theory, viz., that the observed  $\alpha$ - and  $\gamma$ -rays have energies equal to a nuclear energy change plus or minus an energy change of the electronic system, is not necessarily in conflict with ideas based on quantum mechanics. L. L. B.

Rapid registration of small Hoffmann collisions. J. Bøggild (Naturwiss., 1935, 23, 372).— The apparatus consists of an air ionisation chamber (effective vol. 35 litres, pressure 7 atm.), the ionisation current being compensated by a second chamber and a  $\beta$ -ray source. Differences in electrometer readings are registered photographically. A. J. M.

Wave-length of secondary  $\gamma$ -radiation accompanying anomalous absorption of hard y-rays. K. TSU-TUNG (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 85-93).-In view of divergent theories, the absorption coeff. of the secondary  $\gamma$ -radiation associated with the anomalous absorption of  $\operatorname{Th}$ -C" y-rays was determined for the scattering angle 120° for Al, Zn, Sb, and Pb, using a Geiger-Müller counter.  $\lambda$  deduced from the absorption coeff. is 25.4 X for Al and Zn; for Sb and Pb there appears, in addition, a harder component 13.8 X. The ratio of the no. of hard to soft component quanta is 1:23 for Sb and 1:9 for Pb. Results indicate that the Rayleigh scattering of Th-C"  $\gamma$ -rays cannot be present appreciably; the component 25:4 X is attributed to positron and electron annihilation. The hard component is inter-

preted as continuous X-rays produced by scattered electrons and positrons. N. M. B.

Nuclear chemistry. S. FLÜGGE and A. KREBS (Physikal. Z., 1935, 36, 466–480).—A summary of recent work on nuclear transformations, including artificial radioactivity. A. J. M.

Collisions of  $\alpha$ -particles in deuterium. E. POLLARD and H. MARGENAU (Physical Rev., 1935, [ii], 47, 833—842).—Using three different but complementary methods, an investigation of the yields of deuterons emitted from D<sub>2</sub> under Po  $\alpha$ -particle bombardment is reported and discussed.

N. M. B.

Disintegration of the deuteron by impact. J. R. OPPENHEIMER (Physical Rev., 1935, [ii], 47, 845—846).—The probability and neutron yield of the disintegration of deuterons of energy  $> 2 \times 10^6$ e.v. by impact with at. nuclei in passage through matter are calc. N. M. B.

Soft  $\gamma$ -radiation produced on disintegration of lithium by protons. A. ECKARDT, R. GEBAUER, and H. R. VON TRAUBENBERG (Z. Physik, 1935, 95, 210—214). A. B. D. C.

Excitation of the nitrogen nucleus to *H*-emission by polonium  $\alpha$ -rays. H. STEGMANN (Z. Physik, 1935, 95, 72–83). A. B. D. C.

Nuclear transformations of beryllium and boron and the masses of the light elements. M. L. E. OLIPHANT, A. E. KEMPTON, and (LORD) RUTHERFORD (Proc. Roy. Soc., 1935, A, 150, 241— 258).—It is not possible to interpret the results of experiments on the transformation of Be and B by protons and by ions of  $H^2$  on the mass data at present available, but the assumption of a small error in the mass-spectrographic val. for the mass of He<sup>4</sup> brings all the data into agreement. Evidence is found of the existence of two new isotopes, Be<sup>8</sup> and Be<sup>10</sup>.

L. L. B.

Artificial radioactivity produced by neutron bombardment. II. E. AMALDI, O. D'AGOSTINO, E. FERMI, B. PONTECOEVO, F. RASETTI, and E. SEGRÈ (Proc. Roy. Soc., 1935, A, 149, 522-58).— The activation of several elements by neutron bombardment is increased by surrounding the source and activated substance by  $H_2O$  or paraffin wax; the suggested explanation is that the neutrons are slowed down by impacts with H nuclei, and that slow neutrons are more easily captured by some nuclei than fast ones. Some anomalously large absorption cross-sections for slow neutrons, and the production of slow neutrons through the action of non-hydrogenated substances, are described. The results of a systematic investigation of the elements, both as regards the induced activities and the properties with respect to slow neutrons, are tabulated.

L. L. B.

Absorption of slow neutrons. W. EHRENBERG and H. C. SHAN (Nature, 1935, 135, 993-994).--Under the experimental conditions described, slow neutrons are absorbed exponentially by Cd and Ag (see above). This suggests that either the active neutrons are of approx. homogeneous speed, or in the region of their velocity the nuclear cross-section is practically independent of this velocity. L.S.T.

Transformation of aluminium by neutrons. H. KLARMANN (Z. Physik, 1935, 95, 221—226).— Protons of 9 cm. range and a small no. of  $\alpha$ -particles are found. A. B. D. C.

Number and range of nuclear protons ejected from aluminium and nitrogen by  $\alpha$ -rays. H. POSE (Z. Physik, 1935, 95, 84—92). A. B. D. C.

Artificial production of elements of an unknown radioactive family by irradiating thorium with neutrons. (MME.) I. CURIE, H. VON HALBAN, jun., and P. PREISWERK (Compt. rend., 1935, 200, 1841—1843).—Irradiation of Th with neutrons gave four radio-elements with half-life approx. 3.5 hr., and 25, 15, and 1 min. The first and third behave chemically as isotopes of Ac, and the second and fourth as isotopes of Th and Ra, respectively. The existence of the radioactive family  ${}_{92}Ac^{237} \xrightarrow{\alpha}{}_{90}Ac^{233} \xrightarrow{\beta}{}_{91}Ac^{233} \xrightarrow{\beta}{}_{92}Ac^{233} \xrightarrow{\alpha}{}_{90}Ac^{229} \xrightarrow{\alpha}{}_{88}Ac^{225} \xrightarrow{}_{15}$ is suggested. H. J. E.

Artificial transformation of thorium by neutrons. Production of the missing 4n + 1 radioactive series. O. HAHN and L. MEITNER (Naturwiss., 1935, 23, 320).—As a result of the bombardment of Th by neutrons, two different processes occur: (1) a non-reinforced process, to which the substance with half-life 1 min. discovered by Amaldi *et al.* (this vol., 910) belongs. This breaks down into a substance radiating  $\beta$ -rays, with half-life 11—12 min. (2) A reinforced process giving an element of halflife 30 min. These substances are isotopes of Th, and the changes are probably to be represented by (1)  $_{90}$ Th<sup>232</sup>+n $\longrightarrow_{88}$ A<sup>229</sup>+ $\alpha \frac{\beta}{1 \min}_{1 \min}$  89 $B^{229} \frac{\beta}{11 \min}_{11 \min}$  90 $C^{229}$ ; (2)  $_{90}$ Th<sup>232</sup>+n $\longrightarrow_{90}$ Th<sup>233</sup>  $\frac{\beta}{_{30 \min}}$  91 $A^{233}$ . These series are of the new type 4n+1. A. J. M.

Artificial transformation of thorium by neutrons. E. FÖYN, E. KARA-MICHAILOVA, and E. RONA (Naturwiss., 1935, 23, 391).—Th in aq. solution was bombarded with neutrons from Be+Rn, a method of chemical separation being employed to detect the products. After a series of separations with La (for Ac), Ba (for Ra), and Ta (for Pa) there was no increase in the natural  $\beta$ -ray emission of the sample. A. J. M.

Apparent effect of galactic rotation on the intensity of cosmic rays. A. H. COMPTON and I. A. GETTING (Physical Rev., 1935, [ii], 47, 817—821). N. M. B.

Diurnal variation of cosmic rays. J. CLAY and H. R. WOLTJER (Physica, 1935, 2, 582–584).— In equatorial regions there is no diurnal variation of cosmic rays > 0.1% of the total, and, therefore, no variation with siderial time, confirming that cosmic rays are not due to novæ. M. S. B.

Transformations of cosmic radiation in matter. J. CLAY and P. H. CLAY (Physica, 1935, 2, 551-556).—No definite relation has been found between the primary cosmic corpuscular radiation and the secondary radiation produced in Pb. The shower-producing radiations are probably photons. The absorption coeff. of the final corpuscular radiation in Pb is 4 cm.<sup>-1</sup> There appear to be two photon radiations between the primary and final corpuscular radiations. M. S. B.

Secondary effects of cosmic rays on the Hafelekar (2300 m. above sea level). J. A. PRIEBSCH (Z. Physik, 1935, 95, 102-114).

A. B. D. C.

Application of liquid dielectrics to the study of ionisation "jumps" produced by cosmic radiation. C. BIAŁOBRZESKI and I. ADAMZEWSKI (Bull. Acad. Polonaise, 1935, A, 120—128).—Using 1 litre of  $C_6H_{14}$  in an ionisation chamber the frequency of ionisation jumps due to cosmic radiation reaches 37 in 13 hr., about 12% of the jumps being double or more complex. The advantages of liquid dielectric of low mobility are discussed. The surroundings have a considerable influence on the frequency of the jumps, presence of Al being particularly effective. J. W. S.

Neutron-proton interaction. I. Binding energies of the hydrogen and helium isotopes. II. Scattering of neutrons by protons. E. FEENBERG (Physical Rev., 1935, [ii], 47, 850-856, 857-859).-Mathematical. N. M. B.

Mass defect in the heavy elements. M. I. KORSUNSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 112—114).—Light nuclei (up to Ca) are formed of groups of two protons and two neutrons. If each particle moves in the field of all the remaining particles the mass defect  $\infty$  the square of the no. of particles. The curve shows breaks at nuclei formed from an even no. of protons and neutrons.

W. R. A.

General relation between the molecular spectrum and the electrons and electron orbits of the constituent atoms. H. DESLANDRES (Compt. rend., 1935, 200, 1997—2001; cf. this vol., 561).—A review and discussion of the correlation between electron arrangements in molecules and their Raman and infra-red spectra. H. J. E.

Electronic charge from de Broglie wavelengths of electrons. S. VON FRIESEN (Nature, 1935, 135, 1035).—A new method of calculating *e* from the electronic diffraction produced by a crystal of galena combines de Broglie's equation with the formula for the Rydberg const. Preliminary measurements give  $e=(4.796\pm0.010)\times10^{-10}$  e.s.u. L. S. T.

Effective cross-section of the neutrino. M. WOLFKE (Bull. Acad. Polonaise, 1935, A, 107–109).— From the no. of ions produced by neutrinos in an ionisation chamber, the max. possible effective cross-sectional area of the neutrino is  $6 \cdot 6 \times 10^{-33}$  sq. cm., corresponding with a mean free path of  $3 \cdot 9 \times 10^6$ km. in ordinary air. J. W. S.

Detection of neutrinos. M. WOLFKE (Bull. Acad. Polonaise, 1935, A, 19–23).—It is shown theoretically that if a strong  $\beta$ -ray source (e.g., Ra-E) be surrounded by sufficient Pb to absorb all primary  $\beta$ -rays and soft  $\gamma$ -rays, electrons produced by neutrinos should be detectable at the outer surface of the Pb with a counter or Wilson chamber. H. J. E.

Equation of the photon. G. PETIAU (Compt. rend., 1935, 200, 1829-1832).-Mathematical.

H. J. E.

Production of electron pairs and the theory of stellar structure. S. CHANDRASEKHAR and L. ROSENFELD (Nature, 1935, 135, 999).—Deviations from the gas laws may arise from the existence of a definite distribution of positrons and electrons in equilibrium with temp. radiation. L. S. T.

Ratio of the mass of the proton to that of the electron. H. ERTEL (Physikal. Z., 1935, 36, 464–465).—Mathematical. A. J. M.

Dependence of probability of the ionisation  $H_2 \longrightarrow H + H^+ + e + kinetic$  energy, on the orientation of the molecules with respect to the colliding electrons. N. SASAKI and T. NAKAO (Proc. Imp. Acad. Tokyo, 1935, 11, 138—140).— The probability of the above type of ionisation is found to depend on the mol. orientation.

#### A. J. M.

Energy exchange between neon, argon, and mercury atoms and a solid wall. A. A. ZAITZEV and G. V. SPIVAK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 118—125).—Accommodation coeffs. for these gases on a metallic surface have been investigated. and the following vals. obtained : Ne 0-05, A 0-1, Hg 0.58. Substantial increase in these vals. is obtained by adding  $O_2$  or  $CO_2$ . W. R. A.

Statistical error in counting experiments. R. PEIERLS (Proc. Roy. Soc., 1935, A, 149, 467–486). —Mathematical. L. L. B.

Calculations of atomic wave functions. III. Results for beryllium, calcium, and mercury. D. R. HARTREE and W. HARTREE (Proc. Roy. Soc., 1935, A, 149, 210-231).—At. wave functions have been calc. by the method of the self-consistent field (A., 1928, 216) for the normal states of Be, Ca, and Hg, both neutral and doubly ionised. In the case of the neutral atoms, the perturbation of the core by the two valency electrons is not large for Be and Ca, but is considerable for Hg. The differences between the selfconsistent field and the Thomas-Fermi field for neutral Hg are discussed. L. L. B.

Self-consistent field, with exchange, for beryllium. D. R. HARTREE and W. HARTREE (Proc. Roy. Soc., 1935, A, 150, 9—33).—Foch's equations for the self-consistent field of an atom, including exchange effect (Z. Physik, 1930, 62, 795), have been solved numerically for the normal state of neutral Be. The inclusion of the exchange terms has a small effect on the (1s) wave function, and a considerable effect on the (2s) wave function. L. B.

Annihilation radiation of positrons. H. A. BETHE (Proc. Roy. Soc., 1935, A, 150, 129—141).— Mathematical. A fast positron has a large probability of being annihilated during its motion, usually with emission of two quanta. The hard annihilation radiation is practically isotropic if emitted in substances with high at. wt. and it is contended that it is identical with the hard component in the "scattered  $\gamma$ -rays" found by several authors. L. L. B.

Quantisation of the new field theory. II. M. BORN and L. INFELD (Proc. Roy. Soc., 1935, A, 150. 141-166; cf. *ibid.*, 1934, A, 147, 522).—Mathematical. A proof that the quantum mechanics of a particle can be derived from the new field theory.

L. L. B.

Commutating co-ordinates in the new field theory. M. H. L. PRYCE (Proc. Roy. Soc., 1935, A, 150, 166-172).—Mathematical. A co-ordinate vector and an inner angular momentum which obey the simple commutation rules are defined. L. L. B.

Contributions to Born's new theory of the electromagnetic field. E. SCHRÖDINGER (Proc. Roy. Soc., 1935, A, 150, 465–477).—Mathematical. L. L. B.

Relativistic quantum mechanics. K. NIKOL-SKY (Proc. Roy. Soc., 1935, A, 150, 411–415).—The connexion between Dirac's theory of electrons and the Eddington–Born–Infeld theory is obtained.

L. L. B. **Relativistic basis of the quantum theory. III.** H. T. FLINT (Proc. Roy. Soc., 1935, A, 150, 421–441). —Mathematical. Quantum phenomena are shown to correspond with geometrical conceptions which underlie those of the theory of relativity. L. L. B.

Infra-red photography and the spectroscopic determination of [chemical] constitution. R. MECKE (Angew. Chem., 1933, 48, 320-327).--A review of the application of observations on infra-red spectra to constitutional problems, with special reference to the C-H linking. H. J. E.

Filter for obtaining light at wave-length 560 mu. K. S. GIBSON (J. Res. Nat. Bur. Stand., 1935, 14, 545—552).—A combination of 4.55 mm. Corning 351, 5.82 mm. Corning didymium, 1.99 mm. Jena V.G. 3, and 1.94 mm. Jena B.G. 18 glass filters isolates and transmits light of 5600 Å. better than other filters. The characteristics of the filter are detailed.

J. W. S.

Ozone in the Arctic night. E. TÖNSBERG and F. W. P. GÖTZ (Naturwiss., 1935, 23, 354; cf. A., 1929, 419, 624, 1263).— $O_3$  absorption in mid-winter at Tromsö is not exceptionally large (cf. Dauvillier, A., 1934, 1326); max. val. occurs in spring. A. J. M.

Band spectrum of NH. R. W. LUNT, R. W. B. PEARSE, and E. C. W. SMITH (Nature, 1935, 136, 32).— The 2530 Å. band of NH and four weaker bands at 2730, 2835, 2885, and 2980, apparently due to NH<sup>+</sup>, have been observed in the spectrum of discharges through streaming NH<sub>3</sub>. L. S. T.

Ultra-violet absorption spectrum of ammonia. A. B. F. DUNCAN (Physical Rev., 1935, [ii], 47, 822– 827).—Data for bands and intensities in the range 2300—850 Å. are tabulated. The bands down to 1665 Å. are diffuse through predissociation, and below this all are very sharp and show partly resolved rotational fine structure. Continuous absorption, as opposed to that due to pressure broadening, begins at approx. 1200 Å. and is so strong below 1150 Å. that no more bands could be measured accurately, although sharp bands exist down to 1085 Å., leading to a val. of 11.3 volts for the first ionisation potential. Classification in four progressions is given.

N. M. B. Absorption of light by carbon monoxidehæmochromogens.—See this vol., 999.

Intensities of vibration rotation bands. (MISS) J. E. ROSENTHAL (Proc. Nat. Acad. Sci., 1935, 21, 281-285; cf. Dunham, A., 1929, 1126).—The exact expression for the probability of any transition  $v' \leftarrow -v''$  is derived by a simple method for the case of a Morse potential function between the nuclei. Explicit expressions for the ratio of the integrated absorption coeffs. and numerical vals. for HCl, HBr, and HF are given. N. M. B.

Band spectra of ionised hydrogen halides. I. F. NORLING (Z. Physik, 1935, 95, 179–188).—A band spectrum between 3000 and 4000 Å. is ascribed to HBr<sup>+</sup>. A. B. D. C.

Band spectrum of aluminium bromide. P. C. MAHANTI (Indian J. Physics, 1935, 9, 369—382; cf. this vol., 562).—The band spectrum of AlBr is excited in AlBr<sub>3</sub> vapour. The bands have sharp heads degraded towards the red. A classification is given. The isotopic displacements of the bands due to AlBr<sup>81</sup>, AlBr<sup>79</sup> are calc. and agree well with experiment. It is probable that the predissociation which sets in above v'=3 is due to a strong interaction with an unstable and strongly repelling Heitler-London level, thus preventing excitation of higher vibrational states. A. J. M.

Interpretation of the spectra of the monoand di-chlorides of tin. H. TRIVEDI (Indian J. Physics, 1935, 9, 331—345).—The absorption of SnCl<sub>2</sub> vapour was investigated between 6000 and 2000 Å. There are no bands, but three regions of continuous absorption starting at  $\lambda$  4129, 3759, and 2883. There is optical dissociation of SnCl<sub>2</sub> into SnCl and Cl, both products existing in various states of excitation. Only faint fluorescence patches could be obtained after long exposure to 2535 Å. (Hg). The binding in both SnCl and SnCl<sub>2</sub> is ionic. A. J. M.

Absorption spectrum of carbon disulphide. R. K. ASUNDI and R. SAMUEL (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 203—206).—The first predissociation limit of CS<sub>2</sub> is at 2965 Å., corresponding with decomp. into CS and S in the <sup>1</sup> $\Sigma$  and <sup>3</sup>*P* states, respectively. The predissociation limit at 2160 Å. is interpreted as a decomp. into CS (ground <sup>1</sup> $\Sigma$ ) and S (excited <sup>1</sup>*D*). J. G. A. G.

Far ultra-violet absorption spectra and ionisation potentials of the ethyl halides. W. C. PRICE (J. Chem. Physics, 1935, 3, 365—366).—The spectra of EtI, EtBr, and EtCl (1500—1700 Å.) are described. The extrapolated ionisation potentials are : EtI, 9·295 and  $9\cdot885\pm0.005$ , EtBr,  $10\cdot24$  and  $10\cdot56\pm0.1$ . Results support the theory that the dipoles of Me and Et groups have a strong influence in reducing the ionisation potentials in adjacent linkings.

N. M. B. Halochromism of ketones. II. L. C. ANDER-SON and C. M. GOODING (J. Amer. Chem. Soc., 1935, 57, 999-1007; cf. A., 1933, 661).—Solutions of COMe<sub>2</sub>, hexan-y-one, cyclohexanone, dicyclohexyl ketone, cyclohexyl Ph ketone, COPh2, Ph diphenylyl ketone, and didiphenylyl ketone in  $H_2SO_4$  show increased light absorption in the region associated with the CO group. They retain their ketonic structure. Xanthone and fluorenone show a similar change and also possess new bands, which appear to be associated with the stabilisation of the quinonoid structure for these compounds. SnCl<sub>4</sub> produces the same changes as  $H_2SO_4$  on the absorption of xanthone; the production of colour is not due to ether O. The colour of ketone chlorides and H2SO4 or SnCl4 is different from that of ketones and resembles that of triarylcarbinols and their salts. In such solutions the ketone chlorides probably exist in a quinonoid modification. E. S. H.

Absorption spectrum of some organic vapours. C. M. B. RAO and R. SAMUEL (Current Sci., 1935, 3, 549).—Measurements are given to  $\lambda$  1510 Å. for AcCl, AcBr, and CCl<sub>3</sub>·COCl. A. B. D. C.

Optical absorption of substituted benzenes. VI. Methylbenzenes and xylonitriles. H. CON-RAD-BILLROTH (Z. physikal. Chem., 1935, B, 29, 170— 177; cf. A., 1934, 715).—The absorption spectra of methylbenzenes accord with the calculation rule previously described, allowing for the ortho-error, and the variation of the intensity of the absorption max. from one compound to another is similar to what it is for the chlorobenzenes (A., 1932, 1188). Xylonitriles do not obey the rule, although those groups of bands which should have the same frequency lie close together. R. C.

Ultra-violet absorption spectra of some organic compounds (acetylene, anthracene, phenanthrene). H. GOPFERT (Z. wiss. Phot., 1935, 34, 156–173).—Anthracene (I) and phenanthrene (II) were heated to vaporise them. The diffuseness of the (I) spectrum is ascribed to pre-dissociation. The (II) spectrum is different, two sharp-edge systems appearing amongst diffuse bands. The data for  $C_2H_2$  agree mainly with those of Kistiakowsky (A., 1931, 409), but are more detailed. J. L.

Absorption of ultra-violet light by some organic substances. L. MARCHLEWSKI and J. SKUL-MOWSKI (Bull. Acad. Polonaise, 1935, A, 137-145).-Hydrocellulose (I) dissolved in NaOH shows no selective absorption initially, but an absorption band with max. at 3170 Å. gradually appears and shifts towards shorter  $\lambda$ , the max. after 22 hr. being at 2900 Å. The filtrates from the alkaline solutions after acidification with AcOH also show the development of an absorption band at 2600 Å. This change is also accompanied by increases in the Cu and I vals. of the cellulose. The extinction curve of (I) acetate in CHCl<sub>3</sub> solution is similar to that of cellulose acetate, whilst that of (I) benzoate shows a max. at 2758 Å. and a min. at 2622 Å. attributed to the  $C_6H_6$  nucleus. J. W. S.

Absorption spectra of mixed nitrogen-containing compounds and of their isomerides. T. UEMURA and Y. INAMURA (Bull. Chem. Soc. Japan, 1935, 10, 169—182).—The absorption spectra of the following compounds have been investigated : NPh:NPh; NPh:NMe; NPh·NEt; NPh:NPr; NPh:NBu; NPh:N·CH<sub>2</sub>Ph; (CH<sub>2</sub>Ph·N:)<sub>2</sub>; NHPh·N:CH<sub>2</sub>; NHPh·N:CHMe; NHPh·N:CHEt; NHPh·N:CHPr; NHPh·N:CMe<sub>2</sub>; NHPh·N:CMeEt; NHPh·N:CHPh; CH<sub>2</sub>Ph·NH·N:CHPh; NPh:N·NHPh; NPhMe·N:N·NPhMe; (NHPh)<sub>2</sub>; CHPh:N·N:CHPh; NHPh<sub>2</sub>, and CHPh:NPh. When the N-containing radical is a strong chromophore, forming a conjugated double linking with the aromatic nucleus (*e.g.*, NPh:NPh), two very strong absorption bands are obtained, the centres of which are independent of alkyls present. Hydrazones have only one absorption band, the position of which is almost independent of the alkyl group. The absorption is reduced by introduction of Ph into an alkyl. The effects of ·NH· and ·CH:N· groups are discussed. J. W. S.

Electronic spectra of polyatomic molecules. I. Saturated aldehydes. II. Acraldehyde. E. EASTWOOD and C. P. SNOW (Proc. Roy. Soc., 1935, A, 149, 434—446, 446—466).—I. The absorption spectra of the vapours of MeCHO, EtCHO,  $Pr^{a}CHO$ ,  $Pr^{\beta}CHO$ , Bu<sup>\u03c9</sup>CHO, C<sub>6</sub>H<sub>13</sub>·CHO, COMe<sub>2</sub>, and COMeEt have been studied. The results of the vibrational analysis suggest that the electronic transition is effectively the same in all the mols. considered. The electronic structure of the :CO group in these mols. is essentially similar to that of :CO in CH<sub>2</sub>O, both in the ground and upper states. The transition is not localised in the double linking.

II. The absorption spectrum of  $CH_2:CH\cdot CHO$  (I) vapour has been measured under high dispersion. The frequencies of the upper state are 1270 and 500 cm.<sup>-1</sup>, the latter being allotted to a vibration of the  $CH_2$  about the C:C linking. This is supported by observations on the spectrum of CHMe:CH·CHO. The upper state of (I) is different in kind from that of the saturated aldehydes. Nine bands have been resolved into series of rotational lines; each series can be expressed by a single parabolic formula as though it were an isolated R branch. A possible explanation is suggested for the non-appearance of a related P branch, but not for the failure of the various formulæ to yield the same val. for the moment of inertia of the ground state. L. L. B.

Infra-red absorption spectrum of silane. W. B. STEWARD and H. H. NIELSEN (Physical Rev., 1935, [ii], 47, 828—832; cf. A., 1934, 1288).—In the range  $13.0-1.0 \mu$  data and partial resolution are given for bands at 11.0, 4.6, 3.17, 3.23, 5.5, and  $2.3 \mu$ , in decreasing order of intensity. Identifications by analogy with CH<sub>4</sub> are made. The calc. mol. moment of inertia gives  $I_0 = 8.9 \times 10^{-40}$  g.-cm.<sup>2</sup> N. M. B.

Infra-red absorption spectra of nitriles. F. K. BELL (J. Amer. Chem. Soc., 1935, 57, 1023—1025).— The infra-red absorption spectra of aceto-, *n*-butyro-, *n*-valero-, *iso*hexo-, phenylaceto-, benzo-,  $\alpha$ -naphtho-, and succino-nitriles have been examined between 1·0 and 12·0 mµ A characteristic, well-defined absorption band occurs at 4·4 µ in alkyl nitriles and at 4·5 µ in aryl nitriles. This band is traced to the CN linking. A region of characteristic absorption possibly occurs at 7·0 µ. E. S. H.

Light scattering and Raman effect. S. BHAGA-VANTAM (Current Sci., 1935, 3, 526-531).—A summary. Phenomenon of "wings" as a vibrational Raman effect: a correction. E. GROSS and M. VUKS (Nature, 1935, 135, 998; cf. this vol., 564). L. S. T.

Raman spectrum of orthophosphoric acid. M. A. JEPPESEN and R. M. BELL (J. Chem. Physics, 1935, 3, 363; cf. Nisi, A., 1930, 662).—Data are given for the concn. range 50—10 mols.-%. A strong line, showing a frequency change with concn. of about 14 cm.<sup>-1</sup>, appears at all concns. N. M. B.

Rotational Raman scattering in benzene at different temperatures. S. C. SIRKAR and B. B. MAITI (Indian J. Physics, 1935, 9, 323—330).—A reinvestigation of the rotational Raman scattering of liquid  $C_6H_6$  at 30° and 210° has been carried out to explain the discrepancy between the observed and calc. distribution of intensity in the rotational wing accompanying the Rayleigh line. The intensity of the wing is not a max. at the centre of the Rayleigh line, as previously reported, but is zero and attains a max. at 18 and 25 cm.<sup>-1</sup> from the centre at 30° and 210°, respectively. The intensity decreases and the wing extends up to 120 cm.<sup>-1</sup> at 30° and 100 cm.<sup>-1</sup> at 210°. A. J. M.

Raman spectra of amides and anilides in the fused state. I. V. N. THATTE and M. S. JOGLEKAR (Phil. Mag., 1935, [vii], 19, 1116—1121).—Data for HCO·NH<sub>2</sub>, NH<sub>2</sub>Ac, NH<sub>2</sub>Bz, COPh<sub>2</sub>, CO(NH<sub>2</sub>)<sub>2</sub>, and NHPhAc are tabulated. N. M. B.

Raman spectra of decahydro- and tetrahydronaphthalene. S. K. MUKERJI (Phil. Mag., 1935, [vii], 19, 1079—1097).—Using solutions of quinine sulphate and  $m \cdot C_6 H_4 (NO_2)_2$  in  $C_6 H_6$  separately as light filters, 17 new lines for dekalin and 12 for tetralin were measured. Each gave three new anti-Stokes lines at 596, 494, 407, and 162, 265, 1433 cm.<sup>-1</sup>, respectively. Corrections and extensions of assignments of weak frequencies previously reported (cf. Bonino, A., 1932, 7, 1076) are given. N. M. B.

Raman effect. XLII. Raman spectra of naphthalene and its mono-derivatives. H. GOCKEL (Z. physikal. Chem., 1935, B, 29, 79–87; cf. this vol., 681).—The Raman spectra of  $C_{10}H_8$  and  $C_{10}H_7X$  (X=OH, Me, CN, SH, Cl, Br in 1- and 2position and F in 1-position) and of some aliphatic bromides have been determined. R. C.

Raman spectrum of gaseous  $CD_4$ . A. DADIEU and W. ENGLER (Naturwiss., 1935, 23, 355).— $CD_4$ obtained from  $Al_4C_3$  by the action of 99.2%  $D_2O$ , and subsequent purification, shows two Raman lines of frequency 2108 and 2141 cm.<sup>-1</sup> The first is stronger, intensity ratio 5:2. A. J. M.

Raman spectra of deuterobenzenes and the structure of benzene. W. R. ANGUS, C. R. BAILEY, J. L. GLEAVE, A. H. LECKIE, C. G. RAISIN, C. L. WILSON, and C. K. INGOLD (Nature, 1935, 135, 1033–1034).—Raman frequencies obtained for  $C_6D_6$  and  $C_6H_5D$  are compared with those previously recorded (this vol., 806). The  $C_6D_6$  frequencies are consistent with a  $D_{6h}$  symmetry for  $C_6H_6$ . L. S. T.

Phosphorescence process as revealed by the luminescence from solid nitrogen. L. VEGARD (Nature, 1935, 135, 1073).—The Vegard bands in the afterglow of solid N are due to a recombination of N atoms produced from mols. dissociated by the bombarding rays. Phosphorescence and chemi-luminescence appear to be closely related. L. S. T.

Colour distribution in fluorite in relation to crystal structure. H. HABERLANDT and A. SCHIENER (Z. Krist., 1935, 90, 193—214).—Although great variations occur, there is usually an excess or a lack of colour in fluorite crystals in the diagonal planes. There are also colour regularities in zones parallel to (100) and in filaments perpendicular to (100). Microscopic colour periodicities about 1  $\mu$ apart can be seen, corresponding with "mosaic" structure. The colour striations show many apparently homogeneous crystals as in reality an assemblage of smaller units. The presence of impurities is definitely associated with the colour variations.

B. W. R. Electron conduction and colour centres in fluorspar. E. Mollwo (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1934, [ii], 1, 79—89; Chem. Zentr., 1935, i, 670—671).—The absorption spectrum of fluorspar, coloured either electrically or thermally, shows max. at 3750, 5200 Å., the separation of the max. improving with cooling. The colour is due to excess of the cation metal, which can be detected by changes in d, and by direct analysis. A blue coloration was observed in SrCl<sub>2</sub>, colloidal particles being formed on cooling to room temp. H. J. E.

Colour centres of alkali halide crystals. R. W. Pohl (Kolloid-Z., 1935, 71, 257—261).—A summary of published work. E. S. H.

Measurement of number of colour centres in crystals. E. Mollwo and W. Roos (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1934, [ii], 1, 107-113; Chem. Zentr., 1935, i, 525).—A discussion.

H. J. E. Impurities and electrically excited phosphorescence of thin  $Al_2O_3$  layers. H. BETZ (Z. Physik, 1935, 95, 189–197).—An electrolytically formed oxide layer on Al shows phosphorescence in a field of 10<sup>7</sup> volts per cm. The presence of Cr, Cu, Fe, or Mg leaves the intensity of phosphorescence unchanged; Zn decreases it, whilst Mn increases it to an extent dependent on the voltage of formation of the layer. A. B. D. C.

Influence of unequal distribution of phosphorescence centres on Lenard phosphors. V. V. ANTONOV-ROMANOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 105-111).—Theoretical.

W. R. A.

Phosphorescence of calcite. V. LEVSCHIN and M. ALENTZEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 54-57).—A spectroscopic investigation of phosphorescence excited by the 365 mµ Hg line in calcite, aragonite, and stalactites is described. A. B. D. C.

Cathodic phosphorescence phenomena. M. SERVIGNE (Compt. rend., 1935, 200, 2015-2017).--Pptd. CaWO<sub>4</sub> gave feeble blue cathodic phosphorescence compared with natural scheelite. The effect in the pptd. material was much enhanced by heating for 10 min. at 800° and cooling quickly. The blue phosphorescence was intensified by addition of Ag

(optimum 0.1%). Addition of 1% of Sm and Er produced orange-red and green phosphorescences, respectively. H. J. E.

Influence of potassium iodide concentration on the time of decay of the uranine fluorescent radiation. W. SZYMANOWSKI (Bull. Acad. Polonaise, 1935, A, 34—37).—Data are recorded. The applicability of Vavilov's theory is discussed (cf. A., 1929, 489). H. J. E.

Variability of the fluorescence spectrum of a glycerol solution of trypaflavine. MLLE. A. WRZESIŃSKA (Bull. Acad. Polonaise, 1935, A, 38—41).—A band in the fluorescence spectrum at approx. 5000 Å. has been shown by measurements at  $-180^{\circ}$  to 100° to consist of two components, the max. of which vary in position and relative intensity with temp. H. J. E.

Time decrement of light due to polarised fluorescence of dye solutions. A. JABLOŃSKI (Z. Physik, 1935, 95, 53-65).—Perrin's theory of depolarisation is applied to time decrement of fluorescence; this does not generally follow the exponential law. Fluorometer measurements are discussed.

A. B. D. C. Negative polarisation of the phosphorescence of adsorbed dye molecules. A. JABŁOŃSKI (Bull. Acad. Polonaise, 1935, A, 30–33; cf. A., 1934, 584).—Measurements of polarisation in the lowtemp. phosphorescence spectrum of trypaflavine adsorbed on Cellophane are recorded and discussed. H. J. E.

Photomagnetism. D. M. BOSE and P. K. RAHA (Phil. Mag., 1935, [vii], 20, 145—166).—NiSO<sub>4</sub>,7H<sub>2</sub>O crystals and solutions containing V<sup>•••</sup> or V<sup>••</sup> ions show an increase in magnetic susceptibility on absorption of radiation. The photo-magnetic effect of aq. solutions containing various paramagnetic ions follows the order Ni<sup>••</sup>>Cr<sup>••</sup>>Co<sup>••</sup> and approx.  $\infty$  the quenching of the orbital moment of the ions in their ground states. Solutions containing Cr<sup>•••</sup> or Ni<sup>••</sup> in dil. HCl give very small photo-magnetic effects, probably owing to the presence of undissociated paramagnetic mols. in these solutions which absorb the light and in which the orbital moment is equally quenched in the initial and final states. Quant. relations between the light absorption and change in susceptibility are deduced for CrCl<sub>3</sub> solutions. J. W. S.

Surface-force theory of rectification in ionic crystals. S. R. KHASTGIR (Indian J. Physics, 1935, 9, 347-355; cf. this vol., 282). A. J. M.

Dielectric loss of liquid insulators. H. RIECHE (Z. Physik, 1935, 95, 158–178).—Dielectric loss and const. have been measured for transformer oil, PhNO<sub>2</sub>, and  $C_6H_6$  in the frequency range of 50 to  $150 \times 10^6$  hertz, and from  $-80^\circ$  to  $100^\circ$ ; the results agree with Debye's dipole theory rather than Wagner's theory of inhomogeneity. A. B. D. C.

Conductivity-temperature studies on paraffin waxes. W. JACKSON (Trans. Faraday Soc., 1935, 31, 827-835; A., 1934, 585).—Different samples of paraffin wax have a negative coeff. of electrical conductivity over a small temp. range 10-15° below their m.p. The behaviour is apparently due to a change of cryst. form. The instantaneous absorption current passes through a max. with temp. F. L. U.

Mechanism of dielectric loss in paraffin wax solutions at high radio frequencies. W. JACKSON (Proc. Roy. Soc., 1935, A, 150, 197-220).—An attempt to correlate the dielectric properties of solid insulating materials with their chemical and physical constitution. The results of measurements of the variations of power loss and dielectric const. for solutions of cetyl palmitate (I) in a paraffin wax medium over the temp. range  $0-80^{\circ}$  and at frequencies of  $1.80 \times 10^5$ — $1.42 \times 10^7$  cycles per sec. are discussed. The variation of power loss is in good quant. agreement with Debye's theory of dipole orientation. Experimental results point to the conclusion that only a portion of the polar (I) mol. oscillates in the alternating electric field. L. B.

Conductivity of anisotropic liquids. V. FRED-ERIKS, G. MICHAILOV, and D. BENESCHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 208— 212).—The dependence of conductivity on field strength has been investigated for *p*-azoxyanisole and PhCl. W. R. A.

Dipole moment and molecular properties. O. GRABOWSKY (Pharm. Ztg., 1935, 80, 643-646). A summary.

Constancy of two dipole moments in the vapour state and their apparent variation in solution. C. P. SMYTH and K. B. MCALPINE (J. Chem. Physics, 1935, 3, 347–350).—The validity of the solution method for determining dipole moment is considered with reference to possible variation of moment with temp. The moments of heptyl bromide and BuCl in the vapour state are  $2.07\pm0.05$  and  $2.04\pm0.01$ , respectively, showing the absence of appreciable increase in moment with increase in C chain length. Estimated moment vals. for the vapour state are: Pr<sup>a</sup>Br and Bu<sup>a</sup>Br,  $2.04\pm0.03$ ; Pr<sup>a</sup>I and Bu<sup>a</sup>I,  $1.93\pm0.04$ . N. M. B.

Dielectric constants of gases and vapours. II. M. KUBO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 65–73; cf. this vol., 567).—The electric moments and at. polarisation of Pr<sup>a</sup>OH, Bu<sup>a</sup>OH, and allyl alcohol have been calc. from the dielectric consts. of their vapours. W. R. A.

Moments and internal potential energies of two molecules containing movable dipoles. C. P. SMYTH and K. B. MCALFINE (J. Amer. Chem. Soc., 1935, 57, 979–983).—The dielectric consts. of the vapours of trimethylene chloride and  $(CHCl_2)_2$ have been determined. The calc. dipole moments  $(2\cdot10\times10^{-18} \text{ and } 1\cdot36\times10^{-18})$  do not vary over the temp range studied  $(374-485^{\circ} \text{ abs. and } 401-436^{\circ} \text{ abs., respectively})$ . E. S. H.

Dipole moments of ethyl- and phenyl-carbimides. J. R. PARTINGTON and E. G. COWLEY (Nature, 1935, 135, 1038).—Ethyl- and phenylcarbimide in  $C_6H_6$  at 20° give  $P_{2\infty}$  185 and 144 c.c.,  $P_E$  18·3 and 33·9 c.c., and  $\mu$  2·81 and 2·28D, respectively. The results, like the Raman spectra, indicate that ·N:C:O in the carbimides is linear. L. S. T. New formula for molecular polarisation and refraction. P. C. HENRIQUEZ (Rec. trav. chim., 1935, 54, 574—575)—The Clausius-Mosotti expression is regarded as invalid for liquids. From Fairbrother's results (this vol., 13) the mol. polarisation (P) of PhNO<sub>2</sub> in p-xylene is given by P= $(\varepsilon-1)(\varepsilon+4)M/\{(8\varepsilon+7)d\}$ . For 12 "non-associated" substances this relation holds well if  $\varepsilon$  is < 20, and the concn. is < 30 mol.-%. For liquids of  $\varepsilon > 20$ ,  $P=(\varepsilon-1)(\varepsilon+4)M/\{[8\varepsilon+7+(\varepsilon-1)^3 \times 1.7 \times 10^{-3}]d\}$ . Even for pure liquids the deviation is small, dipole moments calc. from data for pure liquis differing by >10% from vals. calc. from data for dil. solution. For  $\varepsilon < 6$ ,  $P=0.60(\varepsilon^{\frac{1}{2}}-1)M/d$ , and the mol. refraction=0.60(n-1)M/d. R. S. B.

cis-Cinnamic acids. F. EISENLOHE and W. HASS (Z. physikal. Chem., 1935, 173, 249—264).— The forms of m.p. 42°, 58°, and 68° have in  $C_6H_6$ solution the same dipole moment,  $1\cdot12\times10^{-18}$  e.s.u. In solution in  $C_6H_6$ ,  $Et_2O$ , and dioxan the forms of m.p. 68° and 42° have the normal mol. wt. The heat of combustion of the acid of m.p. 42° is 1042.7 kg.-cal. per mol. Each form with *trans*-cinnamic acid has the f.-p. diagram of a typical binary system with eutectic. It is suggested that the relation between the three forms is some special kind of rotation isomerism; it is certainly not polymorphism (cf. A., 1930, 471). R. C.

Molecular volume of water in sodium salts. A. ESCRIBANO and E. MOLES (Anal. Fís. Quím., 1934, 32, 494—508).—Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> yields hydrates with 10, 4, 3(?), 2, and 1 H<sub>2</sub>O, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with 5 and 2 H<sub>2</sub>O, and Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> with 2 H<sub>2</sub>O. Density determinations on all the hydrates yield the normal val. for the mol. vol. of the H<sub>2</sub>O, except in the case of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>,2H<sub>2</sub>O (10·3) and Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>,2H<sub>2</sub>O (9·6). H. F. G.

Refractive index of the alkaline chlorides at low concentrations. H. J. WALKE (Phil. Mag., 1935, [vii], 20, 32-44).—At conens. < 0.0005N the refractive index of NaCl, KCl, and LiCl solutions varies linearly with conen., this being interpreted as evidence for complete dissociation below this conen. Between 0.0005 and 0.002N it varies linearly with  $\sqrt{\text{conen.}}$ , suggesting that undissociated mols. may be present in these solutions. J. W. S.

New determination of atomic refractions. I. L. J. N. VAN DER HULST (Rec. trav. chim., 1935, 54, 518-522).—The at. refractions (r) calc. by Eisenlohr (A., 1911, ii, 81) are criticised on the grounds of incorrect mathematical derivation. From the paraffin hydrocarbons and aliphatic nitriles the mol. refraction of CH<sub>2</sub> has been calc. as 4.640 at 20° for 589 m $\mu$ , whence r for C and H=2.590 and 1.025, respectively. Using these vals. the mol. refractions of the paraffin hydrocarbons have been calc., and no "exaltation" appears with higher members, contrary to the results of Eisenlohr. R. S. B.

Molecular refraction, molecular volume, and b.p. in molecular lattices. W. KLEMM (J. pr. Chem., 1935, [ii], 143, 106-114).—The relation between the ratio mol. refraction/mol. vol. and the abs. b.p. of a no. of elements and compounds has been examined. It is a smooth curve for inert gas elements which becomes displaced towards higher b.p. in the case of polyat. mols. without dipole moment. Hydrides of this class  $(CH_4, PH_3, HI)$  lie on the inert gas curve, indicating an inert gas electronic structure. The presence of a dipole moment displaces the relation in the direction of higher b.p. This effect is explained with reference to interat. and interionic forces. In homologous series of saturated hydrocarbons, alcohols, and carboxylic acids, it tends to a const. with increasing b.p. R. S.

Factors modifying the polarisation of liquids. F. R. Goss (J.C.S., 1935, 727-731; cf. this vol., 683).—The previously assumed equality of the mol. anisotropy factors arising from the local asymmetry of the optical and the electrical polarisation field is established for CCl<sub>4</sub>. The "false" orientation polarisation of  $C_6H_6$ , attributed to the presence of co-ordinate links, is measured for the temp. range 10-50°. Several expressions for mol. refraction are compared with reference to temp. independence. N. M. B.

Theory of optical activity. I. General theory of a system of coupled isotropic oscillators. II. Molecules with a binary axis of symmetry. M. BORN (Proc. Roy. Soc., 1935, A, 150, 84-97, 97-105).—I. A development of the theory of rotatory power given previously (A., 1915, ii, 659). The mol. is considered as a set of isotropic oscillators coupled by Coulomb forces, and the interaction is calc. by the perturbation method.

II. A mol. consisting of 2 equal pairs of oscillators perpendicular to each other and to their central line is considered. The theory gives an angle of rotation of the expected order of magnitude.

### L. L. B.

Electrical birefringence of liquid oxygen and nitrogen. R. GUILLIEN (Compt. rend., 1935, 200, 1840—1841).—Data for O (64.05—90.15° abs.) and N (63.29—77.40° abs.) are recorded for  $\lambda$  5461 Å. The vals.  $\propto 1/abs$ . temp., confirming the absence of a permanent electrical moment in the mols. H. J. E.

Rule for calculating the formulæ of acids and bases. M. CARRANZA (Bol. Soc. Quim. Peru, 1935, 1, No. 3, 58-61).—Methods for calculating the formulæ of acids and bases derivable from any given element are deduced from the no. of electrons which can be given or received by the outer electron shell.

E. L.

Transition from metallic to heteropolar linking. U. DEHLINGER (Z. Elektrochem., 1935, 41, 344—346).—Theoretical. An explanation of the fluorspar-lattice structure of AuAl<sub>2</sub>. F. L. U.

The I-I linking in diphenyliodonium iodide. W. V. MEDLIN (J. Amer. Chem. Soc., 1935, 57, 1026-1027).—X-Ray investigation shows that the distance between the I atoms is 3.55 Å., which is compatible with an ionic, but not a covalent, structure. E. S. H.

Linking of HCl. R. SAMUEL (Current Sci., 1935, 3, 549—550).—The covalent nature of this linking is affirmed. A. B. D. C.

Problem of valency. R. F. HUNTER and R. SAMUEL (Chem. and Ind., 1935, 635-637; cf. A.,

1934, 1058).—Difficulties arising in the translation of the theory of co-ordination into wave-mechanical terms are discussed. The limitations of the method of mol. orbitals are considered, and it is maintained that the method should be interpreted as giving, in higher approximations, a pair-bond theory of valency, with strong interaction of electrons within the pair, and weak interaction between adjacent pairs. New band spectroscopic evidence confirms the non-bonding power of the  $s^2$  group. The relation between bond and Raman frequency is discussed. The only method of treating co-ordination by wave-mechanics is to use the method of mol. orbitals as a single electron bond theory. A. J. M.

Number of canonical structures of each degree of excitation for an unsaturated or aromatic hydrocarbon. G. W. WHELAND (J. Chem. Physics, 1935, 3, 356-361).—Results are calc. and illustrated for mols. consisting of a straight chain, a ring, several rings, and an unpaired electron, respectively.

N. M. B. Formation and stability of complex ammines. B. N. SEN (J. Gen. Chem. Russ., 1935, 5, 169–172).— Ammines are formed only by those elements for which the distance D of closest approach of the central atoms is > 2.48 Å. The dissociation temp. T of hexammines is given by  $k=\log (TDV)^{\frac{1}{2}}$ , where V is the ionisation potential. R. T.

Class of perturbations of molecular levels. G. H. DIEKE (Physical Rev., 1935, [ii], 47, 870-876). —The conditions under which perturbations can occur, when the perturbing force is caused by the rotation of the mol., are examined. N. M. B.

Formation of mercury molecules. F. L. ARNOT and J. C. MILLIGAN (Nature, 1935, 135, 999—1000).— Magnetic analysis of ions in Hg vapour at various pressures and voltages shows that diat. mol. ions result from electron impact. The mol. ions are formed by the union of two atoms one of which at least must be excited, a view which reconciles the non-existence of Hg mols. chemically with the band spectra evidence of their presence. L. S. T.

Moles of vibration of butane and pentane. "Free rotation" about carbon-carbon linkings and a new type of stereoisomerism. L. S. KASSEL (J. Chem. Physics, 1935, 3, 326—335).—Mathematical. Rotational investigation of a chain of four C atoms indicates two isomeric forms of  $C_4H_{10}$  with plane C skeletons, and a third form in which the two Et are rotating about the central C·C linking. Vibration frequencies for a five-C chain are calc. Results are in fair agreement with observed Raman and infrared lines. N. M. B.

Spectrum of the normal frequencies of a polar crystal lattice. I. General theory. J. H. C. THOMPSON (Proc. Roy. Soc., 1935, A, 149, 487-505) —Mathematical. The dynamical theory of the vibrations of the particles in a polar crystal lattice is worked out. A determinantal frequency equation, for the determination of a typical set of points of the "frequency spectrum," is obtained in a form in which the coeffs. can be calc. L. L. B. Characteristic vibrations of mechanical models of molecules. II. Four-mass systems. F. TRENKLER (Physikal. Z., 1935, 36, 423-432; cf. this vol., 432).—The form of vibrations and characteristic frequencies of mols. of the types COCl<sub>2</sub>,  $CO_3^{--}$ , trans- and cis-(CHCl)<sub>2</sub>, (CN)<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> have been investigated with mechanical models. The results are in agreement with theory except in the case of the slow deformation vibrations, for which models are inadequate. A. J. M.

Dynamics of molecular crystal lattices. III. Models of vibrating crystals. V. DEITZ and D. H. ANDREWS (J. Franklin Inst., 1935, 219, 703—715; cf. this vol., 811).—The frequencies of vibrating mols. have been studied by mechanical vibration of an appropriate model, and an extension of the method to a complete crystal lattice is described. Models of solid Ne and N<sub>2</sub> (both face-centred cubic) were constructed, containing 15 and 36 unit cells, respectively. Elastic bands represented the forces between each atom and its nearest neighbours, also its next-tonearest neighbours; thus in Ne lattice each "atom" was acted on by eighteen "forces." The model was vibrated mechanically at increasing frequencies. The effect of introducing a heavy "isotope" was studied. B. W. R.

Thermochemistry and physical properties of bromides and hydrosulphides. C. D. WEST (J. Physical Chem., 1935, 39, 493-507).-The lattice energies of alkali bromides and hydrosulphides have been calc. and shown to be similar. The proton affinities of Br' and SH' differ by about 23 kg.-cal. Calc. free energy changes indicate that MSH (M= alkali metal) is increasingly stable as the at. no. of the cation increases, and that the hypothetical LiHS must be thermodynamically unstable. The calc. heats of reaction of M with MSH are in accordance with the observation that MSH is readily decomposed by M, in contrast to the behaviour of M towards MOH. Various thermochemical data for MSH have been calc. from lattice energies. Physical properties of corresponding covalent bromides and hydrosulphides have been compared. Some cyanides have been con-M. S. B. sidered.

Energy constants of a gas in the region of dissociation. F. A. F. SCHMIDT (Forsch. Ingenieurwes., 1934, A, 5, 60–66; Chem. Zentr., 1935, i, 677).—Formulæ are derived for the heat content of a dissociating gas mixture. Data for  $CO_2$ ,  $H_2O$ , and  $NH_3$  are discussed. H. J. E.

**Parachor.** V. DESREUX (Bull. Soc. chim. Belg., 1935, 44, 249–287).—The surface tensions and densities of many halogen-substituted hydrocarbons have been determined and the parachors deduced. The increase in parachor obtained by substitution of H by halogen is not const. and is always < calc., the greatest effects being observed with F. The physical significance of the parachor is discussed, and it is concluded that the anomalies may be due to the compounds not being in strictly comparable states. J. W. S.

Optical reciprocal law applied to X-ray interference. M. VON LAUE (Naturwiss., 1935, 23, 373). -The Maxwell reciprocal law may be applied to radiation proceeding from atoms in a wave field. The two possible cases of the radiation proceeding into and out of the crystal are considered. Similar considerations apply to electron diffraction.

A. J. M. '' Quadratic form '' of inverted polar crystalline space-lattices. V. LINITZKI (Ukrain. Chem. J., 1935, 10, 22–26).—Mathematical. R. T.

Rate of polymorphic transformations. III. Influence of mechanical deformation on rate of transformation. E. COHEN, W. A. T. COHEN-DE MEESTER, and A. K. W. A. VAN LIESHOUT (Z. physikal. Chem., 1935, 173, 169—177; cf. this vol., 688).— The observations accord with the view that a nucleus in a polymorphic metal is to be regarded as a local strain in the lattice. R. C.

Vitreous state. G. HAGG (J. Chem. Physics, 1935, 3, 363-364).—A discussion of a paper by Zachariasen (cf. this vol., 572). N. M. B.

X-Ray investigations on the thermal expansion of solids. II. G. SHINODA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 27–30; cf. B., 1933, 672).— The following thermal expansion coeffs., parallel and perpendicular to the hexagonal axis, respectively, are recorded : Mg  $23\cdot8\times10^{-6}$ ,  $23\cdot5\times10^{-6}$ ; Cd  $50\cdot0\times$  $10^{-6}$ ,  $17\cdot9\times10^{-6}$ ; Zr  $2\cdot5\times10^{-6}$ ,  $14\cdot3\times10^{-6}$ ; Co  $16\cdot1\times10^{-6}$ ,  $12\cdot6\times10^{-6}$ . E. S. H.

Interpretation of Weissenberg photographs in relation to crystal symmetry. D. CROWFOOT (Z. Krist., 1935, 90, 215—236).—Detailed technique is described for interpreting Weissenberg photographs to give the point-group symmetry of the crystal. Charts are reproduced for a special camera size, and particular attention is given to triclinic and monoclinic (a or c axis) photographs. B. W. R.

Interference phenomena in two-dimensional crystals. F. LAVES and W. NIEUWENKAMP (Z. Krist., 1935, 90, 273—278).—A theoretical discussion of the X-ray diffraction to be expected from a twodimensional lattice. B. W. R.

Two-dimensional over-structures. F. LAVES (Z. Krist., 1935, 90, 279–282).—Certain rotation photographs of maucherite, Ni<sub>3</sub>As<sub>2</sub>, are interpreted as indicating the existence of a two-dimensional lattice. B. W. R.

Derivatives of ferric oxide (FeO·OH, FeO<sub>2</sub>Na, FeOCl): determination of their structures. S. GOLDSZTAUB (Bull. Soc. franç. Min., 1935, 58, 6—76). —X-Ray analysis of the natural hydrates of Fe<sub>2</sub>O<sub>3</sub> gives, except in the case of turgite (I), diagrams corresponding with that of either goethite (II) or lepidocrocite (III). (I) gives the hæmatite diagram (cf. A., 1929, 988). Hence in nature there is only one hydrate of Fe<sub>2</sub>O<sub>3</sub>, viz., Fe<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O, which has two different cryst. structures, that of (II) or (III). Thermomagnetic analysis shows that on dehydration (III) gives an unstable  $Fe_2O_2$  which is strongly magnetic, and this has enabled small quantities of (III) to be detected in minerals giving only the X-ray diagram for (II). Larger crystals (2—3 mm.) of Na ferrite (IV) have been prepared by a modification of the method of van Bemmelen and Klobbie (A., 1893, ii, 169). The at. structure of (IV) is discussed (cf. A., 1933, 215). The X-ray diagram of the product of hydrolysis at room temp. is different from that of (II) or of (III).

Goethite from the Restormel mine at Lanlivery, Cornwall, has a 4.64, b 10.0, c 3.03 Å.; space-group  $V_{*}^{Ab}$  bnm. The crystal is built up from units of FeO·OH and the formula should be written FeO·OH, since there are no H<sub>2</sub>O groups in the cryst. structure. Infra-red absorption spectra confirm this by showing only the presence of OH (A., 1933, 13). On dehydration (II) gives, without change of cryst. form, a stable Fe<sub>2</sub>O<sub>3</sub> which is composed of an assemblage of crystallites of hæmatite oriented at 180° to each other.

By heating a mixture of FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> at 350° in a sealed tube for 2—3 weeks larger crystals (d 3.55) of FeOCl are formed. They readily show perfect parallel cleavage and are flexible but not elastic. Their at. structure is discussed (cf. A., 1934, 351). On hydrolysis with warm H<sub>2</sub>O, Cl' is replaced by OH', and (III) is formed without loss of external form or of transparency, indicating that the structure of (III) resembles that of FeOCl. X-Ray examination of (III) confirms this. As in the case of (II) the structural unit is FeO-OH, but the at. arrangement is different.

Lepidocrocite from Siegen has a 3.87, b 12.4, c 3.06 Å., d 3.95, with 4Fe, 4O, and 4OH in the unit cell. The at. arrangement is discussed. Rapid dehydration gives a product with a Debye-Scherrer diagram similar to that of magnetite, whilst that from slow dehydration gives the hæmatite diagram. Both products are magnetic. L. S. T.

Growth of crystals. V. (Supplement.) T. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 497–498).—Sn" ions promote the growth of NaCl crystals in presence of  $\geq 0.004$  mol. ion per 1 mol. NaCl. Large, clear cubes grow in its presence. W. R. A.

Growth of crystals. VII. Influence of cations in the solution on the crystal growth of potassium salts. T. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 499—506).—Influence of cations on the crystal growth of KI,  $K_2SO_4$ ,  $KNO_3$ , and  $KCIO_3$  was studied under the microscope. Except for  $KCIO_3$ , cations which promoted crystal growth were found and are discussed. W. R. A.

Lattice parameters of solid solutions in silver. W. HUME-ROTHERY (Nature, 1935, 135, 1038).— In dil. solid solutions of Cd, In, Sn, or Sb in Ag, alloys of the same equiv. composition (at.-% of solute element  $\times$  valency) have identical lattice parameters. The initial expansion of the Ag lattice produced by an atom of the above elements  $\infty$  the valency. The relation is of the same type as that found for the depression of the f.p. of Ag, and may indicate an effect which  $\infty$  the repulsion between a solute and a solvent ion. L. S. T.

Effect of temperature on cathode-ray interference. H. KAKESITA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 31—35).—With a single crystal of FeS<sub>2</sub> the interference max. are more diffused at 220° than at 25°. With Au foil at 28°, 150°, and 320° the intensity effect increases with the angle of reflexion and with rising temp. E. S. H.

Melting of metal crystals at their boundaries and a theory of recrystallisation of metals. U. YOSHIDA and K. KOYANAGI (Mem. Coll. Sci. Kyoto, 1935, A, 18, 9—16).—When heated to a temp. just below its normal m.p., a metal begins to melt at the crystal boundaries, which become grooved. This is probably due to more rapid evaporation at the crystal boundaries than elsewhere. A crystal also appears to melt more easily where it comes into contact with its melt, and when distorted. A theory of recrystallisation of metals is based on these facts. A. J. M.

Lattice distortion in nickel-iron. W. G. BUR-GERS (Nature, 1935, 135, 1037-1038).—X-Ray diffraction photographs of a Ni-Fe alloy (53 at.-% Fe) distorted by cold working show that compression and stretching change the shape and possibly the size of the unit cell. L. S. T.

Mechanism of the transition in ammonium salts at  $-40^{\circ}$ . J. A. A. KETELAAR (Chem. Weekblad, 1935, 32, 349—350).—Differences observed in the X-ray diagrams of NH<sub>4</sub>Br and NH<sub>4</sub>I are due to change of oscillation in the NH<sub>4</sub> group into rotation. S. C.

Atomic distribution in red and black phosphorus and the crystal structure of black phosphorus. R. HULTGREN, N. S. GINGRICH, and B. E. WARREN (J. Chem. Physics, 1935, 3, 351–355).—Five samples of black P of widely varying age gave identical powder patterns. A sample prepared at room temp. and 35,000 atm. gave the diffuse rings of an "amorphous" X-ray pattern. Another sample, prepared at 300° and 8000 atm., is a new form of P, having the same density as black. At. distribution curves of cryst. and "amorphous" black and red P were practically identical, showing three neighbours of 2.28 Å. and about 12 at 3.6 Å. The structure of black P shows double layers; the cell is side-centred orthorhombic, a 3.31, b 4.38, c 10.50 Å.; 8 atoms per unit cell;  $d_{catc.}$  2.69,  $d_{obs.}$  2.70; space-group  $V_h^{s}$ -Bmab. N. M. B.

Orientation of the crystallites in cast nickel and the changes produced by rolling and recrystallisation. G. TAMMANN and F. LAASS (Z. Metallk., 1935, 27, 86–88).—The crystal orientation in cast Ni and in recryst. rolled Ni sheet is similar to that of Al, in that octahedral planes lie against the cooling surfaces of the casting and in the rolling plane of the annealed sheet. A. R. P.

Molecular arrangement in amorphous antimony. J. A. PRINS (Chem. Weekblad, 1935, 32, 348—349).—Amorphous Sb prepared by electrolysis of SbCl<sub>3</sub> contains occluded SbCl<sub>3</sub>, which keeps the metal in a "dispersed" form. It can be produced in thin layers by distillation in a high vac., but thick layers (< 1000 mµ) crystallise immediately. The electron diffraction pattern corresponds with an at. arrangement similar to that in cryst. Sb, of co-ordination no. 6. S. C.

Crystalline structure of electrolytic white tin. H. HIBATA and Y. TANAKA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 143—152).—X-Ray examination. Sn deposited from a solution of  $SnSO_4$ ,  $H_2SO_4$ , and  $Na_2SO_4$ consists of micro-crystals arranged with the normals to their (111) planes in a common direction, perpendicular to the direction of max. growth of the deposited Sn. Patterns corresponding with two crystals, with one of the (101) planes in common, were detected.

#### E.S.H.

Copper amalgam CuHg with the  $\gamma$ -brass structure. F. SCHOSZBERGER (Z. physikal. Chem., 1935, B, 29, 65—78).—The cubic crystals have a  $9.406 \pm$ 0.004 Å. Hume-Rothery's rule does not hold. If it is attempted to assign to the Cu and Hg atoms a similar arrangement to that in  $\gamma$ -Cu<sub>5</sub>Cd<sub>8</sub> there appear discrepancies between observed and calc. intensities which are present, although less pronounced, in the  $\gamma$ -structures of Cu–Zn and Cu–Cd. R. C.

Structure of the intermetallic compound  $Au_2Pb$ . H. PERLITZ (Acta Comm. Univ. Tartuensis, 1934, 27, No. 11, 12 pp.; Chem. Zentr., 1935, i, 783).— The lattice is face-centred cubic (a 7.91 Å.; 24 atoms in unit cell). Au<sub>2</sub>Pb is related to MgCu<sub>2</sub> and KBi<sub>2</sub>.

H. J. Ĕ.

X-Ray examination of selenium crystals. K. TANAKA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 59-78).— "Metallic" Se has  $a \cdot 360$  Å. and  $c/a \cdot 138$ ; 3 atoms in unit cell; growth occurs most prominently along the trigonal axis. Vitreous and amorphous Se give the same diffraction band and are transformed into the metallic form when annealed at suitable temp. The transition temp., about 74°, has been determined by X-ray examination and confirmed by determinations of d. E. S. H.

Phosphides and arsenides with modified nickel arsenide structure. K. E. FYLKING (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 18, 6 pp.).—Mn, Fe, and Co phosphides and arsenides, prepared by heating the elements in equal mol. proportions for  $\leq$  a day at 610° (for P) or 730° (for As), have lattice structures closely related to that of NiAs, but the metal atoms form zigzag chains instead of straight rows. MnAs differs less from NiAs than FeAs and CoAs. The lattice dimensions of these compounds and parameter vals. for MnP and FeAs are recorded. J. W. S.

Crystal structure of magnetic ferric oxide,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. G. HÄGG (Z. physikal. Chem., 1935, B, 29, 95—103).—If Fe<sub>3</sub>O<sub>4</sub> is oxidised to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at 300° without losing the spinel structure, the length of the edge of the unit cube of the lattice changes continuously from 8.380 for Fe<sub>3</sub>O<sub>4</sub> to 8.322 Å. for Fe<sub>2</sub>O<sub>3</sub>. The increase in O concn. during oxidation is caused by the appearance of unoccupied positions in the Fe atom lattice of the spinel phase; in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> one ninth of the original Fe atom positions are empty. Thewlis' lattice structure for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (A., 1932, 113) is rejected. The belief that  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can be reduced to Fe<sub>3</sub>O<sub>4</sub> by heating at 250° in a vac. (A., 1932, 29) is erroneous. R. C. Crystal structure of the aluminium halides. II. Crystal structure of AlCl<sub>3</sub>. J. A. A. KETE-LAAR (Z. Krist., 1935, 90, 237—255).—AlCl<sub>3</sub> is monoclinic pseudohexagonal,  $a_0$  5·91,  $b_0$  10·24,  $c_0$  6·16 Å.,  $\beta$  71° 21', space-group  $C_2^3$ . The lattice is essentially of layer type, Al<sub>2</sub>Cl<sub>6</sub> being the mol. unit. The structure found from detailed intensity measurement does not agree with previous results (cf. A., 1930, 1503). B. W. R.

Crystal structure of bismuth oxyhalides. F. A. BANNISTER [with M. H. HEY] (Min. Mag., 1935, 24, 49—58).—Minute crystals of BiOCl, BiOBr, and BiOI were prepared by diffusion of solutions  $\operatorname{BiCl}_3$  + HCl etc. into water. They are tetragonal with the same structure as matlockite, BiFCl (A., 1934, 1197). The unit cell contains 2 mols. and has dimensions : for BiOCl, a 3.89, c 7.37 (d 7.717); BiOBr, a 3.92, c 8.11 (d 8.082); BiOI, a 4.01, c 9.14 (d 7.922). The minerals bismoclite (BiOCl) and daubreelite (BiO[OH,Cl]) have a 3.89, c 7.37, and a 3.85, c 7.40 Å., respectively. L. J. S.

Crystal structure of some ammines of the type  $M(NH_3)_2Cl_2$ . C. A. MACGILLAVRY (Chem. Weekblad, 1935, 32, 346—347).—Compounds like  $MX_2,2NH_3$  (M=Hg, Zn, Cd; X=Cl, Br) and  $CuCl_2,2H_2O$  are all of centred lattice type of halogens and  $NH_3$  (unit cell  $4 \times 4 \times 4 \text{ Å}$ .);  $Hg(NH_3)_2Cl_2$  is peculiar in that its X-ray diagram is practically identical with that of Ag. The Cd compounds have a tetragonal twin structure, giving rhombic X-ray diagrams. S. C.

X-Ray study of the cæsium salts of certain 12-heteropoly acids. J. A. SANTOS (Proc. Roy. Soc., 1935, A, 150, 309—322).—The structures of the Cs salts of 12-phospho-, 12-silico-, 12-boro-, and metatungstic acids  $(H_3PW_{12}O_{40},5H_2O, H_4SiW_{12}O_{40},5H_2O, H_5BW_{12}O_{40},5H_2O, and H_6H_2W_{12}O_{40},5H_2O)$  have been studied (cf. A., 1934, 479, 1296). In each case, the Cs salts contained only 3 Cs atoms per mol., and all attempts to prepare salts with > 3 Cs atoms failed. The formulæ deduced are:  $Cs_3PW_{12}O_{40},nH_2O$ ,  $Cs_3H_3W_{12}O_{40},nH_2O$ ,  $Cs_3H_2BW_{12}O_{40},nH_2O$ , and  $Cs_3H_3H_2W_{12}O_{40},nH_2O$ , where n=2 or 0. Corresponding Rb and Tl salts have been prepared, and found to have similar structures. L. B.

Planar structure of quadricovalent cupric compounds. E. G. Cox and K. C. WEBSTER (J.C.S., 1935, 731—733).—Cu disalicylaldoxime has been prepared, and analogy with previously reported compounds (cf. this vol., 684) suggests a planar structure. X-Ray investigation of the cryst. Cu salts of  $CH_2Ac_2$ ,  $CH_2BZAc$ ,  $CH_2(COEt)_2$ , and  $\gamma$ -chloroacetylacetone established their planar configuration by means of space-group considerations, cell dimensions, and optical properties. N. M. B.

Crystal structures of magnesium-aluminium spinels with alumina in excess and of  $\gamma$ -alumina. G. HÄGG and G. SÖDERHOLM (Z. physikal. Chem., 1935, B, 29, 88—94).—The *d* of these spinels indicate that the excess of O is caused by the appearance of unoccupied positions in the metal lattices, the ratio Al : Mg increasing parallel with the excess of O. The edge of the unit cube of MgO,Al<sub>2</sub>O<sub>3</sub> is 8.056 Å. The upper limit of Al<sub>2</sub>O<sub>3</sub> in the stable solid solutions is about 67 mol.-%, whilst the unstable limit is to be regarded as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This latter crystallises in the spinel lattice, cube edge 7.843 Å., but one ninth of the metal atom positions are empty. R. C.

Non-silicates with cristobalite-like structure. T. F. W. BARTH (J. Chem. Physics, 1935, 3, 323— 325).—The cristobalite type of structure is shown to occur in K<sub>2</sub>O,Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O,Fe<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O,Al<sub>2</sub>O<sub>3</sub>. N. M. B.

Crystal structure of the guanidonium halides. III. Structure of guanidonium bromide  $C(NH_2)_3Br$ . W. THELLACKER (Z. Krist., 1935, 90, 256-272).---C(NH<sub>2</sub>)<sub>3</sub>Br is rhombic bipyramidal,  $a_0$  $6.77, b_0$  8.64,  $c_0$  8.30 Å.; 4 mols. in cell; space-group  $V_h^{16}$ . The double refraction of the substance is considered and a set of at. parameters is obtained; the guanidonium ions have their planes parallel to the aaxis and mutually perpendicular. B. W. R.

X-Ray diffraction in some long-chain aliphatic liquids. J. A. PRINS and R. FONTEYNE (Physica, 1935, 2, 573—574).—The strongly polar mols., alcohols and aliphatic acids, show a more conspicuous "inner ring" than other normal long-chain aliphatic compounds. The spacing in the diffraction pattern of cork is 4.4 Å. and not 4.1 Å., as given previously (A., 1934, 948). M. S. B.

The odd-membered *n*-primary alcohols (the  $\alpha \rightarrow \beta$  transition). T. MALKIN (J.C.S., 1935, 726).— The  $\beta$ -forms of the C<sub>15</sub>, C<sub>17</sub>, and C<sub>19</sub> *n*-primary alcohols give two main side spacings (3.7 and 4.2 Å.), whereas the  $\alpha$ -forms give only one (4.2 Å.). Further, the  $\alpha$ -forms are uniaxial, the  $\beta$ -forms are biaxial. These results accord with the view of Wilson *et al.* (A., 1934, 720) that the  $\alpha \rightarrow \beta$  change is due to a change from a vertical rotating ( $\alpha$ ) form to a vertical non-rotating ( $\beta$ ) form. The conclusion of Phillips and Mumford (cf. this vol., 20) that the odd alcohols above C<sub>14</sub> exist in a  $\beta$ -tilted form is not valid.

H. G. M.

Molecular structure and crystal symmetry. Fine structure of triethyl 1:3:5-benzenetricarboxylate. E. HERTEL and E. DUMONT (Z. physikal. Chem., 1935, B, 29, 112—116).—The hexagonal unit cell has  $I_a$  11·3,  $I_c$  20·1 Å. and contains 6 mols. Some crystals have the space-group  $C_{\theta}^2$ , others  $C_{\theta}^3$ , the two species differing in the sense of the twist of the helicohexagyres determining the crystal structure. Although the symmetry of the mol. is  $C_1$  its triangular shape is probably responsible for the mol. arrangement in the crystal. R. C.

Difference in X-ray diffraction patterns of some isomerides. Z. MURO (Mem. Coll. Sci. Kyoto, 1935, A, 18, 79-82).—X-Ray diffraction patterns of d- and l-pinene and -limonene, and of isomerides of the mol. formula  $C_{10}H_{16}$ ,  $C_{10}H_{16}$ ,  $C_{10}H_{18}$ ,  $C_{10}H_{12}O_2$ , and  $C_{10}H_{10}O_2$  were examined. With optical isomerides there is no difference in the form of the pattern, nor in the val. of the distance (d) between the planes. With ordinary isomerides there is a diminution of d accompanied by an increase of diffuseness of the pattern on passing from the normal to the *iso*-compound. In all cases, rise of temp. results in diminution of d and increase of diffuseness. A. J. M. **Crystal structure of** *p*-toluidine. J. WYART (Compt. rend., 1935, 200, 1862—1864).—The crystals are orthorhombic (a 5.98, b 9.05, c 23.3 Å.; 8 mols. in unit cell; space-group  $D_{28}^{16}$ ). The 6 atoms in the nucleus form a regular hexagon of side 1.40 Å. The NH<sub>2</sub> is 1.18 Å. from the C, the C·N linking making an angle of 15° with the plane of the nucleus. This angle for the C·Me linking is 16°, the C—Me distance being 1.48 Å. H. J. E.

Structure of benzoquinone. Quantitative Xray investigation. J. M. ROBERTSON (Proc. Roy. Soc., 1935, A, 150, 106-128).—The crystal is monoclinic, space-group  $P2_1/a$  with 2 centro-symmetrical mols. per unit cell. The planar mols. are nearly parallel and lie almost in the (201) plane. The ring is not a regular hexagon; the C—C distance is about 1.5 Å., C=C about 1.32 Å., and C=O about 1.14 Å. The internal ring angle between single C linkings is 109°, and between double and single linkings 125°. The min. intermol. distance between O atoms is 3.62 Å. between O and C 3.36 Å., and between C and C 3.44 Å. L. B.

X-Ray analysis of the structure of dibenzyl. II. Fourier analysis. J. M. ROBERTSON (Proc. Roy. Soc., 1935, A, 150, 348—362; cf. A., 1934, 1297).—The experimentally determined structure factors for three zones of reflexions have been subjected to a double Fourier analysis. The results indicate that the regular three-dimensional model must be slightly modified, the planes of the C<sub>6</sub> rings being apparently turned 13—16° out of the symmetrical position. The C<sub>6</sub> rings are regular plane hexagon structures. The distance between aromatic C atoms is 1.41 Å., between aromatic C and aliphatic CH<sub>2</sub> 1.47 Å., between the two CH<sub>2</sub> groups 1.58 Å. The angle between the linkings of the CH<sub>2</sub> group is  $109.2-112^{\circ}$ . The min. intermol. distance between aromatic and aliphatic C atoms is 4.10 Å., between aromatic C atoms 3.68 Å. L. L. B.

X-Ray investigation of the crystal structure of *m*-azotoluene. M. PRASAD and P. H. DALAL (Indian J. Physics, 1935, 9, 319–321).—a:b:c=0.8581:1:0.5469;4 mols. in unit cell. A. J. M.

Unidimensional change of the crystal lattice in passing from veronal to dial. E. HERTEL (Z. physikal. Chem., 1935, **B**, 29, 117—120).—The monoclinic crystals of dial have  $I_a$  14.5,  $I_b$  7.1,  $I_c$  21 Å.,  $\beta$  100°, 8 mols. in unit cell, translation group  $\Gamma'_m$ . The monoclinic pseudorhombic crystals of veronal have  $I_a$  14.4,  $I_b$  7.1,  $I_c$  9.7 Å.,  $\beta$  90°, 4 mols. in unit cell, translation group  $\Gamma'_m$ . In the change from veronal to dial the lattice alters in one direction. R. C.

X-Ray crystallography of the toad poisons, bufagin and cinobufagin, and of strophanthidin. (MISS) D. CROWFOOT (Chem. and Ind., 1935, 568— 569).—Data are recorded for bufagin, +EtOH (I), cinobufagin (II), and the A (III) and B (IV) forms of strophanthidin. These confirm the accepted formula for (I), if the *b* axis is the  $\alpha$  optical direction (the reversal compared with the sterol group probably being due to the *tert*.-OH) and the EtOH of crystallisation lies between the ends of the mols. Data for (II) are inconclusive, but suggest a formula C<sub>26</sub>H<sub>34</sub>O<sub>6</sub>. Results for (III) cannot be interpreted owing to decomp., but for (IV) confirm the formula  $C_{23}H_{32}O_6$ ,  $+0.5H_2O$ . R. S. C.

X-Ray study of the hydration and denaturation of proteins. W. T. ASTBURY and R. LOMAX (J.C.S., 1935, 846-851).-X-Ray photographs of ordinary and boiled egg-white, serum-albumin, pepsin, trypsin, zein, casein, tobacco-seed and squash-seed globulin, and edestin from hemp seed, both dry and after adsorption of H2O or EtOH, show inner and outer rings associated, respectively, with side-chain and backbone spacing of polypeptide chains; where spacing changes occur, due to adsorption, the side-chain spacing increases most, and the backbone spacing is almost unchanged. Denaturation by heat results in a sharpening of the backbone reflexion and the appearance of at least one other outer ring indicating a development of a common structural scheme. Results, in general, point to a scheme of crystallites built of parallel, fully-extended polypeptide chains, between which are the principal cross-linkings. N. M. B.

X-Ray diffraction pattern of native cellulose. U. YOSHIDA and C. PARK (Mem. Coll. Sci. Kyoto, 1934, A, 17, 443—447).—The unit cell is monoclinic and contains  $4 C_6 H_{10} O_5$  groups. E. S. H.

Application of X-rays in the investigation of cellulose and its derivatives, with special reference to reaction mechanism. K. HESS and C. TROGUS (Ergebn. tech. Röntgenk., 1934, 4, 21-68; Chem. Zentr., 1935, i, 707-708).—A lecture.

H. N. R.

Structure of liquid and solid mercury studied by cathode-ray diffraction. III. Temperature effect. H. KARESITA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 241–248; cf. this vol., 919).—The patterns of solid and liquid Hg show a face-centred rhombohedral structure. The rings for solid Hg are 10% > those for liquid Hg. E. S. H.

Preparation of thin single crystals of silver and their investigation with electron beams. L. ROYER (Ann. Physik, 1935, [v], 23, 16—17).— The orientation of Ag single crystals formed on a rocksalt base given by Lassen and Brück (this vol., 286) is questioned. The data there given do not agree with the fact that parallel planes in the two crystal lattices should possess approx. equal parameters. A. J. M.

Preparation of thin single crystals of silver and their investigation with electron beams. H. LASSEN and L. BRÜCK (Ann. Physik, 1935, [v], 23, 18—20).—The results of Royer (preceding abstract) are based on the deposition of crystals from solution, the conditions being therefore not comparable with those obtaining in the authors' previous work (this vol., 286). The orientation there described is re-affirmed. A. J. M.

Investigation of effect of oxygen on graphite at high temperatures by means of electron diffraction. H. BOERSCH and L. MEYER (Z. physikal. Chem., 1935, B, 29, 59-64).—Measurements with C filaments coated with graphite show that in the dissolution of O in graphite at high temp. the layer lattice stretches along the c axis like a concertina (cf. A., 1932, 816). R. C. Heat effects in the transformations of cobalt. H. VON STEINWEHR and A. SCHULZE (Z. Metallk., 1935, 27, 90—92).—From measurements made on a 20-kg. cylinder of Co containing Cu 0.24, Fe 1.6, and C 0.007% the heat evolution in the  $\alpha$ - $\beta$  transformation, which extends from 380° to 420°, has been determined as 0.1±0.03 g.-cal. per g. The magnetic change occurs in the range 1070—1125° with heat evolution of 1.2 g.-cal. per g. A. R. P.

Gyromagnetic effect of some ferromagnetic compounds. D. P. R. CHAUDHURI (Indian J. Physics, 1935, 9, 383-414).—The ratio of angular momentum to magnetic moment (g-ratio) of the elementary carriers of ferromagnetism has been determined by the resonance method for  $\text{Fe}_3O_4$ ,  $\text{Fe}_2O_3$ , NiO,  $\text{Fe}_2O_3$ , CuO,  $\text{Fe}_2O_3$ , MnO,  $\text{Fe}_2O_3$ , and 2ZnO,  $3\text{Fe}_2O_3$ . g is in each case < 2, the theoretical val. for the spinning electron, and this is probably due to the fact that the *l*-moment (orbital moment) also enters into ferromagnetic phenomena. A. J. M.

Chemielectric Curie point effect analogous to magnetochemical. J. A. HEDVALL and R. W. PAULY (Z. physikal. Chem., 1935, B, 29, 225-230).— A Curie temp. of 22·0-22·3° is deduced for Na K tartrate from observations on the dissolution relations in EtOH, which change abruptly at this temp. (cf. this vol., 153). R. C.

Influence of mechanical vibrations on the subsequent manifestations of magnetic viscosity. A. V. MITKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 25—29).—The effect of mechanical vibration favours the hypothesis that magnetic viscosity is due to an unstable magnetic state rather than to eddy current effect. A. B. D. C.

Temperature variation of conical indentation hardness of metals. I. J. ENGL and G. HEIDT-KAMP (Z. Physik, 1935, 95, 30-41).—The hardness of mono- and poly-cryst. Cu was determined to 1900° using cones of synthetic corundum crystals.

A. B. D. C.

Young's modulus of aluminium rod composed of large crystal grains. M. SUGIHARA (Mem. Coll. Sci., Kyoto, 1935, 17, 389—396).—Young's modulus of Al rods composed of crystal grains of various sizes has been measured by elongation and by acoustical vibration methods. Whilst the limit of elasticity decreased with size of crystal grain, the modulus remained almost const. W. R. A.

Heat evolved in metallic transformations. III. Iron. H. VON STEINWEHR and A. SCHULZE (Physikal. Z., 1935, 36, 419–423; cf. A., 1934, 725; this vol., 704).—The heat evolved in the magnetic (A2) transformation of Fe (99.97%) is  $4.8\pm0.2$ g.-cal. per g. It takes place over the range 710–790°. The heat evolved in the allotropic (A3) change is  $6.2\pm0.08$  g.-cal. per g. A. J. M.

Twinning in  $\alpha$ -iron. H. O'NEILL (Nature, 1935, 135, 1076-1077).—Attention is directed to prior reports of twinning in  $\alpha$ -Fe (cf. this vol., 811). The greater ductility of mild steel tinplate when cold-rolled and annealed over that which has been hot-rolled and normalised may be due to the more highly

twinned structure probably produced by the former process. L. S. T.

"Recovery" of metals and recrystallisation phenomena in aluminium single crystals. N. J. SELJAKOV and E. I. Sovz (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 125-133).—The "recovery" process produces in single crystals marked changes in the intensity distribution of certain spots on the X-ray plate accompanied with an enhanced definition of the spots. The deformation of the crystals is discussed. W. R. A.

Rotational dispersion of sound in hydrogen. A. S. Roy and M. E. Rose (Proc. Roy. Soc., 1935, A, 149, 511—522).—No variation of the velocity of sound in  $H_2$  is found below frequencies of the order of 10<sup>6</sup> cycles per sec., as predicted by the classical kinetic theory of Jeans, and by the quantum treatment of the inelastic collision between two  $H_2$  mols.

### L. L. B.

Thermo-electric power of the alkali metals in the solid and liquid state, with respect to platinum. E. HEIBER (Ann. Physik, 1935, [v], 23, 111— 136).—The thermo-electric power of Li, Na, K, Rb, and Cs was determined for the solid and liquid elements (Li, solid only). Li and Cs are thermoelectrically positive, the others negative, with respect to Pt. dE/dT shows a jump at the m.p. which is greatest for Cs and Rb, but is within the limit of experimental error for Na and Li. A. J. M.

Effect of a magnetic field on thermal conductivity and viscosity of paramagnetic gases. M. von LAUE (Ann. Physik, 1935, [v], 23, 1—15).— Theoretical. There is no simple connexion between the effect of a magnetic field on these properties of paramagnetic gases. A. J. M.

Influence of an electric field on the thermal conductivity of a solid. G. GROETZINGER (Nature, 1935, 135, 1001).—After solidification in an electric field bees-wax permanently shows a greater thermal conductivity in the direction of the field. Application of an alternating field of 50 cycles produces no such effect. L. S. T.

Thermal conductivity of polyatomic gases. Erratum. A. R. UBBELOHDE (J. Chem. Physics, 1935, 3, 362; cf. this vol., 691).—A correction.

N. M. B.

Direct influence of light on the electrical resistance of metals. A. ETZRODT (Physikal. Z., 1935, 36, 433—441).—The increase in resistance of metals on illumination, reported by Majorana (A., 1932, 898, 1189; 1933, 353, 584; 1934, 114, 555) and assumed to be due to a thermal effect and an inner photo-electric effect, was investigated. It is not possible completely to separate these effects by cooling and increasing the frequency of the incident radiation, but if the temp. coeff. of the resistance is zero, thermal effects should disappear. The effect of temp. on the sp. resistance of wires composed of single crystals of Bi, and of constantan, and the temp. for which temp. coeff. is zero were determined. Parallel determinations of resistance and the Majorana effect showed that the total effect completely disappeared at temp. at which the temp. coeff. is zero; the Majorana effect is thus a thermal effect. A. J. M.

Electrical conductivity of mixed metallic phases at low temperatures (Cu-Pt alloys). H. J. SEEMANN (Z. Physik, 1935, 95, 97–101).— Sp. resistances were measured for Cu-Pt alloys of 70 and 75 at.-% Pt; that at room temp. decreases on tempering at 400—550° due to formation of an ordered cubic structure. Sp. resistance-temp. curves for the 75% alloy are similar to those for Cu<sub>3</sub>Pt, but those for the 70% alloy show anomalies probably due to ferromagnetism. A. B. D. C.

Magnetic properties and critical currents of superconducting alloys. G. N. RJABININ and L. V. SHUBNIKOV (Nature, 1935, 135, 581-582).--Pb-Tl and Pb-Bi alloys lose their superconductivity at low temp. when the magnetic field strength is above a certain val. W. P. R.

Magnetic susceptibility of water and the influence of dissolved salts. B. CABRERA and H. FAHLENBRACH (Anal. Fis. Quim., 1934, 32, 525-537). —The magnetic susceptibility ( $\chi$ ) of H<sub>2</sub>O above 100° is const. at 0.727 ×10<sup>-3</sup>. The variation with temp. below 100° is discussed. The variation of  $\chi$  for KI solutions is due to depolymerisation of the H<sub>2</sub>O and to the deformation of the K' and I' ions under the dipolar action of the H<sub>2</sub>O (hydration effect).

J. W. S.

Diamagnetism of heavy water in the liquid and solid states. B. CABRERA and H. FAHLEN-BRACH (Anal. Fis. Quim., 1934, 32, 538—542).—The general magneto-thermal behaviour of heavy water  $(>99\% D_2O)$  is similar to that of ordinary H<sub>2</sub>O, but the mol. susceptibility, its temp. coeff., and its change with change of state differ in the two cases.

J. W. S.

Cobalt, nickel, and copper complexes of the amides and imides : magneto-chemical studies. L. CAMBI and E. TREMOLADA (Gazzetta, 1935, 65, 322—338).—The structure of many complex compounds of Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> containing amide and imide groups is discussed. Magnetic susceptibility data are recorded. O. J. W.

Diamagnetism of primary alcohols and other organic compounds. B. CABRERA and H. FAHLEN-BRACH (Anal. Fís. Quim., 1934, 32, 543—566).—The magnetic susceptibilities ( $\gamma$ ) of primary alcohols to  $C_{16}H_{33}$ ·OH,  $C_{6}H_{14}$ ,  $C_{6}H_{6}$ , PhNO<sub>2</sub>, AcOH, sec.-BuOH, o-, m-, and p-cresol,  $C_{6}H_{4}$ Me·NO<sub>2</sub>, and p-C<sub>6</sub>H<sub>4</sub>Cl·OH have been measured at various temp. in a "Uviol" glass tube. Like H<sub>2</sub>O, alcohols show an abrupt change of  $\chi$  at the m.p., and on each side of the m.p. there is a temp. range over which  $\chi$  varies considerably with temp. The change in  $\chi$  at the m.p. is related to the electric moment of the mol. The results are discussed with reference to Pascal's additivity theory.

J. W. S.

Magnetic properties of the phenanthroline ferric complexes. G. H. WALDEN, L. P. HAMMETT, and A. GAINES, jun. (J. Chem. Physics, 1935, 3, 364).— The at. susceptibility of the Fe atom in the blue complex  $Fe(C_{12}H_8N_2)_3^{+++}$  obtained only by oxidation of the Fe<sup>II</sup> complex, and in the solid brown salt,  $[Fe(C_{12}H_8N_2)_2(H_2O)(OH)]Cl_2$  obtained by direct interaction of Fe<sup>111</sup> salts and phenanthroline, is  $2446 \times 10^{-6}$ and  $826 \times 10^{-6}$ , respectively. The low val., 1.4 Bohr magnetons, for the magnetic moment in the latter case is attributed to the existence in the single mol. grouping of two or more Fe atoms so oriented that their moments partly neutralise each other. N. M. B.

Determination of the difference of the principal susceptibilities of some rare-earth ethyl sulphates. R. A. FEREDAY and E. C. WIERSMA (Physica, 1935, 2, 575-581).—The differences between the two principal susceptibilities ( $\chi$ ) of the hexagonal crystals of the Et sulphates of Ce, Nd, Pr, and Er have been determined. For Ce, Nd, and Er, which have an odd no. of electrons in the ion, the higher val. of  $\chi$ is along the principal axis and the difference increases rapidly as the temp. falls. Pr has an even no. of electrons in the ion and, at room temp.,  $\chi$  is still the higher along the principal axis. The difference diminishes with fall of temp., and equality is reached at 130° abs.; at lower temp.  $\chi$  along the binary axis becomes the higher. M. S. B.

Magne-crystallic action. III. Organic crystals. K. S. KRISHNAN and S. BANERJEE (Phil. Trans., 1935, A, 234, 265—298; cf. A., 1933, 340).— Using a new method of measuring magnetic anisotropies adaptable to crystals < 1 mg., the principal susceptibilities of 29 org. crystals are tabulated. Mol. orientations in the crystal lattice deduced from the magne-crystallic data agree, in general, with X-ray determinations. The principal susceptibilities of 28 individual mols. are tabulated. N. M. B.

Magnetic susceptibilities of very small crystals. K. S. KRISHNAN and S. BANERJEE (Current Sci., 1935, 3, 548).—The susceptibility of crystals > 0.1 mg. can be determined from their behaviour in a mixture of dia- and para-magnetic solutions.

A. B. D. C.

Magnetochemical investigations. XIV. Magnetic behaviour of some heavy metal compounds of the phthalocyanines. L. KLEMM and W. KLEMM (J. pr. Chem., 1935, [ii], 143, 82–89; cf. this vol., 436).—The magnetic susceptibilities of Ni, Co, Fe, Cu, Zn, Mn, and Mg phthalocyanines have been determined and compared with vals. calc. for at. and ionic linkings. At. linkings can be identified in the case of the Ni, Co, and Fe compounds. The chemical stability of the Cu and Zn compounds indicates a similar structure. Specimens of the Mn and Mg compounds were not sufficiently pure to yield decisive magnetic data, but the replacement of the metal by treatment with  $H_2SO_4$  indicates ionic linkings. R. S.

Rotational heat of ortho-deuterium. K. CLU-SIUS and E. BARTHOLOMÉ (Z. physikal. Chem., 1935, B, 29, 162—169; cf. this vol., 573).—An apparatus for the prep. of o-D<sub>2</sub> is described. The rotational heat at 35—106° abs. has been measured. R. C.

Specific heat of liquid helium. W. H. KEESOM and (MISS) A. P. KEESOM (Physica, 1935, 2, 557— 569, and Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 490).—Sp. heat measurements of He, including measurements under the saturated v.p., have been made (cf. A., 1933, 16). The large change in sp. heat at the  $\lambda$ -point occurs abruptly or in a temp. interval probably  $< 0.0002^{\circ}$ . The absence of latent heat at  $\lambda$ -point is confirmed, but it is difficult to determine here the exact val. of the sp. heat jump; it is probably > is shown by experiment. It is suggested that the  $\lambda$ -transition depends on the interaction between neighbouring atoms. The heat conductivity of He also appears to change abruptly at  $\lambda$ -point. M. S. B.

Atomic heat of nickel from  $1.1^{\circ}$  to  $19.0^{\circ}$  abs. W. H. KEESOM and C. W. CLARK (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 490—491, and Physica, 1935, **2**, 513—520; cf. this vol., 574).—The at. heat > the heat capacity due to the at. lattice as calc. from Debye's law, is > the contribution due to the interaction energy of the ferromagnetism electrons, and is probably connected with the energy of the conduction electrons. N. M. B.

Exact measurement of the specific heats of solid substances at higher temperatures. XVIII. Use of Dewar vacuum vessels in the metal block calorimeter for the control of the cooling rate. F. M. JAEGER, R. FONTEYNE, and E. ROSENBOHM. XIX. Specific heats of zinc, magnesium, and their binary alloy MgZn<sub>2</sub>. T. J. POPPEMA and F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 502—509, 510—520). —XVIII. Difficulties arising from the use of Dewar vessels and precautions necessary for their elimination are discussed.

XIX. Sp. heat data are tabulated for Zn,  $100-360^{\circ}$ , Mg,  $100-550^{\circ}$ , and MgZn<sub>2</sub>,  $100-500^{\circ}$ . Mol. heats of MgZn<sub>2</sub> are in fair agreement with the additive law, but divergences increase with rise of temp. N. M. B.

Low-temperature specific heats. V. Heat capacity of tricalcium phosphate between 15° and 298° abs. J. C. SOUTHARD and R. T. MILNER (J. Amer. Chem. Soc., 1935, 57, 983—984; cf. A., 1934, 135).—Data are recorded for the  $\alpha$  and  $\beta$  forms of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. E. S. H.

Purification and physical properties of organic compounds. VI. Applications and limitations of the specific heat method as a "non-comparative criterion of purity." E. L. SKAU (J. Physical Chem., 1935, 39, 541-544).—Although it is probable that a given compound is pure if the val. of  $(C_p)_{solid}$ increases almost linearly with rise of temp., and is >that of  $(C_p)_{\text{liquid}}$  at the f.p. (cf. A., 1934, 836, 1085), both true and apparent exceptions exist. The former include all the cases of impure samples where the change from the liquid to the solid state takes place completely at const. temp., e.g., a eutectic mixture. The latter are the cases in which the change from the liquid to the solid state takes place over a temp. range which lies completely above the highest temp. for which sp. heat data have been determined. M. S. B.

Heat capacity and v.p. of solid and liquid nitrous oxide. Entropy from its band spectrum. R. W. BLUE and W. F. GIAUQUE (J. Amer. Chem. Soc., 1935, 57, 991—997).—The heat capacity of N<sub>2</sub>O has been determined between 14° abs. and the b.p. Data are m.p. 182·26° abs., b.p. 184·59° abs., heat of fusion 1563 g.-cal. per mol., heat of vaporisation at b.p. 3958 g.-cal. per mol., v.p. of solid (148·48182.26° abs.)  $\log_{10} P = -(1286/T) + 9.13061 - 0.0014038T$ , v.p. of liquid (182.26 - 185.85° abs.)  $\log_{10} P = -(893.56/T) + 6.72158$ . The calc. mol. entropy of the gas at the b.p. is  $47.36 \pm 0.1$  e.u., which is 1.14 units < the val. calc. from spectroscopic data. The mol. entropy of N<sub>2</sub>O at 298.1° abs. and 1 atm., based on band spectra data, is 52.581 e.u. (without nuclear spin entropy), and the abs. entropy 56.947 e.u. E. S. H.

M.p. of calcium, strontium, and barium. F. HOFFMANN and A. SCHULZE (Physikal. Z., 1935, 36, 453-458).—Ca, Sr, and Ba have m.p.  $851^{\circ}$ , 771°, and 704° ( $\pm 1^{\circ}$ ), respectively. A. J. M.

Speed of sublimation and condensation. K. F. HERZFELD (J. Chem. Physics, 1935, 3, 319-323).— For the system crystal-saturated vapour, the equilibrium pressure is changed, in the case of atoms, if the electron wt. in the gaseous state differs from that in the solid state; hence for true metals the speed of sublimation is probably increased, and for nonmetals a reflexion coeff. exists. For mols. the equilibrium pressure is higher than for atoms, resulting probably in an increased speed of sublimation. N. M. B.

Dissociation energy of the carbon monoxide molecule and the sublimation heat of carbon. (A) P. GOLDFINGER and W. LASAREFF. (B) B. ROSEN (Nature, 1935, 135, 1077).—(A) The energy of dissociation of CO into normal atoms calc. from thermochemical and spectroscopic data is  $11\pm0.1$  v.e. This gives 167 kg.-cal. for the sublimation heat of C.

(B) Schmid and Gero's results (this vol., 555) may provide an independent check of the above val.

L. S. T.

Thermal expansion of mono- and poly-crystalline antimony. P. HIDNERT (J. Res. Nat. Bur. Stand., 1935, 14, 523-544).—The average coeff. of linear expansion of monocryst. Sb at 0-100° is  $17.2 \times 10^{-6}$  along the trigonal axis and  $8.0 \times 10^{-6}$  at right angles to this axis. The linear expansion of polycryst. Sb indicates that there is no polymorphic transition between 20° and 560°, and differences observed for different samples are attributed to variations in the average orientation of the crystals.

J. W. S.

Difference in vapour pressure between ortho and para forms of hydrogen isotopes. K. CLU-SIUS, (Z. physikal. Chem., 1935, B, 29, 159—161).— The v.p. of o- and p-D<sub>2</sub> at 20·38° are 262 and 247 mm., whilst those of p- and o-H<sub>2</sub> at 17·13° abs. are 262·0 and 247·1 mm., respectively. It is concluded that in the one-quantum rotational state there is superimposed on the dispersion effect, which is solely responsible for mol. attraction in the zero-quantum state, the interaction of rigid rotating multipoles. Thus the difference in v. p. between o- and p-forms is primarily due to the quadrupole moment of the mol. R. C.

Thermodynamic properties of hydrogen and deuterium. H. C. UREY (Angew. Chem., 1935, 48, 315-320).-Nobel lecture. A review and discussion of data. H. J. E.

Vapour pressure and condensation of radon at low temperatures. L. WERTENSTEIN (Proc. Roy. Soc., 1935, A, 150, 395–410).—Results of measurements of the v.p. of radon at low temp. indicate that the condensation of Rn under usual conditions is not an equilibrium between gas and solid, but is a secondary effect, due to the presence of condensible impurities such as Hg, H<sub>2</sub>O vapour, etc. L. L. B.

Law of Thomson and Gibbs : vapour pressure of small particles. M. VOLMER (Ann. Physik, 1935, [v], 23, 44-46, 49-50).—The method employed by Kossel in deducing the energetics of surfaces (this vol., 161) is criticised. A. J. M.

[Law of Thomson and Gibbs : vapour pressure of small particles.] W. Kossel (Ann. Physik, 1935, [v], 23, 47-48, 50).—A reply to the above. A. J. M.

(A) "Near" and "far" action in the thermodynamic equation of state. (B) Principle of the "dominant action" in the thermodynamic equation of state. W. JACYNA (Bull. Acad. Polonaise, 1935, A, 4—13, 14—19; cf. A., 1934, 1300).— Theoretical. H. J. E.

 $\psi_0$ -value according to the new equation of state. W. JACYNA (Z. Physik, 1935, 95, 252).—This is calc. to be 273.22°. A. B. D. C.

Properties of real gases according to the thermodynamic equation of state. V. Compressibility of helium below the critical state in the range 4.34—2.59° abs. VI. Critical region of helium. W. JACYNA (Z. Physik, 1935, 95, 246— 251, 253—261; cf. A., 1934, 1300).—The crit. coeff. for He is 3.18, and the crit. vol. 0.0151 cu. m. per kg. A. B. D. C.

Measurement of absolute viscosity coefficient by the pendulum viscosimeter method. B. V. ILJIN and V. N. IVANOV (Kolloid-Z., 1935, 71, 265– 267).—Vals. of  $\eta$  for a no. of liquids are in satisfactory agreement with those obtained with the Ostwald viscosimeter. E. S. H.

Temperature coefficient of viscosity of inorganic acid chlorides. G. P. LUTSOHINSKY (Z. anorg. Chem., 1935, 223, 210-212).— $\eta$  for POCl<sub>3</sub> and SbCl<sub>5</sub> varies with temp. according to Batschinsky's formula,  $\eta = C/(v-\omega)$ , where v = sp. vol., and C and  $\omega$  are consts. C and  $\omega/M$  (M = mol. wt.) increase regularly with the at. wt. of the central atom in the chlorides of Si, P, and S, and decrease with rise of at. wt. within one group of the periodic table.

J. S. A.

Viscosity measurements on alicyclic ketones and alcohols [and their acetates]. W. HUCKEL and H. W. WUNSCH (J. pr. Chem., 1935, [ii], 142, 225-231).—Data for 24 compounds over a range of temp. are given. D. R. D.

Critical state. V. Viscosity in critical state. E. SCHRÖER and G. BECKER (Z. physikal. Chem., 1935, 173, 178—197).—A falling-sphere viscosimeter is described permitting determination of the relative viscosity of small amounts of gas or liquid at high pressures and temp. with a precision of 0.5-1% (cf. A., 1934, 750). Measurements have been made with Et<sub>2</sub>O in the crit. region and above at  $184.5-235^{\circ}$ under pressures, p, of 25-75 kg. per sq. cm. The dynamic viscosity  $(\eta)-p$  isotherms resemble d-p isotherms, but intersect when the gas is still liquid, so that even before liquefaction the mechanism of viscosity is predominantly that of liquid viscosity, rather than of gaseous viscosity. The kinematic viscosity  $(\nu)-p$  isotherms in the gaseous region fall rapidly with rising p, whilst those of liquid Et<sub>2</sub>O run parallel to the p axis.  $\eta$  depends on temp. and p, although to a much smaller extent than on d; the higher is d the larger is the (negative) temp. coeff. Measurements with CO<sub>2</sub> at 20° at pressures up to 101 kg. per sq. cm. give  $\nu-p$  isotherms for the liquid which, unlike those of Phillips (A., 1912, ii, 832), are parallel to the p axis. R. C.

Influence of an electric field on the viscosity of liquids. S. DOBINSKI (Bull. Acad. Polonaise, 1935, A, 42—52).—The effect of an electric field on  $\eta$ , observed by various authors, is shown by measurements on 13 liquids (e.g., CHCl<sub>3</sub>, PhNO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>) to be due to ionic impurities. It disappears with progressive purification, and is observed only in polar solvents. Impurities increase  $\eta$  in aliphatic and decrease  $\eta$  in aromatic solvents. H. J. E.

Inner friction of gases in a magnetic field. H. SACK (Helv. phys. Acta, 1934, 7, 639—641; Chem. Zentr., 1935, i, 675).—Data are recorded for  $O_2$ ,  $N_2$ , and their mixtures. H. J. E.

Structure of intermetallic compounds of beryllium with copper, nickel, and iron. L. MISCH (Z. physikal. Chem., 1935, **B**, 29, 42–58; cf. this vol., 816).—The system Cu–Be shows the *compounds* CuBe and CuBe<sub>2</sub>, the latter being stable only in presence of excess of Be. CuBe<sub>2</sub> has the cubic face-centred lattice of MgCu<sub>2</sub>, with 24 atoms in the unit cell. The *compounds* NiBe, cubic body-centred, and Ni<sub>5</sub>Be<sub>21</sub>, apparently with a deformed  $\gamma$ -brass structure, are reported (cf. B., 1929, 724; A., 1929, 996). R. C.

Crystal structure and crystalline configuration of the normal and modified Si-Al alloys. H. KOTÔ (Mem. Coll. Sci. Kyoto, 1935, A, 18, 17-33).—The modification of Si-Al alloys by the addition of Na and substances of similar properties has been investigated. Examination of the micro-structures of the normal and modified alloys shows that Na, K, and Li are very effective as modifying agents, the next most effective being Mg and Ca. The theory that modification is brought about by volatile elements is disproved by the fact that P, S, Se, Te, and As give no appreciable effect. Bi and Sb, which are immiscible with both Si and Al, produce no modification. Hence the ternary constituents theory which attributes modification to the separation of the agent from the Si-Al alloy on cooling cannot be correct. Thermal analysis of the normal and modified alloys indicates that supercooling is more marked with the former than the latter. X-Ray examination of the alloys shows that the actual cryst. structure does not always agree with that deduced from photomicrographs. Although Na and Li both modify Si-Al alloys, X-ray analysis shows that Na is not miscible with Si and Al, but that Li forms solid solutions and compounds with these elements. A. J. M.

Systematic studies in combination. LXIV. Combining power of platinum and phosphorus. W. BILTZ, F. WEIBKE, and E. MAY [with K. MEISEL] (Z. anorg. Chem., 1935, 223, 129—143).—The phase diagram confirms the existence of PtP<sub>2</sub>. There is also a subphosphide,  $Pt_{20}P_7$ . Its existence is confirmed by X-ray examination and it is the compound responsible for the destruction of Pt apparatus by heating in contact with P compounds, since the eutectic mixture of Pt with  $Pt_{20}P_7$ , containing 3.8 at.-% P, melts at 588°. M. S. B.

Crystallisation of binary eutectic systems. E. RAUB (Z. Metallk., 1935, 27, 77-83).-The grain structure of a cast eutectic alloy resembles that of a pure metal, the type and size of the grains being determined chiefly by those of the predominating constituent, other conditions being equal. The structure has little effect on the mechanical properties when there are great differences between the workability of the constituents, but has a determining effect when both constituents have similar mechanical properties, the eutectic in this case behaving like a pure metal and the distribution of the phases having little effect on the properties. In cold-working and recrystallisation on annealing the structure is deformed and re-formed in a similar manner to that of a metal and solid solution alloys, the recrystallisation grains being formed about the predominating constituent in such a way that the annealed sheet shows characteristic anisotropic phenomena which are ascribed to the setting up of an ordered recrystallisation position of that constituent. These phenomena are illustrated by photomicrographs and tables showing the properties of the Ag-Cu eutectic after various thermal and mechanical treatments. to noiserson A. R. P.

Constitution of magnesium-zinc-silicon alloys rich in magnesium. E. ELCHARDUS and P. LAF-FITTE (Compt. rend., 1935, 200, 1938—1940; cf. A., 1934, 22).—The unstable compound Mg<sub>4</sub>Si (m.p. 932°) forms a labile system (Mg-MgZn<sub>2</sub>-Mg<sub>4</sub>Si) which gives a ternary eutectic (m.p.  $314^{\circ}$ ; Mg 51·85, Zn 47·7, Si 0·45%). In the binary system Mg-Si, Mg<sub>4</sub>Si forms a eutectic (m.p.  $575^{\circ}$ ; 2·7% Si).

H. J. E.

Iron-nickel-copper alloys of high initial permeability. O. VON AUWERS and H. NEUMANN (Wiss. Veröff. Siemens-Werken, 1935, 14, 93—108).— Examination has shown a zone of high initial magnetic permeability comprised by the region Ni 80, Fe 20% to Ni 40, Cu 50, Fe 10%. Over the greater part of this region the sign of magnetostriction is reversed. E. S. H.

System cobalt-iron-titanium. W. Köster and W. GELLER (Arch. Eisenhüttenw., 1934—1935, 8, 471—472).—The system up to 22% Ti has been examined by micrographic and pptn.-hardening methods. The two compounds Co<sub>3</sub>Ti and Fe<sub>3</sub>Ti form a continuous series of solid solutions (I) and the solubility of these compounds in the  $\alpha$ - and  $\gamma$ -Fe-Co phases decreases with fall in temp. to a val. corresponding with 2% Ti at room temp. The eutectic equilibrium liquid  $= \alpha + \text{Fe}_3\text{Ti}$  in the Fe-Ti system and the peritectic reaction liquid  $+\alpha = \gamma$  in the Fe-Co system are displaced to lower temp. by the addition of Co and Ti, respectively, and merge at 1150° into a plane of 4-phase equilibrium : liquid  $+\alpha$ -solid solution  $\implies$  (I)  $+\gamma$ -solid solution. From this plane as the temp. falls there extends a field of 3-phase equilibrium : liquid  $\implies \gamma + (I)$ , which terminates in the Co-Ti eutectic. A. R. P.

Equilibrium diagram for quaternary alloys. V. FISCHER (Z. Metallk., 1935, 27, 88–89).—A method of representing the equilibria on a plane orthogonal co-ordinate system is illustrated graphically with reference to the Mn–Cu–Fe–Ni system. A. R. P.

Viscosity of mixtures of hexane and nitrobenzene in the neighbourhood of the critical point of dissolution. (MLLE.) Z. SZAFRAŃSKA (Bull. Acad. Polonaise, 1935, A, 110—119; cf. Drapier, A., 1911, ii, 968).—Anomalies in the viscosity-concn. curves for  $C_6H_{14}$ -PhNO<sub>2</sub> mixtures are observed only in concn. regions where opalescence is observed. The irregularities observed by Drapier are attributed to turbulent motion. J. W. S.

Internal friction of fused metals and alloys. VI. Internal friction of Pb, Cd, Zn, Ag, Sn, K, Na; structure viscosity of amalgams. K. GERING and F. SAUERWALD (Z. anorg. Chem., 1935, 223, 204—208).—A pressure viscosimeter for determining  $\eta$  for molten metals is described. The dependence of  $\eta$  on pressure in the case of amalgams at low pressure (Köhler, A., 1933, 895) has been confirmed, and also observed in pure Hg at very low pressures. In the case of amalgams the effect is explained by the existence of small crystals in suspension, whilst the effect in Hg is due to the large rôle played by surface tension and similar phenomena when the pressure is very low. M. S. B.

Calorimetric analysis of a binary mixture. R. N. M. A. MALOTAUX (Chem. Weekblad, 1932, 32, 348; cf. A., 1933, 465; 1934, 951; B., 1934, 354). S. C.

Magnetic measurements on molecular compounds in solution with a modified form of Decker's balance. S. S. BHATNAGAR, M. B. NEVGI, and G. TULI (Indian J. Physics, 1935, 9, 311— 317).—The stability of mol. compounds in solution has been investigated by determining the diamagnetic susceptibility ( $\chi$ ) of the picrates of anthracene,  $C_{10}H_8$ , 1- $C_{10}H_7$ Me, and phenanthrene in the solid state and in solution in  $C_6H_6$ . In the latter case,  $\chi$  does not vary appreciably with concn., but is < the val. for the solid substances, being nearer that given by the mixture law, thus indicating dissociation in solution. A. J. M.

Simultaneous formation of double and triple complexes in dipole association. I. SAKURADA (Z. physikal. Chem., 1935, B, 29, 104—111; cf. A., 1934, 475).—Assuming that in dipole association dipole-free double and triple complexes are formed simultaneously and that the mass law is valid, a method of calculating the equilibrium consts. of the two kinds of association from dielectric data is described. The formation of such complexes in various binary mixtures is deduced. From the temp. coeff. of the association const. the heat of association is calc. Hertel and Dumont's criticism (this vol., 430) is discussed. R. C.

Calculation of molar polarisation of solutes at infinite dilution with Hedestrand's formula. M. M. Отто (J. Amer. Chem. Soc., 1935, 57, 1147).— The formula is applicable even to certain substances for which the dielectric const. and d are not linear functions of concn. E. S. H.

Relation between molecular polarisation in solution and the dielectric constant of the solvent. R. J. W. LE FÈVRE (J.C.S., 1935, 773-776).—Vals. of  $d^{25}$  and of the dielectric const.,  $\varepsilon$ , at 25° for NH<sub>2</sub>Ph, NHPhMe, NPhMe<sub>2</sub>, quinoline, *iso*quinoline, and C<sub>5</sub>H<sub>5</sub>N are recorded. The expression  $_0P_1/_0P_2=K(\varepsilon_2+2)/(\varepsilon_1+2)$ , in which  $_0P_1$  and  $_0P_2$  are the orientation polarisations of a solute mol. in two media of dielectric consts.  $\varepsilon_1$  and  $\varepsilon_2$  respectively, has been applied to : (a) pairs of solutions, (b) solutions and the corresponding solutes in the vapour states, and (c) solutions and the (liquid) solutes in bulk. In case (a), published data for polar and non-polar solvents afford vals. of K between 0.92 and 1.09 (cf. this vol., 240), in case (b), K lies between 1 and 1.7, but H<sub>2</sub>O and EtOH afford vals. between 3.3 and 4.3. The theoretical basis of the expression is discussed and leads to K=1. J. G. A. G.

Conductivity and density in the system fused KCl-MgCl<sub>2</sub>. S. KARPATSCHEV, A. STROM-BERG, and O POLTORATZKAJA (J. Gen. Chem. Russ., 1935, 5, 189—196).—The relations indicate the compound 2KCl,MgCl<sub>2</sub>. R. T.

Vapour pressures and activities of completely and incompletely miscible binary and ternary alloys with one and two volatile components. K. JELLINEK and H. A. WANNOW (Z. Elektrochem., 1935, 41, 346—362; cf. this vol., 168).—V.p. for the following liquid alloys have been measured and the activities of the respective volatile components calc.: Sn-Zn, Sn-Cd, Sb-Zn, Pb-Zn, Cd-Zn, Sn-Sb-Zn, Sn-Pb-Zn, Sn-Cd-Zn. F. L. U.

Distillation of azeotropic mixtures. W. SWIENTOSLAWSKI (J. Chim. phys., 1935, 32, 293-299).—The b.p. of a mixture of two binary homo-azeotropes, AC and BC, e.g.,  $C_6H_6$ -EtOH and PhMe-EtOH, is always < that of the azeotropic agent C, and lies between the b.p. of AC and BC. With insufficient C, the proportion of AC and BC distilling depends on [C] as well as on [A] and [B]. The difference between the b.p. of the homoazeotropes is < that between the b.p. of A and B. Small quantities of C<sub>6</sub>H<sub>6</sub> and PhMe can be removed from xylene by distilling with the appropriate quantity of MeOH. A method has been devised for determining whether four substances forming two ternary azeotropes also form a quaternary azeotrope. A mixture of the ternary azeotropes C<sub>6</sub>H<sub>6</sub>-EtOH-H<sub>2</sub>O (I), b.p. 64.676°, and PhMe-EtOH-H<sub>2</sub>O behaves as a binary mixture of two chemical individuals. The mixture of azeotropes (I) and C<sub>6</sub>H<sub>6</sub>-Pr<sup>β</sup>OH-H<sub>2</sub>O, b.p. 66·141°, does not form a quaternary azeotrope although it shows a positive deviation from Raoult's law. The degree of dehydration achieved by azeotropic agents depends on the nature of the substances involved.

J. G. A. G. Polymorphism in FeS-S solid solutions. I. Thermal study. H. S. ROBERTS (J. Amer. Chem. Soc., 1935, 57, 1034-1038).-The solid solutions extending from FeS to approx. FeS<sub>1.14</sub> appear in 6 different forms between room temp. and 575°. A reversible transformation occurs between 315° and  $318^{\circ}$ , and there is evidence that the form b, stable just above 318°, is not the form a, which is synthesised at 550-575°. In the compound FeS the form c, stable just below 315°, is transformed between 144° and 139° into a form d, which appears to be the stable form of all the solid solutions at room temp. This transformation temp. falls with increasing S content. From FeS to approx. FeS<sub>1.05</sub> the transformation is between d and c; at the latter point an intermediate form e appears, and beyond approx.  $\text{FeS}_{1.07}$  the transformation is between d and f. The transformation temp.  $c \Longrightarrow e$  and  $e \Longrightarrow f$  are raised by increasing S content, reaching the limit of solid solution a few degrees below the  $b \implies c$  transformation. E. S. H.

(A) Position of the region of non-miscibility of binary systems in the surface tension-concentration diagrams. (B) Physico-chemical nature of binary liquid mixtures at the lower critical temperature. R. V. MERTZLIN (J. Gen. Chem. Russ., 1935, 5, 155—160, 161—168).—(A) The anomaly at the upper crit. temp. is ascribed to increase in the activity of capillary-active solutes with falling temp., in conjunction with a low temp. coeff. of solubility.

(B) Systems at the lower crit. temp. are of the irrational type; the principle of corresponding states is applicable to them. R. T.

Influence of a current of hot water on air and radon dissolved in cold water. M. GESLIN (Compt. rend., 1935, 200, 2204—2206).—Dissolved gases are partly extracted from cold  $H_2O$  by the passage of a stream of hot  $H_2O$  containing  $CO_2$ . H. J. E.

Anomalous diffusion in true solution. H. FREUNDLICH and D. KRÜGER (Trans. Faraday Soc., 1935, 31, 906—913).—Concn. gradients may cause diffusion of uniformly distributed substance, owing to mutual change in solubility of the solutes. A thin layer of liquid on the border of the solution may therefore become less dense that the solution above it and lead to convection currents which disturb normal diffusion. It is found that diffusion anomalies disappear when the upper layer is sufficiently lighter than the lower. J. W. S.

Variation of the permeability of palladium to hydrogen just below 200°. V. LOMBARD and C. EICHNER (Compt. rend., 1935, 200, 1846—1848; cf. A., 1934, 1302).—A rapid increase in permeability is observed at approx. 180°. H. J. E.

Nitrates of lanthanum, and their solubilities in water. J. N. FRIEND (J.C.S., 1935, 824-826).— La(NO<sub>3</sub>)<sub>3</sub>,6H<sub>2</sub>O exists in two forms, and the transition point is 43° approx. Solubilities have been determined between 0° and the m.p. of the  $\beta$ -form, 65.4°. J. G. A. G. Solubility of sodium bromide in acetone. L. E. SWEARINGEN and R. T. FLORENCE (J. Physical Chem., 1935, 39, 701—707).—The solubility of NaBr in COMe<sub>2</sub> is markedly increased by the presence of LiClO<sub>4</sub> or Ca(ClO<sub>4</sub>)<sub>2</sub>, and is much > that predicted by the interionic attraction theory of Debye and Hückel. F. L. U.

Titration of *p*-hydroxybenzoic acid. A. Osol and M. KILPATRICK (J. Amer. Chem. Soc., 1935, 57, 1053).—Revised vals. for the solubility of *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H are given (A., 1934, 29), based on an improved method of titration. E. S. H.

Solubility of gold in ferric sulphate and its geological applications. R. L. MILNER (Proc. Nova Scotian Inst. Sci., 1934, 18, 267–271).—Au is slightly sol. in  $Fe_2(SO_4)_3$  solution and readily sol. in the presence of  $H_2SO_4$ . C. W. G.

Solubility of lead in mercury. H. E. THOMPSON, jun. (J. Physical Chem., 1935, 39, 655–664).—The solubility of Pb in Hg has been determined over the range 20—70°. The at. fraction of Pb in the saturated solution at  $T^{\circ}$  abs. is given by 0.5893-0.004115T+ $0.000007354T^{2}$ . F. L. U.

Solubility of sodium in aluminium. E. SCHEUER (Z. Metallk., 1935, 27, 83–85).—The solubility of Na in Al (Si 0·1, Fe 0·2%) rises linearly from 0·10 to 0·12% between 700° and 800°, whereas that in silumin rises from 0·08% at 600° to 0·13% at 750°, then decreases to 0·11% at 800°. In the 5% Mg– Al alloy it is 0·17% at 700° and 0·21% at 800°, and in the 8% Cu–Al alloy 0·15% at 700° and 0·18% at 800°. The presence of Fe and Si has no effect on the solubility. In the solid alloys the Na appears as a new phase; no evidence of solid solubility of Na in Al could be obtained. A. R. P.

Solubility of potassium fluorotantalate in aqueous hydrogen fluoride. A. V. BABAEVA and T. A. ARTSCHAKOVA (J. Gen. Chem. Russ., 1935, 5, 220—223).—The solubility of  $K_2TaF_7$  increases with increasing [HF], to a greater extent at higher than at lower temp. R. T.

Solubility of sucrose and lime in their concentrated solution at 30°. K. SUZUKI (J. Soc. Chem. Ind. Japan, 1935, 38, 177–178B).—Data are given for the solubility of sucrose + CaO in  $H_2O$ , and in presence of Na phosphate. J. S. A.

(A) Solubility of sodium sulphate in aqueous ammonium carbonate at  $32.5^{\circ}$ . (B) Mutual system Na<sub>2</sub>SO<sub>4</sub>-NH<sub>4</sub>HCO<sub>3</sub>-H<sub>2</sub>O at low temperatures. A. P. BELOPOLSKI (J. Appl. Chem. Russ., 1935, 8, 193-194, 195-211).-(A) [with V. V. URUSOV]. The solid phase is Na<sub>2</sub>SO<sub>4</sub> at [(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>] < 33.6 g. per 100 g. of H<sub>2</sub>O.

(a) Constant phase is reasonable of the phase of the

Mutual solubility of aluminium, sodium, potassium, and iron nitrates in water in presence of nitric acid. I. A. J. SASLAVSKY, J. L. ETTINGER, and E. A. ESEROVA (Z. anorg. Chem., 1935, 223, 277–287).—Isotherms in the system Al(NO<sub>3</sub>)<sub>3</sub>-KNO<sub>3</sub>-NaNO<sub>3</sub>-H<sub>2</sub>O and its partial ternary systems have been studied at 0°, 20°, 40°, and 60°. Solid phases are  $KNO_3$ ,  $NaNO_3$ , and  $Al(NO_3)_3,9H_2O$ , with no formation of double compounds or mixed crystals. J. S. A.

Relation between separate and common solubility of the components of a ternary system. E. I. AKUMOV (J. Gen. Chem. Russ., 1935, 5, 131— 142).—Relationships between the solubility of the individual components of a ternary system, separately and together, have been derived. R. T.

(A) Theory of  $L_p$  [solubility product]. (B) Influence of hydrolysis on solubility. N. A. TANA-NAEV (J. Appl. Chem. Russ., 1935, 8, 346-351, 352-355).—(A) For any sparingly sol. salt,  $M_mA_n$ ,  $L_i = (L_p/m^m n^n)^{1/(m+n)}$ , where  $L_i$  is the ionic solubility, and  $L_p$  the product of the conces. of the ions. (B) The concent of M' in solutions of the sparingly

(B) The concn. of M' in solutions of the sparingly sol. salt MA is given by  $[M'] = \sqrt{[L_i/(1-\alpha)]}$ , where  $\alpha$  is the fraction of salt hydrolysed. R. T.

Influence of salt or acid hydrophilic colloids on the solubility of sparingly soluble acids and bases. II. Gelatin. H. BRINTZINGER and A. SCHALL (Kolloid-Z., 1935, 71, 302—307; cf. A., 1934, 1066).—The influence of gelatin (I) and acid on the solubility of salicylic, benzoic, and anthranilic acids, o-, m-, and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, and strychnine has been determined. In all cases an increase of solubility is observed; this is traced to the presence of CO<sub>2</sub>H and NH<sub>2</sub> in the mol. of (I). The different results obtained with gum arabic are explained by the absence of NH<sub>2</sub>. E. S. H.

Solubility of sparingly soluble substances in colloid solutions. H. BRINTZINGER and A. SCHALL (Kolloid-Z., 1935, 71, 300—302).—A discussion of the factors involved. E. S. H.

Distribution of (A) phenylacetic acid between two contiguous liquid phases, (B) chloroacetic acids between water and halides of saturated hydrocarbons, (C) malonic and ethylidenelactic acid between water and saturated monobasic aliphatic alcohols. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1935, 5, 60–62, 63–68, 69–72).— (A) [with A. BEKTUROV]. Data are given for  $CH_2Ph \cdot CO_2H - H_2O$ , -PhMe, -PhNO<sub>2</sub>, and -iso- $C_3H_{11} \cdot OH$ , at 25°.

(B) [with F. S. KULIKOV]. Data are given for  $CH_2Cl \cdot CO_2H$ - and  $CHCl_2 \cdot CO_2H$ - $H_2O$ - $CCl_4$ , -EtBr, and -MeI, and for  $CCl_3 \cdot CO_2H$ - $H_2O$ -MeI, at 25°.

(c) [with A. BEKTUROV]. Data are recorded for  $CH_2(CO_2H)_2-H_2O-Bu^{\beta}OH$ , -n- and -iso- $C_5H_{11}$ ·OH, and for ethylidenelactic acid- $H_2O$ -iso- $C_5H_{11}$ ·OH, at 25°. R. T.

Passage of helium through compact solids. (LORD) RAYLEIGH (Nature, 1935, 135, 993).—He passes through vitreous  $B_2O_3$  but not vitreous borax at room temp. Single crystals of various substances are impervious to He at room temp. The provisional positive result reported for a crystal of beryl (this vol., 159) is withdrawn. L. S. T.

Adsorption. A. GANGULI (Kolloid-Z., 1935, 71, 275-279).—A discussion of published work.

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Adsorption of alkali metals on metal surfaces. IV. Adsorption of atoms next to ions. V. Influence of temperature on the normal photoelectric effect. J. H. DE BOER and C. F. VEENEMANS (Physica, 1935, 2, 521-528, 539).—IV (cf. A., 1934, 1066; this vol., 27). The metal is adsorbed as ions only until a certain val. of the covering fraction 0 is reached. Above this val. adsorption takes place in the form of atoms. The arrangement of adsorbed atoms is such that photo-electric emission is diminished. At still higher vals. of 0 the emission is increased, hence the at. dipoles are reversed in the later stages. The possible position of the atoms in relation to the ions, and the direction and magnitude of the dipoles are discussed. A more exact calculation is made of the val. of  $\theta$  at which at. adsorption sets in for Cs on W.

V. At low vals. of  $\theta$  for adsorbed ions photoelectric emission increases exponentially with  $\theta$  in white light. At higher vals., for adsorbed atoms, emission increases more slowly and reaches a max. Rise of temp. increases the dipole moment of adsorbed ions and diminishes the induced dipole of adsorbed atoms; the emission changes in the corresponding direction in each case. This is demonstrated by the behaviour of Na on W. The effect is reproducible, but in the first heating a surface migration effect is observed. M. S. B.

Adsorption of vapours of ketones and esters by activated charcoal. J. N. PEARCE and A. C. HAN-SON (J. Physical Chem., 1935, 39, 679-691; cf. A., 1934, 593).—The adsorption of vapours of three ketones and four esters by activated C, measured at several temp. between 0° and 182°, conforms to Langmuir's equation for adsorption at plane surfaces for pressures  $\geq 200$  mm. For both series of compounds the amount of vapour adsorbed at pressures  $\geq 0.8$  mm. increases with increase of the b.p. or of the van der Waals const. a. At higher pressures the order is reversed. Dipole moment is without influence. F. L. U.

Essential structural discontinuities in certain adsorbed films. J. K. ROBERTS (Nature, 1935, 135, 1037).—The adsorption of diat. gas mols. on solid surfaces is discussed. The adsorbed films are not continuous : certain single atoms remain bare and may show catalytic activity. Confirmatory experimental evidence of these views in the case of  $O_2$  on W has been obtained. L. S. T.

Alteration of the adsorption of dyes on nickel wires on transition of the wire from the hard to the soft state. G. TAMMANN (Z. anorg. Chem., 1935, 223, 222—224).—A rapid decrease in the adsorptive power of Ni wires for dyes (cf. A., 1934, 956) occurs over the same temp. range (500—600°) as the recovery of cold-worked Ni, the magnetic crit. temp., and the first perceptible recrystallisation, with which the effect is correlated. J. S. A.

Surface behaviour of zeolites. V. R. DAMERELL and R. CADLE (J. Physical Chem., 1935, 39, 693— 694; cf. A., 1932, 680).—Experiments on the dehydration of scolecite and analcite indicate that  $H_2O$  is lost only from the surface portions of the zeolite lattice. F. L. U. Active oxides. XC. Enhanced sorptive power of nascent zinc chromite. J. HAMPEL (Z. anorg. Chem., 1935, 223, 297–304).—The sorptive power towards Congo-red, acid fuchsin, and eosin of equimol. mixtures of ZnO and  $Cr_2O_3$ , heated at different temp., is much > that of either component, and passes through a max. in the neighbourhood of the max. in catalytic properties and magnetic susceptibility. The low sorptive power of cryst. ZnCr\_2O\_4 increases at high temp., probably due to volatilisation of ZnO from the surface. J. S. A.

Liberation of bromine and iodine from adsorption on active charcoal. V. A. PIANKOV (J. Appl. Chem. Russ., 1935, 8, 238-245).—Active C may adsorb 40% of its wt. of I from EtOH, and 65% from aq. solution. Most of the I is recovered by heating at 300°, but the last traces are obtainable only by burning the C. The desorption curves present certain differences according to whether the I was adsorbed from aq. or EtOH solution. C adsorbs  $\geq 25\%$  of its wt. of Br from aq. solutions; 50-60% is liberated at 100°, and the remainder at 400°. HBr behaves similarly to Br in the above respects.

R. T.

Heat of adsorption of vapours from a current of air by active charcoal at 24°. P. K. MIGAL (J. Gen. Chem. Russ., 1935, 5, 197—210).—The heat (q)-time curves, after a short induction period, are rectilinear for MeCl, CHCl<sub>3</sub>, CCl<sub>4</sub>, MeI, CS<sub>2</sub>, and MeOH corresponding with  $q = kcv(t-t_0)$ , where c is the concn. of vapour, v its rate of flow, and  $t_0$  is the time at the end of the induction period. R. T.

Porosity of charcoal. A. KING (Trans. Faraday Soc., 1935, 31, 935—937).—It is suggested that the porosity of a charcoal depends partly on the extent of inhibition of crystal growth during its prep., and that charcoals (e.g., sugar) which evolve only small amounts of gas after they are solidified are less porous and less active than wood charcoals where transformation occurs in the solid state throughout. Molasses charcoal is much more active than sugar charcoal, in accord with this theory. Activation of charcoal probably consists essentially in the removal by oxidation of hydrocarbons from the surface, yielding free valencies, as well as increasing the surface area of the charcoal. J. W. S.

Sorption of propyl and butyl alcohols by silica gel. A. FOSTER (Proc. Roy. Soc., 1935, A, 150, 77-83).—The isothermals for the adsorption of Pr<sup>a</sup>OH, Pr<sup>\$</sup>OH, and Bu<sup>a</sup>OH by SiO<sub>2</sub> gel at 25° are similar to those for MeOH and EtOH (A., 1934, 1169). A small hysteresis area is found just before saturation, the extent of which shows little variation. The relative pressure at which the hysteresis occurs diminishes from MeOH to BuOH, but the capillary radius calc. from these pressures by means of the Kelvin equation remains const. at about 15 Å.

L. L. B.

Spectro-photometric study of the adsorption of copper in ammoniacal solutions by precipitated ferric hydroxide. (MME.) L. S. MATHIEU-LEVY (Compt. rend., 1935, 200, 1934—1936; cf. this vol., 819).—Data are recorded for the variation of the extinction coeff. with [NH<sub>3</sub>] and with the Cu adsorbed. Cu is adsorbed both as  $[Cu(NH_3)_4]^{"}$  and as colloidal  $Cu(OH)_2$ . H. J. E.

Change in the capacity for [ionic] exchange of colloidal clay. II. A. L. S. BAR and H. J. C. TENDELOO (Rec. trav. chim., 1935, 54, 566-569; cf. this vol., 32).—The capacity for ionic exchange of 4 colloidal clays agrees with the formula of Verwey,  $dy/d \log c$ =const., where y=adsorbed OH' and c=[OH']. The precise mechanism of the exchange is uncertain. R. S. B.

Heat of wetting. I. Influence of adsorbed ions. A. DUMANSKI and M. TSCHAPEK (Kolloid-Z., 1935, 71, 279–282).—The influence of adsorbed Fe<sup>•••</sup>, Ca<sup>••</sup>, Mg<sup>••</sup>, NH<sub>4</sub><sup>•</sup>, K<sup>•</sup>, Na<sup>•</sup>, and H<sup>•</sup> on the heat of wetting of activated C, SiO<sub>2</sub> gel, and permutite by H<sub>2</sub>O has been determined. Part of the apparent heat of wetting is due to heat of hydration of the ions. The ratio of heat of hydration to heat of wetting is the greater, the more hydrophobic is the adsorbent. The influence of a given cation on heat of wetting varies with the adsorbent. E. S. H.

Determination of surface of powders in the light of heat of wetting ; apparatus for determination of heat of wetting of polished metal surfaces by oil. H. HERBST (Kolloid-Z., 1935, 71, 282—290).— Sources of error in the determination of the surface of a powdered metal by means of adsorption measurements are pointed out. Such errors invalidate measurements of heat of wetting of metal powders by oil as a guide to lubricating efficiency. An apparatus for the direct determination of heat of wetting, using a polished metal surface of known area, is described. E. S. H.

Wetting power of metals of low m.p. for metals of high m.p. G. TAMMANN and A. RÜHENBECK (Z. anorg. Chem., 1935, 223, 192—196).—It is shown that, of two metals miscible in the solid state, the more easily fusible one in the molten state will wet the other (solid) metal at temp. above that at which a change of structure takes place in the latter. This is illustrated by the behaviour of Sn, Pb, and Bi towards electrolytic Fe, Ni, W, Mo, Ta, and Cu, and also of Ag towards electrolytic Fe. Wetting by a fused drop is usually preceded by dome formation (cf. A., 1930, 1365). M. S. B.

Surface tensions and partial vapour pressures of aqueous aniline solutions. J. C. SPEAKMAN (J.C.S., 1935, 776-779).—The data refer to 0— 0.356M solutions at 20°, and correspond with an area per mol. of  $23.4 (\pm 0.3)$  sq. Å. This is consistent with the formation of a unimol. film composed entirely of NH<sub>2</sub>Ph mols. at the surface. J. G. A. G.

Surface tension of system sulphuric acidwater. L. SABININA and L. TERPUGOV (Z. physikal. Chem., 1935, 173, 237—241).—Measurements have been made at 10—50°. The temp. coeff. of the surface tension is a min. and the deviation from additivity at all temp. reaches a max. at  $H_2SO_4, 2H_2O$ . There is no indication of the existence of any other compound. R. C.

Dimensions of the sodium palmitate molecule from a study of surface tensions in dilute aqueous solutions. E. R. WASHBURN and G. W. BERRY (J. Amer. Chem. Soc., 1935, 57, 975–977).—The equilibrium surface tension-concn. curve for aq. Na palmitate has been determined by the capillary-rise method. The dimensions of the Na palmitate mol. calc. from the min. of this curve are  $23 \times 10^{-8}$  cm.  $\times 62 \times 10^{-8}$  cm.  $\times 3.7 \times 10^{-8}$  cm. E. S. H.

Films built by depositing successive unimolecular layers on a solid surface. K. B. BLODGETT (J. Amer. Chem. Soc., 1935, 57, 1007-1021).-The building of films of palmitic, stearic, and arachidic acids and their Ca, Mg, Sr, Ba, Pb, and Zn soaps on surfaces of glass, Cr, Ni, brass, steel, cast Fe, Ag, and Pt, by transferring unimol. layers from a H<sub>2</sub>O surface, is described. Two different types of layers of Ca stearate were observed, depending on the  $p_{\rm H}$  and temp. of the H<sub>2</sub>O from which the films were transferred. Films built in steps of odd-numbered layers showed interference colours when viewed in white light; a single layer could be seen on polished Cr by means of polarised light. The thickness of step-films was measured by the interference of reflected monochromatic light; n was determined from the polarising angle, measured by a new method. The results show the thickness to be slightly > the long spacings of the corresponding fatty acids as deter-mined by the X-ray method. The m.p. of Ba stearate films show that those taken from  $H_2O$  of  $p_{\rm H}$  8.5 probably consist of neutral stearate, whilst those taken from H<sub>2</sub>O of  $p_{\rm H}$  6.9 are acid stearate.

E. S. H.

 Theory of flotation.
 I. W. WARK (Z. physikal.

 Chem.;
 1935,
 173,
 265—283).—Polemical against

 Ostwald (A., 1934, 958).
 R. C.

Dielectric potentials at the solution-air interface. B. KAMIENSKI (Bull. Acad. Polonaise, 1935, A, 129—136).—A dynamical jet method is described, particularly suitable for measuring the dielectric potentials at the solution-air interface of solutions of very active substances. The potential for 0.01*M*quinine hydrochloride changes from 0.055 volt at  $p_{\rm H}$  2.2 to 0.464 volt at  $p_{\rm H}$  7, the curve showing inflexions at  $p_{\rm H}$  4.15, 5.6, and 6.8. 0.001*M*-Quinine hydrochloride has a potential of 0.175 volt at the  $p_{\rm H}$ of blood. J. W. S.

Arrangement for studying the conditions within diffusion layers. T. TEORELL (Science, 1935, 81, 491).—Experiments with a "multimembrane" arrangement of Cellophane or collodion sheets show that the relation of the ionic concns. is qualitatively, at least, in accord with the Planck-Plettig predictions. The method has also been applied to diffusion systems associated with chemical reaction. L. S. T.

Metal membranes. N. V. KULTASCHEV and F. A. SANTALOV (Z. anorg. Chem., 1935, 223, 177– 184).—Cu membranes have been prepared by heating a Cu-Zn alloy until the Zn has volatilised. Such membranes are permeable to Cl',  $SO_4''$ , and  $CO(NH_2)_2$ , but not to glucose. The permeability is greatly increased by the action of 25% aq. HNO<sub>3</sub>. H<sub>2</sub>O can be forced through at a pressure of 1 atm. For cells in which the electrode solutions were separated by a Cu membrane, evidence of the existence of a membrane potential could be obtained. A Ag membrane, similarly prepared, showed similar properties. Having a larger pore vol. it was permeable to glucose also, but not to methylene-blue.

M. S. B.

Condition of substances dissociated in concentrated sulphuric acid. C. R. DE ROBLES and E. MOLES (Anal. Fis. Quim., 1934, **32**, 474–493).— The cryoscopic const. of  $H_2SO_4$ , m.p. 10.52°, determined by measurements with solutions of PhNO<sub>2</sub>, picric acid, CCl<sub>3</sub>·CO<sub>2</sub>H, and trinitrotoluene, is 65.4. HClO<sub>4</sub> yields normal results. When an excess of SO<sub>3</sub> is present I forms a compound  $I_2SO_3$ . HNO<sub>3</sub> yields HSO<sub>4</sub>NO,H<sub>2</sub>O and O, the observed mol. wt. being 23. With S<sub>2</sub>Cl<sub>2</sub> low vals. (105) are obtained, and decomp. occurs. Tetralite (2:4:6-trinitrophenylmethylnitroamine) forms a salt which yields 3 ions. H. F. G.

Association of water and deuterium oxide in dioxan solution. R. P. BELL and J. H. WOLFENDEN (J.C.S., 1935, 822-824).—The f.p. of 0.1—1.8M- $H_2O$ ,  $-D_2O$ , and -PhCl in dioxan show that  $H_2O$  and  $D_2O$  depart considerably from the laws of ideal solutions. The vals. of the osmotic coeffs. are consistent with Fuoss' treatment of dipole interaction (A., 1934, 728), and the assumption of a small difference of effective radius due to difference of zero-point energy accounts for the association factor for  $D_2O$  being approx. 3% > for  $H_2O$  at the same mol. concn. J. G. A. G.

F.-p. depression and constitution. W. HUCKEL, K. KUMETAT, and H. SEVERIN (Annalen, 1935, 518, 184-203) .- Determination of the cryoscopic const. of cyclohexane (I), C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>, and CHBr<sub>3</sub> for a variety of solutes shows that it often deviates considerably from the theoretical val. and also frequently varies with concn. Such variation is not observed (with any one solute) in all solvents, and the above anomalies are due mainly to the formation of solid solutions and different partition vals. between the liquid and solid phases. In (I) the trans-forms of dicyclic ring systems give higher vals. for cryoscopic const. than do the cis-forms, but trans-decahydronaphthalene gives an almost normal (const.) val. The implications of these results are discussed, so-called "association" anomalies being due frequently not to dipole association but to solid solution formation. Abnormal vals. of cryoscopic const. may also arise from vol. changes on dissolution. J. W. B.

Molecular arrangement and X-ray diffraction in ionic solutions. Errata. J. A. PRINS (J. Chem. Physics, 1935, 3, 362; cf. this vol., 443).—A correction. N. M. B.

X-Ray evidence on the ionic arrangement in thorium nitrate solutions. J. A. PRINS and R. FONTEYNE (Physica, 1935, 2, 570–572).—Measurements have been made of the diffraction halo of aq. Th(NO<sub>3</sub>)<sub>4</sub> of different concn. The results may be accounted for by assuming that each Th<sup>\*\*\*\*</sup> is heavily hydrated so as to form a close-packed arrangement, NO<sub>3</sub>' finding a place somewhere between.

M. S. B.

Variation with concentration of equivalent refraction of some salts and acids in aqueous solution. R. LUHDEMANN (Z. physikal. Chem., 1935, B, 29, 133-149).—The variation of apparent equiv. refraction, R, with concn., c, in g.-equiv. per 1000 g.  $H_2O$  has been examined at 25° at concns. from N to saturation at 10°. For HI R falls with rising c more rapidly than for any strong electrolyte hitherto examined. With HCO<sub>2</sub>Na R is const. for  $c=1-2\cdot5$ . For HIO<sub>3</sub> and LiIO<sub>3</sub> R is a max. at concns. of  $\sim7$  and 2.75, respectively. With HNO<sub>3</sub> the equiv. dispersion in the visible falls rapidly with increasing c. R. C.

Non-additivity of equivalent refraction of strong electrolytes at large concentrations. K. FAJANS and R. LÜHDEMANN (Z. physikal. Chem., 1935, B, 29, 150—157).—Extrapolation to zero conen. of available data for the rate of change with conen. of the apparent equiv. refraction, R, at conens. above 1.5 g.-equiv. per 1000 g. of H<sub>2</sub>O has shown for 29 electrolytes additivity of R at zero conen., thus justifying the extrapolation. Examples are, however, given showing that in general R and its variation with conen. are not additive at higher conens.

R. C. What is a colloid ? J. W. MCBAIN (Nature, 1935, 135, 1033).—Association is regarded as the characteristic factor in the colloidal state. The case of longchain mols. is discussed. In concest. > 0.1N association is predominant in the simple sulphonic acids and is responsible for an increase in conductivity, f.p. lowering, and e.m.f. with concen. L. S. T.

Preparation of colloidal metals. A. M. THOMAS and E. B. WEDMORE (Nature, 1935, 135, 1001).—A method for the prep. of colloidal suspensions of liquid metals and alloys in semi-conducting media is described. L. S. T.

Preparation of colloid solutions by the silent electrical discharge. III. S. MIYAMOTO (Kolloid-Z., 1935, 71, 297-300; cf. A., 1934, 841, 1305).---Sols of Se and Te in  $H_2O$  and EtOH, and hydrosols of  $MnO_2$  have been prepared by the action of the silent electric discharge. The stability of the sols and the influence of protective colloids have been studied.

E. S. H.

Validity of Rayleigh's formula for colloid systems. L. V. SMIRNOV (Kolloid-Z., 1935, 71, 261-265).—For white, non-metallic colloid systems the power to which  $\lambda$  is raised in the Rayleigh formula falls from 3.8 to 1.3 as the radius of particle is increased from 60 to 200 mµ. E. S. H.

Cryolysis, diffusion, and particle size. I. Experiments with sodium oleate, ovalbumin, and polyacrylic acid. F. E. M. LANGE and F. F. NORD (Biochem. Z., 1935, 278, 173—190; cf. A., 1931, 389). —The changes produced by freezing (to  $-79^{\circ}$  or lower) and subsequent thawing in the rates of diffusion of these substances (in biological conens.) indicate that, with high conens., the state of aggregation is increased by freezing, whilst with low conens. it is decreased. A partial explanation is thus provided of the behaviour of colloidal materials (enzymes, soil). W. McC.

Structure of the gelatinous ortho-ferric hydroxide obtained by oxidising ferrous carbonate. A. KRAUSE and L. SKORUPSKA (Rocz. Chem., 1935, 15, 114—121).—The gel obtained by adding  $H_2O_2$  to an aq. suspension of freshly pptd. FeCO<sub>3</sub> is probably  $Fe(OH)_2 \cdot O \cdot [FeO \cdot OH]_4 \cdot FeO$ . R. T.

Changes in the refractive index of mixed alumina and silica gels under the influence of water and alkali. J. H. HELLMERS and R. KOHLER (Z. Pflanz. Düng., 1935, 39, 38—44; cf. B., 1934, 1074).—A microscopically uniform mixture of  $Al_2O_3$ (I) and SiO<sub>2</sub> (II) gels is obtained by shaking the two components in N-NaOH. The *n* of the product varies with the composition of the mixture and with the proportion of adsorbed Na. No evidence was obtained of the formation of compounds of (I) and (II) on mixing Na silicate with AlCl<sub>3</sub> solution. The *n* of naturally occurring compounds of similar composition is discussed. A. G. P.

Combination of iodine with starch. S. V. NEDZVETSKI (Bull. Acad. Sci. U.R.S.S., 1934, 7, 1561—1569).—On adding I in KI to starch solution  $\eta$  remains const. up to a definite % of I and then rises rapidly. The point of change depends on the ratio starch/I and not on the concns. of the components. The stability of starch iodide towards electrolytic coagulants falls rapidly as soon as  $\eta$  increases. After coagulation the I is entirely retained by the starch. It is inferred that combination is at first "chemical," and is followed by adsorption of I. R. S. B.

Viscosity and plasticity of disperse systems. V. Plastic-viscous properties of peat. M. P. VOLAROVITSCH, N. N. KULAKOV, and A. N. ROMANSKI (Kolloid-Z., 1935, 71, 267—274; cf. this vol., 701).— A capillary viscosimeter for use with systems composed of peat and  $H_2O$  is described. Determinations of plasticity const., flow resistance, and  $\eta$  have been made, and their dependence on the  $H_2O$  content of the system has been investigated. Bingham's theory of plastic streaming is applicable. E. S. H.

Ionic exchange in relation to stability of colloidal systems. H. JENNY and R. F. REITEMEIER (J. Physical Chem., 1935, 39, 593—604; cf. A., 1932, 992).—For Putnam clays the  $\zeta$ -potential is the higher, the smaller are the adsorbed cations, when the latter are of the rare gas type and of equal valency. The extent of the ionic exchange occurring when clays stabilised by different types of ions are brought in contact with various electrolytes, and its relation to the coagulation val. of the latter, are discussed.

F. L. U. Lyophilic colloids. VII. Fractionation of agar and physico-chemical properties of the fractions. S. M. LIEPATOV and A. A. MOROSOV (Kolloid-Z., 1935, 71, 317—324; cf. this vol., 701).— Agar has been fractionated by progressive dialysis. The ash content,  $p_{\rm H}$ , osmotic pressure, swelling, solubility, and heats of swelling and hydration of the fractions have been determined. The fractions differ in degree of association; the more highly associated fractions contain less Ca<sup>\*\*</sup>. The heat of chemical hydration of agar is > that of gelatin, cellulose, or starch, although the heat of total solvation is less. E. S. H.

Influence of hydrophilic colloids on structure formation in ferric hydroxide sols. G. FUCHS

Polysaccharoprotein sols. S. J. VON PRZYLECKI, H. ANDRZEJEWSKI, and E. MYSTKOWSKI (Kolloid-Z., 1935, 71, 325–333).—Measurements of turbidity and  $\eta$  have been made for solutions of several proteins, polysaccharides, and their mixtures. Departures from additivity on mixing several of the pairs are noted. These observations are discussed in relation to the mode of combination of the components.

E. S. H. Rhythmic reactions in silicic acid gels. F. TABOURY and G. JAUNEAU (Bull. Soc. chim., 1935, [v], 2, 971—982).—The period of gelatinisation of SiO<sub>2</sub> by the addition of HNO<sub>3</sub> or H<sub>2</sub>CrO<sub>4</sub> to Na<sub>2</sub>SiO<sub>3</sub> increases with the dilution and becomes a min. with increasing [neutral salt]. The rate of penetration of CuSO<sub>4</sub> into gels containing K<sub>2</sub>CrO<sub>4</sub>, and the formation of CuCrO<sub>4</sub> rings has been studied in relation to the [K<sub>2</sub>CrO<sub>4</sub>] and [neutral salt]. Rhythmic pptn. of Ag<sub>2</sub>CrO<sub>4</sub>, which has been similarly studied, is favoured by an impurity (e.g., NaBr) which produces a ppt. more insol. than Ag<sub>2</sub>CrO<sub>4</sub>. The distances of successive rings from the origin are in agreement with the equations previously applied (A., 1932, 225).

R. S. Electrokinetics. XIV. Critical comparison of electrophoresis, streaming potential, and electroosmosis. H. B. BULL (J. Physical Chem., 1935, 39, 577-583; cf. A., 1934, 143).—The three methods give the same val. for the ζ-potential of surfaces covered with gelatin or ovalbumin, but not for surfaces of quartz or cellulose. A cell for electrophoresis is described. F. L. U.

Comparison of electrophoretic, electroosmotic, and stream potential isoelectric points at glass and gelatin surfaces. B. MONAGHAN, H. L. WHITE, and F. URBAN (J. Physical Chem., 1935, 39, 585—591).—The isoelectric concess of Th<sup>\*\*\*</sup>, Fe<sup>\*\*\*</sup>, and Al<sup>\*\*\*</sup> for Pyrex glass given by electroosmosis and electrophoresis are several times > those given by streaming potential measurements. All three methods give the same isoelectric [H<sup>\*</sup>] for gelatin. It is inferred that only the diffuse component of the double layer is moved by hydrostatic forces, whilst both the diffuse and the outer Helmholtz layers move in an electric field. F. L. U.

Influence of electrolyte concentration on the ratio of electro-osmotic to electrophoretic mobilities. H. L. WHITE, B. MONAGHAN, and F. URBAN (J. Physical Chem., 1935, **39**, 611-622; cf. preceding abstract).—The ratio (R) of electro-osmotic velocity to the electrophoretic velocity of glass and of gelatin-covered particles of  $1-3 \mu$  diam. is > 3 in distilled H<sub>2</sub>O, but decreases with increasing [KCl] to 1 for conces.  $10^{-3}-10^{-2}M$  and higher. The causes are discussed. F. L. U.

Electrical charges of activated carbons. H. L. OLIN, J. D. LYKINS, and W. F. MUNRO (Ind. Eng. Chem., 1935, 27, 690—693).—Cataphoretic velocities have been measured for Brownian particles of various types of activated C suspended in solutions of  $p_{\pi}$ 1.5—12.0. At each  $p_{\pi}$  val. many results are averaged and the resulting curves show two isoelectric points for each sample. There is a remarkable similarity between relative adsorptive capacities and drift

(Kolloid-Z., 1935, 71, 307-316).—Viscosity-pressure curves show that albumin causes coagulation structure formation in  $Fe(OH)_3$  sols, which is followed after a time by spontaneous peptisation. The former is due to the fixing of Fe<sup>...</sup> by the albumin, thus involving desorption of the stabilising ions. The subsequent peptisation is due to the formation of  $NH_2$ -acids from the albumin. Independent experiments show that  $\alpha$ -alanine destroys the Fe(OH)<sub>3</sub> structures. Starch causes similar structure formation in Fe(OH)<sub>3</sub> sols, through the binding of H<sup>\*</sup> in the intermicellar liquid. E. S. H.

Action of electrolytes on hydrophobic colloids. H. R. KRUYT (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 464-470).—The distinction between potential- and non-potential-determining ions is discussed and illustrated by data for the flocculation of negatively-charged AgI sol, flocculated by  $Al(NO_3)_3$ and  $K_2SO_4$ . The antagonistic effect of the  $K_2SO_4$ causes a high concn. of the Al ion, the activity of which, however, decreases along the flocculation curve. N. M. B.

Thixotropy, influenced by the orientation of anisometric particles in sols and suspensions. H. FREUNDLICH and F. JULIUSBURGER (Trans. Faraday Soc., 1935, **31**, 920–921).—Thixotropic sols (e.g.,  $V_2O_5$  sol) or suspensions (e.g.,  $CaSO_4, 2H_2O +$  $H_2O$ ) containing anisometric particles solidify in a few sec. when the particles are oriented by gentle movement, whereas up to 1 hr. is required for spontaneous solidification. The term "rheopexy" is suggested for the phenomenon. J. W. S.

Refractive index of hydrosols of pectin substances. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1935, 5, 185–188). R. T.

Physical chemistry of proteins in non-aqueous and mixed solvents. II. Electrochemical properties of protein solutions in glacial organic acids. D. M. GREENBERG and C. E. LARSON (J. Physical Chem., 1935, 39, 665-677; cf. A., 1930, 1118).—Casein, edestin, gelatin, and deaminised gelatin do not increase the electrical conductivity of anhyd. lactic acid, and the increase of that of AcOH is too small to permit the assumption of salt formation. The large increase observed with HCO<sub>2</sub>H is due to formation of protein formates, the conductivities and transport nos. of which have been measured. The solvent action of the three acids is not primarily dependent on their ability to form charged protein ions. F. L. U.

Isoelectric point of isinglass. H. FREUNDLICH and P. S. GORDON (Trans. Faraday Soc., 1935, 31, 915—919).—The isoelectric point of isinglass (I) in aq. solution, as measured by the cataphoretic velocity of quartz particles coated with (I) in buffer solutions, is  $p_{\rm H} 5.9$ . The sedimentation vol. of quartz particles in buffer solutions containing (I) is a max. at  $p_{\rm H}$ 5.8—6.0, but the abs. vol. is dependent on the presence of air, decreasing to half on evacuation. This decrease is only about 10% in absence of (I). The vol. of the sediment formed in a vac. increases only slightly on shaking with air. Similar results were obtained with gelatin, ovalbumin, and hæmoglobin. J. W. S.

velocities, especially with high  $p_{\rm H}$  vals. For this reason the method offers promise of usefulness in C. I. evaluating adsorptive C.

Derivation of thermodynamical relations for a simple system. A. N. SHAW (Phil. Trans., 1935, A, 234, 299-328).-A new procedure is developed whereby thermodynamic relations for a system which requires only three related variables for its description may be rapidly deduced. Compact tables are given which contain data for a great variety of transformations and illustrations of the use of the tables are provided by transformations connected with the theory of perfect gases, radiation in an enclosure, and saturated vapour. R. S. B.

Parachor and entropy of metallic elements. B. N. SEN (J. Chim. phys., 1935, 32, 300-302; cf. A., 1934, 719).-A formula is deduced whereby vals. for the entropy of metals calc. from the parachors are, in general, in good agreement with accepted vals. J. G. A. G.

Ethane-ethylene-hydrogen equilibrium. H. A. SMITH and W. E. VAUGHAN (J. Chom. Physics, 1935, 3, 341-343).-A statistical calculation of the equilibrium consts. over the temp. range 400-700° gives vals. < experiment by the factor 2. The discrepancy probably lies in the calc. entropy of free rotation in  $C_2H_4.$ N. M. B.

Interpretation of reaction between allylthiocarbimide and piperidine. W. HEROLD (Z. physikal. Chem., 1935, B, 29, 121-126).-The equilibrium const. has been derived from Kremann and Riebl's absorption data (A., 1933, 885) and shows reaction to go almost to completion. The results suggest that the product of reaction is a substituted thiocarb-R. C. amide.

Dissociation constants of some polybasic acids. W. R. MAXWELL and J. R. PARTINGTON (Trans. Faraday Soc., 1935, **31**, 922–935).—The dissociation consts. of  $C_6(CO_2H)_6$ ,  $C_6H(CO_2H)_5$ , 1:2:3- $C_6H_3(CO_2H)_3$ , o- and  $m \cdot C_6H_4(CO_2H)_2$ , and BzOH are in the ratio 500:250:25:15:3:1, indicating the tendency of one CO2H to promote ionisation of another and the effect of inter-group distance. The tendency of an ionised CO<sub>2</sub>H to hinder ionisation of a further CO<sub>2</sub>H is shown by the fact that dissociation consts. of the last  $CO_2H$  of the above compounds are in the ratio 10:35:120:500:2500:6000.

J. W. S.

Hydrolysis of the aluminium benzenesulphonates. V. CUPR and B. SLIVA (Publ. Fac. Sci. Univ. Masaryk, 1935, No. 200, 3-13; cf. A., 1931, 910).-The  $p_{\rm H}$  of 0.01–0.5N solutions of (PhSO<sub>3</sub>)<sub>3</sub>Al,9H<sub>2</sub>O, p-(OH·C<sub>6</sub>H<sub>1</sub>·SO<sub>3</sub>)<sub>2</sub>Al,9H<sub>2</sub>O, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and AlCl<sub>3</sub> during hydrolysis is  $-0.54 \log [A1^{\cdot\cdot\cdot}]+2.65$ . The following salts have been prepared from  $Al_2(SO_4)_3$  and the appropriate Ba salts:  $p \cdot (C_6H_4Me \cdot SO_3)_3Al,9H_2O$ ;  $p \cdot (C_6H_4Cl \cdot SO_3)_3Al,9H_2O$ ;  $p \cdot (C_6H_4Br \cdot SO_3)_3Al,9H_2O$ ;  $2 : 1 : 4 \cdot (NO_2 \cdot C_6H_3Me \cdot SO_3)_3Al,12H_2O$ ;  $3 : 6 : 1 \cdot (NO_2 \cdot C_6H_3Cl \cdot SO_3)_3Al,9H_2O$ ;  $m \cdot (NO_3 \cdot C_6H_3Cl \cdot SO_3)_3Al,9H_2O$ ;

 $m \cdot (NO_2 \cdot C_6 H_4 \cdot SO_3)_3 Al, 9H_2O.$ F. R. G.

Nature of the ceric sulphates. E. G. JONES and F. G. SOPER (J.C.S., 1935, 802-805).-Ce(SO<sub>4</sub>)<sub>2</sub> and  $Ce(SO_4)_2, 4H_2O$  coexist in contact with a solution con-

taining 57—62% of SO<sub>3</sub>.  $Ce(SO_4)_2$  forms metastable solutions in H<sub>2</sub>O, which, on mixing with conc. H<sub>2</sub>SO<sub>4</sub>, give two salts,  $H_4Ce(SO_4)_4$  (English red) and  $H_2Ce(SO_4)_3$ (orange), which gradually change to  $Ce(SO_4)_2$ . There is no evidence of migration of Ce to the cathode in solutions 0.5-20N with respect to  $H_2SO_4$  and 0.01-0.13M with respect to  $Ce(SO_4)_2$ , either alone or with added K, Na, and Li sulphates. The coloured Ce ions migrate to the anode. In N-H<sub>2</sub>SO<sub>4</sub>, the Ce is present chiefly as H<sub>3</sub>Ce(OH)(SO<sub>4</sub>)<sub>3</sub>, and the colour of the solution decreases rapidly in < 0.4N-H<sub>2</sub>SO<sub>4</sub>. This is probably correlated with hydrolysis of the sulphato-cerate anion and the ultimate pptn. of the J. G. A. G. basic salt HCe(OH)<sub>3</sub>SO<sub>4</sub>.

Cryoscopy of mixtures of nitrogen peroxide and bromine. A. PERRET and R. PERROT (Compt. rend., 1935, 200, 2166-2168).-The f.-p. curve given affords no evidence for the existence of NO<sub>2</sub>Br. H. J. E.

Equilibrium in the system Be(NO<sub>3</sub>)<sub>2</sub>-HNO<sub>3</sub>-H<sub>2</sub>O. A. V. NOVOSSELOVA and N. D. NAGORSKAJA (Bull. Soc. chim., 1935, [v], 2, 967-971).—The solubility of  $Be(NO_3)_2$  in aq.  $HNO_3$  at 0° and 20° has been determined. Hydrates with 4, 3, 2, and 1 H<sub>2</sub>O have been identified. The last three give metastable forms. R. S.

System water-sodium pentaborate. A. P. ROLLET and P. CHUNG-MING (Bull. Soc. chim., 1935, [v], 2, 982-985).-The solubility of Na<sub>2</sub>O,5B<sub>2</sub>O<sub>3</sub> in H<sub>2</sub>O has been determined. There is an ice-salt eutecticat  $-1.7^{\circ}$  and the transition  $Na_2O_{,5}B_2O_{3,1}OH_2O$  $\longrightarrow Na_2O_{,5}B_2O_{3,2}H_2O$  occurs at 100°. R. S.

System water-sodium pentaborate-sodium chloride. P. CHUNG-MING (Bull. Soc. chim., 1935, [v], 2, 985-993; cf. preceding abstract).-The saturated solution is in equilibrium with the solid phases NaCl,  $Na_2O_{,5}B_2O_{3}, 10H_2O$  (I), and  $Na_2O_{,5}B_2O_{3}, 2H_2O$ at  $55^{\circ}\pm3^{\circ}$ , and with NaCl, NaCl, 2H<sub>2</sub>O, and (I) at  $-1.3^{\circ}$ . (I) is metastable above  $55^{\circ}$ . There is a ternary eutectic ice-NaCl,2H<sub>2</sub>O-(I) at -22.7°. A saturated solution of NaCl and Na<sub>2</sub>O,5B<sub>2</sub>O<sub>3</sub> deposits only pentaborate on cooling between  $100^{\circ}$  and  $-1.3^{\circ}$ . R. S.

Vapour pressure and dehydration of unstable salt hydrates. Sodium perborate. T. I. TAYLOR and G. G. TAYLOR (Ind. Eng. Chem., 1935, 27. 672—680).—Commercial Na perborate (I) is represented by NaBO<sub>3</sub>, $4H_2O$  or more correctly NaBO<sub>2</sub>. $H_2O_2$ , $3H_2O$ . The  $H_2O$  v.p. of a mixture of (I) with NaBO<sub>2</sub>,  $H_2O_2$  at temp. up to 50° is given by log  $p=12\cdot19-3286/T$ . Rate of dehydration at a given temp. is governed by (1) rate of nucleus formation, (2) rate of linear propagation of interface, (3) size and shape of reactant particles, (4) rate of removal of H<sub>2</sub>O vapour. In dehydration at atm. pressure the rate of removal of H<sub>o</sub>O is the controlling factor until about 70% of the  $H_2O$  is removed. On heating to 90° the available O in (I) increases from 10% to 16%, but at higher temp. diminishes rapidly with O evolution. The solubility rises continually with heating. C. 1.

Ammines of thorium bromide. R. C. Young (J. Amer. Chem. Soc., 1935, 57, 997-999).-The system has been studied by the tensimetric method at 0° and 25°. The equilibrium  $\text{ThBr}_4,20\text{NH}_3 \Longrightarrow$  $\text{ThBr}_4,14\text{NH}_3+6\text{NH}_3$  has been established. The decomp. pressures of the ammines have been measured. E. S. H.

Thermal analysis of binary systems of antipyrine and resorcinol with certain organic compounds.—Sce this vol., 971.

Thermal equilibrium in ternary systems. IV. Antipyrine-phenacetin-salol. Thermal equilibrium in the system  $\beta$ -naphthol- $\beta$ -naphthylamine.—See this vol., 970.

Equilibria in the system  $NiCl_2-H_2O-HCl$ . A. V. BABAEVA and T. A. ARTSCHAKOVA (J. Gen. Chem. Russ., 1935, 5, 216—219).—The solid phase at 20°, for [HCl] from 0 to 21·2%, is  $NiCl_2,6H_6O$ , and  $NiCl_2,4H_2O$  (I) at higher [HCl]; at 80° only (I) is formed. R. T.

Equilibria in the system  $Na_2O-HF-H_2O$ . N. D. NAGORSKAJA and A. V. NOVOSELOVA (J. Gen. Chem. Russ., 1935, 5, 182—184).—The solubility of NaF falls rapidly with rising [NaOH]; the relations show little change between 0° and 94°. R. T.

System  $Na_2SO_4-Al_2(SO_4)_3-H_2O$ . J. T. DOB-BINS and J. A. ADDLESTON (J. Physical Chem., 1935, 39, 637-642; cf. A., 1932, 341).—Isotherms for 0°, 30°, and 42° are given. Na alum is formed as a solid phase at 30° and 42°, but not at 0°. F. L. U.

System CaO-SiO<sub>2</sub>-H<sub>2</sub>O. R. NACKEN and R. MOSEBACH (Z. anorg. Chem., 1935, 223, 161–173).— Ca<sub>3</sub>SiO<sub>5</sub> is gradually decomposed by H<sub>2</sub>O forming successively, with increasing quantities of H<sub>2</sub>O, 2CaO,SiO<sub>2</sub>,H<sub>2</sub>O, 3CaO,2SiO<sub>2</sub>,3H<sub>2</sub>O, and

CaO,SiO<sub>2</sub>,2H<sub>2</sub>O. No appreciable dissolution of SiO<sub>2</sub> is indicated. Marked variation in solubility of CaO with fineness of division was observed. The most probable val. for the solubility at 20° is 1.2100 g. per litre. By grinding in contact with H<sub>2</sub>O a supersaturation of 23% may be obtained. M. S. B.

Felspar system and the weathering of felspar to kaolin. M. HOLLENWEGER and H. RUMPELT (Z. techn. Physik, 1934, 15, 318—323; Chem. Zentr., 1935, i, 539).—M.-p. data are recorded for the system  $K_2O-Al_2O_3$ -SiO<sub>2</sub>. The free alkali formed on heating felspar samples for 24 hr. at 80° with H<sub>2</sub>O is correlated with the equilibrium diagram. Weathering is discussed. H. J. E.

Ternary systems water, allyl alcohol, and salts at 25°. P. M. GINNINGS and M. DEES (J. Amer. Chem. Soc., 1935, 57, 1038—1040).—Data for systems of H<sub>2</sub>O and allyl alcohol (I) with  $(NH_4)_2HPO_4$ , Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, MgSO<sub>4</sub>, NaNO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaCl, SrCl<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>,  $(NH_4)_2SO_4$ , and CdSO<sub>4</sub>, respectively, are recorded. (I) is more difficult to salt out than Pr<sup>a</sup>OH or Pr<sup>g</sup>OH. E. S. H.

System aniline-formic acid-water. J. R. POUND and A. M. WILSON (J. Physical Chem., 1935, 39, 709-719).—Equilibria at 15° have been determined. The only solid phase is aniline formate (I). The transformation of the liquid mixtures and of solid crystals of (I) into formanilide has been studied. .F. L. U. System alkali oxide-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>. III. Action of CO<sub>2</sub> and  $K_3CO_3$  on potassium diand tetra-silicate. C. KROGER and E. FINGAS (Z. anorg. Chem., 1935, 223, 257—276).—Equilibria on the SiO<sub>2</sub>-rich side of the  $K_2O-CO_2$ -SiO<sub>2</sub> system have been investigated between 200° and 900° by measurement of the equilibrium pressure of CO<sub>2</sub>. The phase-rule diagram (cf. A., 1933, 916) is completed by the equilibria in the system  $K_2Si_4O_9$ +  $K_2CO_3=CO_2$ +mixed crystals of  $K_2CO_3$  with  $K_2Si_2O_5$ . Heats of formation of  $K_2SiO_3$ ,  $K_2Si_2O_5$ , and  $K_2Si_4O_9$ are calc. from the tensimetric data. J. S. A.

Heats of dilution and heats of vaporisation of D<sub>2</sub>O-H<sub>2</sub>O mixtures. E. DOEHLEMANN and E. LANGE (Z. physikal. Chem., 1935, 173, 295-312; cf. A., 1934, 1071).—There is no heat effect on mixing  $COMe_2$  and  $CO(CD_3)_2$ . The integral heat of dilution on mixing  $H_2O$  and  $D_2O$  is considerable and increases linearly with the D content of the mixture. The partial mol. heats of dilution of H<sub>2</sub>O and D<sub>2</sub>O and the partial mol. heats of vaporisation have been calc. All these data agree with the assumption that the cause of the heat of mixing is not van der Waals forces, but  $H_2O + D_2O \longrightarrow 2HDO - 32$  g.-cal. If the heat of this reaction in the gaseous state is -156 g.-cal. the van der Waals part of the partial mol. heat of evaporation of HDO is not the mean of the corresponding vals. for  $D_2O$  and  $H_2O$ . If it is the mean, the heat of the above reaction must be the same in both gaseous and liquid states. The mol. heats of vaporisation of the solution have been cale. R. C.

Heat of dissolution of magnesium oxide in nitric acid, and of zinc oxide and silver oxide in hydrofluoric acid as dependent on the concentration of acid. Specific heat of hydrofluoric acid solutions. A. PRANSCHKE and H. E. SCHWIETE (Z. anorg. Chem., 1935, 223, 225–233).—The heats of dissolution of MgO in 2N-, 4N-, 5N-, and 9N-HNO<sub>3</sub>, and of ZnO and Ag<sub>2</sub>O in 5N-, 10N-, 18N-, and 23N-HF, at 18° have been measured, and the sp. heat of aq. HF (9.8–40.7%) at 18° has been determined. J. S. A.

Salt effect in concentrated solutions. Change in the heat of dissolution of potassium chloride by other electrolytes. C. DRUCKER (Arkiv Kemi, Min., Geol., 1935, 11, A, No. 18, 27 pp.).—The effect of HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, LiCl, NaCl, KCl, NH<sub>4</sub>Cl, KI, MgCl<sub>2</sub>, CaCl<sub>2</sub>, BaCl<sub>2</sub>, CdCl<sub>2</sub>, LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, Be(NO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, La(NO<sub>3</sub>)<sub>3</sub>, NaOAc, KOAc, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub> on the heat of dissolution of KCl has been investigated. The greatest decrease occurs in presence of NO<sub>3</sub>' and SO<sub>4</sub>'', and much less decrease with Cl' and especially OAc'. In general, bivalent cations have a greater effect than univalent cations. J. W. S.

Thermodynamics of system sulphur dioxidewater. W. A. ROTH (Z. physikal. Chem., 1935, 173, 313—318).—The heat of dissolution of SO<sub>2</sub> in H<sub>2</sub>O consists of heat of dissolution without hydration (=heat of condensation), heat of hydration, and heats of first and second dissociation. Since the second dissociation is negligible, if hydration is complete the heat of dissociation should be a linear function of the degree of first dissociation. From the deviation from linearity observed at higher concus. the hydration const. has been calc., permitting the derivation of a formula for heat of dissolution valid for solutions containing 37.5-7500 mols. of H<sub>2</sub>O per mol. of SO<sub>2</sub> with an average error of 0.3%. Component parts of the heat of dissolution derived by the reaction isochore (this vol., 25) are less trustworthy than the calorimetric vals. R. C.

Thermochemistry of ammonium arsenates. A. DE PASSILLÉ (Compt. rend., 1935, 200, 1852– 1854).—Data for heats of neutralisation of  $H_3AsO_4$  by aq. NH<sub>3</sub> and for heats of dissolution of the products at 15° are recorded, and vals. for the heats of formation of NH<sub>4</sub>H<sub>2</sub>AsO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HAsO<sub>4</sub>, (NH<sub>4</sub>)<sub>3</sub>AsO<sub>4</sub>, and (NH<sub>4</sub>)<sub>3</sub>AsO<sub>4</sub>,3H<sub>2</sub>O are calc. H. J. E.

Electrical conductivity of extremely dilute solutions. M. HŁASKO and A. SALIT (Bull. Acad. Polonaise, 1935, A, 189–200).—A method is developed for the measurement to  $\pm 2\%$  of the electrical conductivity of solutions of concn. down to  $10^{-7}N$ , and for the direct determination of the limiting mol. conductivity of strong electrolytes. The Kohlrausch extrapolation formula is applicable to the calculation of the limiting mol. conductivity of both strong and weak electrolytes. Data are given for solutions of KOH,  $H_2SO_4$ , AcOH, and  $NH_3$ . J. W. S.

Conductivity of alkali hydroxides in very dilute aqueous solutions. M. HŁASKO and A. SALITÓWNA (Rocz. Chem., 1935, 15, 153—162).—Direct measurements show that  $\lambda_{x}$  is attained at the following concess.: LiOH  $2 \times 10^{-6}N$ , NaOH  $4 \times 10^{-6}N$ , KOH  $5 \times 10^{-6}N$ , RbOH  $8 \times 10^{-6}N$ , CsOH  $10^{-5}N$ ; these results differ by 0.2% from those calc. from Kohlrausch's formula. The transport nos. of the ions are K' 74.7, Li' 40.0, Na' 50.9, Rb' 77.6, and Cs' 78.4. R. T.

A.c. and d.c. surface conductivity measurements in Pyrex slits. F. URBAN, S. FELDMAN, and H. L. WHITE (J. Physical Chem., 1935, 39, 605— 609; cf. A., 1932, 699).—The surface conductivities of dil. aq. KCl in slits formed by cracking Pyrex flasks agree with those previously found for capillaries. There is thus no difference in the surface conductivities of fused and fractured glass. The apparent sp. conductivity is lower with d.c. than with a.c.; this is due to membrane potentials. F. L. U.

Electrolysis of solid alloys. W. JOST and R. LINKE (Z. physikal. Chem., 1935, B, 29, 127–132).— When a current is passed through a glowing wire of a Au–Pd alloy Au accumulates at the anode and Pd at the cathode end. The transport no. of Pd at 900° is  $\sim 10^{-11}$  (cf. this vol., 158). R. C.

Electrochemical investigation of solid cadmium-antimony alloys. A. ÖLANDER (Z. physikal. Chem., 1935, 173, 284–294).—Electrode potentials of alloys in contact with molten mixtures of NaOAc, KOAc, and  $Cd(OAc)_2$  at 240–290° have been measured. The stable intermediate phase CdSb exhibits a region of homogeneity extending from 50.0 to 50.5 at.-% Cd. The degree of disorder of the lattice of this compound is calc. to be 0.00005 at  $250^\circ$ , but must rise continuously with the temp. R. C.

Diffusion potentials. II. V. CUPR (Publ. Fac. Sci. Univ. Masaryk, 1934, No. 197, 1–14; cf. A., 1934, 149).—Theoretical. Planck's equation satisfies the relation formerly deduced when (a) the solutions in contact have the same concn. and cation (anion), or cations (anions) of the same mobility, (b) the solutions contain the same electrolyte in different concns., or (c) the diffusion potential between both solutions is zero. E. S. H.

Current-producing processes in concentration gradients in solid electrolytes. W. SCHOTTKY (Wiss. Veröff. Siemens-Werken, 1935, 14, 1-19).— Theoretical. The conditions under which an e.m.f. is produced by concn. differences in solid solutions, such as Na in NaCl etc., are discussed. E.S. H.

Electrometric studies of the precipitation of hydroxides. XIII. Constitution of aqueous solutions of silver oxide in ammonia, mono-, di-, and tri-methylamine and -ethylamine, pyridine, and ethylenediamine; dissociation constants of amines. H. T. S. BRITTON and W. G. WILLIAMS (J.C.S., 1935, 796-801).-The dissociation consts., K, of the amines determined potentiometrically at 18° are of the same order as recorded vals.  $K_{b_1}$  and  $K_{b_1}$  of  $(\cdot CH_2 \cdot NH_2)_2$  are  $1 \cdot 14 \times 10^{-4}$  and  $1 \cdot 13 \times 10^{-7}$ , respectively. The solubilities were determined at  $15^{\circ}$  in 0.04—3.1N-aq. solutions of the bases, and from the e.m.f. of the cell Ag|complex solution|sat.  $KNO_3|N$ -calomel, the instability consts.  $K_1 =$  $[Ag'][B]^2/[AgB_2']$  were calc. These vals. show that the order of the co-ordinating tendencies of amines (except  $NH_2Ph$ ) with respect to Ag is primary > sec. > tert. Electrometric and conductometric titrations show the presence of bases,  $Ag(B)_2OH$ , similar in strength to NaOH. The strength of these complex bases is independent of the strength of the NH<sub>3</sub> base in the complex cation. J. G. A. G.

Polarographic studies with the dropping mercury cathode. XLVII. Passivation of small mercury anodes. V. MAJER (Coll. Czech. Chem. Comm., 1935, 7, 215—227).—In the polarographic investigation of aq. solutions of KCl and of KBr with small anodes, new passivity phenomena have been observed, which are due to the formation of anodic films of Hg<sub>2</sub>Cl<sub>2</sub> and Hg<sub>2</sub>Br<sub>2</sub>, respectively. These surface films of thickness  $146\pm20$  Å. act like a resistance of  $10^6$ — $10^7$  ohms. The theory of the passivation of small Hg anodes is discussed.

O. J. W.

Polarographic studies with the dropping mercury electrode. II. Absolute determination of reduction and depolarisation potentials. J. HEYROVSKY and D. ILKOVIO (Coll. Czech. Chem. Comm., 1935, 7, 198—214).—In analytical applications of the polarographic method some uncertainty occurs in fixing the position of the characteristic bend in the current-potential curve. This uncertainty is eliminated and a const. val. of the electrode potential obtained by taking the potential at the point where the current is equal to half the limiting current (diffusion current). This potential is characteristic of the electrolytic process and is independent of the concn. of the solution, sensitivity of galvanometer, rate of dropping of Hg, scale of co-ordinates, and height of diffusion current. O. J. W.

Intensity of the diffusion current in relation to the size and period of renewal of the cathode surface. G. SEMERANO (Gazzetta, 1935, 65, 289— 298).—The dependence of the intensity of the diffusion current on the size of the dropping Hg cathode and on the rate of dropping has been studied for the deposition of Cd and of Ba. With increasing size of drops or rate of dropping the waves of the diffusion current are increased in height and the deposition potentials of the metallic ions become more positive. The thickness of the diffusion layer around the cathode is calc. to be  $36-65 \mu$ . The weight of the Hg drops is probably const. Means for increasing the precision of the polarographic method are described. O. J. W.

Reduction of deoxybenzoin and of benzoin at the dropping Hg cathode. G. SEMERANO (Gazzetta, 1935, 65, 273–288).—The reduction potentials of deoxybenzoin and of benzoin dissolved in 0·1*N*-NH<sub>4</sub>Cl in 50% EtOH are -1.129 and -1.061 volts, respectively (referred to *N*-calomel cell). From the form of the polarisation curve and the displacement of the reduction potential with concn. of reducible substance and of H<sup>+</sup>, it is concluded that the reduction process is univalent and leads to the corresponding pinacols. A method is proposed for determining the constitution of isomeric benzoins. The solubility of benzoin in H<sub>2</sub>O is  $1.75 \times 10^{-4}$  mol. per litre.

0. J. W.

Simultaneous discharge of hydrogen ion and metal ions from solutions of complex cyanides. O. ESSIN, A. BALABAJ, and A. MATANZEV (Z. physikal. Chem., 1935, 173, 216—222).—The equation previously derived (this vol., 450) has been confirmed by measurements of the simultaneous discharge of H<sup>\*</sup> and Zn<sup>\*\*</sup> from solutions of K<sub>2</sub>Zn(CN)<sub>4</sub> and published data for the simultaneous discharge of H<sup>\*</sup> and metal ions from solutions of other complex cyanides. The results permit calculation of  $\gamma$  coeffs. of Volmer's equation (A., 1930, 1376) for several ions. R. C.

Influence of light on the anodic polarisation of tungsten. J. P. E. DUCLAUX (Compt. rend., 1935, 200, 1838-1840).—Ultra-violet light produces depolarisation of a W electrode, polarised in conc. aq.  $H_2SO_4$ , the increase in current depending on the applied voltage. The max. sensitivity is at 3650 Å. The effect of light falls to approx. 10% of its initial val. after 24-48 hr. H. J. E.

Anodic behaviour of alcohols in alkaline solutions. S. KOIDZUMI (Mem. Coll. Sci. Kyoto, 1934, A, 17, 329—379).—Current-potential curves for anodes of Pt, Pd, Au, Rh, Ag, Ni, Cu, Ir, and C in solutions containing  $H_2O$ , NaOH, and MeOH or EtOH have been determined and the products of electrolysis analysed. The evolution of  $H_2$  and hydrocarbons has been observed at the anode; the mechanism is discussed on the basis of the electronic theory, assuming adsorption and splitting of org. ions at the anode. Periodic variations of c.d. and p.d., accompanied by the intermittent formation of a yellow film (possibly an aldehyde resin), were observed under certain conditions. E. S. H.

Kinetics of exothermal reactions. III. Role of the walls in chain reactions. N. N. SEMENOV (Acta Physicochim. U.R.S.S., 1934, 1, 525-534).— There is a large class of gas reactions which are at the same time homogeneous and heterogeneous. They are particularly sensitive to the state of the surface, on which not only chain breaking, but also branching, occurs. The oxidation of hydrocarbons, which is a reaction of this class, is discussed.

0. J. W.

Theory of termolecular reactions. H. GER-SHINOWITZ and H. EYRING (J. Amer. Chem. Soc., 1935, 57, 985—991).—Theoretical. Assuming that the rate of termol. homogeneous gas reactions is determined by the concn. of an activated complex of the three mols. involved, in which the individual mols. cannot rotate, the calc. rates for the reactions of NO with  $O_2$ ,  $Cl_2$ , and Br are in good agreement with experiment. The negative temp. dependence of the NO- $O_2$  reaction follows from the theory.

E. S. H.

Attempt to follow the course of a reaction by potentiometric measurements. J. A. REUTER-SKIOLD (Svensk Kem. Tidskr., 1935, 47, 121–141).— A potentiometric method using glass electrodes for following the cleavage of  $(\cdot CH_2 \cdot CO_2 \cdot CH_2 \cdot CO_2H)_2$  in alkaline solution is described. Correction formulæ are derived. The method is specially applicable in solutions with low [OH']. M. S.

Ignition of hydrogen and oxygen by electric sparks in different reaction vessels. M. MIVA-NISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 52—58).—The lower crit. ignition pressures  $p_c$  of  $2H_2+O_2$  for different igniting currents in vessels of glass, quartz, and Al are given.  $p_c$  was lowest in the glass vessel, in which the pressure decrease was > theoretical. This is accounted for by the interaction of reaction chains with the Na of the glass, which can be detected in the flame spectrum. The no. of such chains  $\propto p_c^2$ . R. S.

Critical phenomena in the oxidation and selfinflammation of hydrocarbons. A. EGERTON and A. R. UBBELOHDE (Nature, 1935, 135, 997–998). L. S. T.

Initial stages of combustion of hydrocarbon fuels. K. I. IVANOV and V. K. SAVINOVA (J. Appl. Chem. Russ., 1935, 8, 64—92).—The products of heating mixtures of air and PhMe, methylcyclohexane (I), and *n*-heptane at 250—650° have been identified and determined. PhMe ignites at 633°, after an initial stage (> 590°) of production of aldehydes (chiefly CH<sub>2</sub>O), alcohols, and acids; peroxides are not formed. The ignition temp. falls with increasing relative concn. of PhMe in the mixture. Production of 1- and 2-C oxy-compounds commences at 315°, is at a max. at 350—450°, and falls from 450° to the ignition point (530°), with corresponding increase in CO and CO<sub>2</sub> production. In the case of *n*-C<sub>7</sub>H<sub>16</sub>, the initial stage of oxidation commences at 252°, passes through a max. at 370°, and falls with approach to the flash point (515—580°); peroxide (including  $H_2O_2$  and  $OH \cdot CH_2O_2R$ ) formation varies similarly. The peroxides decompose at 110— 115°, with formation of ketones, aldehydes, alcohols, acids, CO, and CO<sub>2</sub>; the view is expressed that the initial stage consists chiefly in the formation and thermal decomp. of the peroxides. R. T.

Induction period in the oxidation of propane. W. P. MUNRO (J. Amer. Chem. Soc., 1935, 57, 1053— 1054).—The effect of composition and total pressure on the lowest temp. of reaction and on the temp. coeff. has been investigated. The mechanism is discussed. E. S. H.

Relative rates of combination of light and heavy hydrogen with ethylene. R. N. PEASE and A. WHEELER (J. Amer. Chem. Soc., 1935, 57, 1144— 1145).—The ratio of the rates for H<sub>2</sub> and D<sub>2</sub>, using a Cu catalyst, is 1.59 at 0° and 1.04 at 306°; in the homogeneous reaction the ratio is 2.10 at 524° and 2.0 at 560°. The influence of exchange is being investigated. E. S. H.

Chain process in the reaction between  $SO_2$  and  $O_3$ . I. Oxidation of aqueous  $SO_2$  by ozone. S. S. VASILIEV, M. V. FROLOV, L. I. KASCHTANOV, and T. L. KASTORSKAJA (J. Gen. Chem. Russ., 1935, 5, 149—154).—The no. of mols. of  $SO_2$  oxidised per mol. of  $O_3$  rises from 1 to 5 as the  $[SO_2]$  rises from 0.02 to 0.5N. An optimum  $[O_3]$  in the gas exists for each  $[SO_2]$  in the solution; the most efficient oxidation (13 mols. of  $SO_2$  per mol. of  $O_3$ ) was obtained with 0.067%  $O_3$  and 0.1N-H<sub>2</sub>SO<sub>3</sub>. The results point to inductance of the reaction  $2SO_2+O_2\longrightarrow 2SO_3$  by the reaction  $3SO_2+O_3\longrightarrow 3SO_3$ . R. T.

Homogeneous unimolecular decomposition of gaseous alkyl nitrites. III. Decomposition of *n*-propyl nitrite. E. W. R. STEACLE and G. T. SHAW (J. Chem. Physics, 1935, 3, 344-347; cf. A., 1934, 847),-The thermal decomp. is homogeneous and of the first order in the temp. range 170-210°. The reaction is PrONO = NO + 0.5EtCHO + 0.5PrOH. The reaction rate is given by  $k=2.75\times10^{14}e^{-37,650/RT}$ sec.-1 Comparison shows that kMe: Et : Pr = 1:1.95:4.07; the increased rate for higher members of the series is probably due to participation of extra vibrational degrees of freedom. N. M. B.

Relation between explosiveness and chemical structure. V. PLETZ (J. Gen. Chem. Russ., 1935, 5,173—178).—8 groups of explosives are distinguished, containing "explosophores" (·NO<sub>2</sub>, ·ONO<sub>2</sub>, ·N:N·, ·NCl<sub>2</sub>, C:N·, etc.) and "auxexploses." R. T.

**Explosion of ethyl azide.** H. C. CAMPBELL and O. K. RICE (J. Amer. Chem. Soc., 1935, 57, 1044— 1050).—The pressure limit for explosion has been determined as a function of temp. The crit. pressure is raised by decreasing the size of the reaction vessel, and by the addition of He; addition of  $CO_2$  has no effect. The Semenov theory is in satisfactory agreement with the data. The reaction is compared with the explosion of azomethane. E. S. H.

Mechanism of additions to double linkings. I. Thermochemistry and kinetics of a diene synthesis. A. WASSERMANN (J.C.S., 1935, 828-839). The heats of the 1:4-addition of benzoquinone (I) to cyclopentadiene (II) and of the hypothetical 1:2-addition have been calc. Both reactions are exothermic and there is no thermodynamic reason for the preferential 1:4-addition. The kinetics of the (I)-(II) reaction have been investigated. A second-order association is involved, which is relatively insensitive to catalysts, light, or a magnetic field. The activation energy in EtOH or in  $C_6H_6$  is 13—14 kg.-cal. The dipole-induction energy for different mutual orientations of the two reacting mols. has been calc. For orientations which might lead to 1:4addition the induction energy is > for those suitable for 1:2-addition. Heats of combustion are recorded. O. J. W.

Benzoin reaction. I. Reaction between pure benzaldehyde and pure potassium cyanide. D. R. NADKARNI, S. M. MEHTA, and T. S. WHEELER (J. Physical Chem., 1935, 39, 727—739).—Pure dry PhCHO and KCN yield benzoin at 100° and, more slowly, at 30°, provided that a certain min. quantity of KCN is used. A rapid homogeneous autocatalytic reaction and a slow heterogeneous reaction occur simultaneously. The results are treated mathematically and the mechanism of the reaction is discussed. F. L. U.

Rate of hydrolysis of chlorine. E. A. SCHILOV and G. V. KUPINSKAJA (Compt. rend. Acad. Sci., U.R.S.S., 1935, 2, 222—224).—Electrical conductivities of Cl<sub>2</sub> solutions show that Cl<sub>2</sub> is hydrolysed rapidly at 0°. W. R. A.

Rate of absorption of carbon dioxide. Effect of concentration and viscosity of normal carbonate solutions. L. B. HITCHCOCK and H. M. CADOT (Ind. Eng. Chem., 1935, 27, 728-732).-The initial rate of absorption of pure CO2 by stirred solutions of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> follows an equation of the type  $dV/Ad0 = K(C_i + C_s)^b/z$ , where  $C_i$ ,  $C_s$  are interfacial and main-body concess. Max. occur at 1.5N for  $Na_2CO_3$  and 2.9N for  $K_2CO_3$ , after which increasing viscosity (z) causes a decrease. Consts. obtained experimentally are about 10% lower for  $Na_2CO_3$ than for K<sub>2</sub>CO<sub>3</sub>. Except at very low concns. the rate of absorption is only a fraction of that with NaOH or KOH, but it is much > with pure  $H_2O$ . Very discordant statements on these matters in the lit. are due to varying absorption conditions. The rate measured by the authors is not the true initial rate, but the "steady initial rate " attained in > 1 sec. C. I.

Ester hydrolysis in pure water. W. POETHKE (Ber., 1935, 68, [B], 1031—1037).—In pure H<sub>2</sub>O the rate of hydrolysis of  $HCO_2Et \propto [H]$ . Addition of  $HCO_2$ Na retards the change. Hydrolysis of EtOAc in pure H<sub>2</sub>O is not appreciable until after some days, its incidence appearing to depend on unidentified impurities.  $CO_2$  hastens the incidence, but is without further effect. The absence of non-catalysed change is further established by the stability of H<sub>2</sub>O in pure EtOAc. H. W.

Influence of temperature on the velocity of ionic reactions. II. A. VON KISS and R. KUKAI (Z. anorg. Chem., 1935, 223, 149—160; cf. A., 1934, 603).—The velocity of the reaction between OH' and the acetylglycollate ion has been measured at 5—45° without addition of salt and also in aq. NaCl, NaNO<sub>3</sub>,

 $NaClO_3$ ,  $Na_2SO_4$ , KCl, KNO<sub>3</sub>,  $K_2SO_4$ ,  $BaCl_2$ , and  $Ba(NO_3)_2$  of different concn. The Bronsted-Debye-Hückel relation is followed throughout the temp. range in presence of Na<sup>\*</sup> for ionic strength 0.0014-0.03, and, under the same conditions, the van 't Hoff temp. coeff. is independent of the ionic strength. The coeff. is lowered by Li' and raised by Ca"; addition of neutral salts in dil. solution depresses it, but when the salts are more conc. their action is sp. It decreases also with rise of temp., and for the Bronsted kinetic activity coeff. is approx. 1. In N-NaNO<sub>3</sub> the relation between log k and the salt concn. is linear. For const. salt concn. log  $k \propto 1/T$ . Without addition of neutral salt the activation energy of the reaction for the whole temp. range is 12,660 g.-cal. in presence of K' and Na'. Ca" gives a val. 8.6% higher. Addition of neutral salts lowers the activation energy in dil. solution. In conc. solutions the action is sp. In general, activation energy diminishes with rise of temp. The effect of neutral salts on the collision no. is > on the activation energy, but there is no simple connexion between the two. M. S. B.

Kinetics of keto-enol transformations. I. P. KRIVOBABKO and I. A. SCHTSCHERBAKOV (Ukrain. Chem. J., 1935, 10, 1—3).—The kinetics of the reaction COPhMe  $\implies$  OH·CPh:CH<sub>2</sub> are conveniently studied cryoscopically, by measuring the f.p. of the products obtained when a freshly-distilled sample of COPhMe is maintained at 20° and 25° for 0—168 hr. The temp. coeff. is 2.48, and the heat of activation is 31,496 g.-cal. R. T.

Reaction kinetics of sulphonation by sulphuric acid containing water.—See this vol., 863.

Relative rates of formation of some organomagnesium and -lithium compounds. H. GIL-MAN, E. A. ZOELLNER, J. B. DICKEY, and W. M. SELBY (J. Amer. Chem. Soc., 1935, 57, 1061-1063). Formation of simple Mg alkyl bromides is more rapid than that of the simple aryl compounds. The rate of formation of MgBueHal increases in the order Hal= Cl < I < Br, of MgRBr (R=n-alkyl) as the chain length decreases, and in the order  $Bu^{\beta} < CH_2 Pr^{\beta} <$ Bu<sup> $\alpha$ </sup> and  $\beta - \langle \alpha - C_{10}H_7 \rangle$  other aryl groups. o-, m-, and p-Tolyl compounds are equally readily formed. The rate of formation of LiR follows in general the reactivity of the RHal, but complications may be caused by a Wurtz reaction with excessively active compounds. Li aryl compounds are formed in lower yields than are the alkyl compounds. In general, Li compounds are more rapidly formed than are Mg compounds, although the final yield may be lower. **R. S. C.** 

Removal of hydrogen and acid radicals from organic compounds by means of bases. I. Removal of hydrogen chloride from aldchloroimines by sodium hydroxide. Rates of reaction in alcoholic solution. C. R. HAUSER, J. W. LE MAISTRE, and A. E. RAINSFORD (J. Amer. Chem. Soc., 1935, 57, 1056—1059).—The rate of loss of HCl from aldchloroimines is bimol., being  $\infty$  the amount of base and also affected by the strength of the base. It bears no relation to the temp. of instantaneous decomp., but is roughly parallel to the k of the corresponding acid, except for *o*-compounds, where steric factors may interfere. Reaction thus probably proceeds by removal of  $H^+$  by the base and subsequent ejection of Cl<sup>-</sup>. k is determined for 17 aldehloroimines in 92.5% EtOH, for 4 in dioxan at 0°, and for 5 in 92.5% EtOH at 35°. Heats of activation for the last-mentioned 5 compounds are cale. R. S. C.

Kinetics of polymorphic transformation of quartz. A. H. SCHTSCHUKAREV, N. S. KASJAN, and V. D. TZIGLER (Ukrain. Chem. J., 1935, 10, 35–43).—The velocity coeffs. of the reaction of transformation of quartz into cristobalite correspond equally well with a uni- and bi-molecular reaction. The reaction is catalysed by a no. of "mineralisers" (CaO, Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, NaCl). R. T.

Corrosion of zinc in water in presence of oxidising agents. I. F. KROCHMAL (Rocz. Chem., 1935, 15, 122-135).—Corrosion of Zn immersed in  $H_2O$  saturated with  $O_2$  varies with the cryst. structure of the samples; reproducible results are obtained more readily with coarsely than with finely cryst. samples. R. T

Reaction in ethylene-hydrogen mixtures induced by oxygen. R. N. PEASE and A. WHEELER (J. Amer. Chem. Soc., 1935, 57, 1147).—Small amounts of  $O_2$  cause greatly increased initial reaction rates in the homogeneous reaction at 538°.

E. S. H.

Iodine ion catalysis of deuterium peroxide. E. ABEL, O. REDLICH, and W. STRICKS (Monatsh., 1935, 65, 380–385; cf. A., 1934, 1075).—The velocity of decomp., k, of  $H_2O_2$  in 60–90%  $D_2O$ solution in presence of I' was measured interferometrically at 25° and 8·3°. k for  $H_2O_2 > k$  (HDO<sub>2</sub>)> k ( $D_2O_2$ ), but the energies of activation are identical in spite of the difference of zero point energy. An explanation is advanced. J. S. A.

Action of arsenic acid and arsenates on hydrogen peroxide. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1935, [vi], 21, 454-460).— $H_3AsO_4$ , unlike  $H_3PO_4$ , accelerates the decomp. of aq.  $H_2O_2$ . Na $H_2AsO_4$  has a similar action to  $H_3AsO_4$ ; decomp. by Na<sub>2</sub>HAsO<sub>4</sub> is not as great as that caused by Na<sub>2</sub>HPO<sub>4</sub>. Decomp. is more rapid with increasing concn. of As compound. The formation of perarsenates was not observed. E. W. W.

Oxidation of sulphites. E. SERNAGIOTTO DE CASAVECCHIA (Chim. e l'Ind., 1935, 17, 220–223).— Experiments on the oxidation of sulphites, with and without the presence of catalysts, are described. The oxidation by O<sub>2</sub> follows the mass-action law.

O. J. W. Catalytic action of silver ions on the velocity of oxidation of acetone by persulphates. E. BEKIER and S. W. KIJOWSKI (Rocz. Chem., 1935, 15, 136— 152).—The process consists of the slow reaction  $S_2O_8''+Ag' \rightarrow 2SO_4''+Ag'''$ , and of the instantaneous one  $COMe_2+4Ag''+Ag'''$ , and of the instantaneous one  $COMe_2+4Ag'''+3H_2O \rightarrow OAc'+4Ag'+$  $9H'+CO_2$ . The reaction is within wide limits  $\infty$ [Ag'] and [ $S_2O_8''$ ], but not  $\infty$  [COMe<sub>2</sub>]; the velocity coeff. is expressed by the Brönsted-Debye-Hückel equation. R. T. Specificity of iron as a catalyst for the reaction between hydrogen peroxide and pyrogallol. A. WASSERMANN (J.C.S., 1935, 826–828).—The reaction between  $H_2O_2$  and pyrogallol as catalysed by FeCl<sub>3</sub> has been followed spectrophotometrically under various conditions. The FeCl<sub>3</sub> is about 3000 times as effective as a catalyst for this reaction as for the decomp. of  $H_2O_2$ . The main product of the reaction is a brownish dye, the max. colour being developed after 8—10 min. The dependence of the dye formation on [H'] and  $[H_2O_2]$  and on the temp. has been investigated. O. J. W.

Specificity of enzyme catalysis. A. E. BRAUN-STEIN (Acta Physicochim. U.R.S.S., 1934, 1, 535– 550).—A general survey. O. J. W.

Adsorption and catalysis. J. E. NYROP (J. Physical Chem., 1935, 39, 643-653; cf. A., 1932, 553).—Theoretical. The influence of ionisation potential on adsorption and catalysis by metals is discussed. F. L. U.

Formation of acetone from acetaldehyde and water.—See this vol., 963.

Role of adsorbed atoms in heterogeneous catalysis. S. ROGINSKI (Acta Physicochim. U.R.S.S., 1934, 1, 473—482).—The adsorption of mol. and at. H at various metallic and non-metallic surfaces is discussed. The assumption that in catalytic hydrogenation  $H_2$  is split up into H atoms in the adsorption stage appears to be unnecessary.

0. J. W.

Ageing of thin layers of catalysts. D. DOBIT-SCHIN and A. V. FROST (Acta Physicochim. U.R.S.S., 1934, 1, 503—510).—The gradual decrease in the catalytic activity of thin Pd layers for the hydrogenation of  $C_2H_4$  is accompanied by a sintering process in which the Pd crystals increase in size from < 40 Å. to 250—1000 Å. With increase in size of the crystals there is no appreciable change in the amount of  $H_2$ that can be adsorbed by a given surface, but the rates of adsorption and of desorption of the  $H_2$  are decreased. The sintering process is retarded by  $H_2$  and other gases, but is accelerated by rise in temp. O. J. W.

Variable activity of catalytic surfaces. H. S. TAYLOR (Acta Physicochim. U.R.S.S., 1934, 1, 397-406).—Evidence for the non-uniformity of catalytic surfaces and the theory of activated adsorption are discussed. O. J. W.

Mechanism of adsorption catalysis. S. ROGIN-SKI (Acta Physicochim. U.R.S.S., 1934, 1, 651-684).—A general discussion of surface reactions (energy exchanges, activation energies, kinetics).

0. J. W.

Heterogeneous catalysis. I. Activated adsorption of hydrogen by carbon. R. KLAR (Z. Elektrochem., 1935, 41, 457–458).—A criticism of recent work (cf. this vol., 696). E. S. H.

Activated adsorption of hydrogen on charcoal and its influence on the catalytic activity of charcoal. R. BURSTEIN and P. KASCHTANOV (Acta Physicochim, U.R.S.S., 1934, 1, 465-472).—The rate of ortho-para-H<sub>2</sub> conversion on charcoal "poisoned" by activated adsorption of H at temp. of 300°, 500°, and 700° is considerably decreased. The conversion at high temp. does not take place through an intermediate stage of activated adsorption, and the above-mentioned decrease in the rate is not due to a change in the van der Waals adsorption. The H atoms formed in the activated adsorption process are so tightly bound by the charcoal surface that they do not hydrogenate adsorbed  $C_2H_4$ .

0. J. W.

Catalysts for destructive hydrogenation. II. Kinetics of the hydrogenation of aromatic hydrocarbons on  $MoS_2$ . L. ALTMANN and M. NEMTZOV (Acta Physicochim. U.R.S.S., 1934, 1, 429—448; cf. A., 1934, 609).—The hydrogenation of PhMe on  $MoS_2$  at high pressures and temp.  $> 460^{\circ}$  is of the first order with respect to H<sub>2</sub> and of zero order with respect to PhMe. For pressures of H<sub>2</sub> of 50—250 atm., log  $K=6.87+\log (P_{\rm H}\times273/T)-5058/T$ , where K=quantity of PhMe hydrogenated per min. for 1 kg. of MoS<sub>2</sub>. The apparent activation energy at 400—460° is 23—100 g.-cal. The advantages of nonmetallic catalysts for destructive hydrogenation are indicated. The velocity of hydrogenation for different hydrocarbons at 420° increases in the order  $C_3H_6 <$  $C_6H_3Me_3 < C_6H_4Me_2 < PhMe < C_{10}H_8$ . O. J. W.

Mechanism of catalytic hydrogenation. O. SCHMIDT (Ber., 1935, 68, [B], 1098-1107).-In the hydrogenation of C<sub>2</sub>H<sub>4</sub> in presence of Rb, Cs, Ca, Sr, or Ba, activation of H occurs through H<sup>-</sup> at the surface, whereas in presence of Cr, Mn, Re, Fe, Co, Ni, Cu, Pd, or Pt it takes place through H<sup>+</sup> within the metal, in the metallic solution as a typically electrolytic process for which the energy of solvation of H<sup>+</sup> can be determined. The processes in this metallic solution depend on the heat of solvation of  $H^+$ , the work of recession, and the ease of transition,  $R^{++} \Longrightarrow R^+$ . The electrolytic dissociation process within the metal has no relationship to the nature of the surface or the presence of edges or points. The conceptions of "outer" and "inner" surfaces are here inapplicable by reason of the wide differences of the external and internal forces. Both H<sup>-</sup> and H<sup>+</sup> can pass into H, for which the heat of solvation and, particularly, the differences in the heat of solvation at the outer surface and in the interior, are appreciably smaller. It depends on individual conditions whether hydrogenation occurs at the place where H ions are formed or where H atoms are produced.

In the reduction of PhNO<sub>2</sub> at Ag, Au, Pb, or Cu the primary action is the formation of PhNO<sup>•</sup> or PhN: and metallic oxide which is reduced by H. The mechanism of the change PhNO<sup>•</sup> or PhN:  $\longrightarrow$  NH<sub>2</sub>Ph is unknown. A similar initial stage is probably found in the conversion of CO<sub>2</sub> or CO into CH<sub>4</sub> in presence of Ni or Co. H. W.

Dehydrogenation of succinic acid by charcoal. Model of the mode of reaction of succinodehydrase. B. TAMAMUSHI and H. UMEZAWA (Acta Phytochim., 1935, 8, 221–230).—The transformation of (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> (I) into fumaric acid (II) by O<sub>2</sub> or methylene-blue (III) is accelerated by animal charcoal or carboraffin, the ash and Fe in which appear responsible for the change. The reversibility of the change, (I)+(III)  $\Longrightarrow$  (II)+leucomethylene-blue is established by the Thunberg–Quastel method, although equilibrium is only slowly attained and its position greatly displaced in the direction of oxidation. Charcoal behaves like an enfeebled succinodehydrase. The restrictive action of KCN, amyl alcohol, and  $O'C_6H_4'O$  is similar in the model and biological reactions. H. W.

Finely-divided metals [as catalysts and adsorbents] and a method for their preparation. E. G. INSLEY (J. Physical Chem., 1935, 33, 623–636).—A method of preparing finely-divided Cu, Co, Ni, and Fe from their amalgams is described. The adsorptive capacity for  $H_2$ ,  $C_2H_4$ , and  $C_2H_6$ , and the ability to promote hydrogenation of  $C_2H_4$  shown by specimens prepared from amalgams are comparable with those shown by the same metals prepared by reduction of their oxides by  $H_2$  at a low temp. The adsorption of  $H_2$  by Ni between  $-80^\circ$  and  $150^\circ$  has been measured. F. L. U.

Reactivity of gaseous nickel carbonyl. S. S. URAZOWSKI and N. A. JAKIMKIN (Ukrain. Chem. J., 1935, **10**, 44–50).—The reactions  $CO+3H_2 \rightarrow CH_4+H_2O$  and  $2CO \rightarrow CO_2+C$  are more powerfully catalysed by Ni(CO)<sub>4</sub> at its decomp. temp. (150°) than by other Ni catalysts. The reaction CO+ $CH_4 \rightarrow MeCHO$  is not catalysed by Ni(CO)<sub>4</sub>. R. T.

Role of rhodium in increasing the resistance of platinum gauze. I. E. ADADUROV (Ukrain. Chem. J., 1935, 10, 106—117).—Corrosion of Pt used as catalyst in the reaction  $NH_3+O_2 \rightarrow NO+H_2O$  is associated with adsorption of  $H_2$ , followed by its entrance into the space lattice. In general, metals with an edge-centred cubic lattice for which a >3.903 Å. absorb  $H_2$ , whilst those with a < 4.070 Å. do not. Abolition of absorption of  $H_2$  without loss of catalytic power can be effected by using alloys of Pt with Rh or Ag, but not with Au. R. T.

Preparation of platinum oxide catalyst from spent material. E. L. BALDESCHWIELER and L. A. MIKESKA (J. Amer. Chem. Soc., 1935, 57, 977— 978).—A satisfactory Pt hydrogenation catalyst can be prepared from spent material by a modification of Wichers' purification method (A., 1921, ii, 648).

É. S. H.

Influence of the solvent on the velocity of decomposition of hydrogen peroxide by means of platinum. II. T. S. GLIKMAN (Bull. Acad. Sci. U.R.S.S., 1934, 7, 1593—1598).—The velocity of decomp., v, of  $H_2O_2$  in  $H_2O$ -COMe<sub>2</sub> by platinised Pt is given by  $v=1/(k_1+k_2c)$ , where  $k_1$  and  $k_2$  are consts. and c=concn. of  $H_2O$ , vals. of v being observed under comparable conditions. v is negligible with 10—15% of  $H_2O$  and then increases with c. The reaction differs from that in  $H_2O$ -Et<sub>2</sub>O in the absence of a max. val. of v, and in the smaller influence of changes in c on v. Rotating the Pt plate does not influence v. R. S. B.

Catalytic action of platinum and manganese dioxide on benzoyl peroxide and perbenzoic acid. F. I. BERESOVSKAJA and O. SEMICHATOVA (Bull. Acad. Sci. U.R.S.S., 1934, 7, 1583—1592).—Platinised and spongy Pt catalyse the decomp. of  $Bz_2O_2$  and  $BzO_2H$  in  $Et_2O$ , but  $MnO_2$  has no action on  $Bz_2O_2$  and is less effective than Pt with  $BzO_2H$ . It follows that reaction with  $Bz_2O_2$  does not proceed by way of  $BzO_2H$ produced from  $Bz_2O_2$  by hydrolysis, since no reaction occurs with  $MnO_2$  and  $Bz_2O_2$  even in presence of a little  $H_2O$ . The inability of  $MnO_2$  to decompose  $Bz_2O_2$  is discussed. R. S. B.

Velocity of oxidation of ammonia at a platinum gauze. V. I. ATROSCHTSCHENKO (J. Appl. Chem. Russ., 1935, 8, 25—34).—Formulæ connecting the time of contact with the Pt surface, temp., pressure, concn. of NH<sub>3</sub>, etc. are derived. R. T.

Surface reactions at very low pressures. I. Platinum-chlorine. B. Reactions at the surface of the finely-divided metal. C. NOGAREDA (Anal. Fís. Quím., 1934, **32**, 396—431).—Sublimed Pt at 0° adsorbs a unimol. layer of Cl<sub>2</sub>, which is stable up to 150°. When the film, at 0°, is brought in contact with Cl<sub>2</sub> activated by contact with Pt at temp. > 200°, reaction occurs with formation of PtCl<sub>4</sub>, in accordance with the equation  $-dp/dt=ap(p_0-p)^n$ , where  $p_0$  is the initial pressure (0.02 mm.), and n varies between 0 and 1 according to the area of the film and its degree of saturation. The activation energy is 14—15 kg.-cal. The reaction does not progress beyond the surface layer. If the PtCl<sub>4</sub> film is reduced at 400°, the product requires an activation energy of about 18 kg.-cal., and the adsorptive power is about one half that of the sublimed Pt.

H. F. G.

Surface reactions at very low pressures. II. Platinum-bromine. C. NOGAREDA (Anal. Fís. Quím., 1934, 32, 567-589).—Br<sub>2</sub> mols. are dissociated by a Pt wire at 950-1250°, the energy of activation being 43,000 g.-cal. per mol. of dissociated Br. The results are in accord with a limiting adsorption mechanism. Above 1200° Br atoms attack the Pt yielding PtBr<sub>2</sub> and PtBr<sub>4</sub>, which condense on the walls of the vessel. A sublimed layer of Pt adsorbs a limiting unimol. Br<sub>2</sub> film at 0°, stable to 150°, but a wall coated with Pt and maintained at 0° is attacked superficially by Br<sub>2</sub> mols. when a wire in the reaction vessel is heated to 250° and yields a surface film of PtBr<sub>4</sub> which protects against further attack. The energy of activation of the reaction with sublimed Pt at 250-500° is 14,000-16,000 g.-cal. Reduced Pt possesses about half the adsorptive power and reactivity of the same surface of a sublimed layer. The behaviour with such layers is attributed to a sintering of the sublimed Pt. J. W. S.

Contact sulphuric acid manufacture. IV. Platinum catalyst on magnesium sulphate.—See B., 1935, 589.

Mechanism of the catalytic oxidation of CO on MnO<sub>2</sub>. J. ZELDOVITSCH (Acta Physicochim. U.R.S.S., 1934, 1, 449—464).—The adsorption of CO, of O<sub>2</sub>, and of CO<sub>2</sub> on finely-divided MnO<sub>2</sub> has been studied. All three gases show an instantaneous mol. adsorption, which for CO and O<sub>2</sub> is appreciable only below 0°. The heats of adsorption for this stage are 2600, 2300, and 5500 g.-cal. per mol. for CO, O<sub>2</sub>, and CO<sub>2</sub>, respectively. With CO there is a further slow activated or chemical adsorption, and for this stage the heat of adsorption agrees with the heat of the reaction :  $MnO_2+CO=MnO+CO_2+41,000$  g.-cal. The heat of activation for the adsorption of CO on  $MnO_2$  is 8000 g.-cal. The mechanism of the oxidation reaction is discussed. O. J. W.

Catalytic oxidation of carbon monoxide on manganese dioxide. S. ROGINSKI and J. ZELDO-VITSCH (Acta Physicochim. U.R.S.S., 1934, 1, 554— 594; cf. preceding abstract).—More detailed data are given regarding the mol. adsorption of  $O_2$ , CO, and CO<sub>2</sub> on MnO<sub>2</sub>, and of the activated adsorption of  $O_2$  and CO. O. J. W.

Mechanism of catalytic oxidation of carbon monoxide. II. S. ROGINSKI and J. ZELDOVITSOH (Acta Physicochim. U.R.S.S., 1934, 1, 595-610; cf. preceding abstracts).—The kinetics of the activated adsorption of CO on  $MnO_2$  are described in more detail. The CO may be oxidised either by  $MnO_2$  or by gaseous  $O_2$  and both mechanisms are discussed. O. J. W.

Action of chlorine on [a mixture of coal and] titanium dioxide. A. V. PAMFILOV, A. S. CHUD-JAKOV, and E. G. STANDEL (J. pr. Chem., 1935, [ii], 142, 232–236).—The action proceeds most rapidly at 400–420°, using  $MnO_2$  as catalyst. Approx. 80% of the  $Cl_2$  is converted into TiCl<sub>4</sub> and 15% into COCl<sub>2</sub>. D. R. D.

Catalysts for oxidation of ammonia to oxides of nitrogen.—See B., 1935, 590.

Alumina as catalyst of hydrocyanic acid formation [from carbon monoxide and ammonia].— See B., 1935, 589.

Zinc oxide-chromium oxide catalysts for methyl alcohol synthesis.—See B., 1935, 583.

Catalytic oxidation of ethyl alcohol.—See B., 1935, 584.

Influence of crystalline addenda on the decomposition temperature of carbonates. B. SREBROW (Kolloid-Z., 1935, 71, 293—297).—The decomp. temp. of MnCO<sub>3</sub>, NiCO<sub>3</sub>, CoCO<sub>3</sub>, ZnCO<sub>3</sub>, CdCO<sub>3</sub>, and PbCO<sub>3</sub> are lowered by addition of the oxides of Mn, Fe, Co, Ni, Mg, etc. The observations are similar to those of Balarev and Lukova (A., 1930, 1110) for the decomp. of CaCO<sub>3</sub>. E. S. H.

Comparison of the polymerising and adsorptive powers of silicates. J. M. SLOBODIN (J. Appl. Chem. Russ., 1935, 8, 35–43).—SiO<sub>2</sub> gel and silicates (floridin, kaolin, and various clays) activated at < 200° or at > 600° do not catalyse polymerisation of *iso*butylene. The adsorptive properties of the silicates are unaffected by temp. > 650°. R. T.

Electrolytic reduction of oxygen to hydrogen peroxide. E. MÜLLER and K. MEHLHORN (Z. anorg. Chem., 1935, 223, 199–203).—An apparatus for the electrolytic reduction of  $O_2$  to  $H_2O$  is described. A 3% solution of  $H_2O_2$  was obtained with a 50% efficiency. M. S. B.

Anodic behaviour of tin in electrolysis in sodium stannate solution. G. HANSEL [with A. GREVEL] (Z. Elektrochem., 1935, 41, 314—321).— Measurements of the anode potential of Sn during electrolysis of Na stannate solutions are recorded. The c.d., temp., [Na stannate], and [NaOH] were varied. A compact and satisfactory cathode deposit is obtained when a film of  $\text{SnO}_2$  is preformed on the anode, and when the latter dissolves directly as  $\text{Sn}^{\text{\tiny eff}}$ . Procedure for realising these conditions is described. F. L. U.

Electrolysis of aqueous solutions of ammonium chloride. F. JRSA (Z. Elektrochem., 1935, 41, 321-330).—Over a wide range of concn. and of c.d. the end-product in the anolyte is NHCl<sub>2</sub>, formed by the action of Cl<sub>2</sub> on the NH<sub>2</sub>Cl produced at first. The order of increasing efficiency of the anode material is graphite<Fe<sub>3</sub>O<sub>4</sub><Pt. Solutions containing NH<sub>3</sub> give a lower yield. Very little NHCl<sub>2</sub> is formed unless a diaphragm is used. NCl<sub>3</sub> is produced only in conc. solutions at 35-40° and at low c.d., when the liquid is unstirred. F. L. U.

Titanium alum. J. MEYER and H. MEISSNER (J. pr. Chem., 1935, [ii], 143, 70-81).—The prep. and electrolytic reduction of  $Ti(SO_4)_2$  are described. A Hg or Pb cathode gives the best result. Pt catalyses the change  $Ti^{\cdots} \rightarrow Ti^{\cdots}$ . The influence of different  $[H_2SO_4]$  on the stability of  $Ti_2(SO_4)_3$  has been studied. Autoxidation occurs when  $[H_2SO_4]$  is small.  $CsTi(SO_4)_2, 12H_2O$  has been prepared by addition of aq.  $Ti_2(SO_4)_3 + H_2SO_4$  to aq.  $Cs_2SO_4$  in an atm. of  $CO_2$ . Pure RbTi $(SO_4)_2, 12H_2O$  could not be obtained, and attempts to prepare K Ti,  $NH_4$  Ti, and Tl Ti alums (I) failed. It is suggested that in stable alums the ratio M'/M<sup>\combox</sup> lies between 2 and 3, whereas in (I) M'/M<sup>\combox</sup> is < 2.

Anode effect in the electrolysis of melts. II. H. VON WARTENBURG and G. WEHNER (Z. Elektrochem., 1935, 41, 448—450; cf. A., 1926, 912; 1928, 371).—The anode effect previously described is not electrical in origin, but is due to alteration of the interfacial tension at the electrode-melt boundary by the presence of oxide. E. S. H.

Preparation of cerium by electrolysis of its fused salts. S. I. SKLJARENKO and J. P. VIRSKI (J. Appl. Chem. Russ., 1935, 8, 44-48).—Ce is obtained by a modification of Billy and Trombe's method (A., 1933, 1253). R. T.

Electrochemical preparation of aluminium oxide from aqueous aluminium sulphate. V. PLOTNIKOV, D. ZOSIMOVITSCH, O. KUDRA, and I. PODORVAN (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1935, 1, 251—267).—Al(OH)<sub>3</sub> containing 2% of SO<sub>3</sub> is obtained in 108% yield (on current) by electrolysing 10% aq. Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>,18H<sub>2</sub>O containing 1% of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (150 min.; 30°; 0.5 amp., 5.5 volts), when the vol. of anolyte is 6 times that of the cathode. The final [H<sub>2</sub>SO<sub>4</sub>] of the anolyte is raised to 23% by interposing two diaphragms between the electrodes. R. T.

Electrochemical study of the system AlBr<sub>3</sub>-KBr in ethyl bromide. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Gen. Chem. Russ., 1935, 5, 224—226).— Cryst. Al is deposited at the cathode, and Br is liberated at the anode; the decomp. potential is 2.02volts. R. T.

Effect of chemical reactions on the cathode and anode in an arc discharge. A. VON ENGEL (Naturwiss., 1935, 23, 305-306).—The calculation of the temp. of a metal anode in an arc discharge is outlined. The effect of chemical reaction between the anode and the gas in which the arc is struck on the heat-resistance of the anode is discussed.

A. J. M.

Heterogeneous chemical reactions in the silent electric discharge. XIII. Reactions between hydrogen and solid inorganic compounds. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1935, **10**, 199– 204).—H<sub>2</sub>SeO<sub>3</sub> yields Se; H<sub>2</sub>SeO<sub>4</sub> yields H<sub>2</sub>SeO<sub>3</sub> and Se; Na<sub>2</sub>SeO<sub>4</sub>,10H<sub>2</sub>O yields Na<sub>2</sub>SeO<sub>3</sub> and Se; H<sub>2</sub>TeO<sub>3</sub> yields Te; Na<sub>2</sub>TeO<sub>3</sub> yields Te and NaOH; H<sub>2</sub>TeO<sub>4</sub>,2H<sub>2</sub>O yields Te and H<sub>2</sub>TeO<sub>3</sub>; K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> yields K<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>S, and S; Ag<sub>2</sub>CO<sub>3</sub> yields Ag and CO<sub>2</sub>; LiClO<sub>3</sub>,0·5H<sub>2</sub>O yields LiCl; and NaBrO<sub>2</sub> yields NaBr. J. W. S.

Catalytic influence of mercury vapour on the cracking of methane by the glow discharge. 'N. I. KOBOZEV, S. S. VASILIEV, and E. E. GALBRAICH (Compt. rend. Acad. Sci. U.S.S.R., 1935, 2, 235-243).—With electrodes of Al, Cu, Zn, Pb, or Fe about 1.5% of CH<sub>4</sub> is transformed by the glow discharge into ethylenic and acetylenic compounds. Under the same conditions but with Hg electrodes the conversion is 5.2%, increased to 14% by use of intermediate Hg electrodes or by warming the latter. Dissolution of Na in the Hg annihilates the change. The effect is ascribed to activation of the Hg vapour from which the energy is transferred to the CH<sub>4</sub> mols. H. W.

Photochemical effect of nitrogen dioxide on the combination of hydrogen and oxygen. M. MIYA-NISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 47–51).—H<sub>2</sub>O is produced when the mixture  $2H_2+O_2+NO_2$  is illuminated with monochromatic light in the region 2000—4000 Å. R. S.

Decomposition of hydrogen peroxide by the irradiation of its aqueous solution with X-rays. H. FRICKE (J. Chem. Physics, 1935, 3, 364—365).— The reaction is  $2H_2O_2=2H_2O+O_2$ ; no detectable  $H_2$  is formed. For the concn. range 0.0001—0.1 mols. per litre and X-ray intensities 3—15r per sec., the no. of mols. decomposed per unit dosage  $\propto \sqrt{(\text{concn.}/X\text{-ray intensity})}$ . The temp. coeff. rises with temp. Data are compared with results for the decomp. of  $H_2O_2$  by light, and indicate that the primary process is the activation of  $H_2O$  mols. followed by the transfer of energy to the  $H_2O_2$ . N. M. B.

Photosynthesis of hydrogen chloride. J. C. POTTS and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1935, 57, 1027—1032).—Experiments over the range 140—300° abs. show that at room temp. the rate law of Bodenstein and Unger (A., 1931, 319) is valid, save for a small correction for an inhibiting action by the HCl formed. At temp. below 172° abs. the rate depends on the  $\sqrt{(light absorbed)}$ . The temp. coeff. of the reaction has been determined at room temp. and at lower temp. E. S. H.

Photochemical reactions of adsorbed iodine molecules. A. TERENIN (Acta Physicochim. U.R.S.S., 1934, 1, 407–428).—The discoloration by the action of light of a layer of  $I_2$  adsorbed on TII is attributed to the photodissociation of the adsorbed  $I_2$  mols. The liberated I atoms are then bound by  $TI^+$  ions. The max. discoloration is produced by light of about 5600 Å. The presence of adsorbed  $H_2$  or  $O_2$  mols. on the surface causes marked shifts of the active wave-lengths, but  $N_2$  has no effect. This is ascribed to photochemical reactions between adsorbed  $I_2$  and  $H_2$  or  $O_2$ , with the formation of HI and of I oxide, respectively. The absorption spectrum and potential energy diagram of  $I_2$  in the adsorbed state are discussed. O. J. W.

Oxidation of the nitrite to the nitrate ion by the irradiation of its aqueous solutions with X-rays. H. FRICKE and E. J. HART (J. Chem. Physics, 1935, 3, 365).—The amount of  $NO_2'$  oxidised is independent of the concn. and of the  $p_{\rm H}$ . The transformation is due to  $H_2O$  mols. activated by X-rays, according to  $NO_2' + (H_2O)_{\rm act} = NO_3' + H_2$ . N. M. B.

Mercury-photosensitised polymerisation of aceylene and acetylene-d<sub>2</sub>. J. C. JUNGERS and H. S. TAYLOR (J. Chem. Physics, 1935, 3, 338— 340).—The rate of reaction is 30% greater with  $C_2H_2$ than with  $C_2D_2$  for the pressure range 0.1—4 cm. At low pressures the rate  $\propto$  pressure, but in the range 0.7—4 cm. is independent of the pressure and is determined by the intensity of the absorbed resonance radiation. The quantum yield is approx. 6.5 for  $C_2H_2$  and 5 for  $C_2D_2 <$  the yield for  $C_2H_2$  at the same temp. in the photochemical reaction. N. M. B.

Discoloration of silver iodide by aqueous ammonia. W. LANGE (Z. anorg. Chem., 1935, 223, 174—176).—By treatment with  $5\cdot34$ — $30\cdot7\%$  aq. NH<sub>3</sub>, AgI forms a white compound AgI, $0\cdot5$ NH<sub>3</sub>. It turns deep violet on exposure to light, evolves NH<sub>3</sub> on keeping, and has the same composition as the ammine obtained by the action of gaseous NH<sub>3</sub> on AgI. M. S. B.

Action of aqueous solutions on photographic latent images of varying ages. C. JAUSSERAN (Compt. rend., 1935, 200, 2076—2078).—Data are recorded for changes in density of the image with varying times between exposure and development. Immersion in  $H_2O$ , aq. Na<sub>2</sub>CO<sub>3</sub>, aq. Na<sub>2</sub>SO<sub>3</sub>, or a desensitising solution between exposure and development arrests development of the latent image if the time is not too long. H. J. E.

Density surface of [a solid diagram representing] the Villard effect. III. H. ARENS (Z. wiss. Phot., 1935, 34, 125—135; cf. A., 1934, 374).—The density surfaces have been determined, and are illustrated, for a fine-grain and a large-grain unsensitised normal emulsion. The results produced by pre-exposure to X-rays, followed by various white light exposures, are compared with the theoretical "additive" results. At low intensities of the white light the actual densities, with the fine-grain emulsion, are > the additive figure, whereas at high intensities they are lower; the positions of the solarisations are also abnormal. J. L.

Polymerisation of deutero-acetylene by alpharays. S. C. LIND, J. C. JUNGERS, and C. H. SCHIF-LETT (J. Amer. Chem. Soc., 1935, 57, 1032–1034).— The no. of mols. polymerised per ion pair is the same for  $C_2H_2$  and  $C_2D_2$ . E. S. H.

Chemical action produced by alpha-particles : combination of deuterium and oxygen. S. C. LIND and C. H. SCHIFLETT (J. Amer. Chem. Soc., 1935, 57, 1051-1052).-The rate of combination of  $O_2$  with  $D_2$  is 25-30% < with  $H_2$ . E. S. H.

Increase of chemical reactivity during phase changes in solid substances. J. A. HEDVALL (Z. Elektrochem., 1935, 41, 445-448) .- Mainly a discussion of published work (cf. this vol., 589)

E. S. H.

Recombination of hydrogen atoms in presence of hydrogen chloride. W. H. RODEBUSH and M. L. SPEALMAN (J. Amer. Chem. Soc., 1935, 57, 1040-1043).—The recombination appears to be due to the reaction  $H+HCl=H_2+Cl$  (i) followed by the rapid reaction H+Cl=HCl (ii). (i) probably takes place in the gas phase and on the walls, whilst (ii) occurs on the walls only. E. S. H.

Concentration of the heavier isotope in carbohydrates. T. TITANI and M. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 205; cf. this vol., 458).-H<sub>2</sub>O obtained by combustion of cane- and of beet-sugar is respectively 7.4 and 6.5 p.p.m. heavier than normal H2O. H2O from the combustion of substances consisting principally of glucose, lactose, starch, dextrin, galactose, mannose, or cellulose averages 6 p.p.m. heavier than normal H<sub>2</sub>O. J. W. S.

Stability of hydrogen peroxide solution.-See B., 1935, 628.

Action of water on anhydrous sodium metaphosphates. A. BOULLE (Compt. rend., 1935, 200, 1403-1405; cf. this vol., 571, 591).-Action of H<sub>2</sub>O on metaphosphate A' yields a solution of trimetaphosphate A (I) and a residue of an insol. product (metaphosphate  $B_1$ ) which has X-ray structure identical with that of metaphosphate B (II), but passes slowly into colloidal solution, whereas (II) slowly yields a solution of (I). Evaporation of aq. (I), after boiling under reflux for several days, yields NaH<sub>2</sub>PO<sub>4</sub>. A solution of metaphosphate C redeposits the same amorphous form. J. W. S.

Purification and preservation of sodium and potassium in the silvery state. I. I. PRUNDEANU (Bul. Chim. Soc. Romane, 1934, 37, 141-142).-The metal is melted under pure light petroleum, stirred to remove surface crusts and produce bright globules, cooled, and transferred to melted paraffin wax for preservation. A. R. P.

Silver-mercuric complex. J. BOUGAULT and E. CATTELAIN (Bull. Soc. chim., 1935, [v], 2, 996-1000).—The prep., properties, and analysis of  $Hg(CN)_2$ ,  $AgNO_3$ ,  $2H_2O$  are described. It loses  $2H_2O$  above 100°. CN' was determined by oxidation to CNO' with KMnO<sub>4</sub> and the N liberated as NH<sub>3</sub> by  $H_2SO_4$ , whilst the NO<sub>3</sub>' was obtained as NH<sub>3</sub> by reduction with Devarda's allow R. S. reduction with Devarda's alloy. R. S.

Active oxides. LXXXV. Intermediate steps in the transformation of a mixture of magnesium oxide and chromic oxide into magnesium chromite. T. MEYER and G. F. HUTTIG [with O. HNEVKOVSKY and H. KITTEL] (Z. Elektrochem., 1935, 41, 429-435; cf. this vol., 440).-Measurements

of d, the catalytic influence on the decomp. of  $N_2O_1$ , and magnetic susceptibility, and X-ray examination confirm the existence of active, intermediate states. E. S. H.

Formation of hydrogen carbonates in the system CaCO<sub>3</sub>-H<sub>2</sub>O-CO<sub>2</sub>-K<sub>2</sub>SO<sub>4</sub>. A. P. BUNTIN and M. M. BIKOV (J. Appl. Chem. Russ., 1935, 8, 19-24).-The formation of H carbonates in the system  $CaCO_3-H_2O-CO_2$  is augmented by adding  $K_2SO_4$ , as a result of the reaction  $Ca(HCO_3)_2 + K_2SO_4 \rightarrow 2KHCO_3 + CaSO_4$ , which shifts the equilibrium of the reaction  $CaCO_3 + H_2O + CO_2 \equiv Ca(HCO_3)_2$ . R. T.

Preparation of phosphorescent zinc sulphide. N. Z. ANDREEV (J. Appl. Chem. Russ., 1935, 8, 49-51).-ZnS is pptd. from aq. ZnSO<sub>4</sub> containing KOAc and AcOH, at 75°, the suspension is boiled, an equal vol. of cold 1.5% NaCl is added, the ppt. is collected, dried, and heated at 900° with traces of CaCl<sub>2</sub>, BaCl<sub>2</sub>, MgCl<sub>2</sub>, Na<sub>2</sub>WO<sub>4</sub>, and In (or Cs, Rb, Os, Tl, U, or Th). R. T.

Reactions in the solid state at high temperatures. XII. W. JANDER and K. F. WEITENDORF (Z. Elektrochem., 1935, 41, 435-444; cf. A., 1934, 741).-The reaction between ZnO and Cr2O3 has been studied by measurements of the sp. vol., catalytic effect on the decomp. of  $CH_4$ , solubility in HCl and  $H_2SO_4$ , sorption of methylene-blue and fuchsin, electrical conductivity, and X-ray structure. The existence of intermediate stages before the formation of  $ZnCr_2O_4$  has been established. E. S. H.

Complex compounds of 2:4:6-triaminotoluene. F. HEIN and F. WAGNER (Ber., 1935, 68, [B], 1116-1122).-By treatment of the requisite salt with a slight excess of  $2:4:6-C_6H_2Me(NH_2)_3$  (=R) when a sight excess of  $2.4 \cdot 0.06_{6}$  in  $(M1_{2/3} (=10))$ in absence of  $H_2O$  the following complex salts are obtained:  $CdI_2, R, 0.5COMe_2$ ;  $ZnCl_2, 2R$ ;  $CdBr_2, 2\frac{1}{3}R, 0.5COMe_2$ ;  $HgCl_2, R, 0.52COMe_2$ ;  $2ZnCl_2, 2\frac{1}{3}R, 2COMe_2$ ;  $SbCl_3, 2\frac{1}{3}R, 0.5EtOH$ ; SbCl\_2, 21R, 10.4Cl\_2, 2H2Cl\_2, 2H2Cl\_2, CoCl\_5R, 0.5EtOH;

 $SbCl_3, 2\frac{1}{3}R, \frac{1}{3}CHCl_3; 3HgCl_2, 3\frac{1}{3}R; CoCl_2, 5R, COMe_2;$ FeCl<sub>2</sub>, FeCl<sub>3</sub>, 5<sup>1</sup><sub>3</sub>R, 2COMe<sub>2</sub>;

2[(CrCl<sub>2</sub>OEt)<sub>3</sub>,CrCl(OEt)<sub>2</sub>,2COMe<sub>2</sub>],5R. The presence of fractions of a mol. of base is simply explained by the assumption that all three NH<sub>2</sub> groups of an individual mol. are involved in the complex union.

H. W.

Dry purification of mercury. ZIENER (Glas u. App., 1934, 15, 187-189; Chem. Zentr., 1935, i, 540).—The Hg is treated in a 1—1.5-litre flask first at room temp. and then at 100-105° with an air stream. Hg vapour is subsequently removed from the cooled air stream by active C containing I. H. J. E.

Behaviour of mercuric cyanide towards bases. F. REIFF, P. PÖHLS, and W. OVERBECK (Z. anorg. Chem., 1935, 223, 113-120).-Hg(CN), dissolves in conc. aq. KOH; transport measurements indicate the existence of a complex anion containing Hg and confirm Hofmann's formula for the hydroxy-salt [Hg(CN)<sub>2</sub>OH]K.H.O. The free acid is not present in aq. Hg(CN)<sub>2</sub> and there is no salt formation with insol. or slightly sol. metal hydroxides or with aq. NH3. Salts of NMe<sub>4</sub>OH, C<sub>5</sub>H<sub>5</sub>N, and dioxan, corresponding with the K salt, have been prepared. Transport measurments also show that CN·Hg·OH is not a hydroxy-salt of the composition [Hg(CN)<sub>2</sub>(OH)<sub>2</sub>]Hg,

but it forms the ions (HgCN)' and OH'. The formation of the compound  $[Cr(SCN)_4(NH_3)_2]$ HgCN with Reinecke's salt confirms the existence of the complex cation. M. S. B.

Preparation, analysis, and qualitative study of  $HgSO_4,2HgS$ . G. L. CHABORSKI and E. POTAMIAN (Bul. Chim. Soc. Romane, 1934, **37**, 153—164).— Digestion of HgS with conc.  $H_2SO_4$  at 145° affords white  $HgSO_4,2HgS$  after washing and drying at 130°. Alkalis extract the  $SO_4''$ , halogen acids convert it into yellow compounds which redden on heating, and  $BaCl_2$  gives a mixture of HgS and  $BaSO_4$ . Methods of analysis are described.

A. R. P.

Complex compounds of mercuric cyanide. R. UZEL (Coll. Czech. Chem. Comm., 1935, 7, 159– 182).—The prep. of compounds  $M(NH_3)_4[Hg(CN)_2X]_2$  $(M=Cu, Zn, Cd, Ni, and X=Br, I, CNS, N_3)$ , of  $Cu en_2[Hg(CN)_2X]_2$ , and of  $M en_3[Hg(CN)_2I_2]$  (M=Zn, Cd, Ni) is described. The formation of the sparingly sol. salts of the last type is characteristic of iodides. Zn can be determined gravimetrically as  $Zn(NH_3)_4[Hg(CN)_2I]_2$ . O. J. W.

Thermal decomposition of aluminium nitrate. A. A. JAKOVKIN, S. S. MARKOV, and E. A. KREMLEVA (J. Appl. Chem. Russ., 1935, 8, 212–220).—The non-fusible salt,  $Al_2O_3,N_2O_5,6H_2O$ , crystallises from aq. basic Al nitrate (I) at 140°; the salt  $3Al_2O_3,N_2O_5,6H_2O$  is obtained by heating (I) in a current of air at 200°, or in presence of HNO<sub>3</sub> vapours at 225°. (I), when heated, evolves  $H_2O$  and HNO<sub>3</sub> vapours in the proportion 6 : 1 at < 225°, and chiefly the latter at higher temp. At 318° decomp. is complete after 6 hr., the residue corresponding with AlO(OH), and containing 15% of  $H_2O$ , whilst at 340° it contains 9.41%  $H_2O$  and 1.29% of  $N_2O_5$ .

Surface chemistry of tin. A. KUTZELNIGG (Z. Elektrochem., 1935, 41, 450–453).—Sn containing Sb is coloured black by aq. FeCl<sub>3</sub>; a residue is obtained after dissolution in conc. HCl. 0.1% Sb in Sn can be detected by this method. The presence of 0.01% Sb accelerates the dissolution of Sn in hot, conc. HCl, whilst Bi retards it. Sn is readily dissolved by alcoholic I. Evidence for the existence of an oxide film on Sn is adduced. E. S. H.

Decomposition of tin dioxide, insoluble sulphates, and the corresponding minerals. G. L. CHABORSKI and D. PIRTEA (Bul. Chim. Soc. Romane, 1934, 37, 129–132).—SnO<sub>2</sub> is reduced to Sn and PbSO<sub>4</sub> to PbS by heating in NH<sub>3</sub> at 700–800°. CaSO<sub>4</sub>, SrSO<sub>4</sub>, and BaSO<sub>4</sub> may be similarly reduced to the corresponding sulphides at  $> 1000^\circ$ , the ease of reduction decreasing in the order given.

#### A. R. P.

Chemical reactions with active nitrogen (formation of mercurous nitride, gallium nitride, and reactions with amalgams). E. TIEDE and H. G. KNOBLAUCH (Ber., 1935, 68, [B], 1149—1154).—  $Hg^{I}$  nitride is produced by the action of active N on cold, well-agitated Hg. Unless special precautions are taken, the trace of O necessary for activation of N gives rise to O<sub>3</sub>, causing production of HgO. Molten Ga also yields a nitride which differs from GaN, since it is attacked by  $H_2O$  and loses N at 150°/1 atm. Amalgams of K, Na, Pb, Zn, Sn, or Cd (1%) yield exclusively nitride, only the Hg entering into reaction. With Na-Hg (85%=Na) production of azide in addition to nitride is observed. Li-Hg with mol. or active N gives only nitride. K-Na (5:1) gives azide and nitride. H. W.

Red ammonium chloride. F. PAVELKA (Kolloid-Z., 1935, 71, 291—292).—The red crystals of NH<sub>4</sub>Cl, obtained by crystallisation of solutions containing NH<sub>4</sub>Cl and FeCl<sub>3</sub>, contain FeCl<sub>3</sub>, which is taken up in accordance with the adsorption isotherm. The colour varies more with the size of the crystals than with the FeCl<sub>3</sub> content. E. S. H.

Mechanism of the action of liquid ammonia on phosphorus pentachloride. H. MOUREU and P. Rocquer (Compt. rend., 1935, 200, 1407—1410; cf. A., 1934, 158).—Action of excess of liquid NH<sub>3</sub> on PCl<sub>5</sub> in a vac. yields a product with a dissociation pressure at 0° of 1036 mm., equal to that of NH<sub>4</sub>Cl,3NH<sub>3</sub>. After the removal of this NH<sub>3</sub> the pressure falls to 300 mm. From the vols. of NH<sub>3</sub> removed under the two conditions it is concluded that the primary reaction is  $PCl_5+10NH_3=5NH_4Cl$  $+P(NH_2)_5$ , and that below 300 mm. at 0° the  $P(NH_2)_5$  decomposes irreversibly yielding  $PN_3H_4$ , which polymerises as produced and at 400° and 0·1 mm. yields  $PN_2H$ . J. W. S.

Hydrogen diarsenide : As  $_{2}$ H<sub>2</sub>. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1020-1024).—The prep. and properties of As  $_{2}$ H<sub>2</sub> are described and the rate of decomp. has been investigated. Decomp. is complete after 15 days' exposure to the air in the dark. R. S.

Precipitation of protoactinium with titanium. (MLLE.) H. ZAVIZZIANO (Compt. rend., 1935, 200, 1843—1845).—Pa is pptd. almost quantitatively with Ti by hydrolysis of slightly acid  $Ti(SO_4)_2$  solution. Details are given for the separation of Pa from a mineral by this method. H. J. E.

Technical extraction of protoactinium.—See B., 1935, 590.

Complexity of the reaction between ozone and potassium iodide. J. GUÉRON and M. PRETTRE (Compt. rend., 1935, 200, 2084–2086).—Action of  $O_3$  on aq. KI, buffered to  $p_{\rm H}$  7, forms I and KIO<sub>3</sub>, the latter liberating equiv. I on acidification before titrating with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. When 5% ozonised O<sub>2</sub> is passed into conc. aq. KI through a sintered glass plate, only KIO<sub>3</sub> is formed. H. J. E.

[Formula of] hydrofluoric acid. H. MULLER (Compt. rend., 1935, 200, 2080—2082; cf. A., 1932, 691; this vol., 824).—From the lowering of the eutectic temp. for the ice–KNO<sub>3</sub> system, the formula is HF and not  $H_2F_2$ . With KF,HF, the complex ion  $HF_2'$  is formed in conc. solution. Cornec's method (A., 1913, ii, 840) was applied in studying the neutralisation of HF by KOH. H. J. E.

Origin of polyhalides and polysulphides. M. M. PLATONOV (Ukrain. Chem. J., 1935, 10, 51— 56).—Poly-halides and -sulphides are represented as anhydrides in which O is replaced by S or by  $X_2$ . R. T.

Oxides of manganese. Structure of mixed crystals. P. DUBOIS (Diss., Paris, 1935).-All methods of prep. yield the same form of MnO, identical with manganosite. Mn<sub>3</sub>O<sub>4</sub>, prepared by thermal decomp. of Mn<sup>II</sup> salts, has a crystal structure identical with that of hausmannite. Mn<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O, identical in structure with manganite, can be obtained by oxidation of  $MnSO_4$  with  $H_2O_2$  in alkaline solution. At 300° in air it yields  $MnO_2$  and in a vac.  $\alpha$ - $Mn_2O_3$ , which is converted into the normal form,  $\beta$ -Mn<sub>2</sub>O<sub>3</sub>, at 600°.  $\beta$ -Mn<sub>2</sub>O<sub>3</sub> has the same structure as braunite. Thermal decomp. of Mn(NO<sub>3</sub>)<sub>2</sub> or oxidation of a-Mn<sub>2</sub>O<sub>3</sub> in warm air yields the anhyd.  $\beta$ -MnO<sub>2</sub>, identical with pyrolusite. It decomposes at 550—600°, yielding  $\beta$ -Mn<sub>2</sub>O<sub>3</sub>. The spontaneous decomp. of HMnO<sub>4</sub>, and reduction of  $KMnO_4$  by  $MnSO_4$  or  $H_2O_2$ , yield highly hydrated  $\alpha$ -MnO<sub>2</sub>, which is always associated with  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> or  $Mn_2O_3, H_2O$  and which loses  $H_2O$  progressively up to 500° and  $O_2$  from 250°. No individual hydrate could be identified. At 500° it gives impure  $\beta$ -MnO<sub>2</sub>. Thermal decomp. of Mn<sup>II</sup> salts gives a mixture of  $\beta$ -MnO<sub>2</sub> and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>. On addition of KMnO<sub>4</sub> to MnSO4 under certain conditions a product is obtained of composition MnO<sub>1.87</sub>, of distinct crystal structure similar to that of the product of decomp. of  $\alpha$ -MnO<sub>2</sub> similar to that of the product of decomp. of  $\alpha$ -MhO<sub>2</sub> in a sealed tube at 400°, suggesting the existence of an oxide between Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>. Other products intermediate in composition are mixtures or ad-sorption complexes. The irreversibility of the reaction 4MnO<sub>2</sub>=2Mn<sub>2</sub>O<sub>3</sub>+O<sub>2</sub> above 500° is attributed to transition into the β-forms which are non-reactive. J. W. S.

New complex compound. N. A. TANANAEV (Ukrain. Chem. J., 1935, 10, 19-21).-A reddishbrown ppt. of Mn(AgHgC<sub>2</sub>O<sub>4</sub>)<sub>3</sub> (I) is obtained when an acid solution of Mn, Ag, and Hg nitrates is added to aq.  $H_2C_2O_4$ . (I) yields Mn<sup>\*\*</sup>, Hg<sup>\*\*</sup>, AgCl, and Hg-Ag with HCl, and Mn<sup>\*\*</sup>, MnO<sub>3</sub><sup>\*\*</sup>, Hg<sup>\*\*</sup>, Ag(NH<sub>3</sub>)<sub>2</sub>, R. T. and Hg-Ag with aq. NH<sub>3</sub>.

Double salts of rhenium trichloride with rubidium and cæsium chloride. W. GEILMANN and W. WRIGGE (Z. anorg. Chem., 1935, 223, 144-148).—The prep. of the insol. salts  $RbReCl_4$  and  $CsReCl_4$ , formed in the microchemical detection of Re, is described. Their composition (cf. Noddack, A., 1934, 44) has been confirmed. They are decomposed by heat into M2ReCl6, Re, and ReCl3. K forms a sol. salt of corresponding formula.

M. S. B.

Amorphous and crystallised hydrated oxides and oxides. XXI.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O, goethite or needle ironstone, and the conversion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O into α-Fe<sub>2</sub>O<sub>3</sub>. A. KRAUSE (Z. Elektro-chem., 1935, 41, 337-339; cf. A., 1934, 1083).--The name goethite should be retained for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O whether natural or artificial. Needle ironstone is also suitable for the former, but not for the latter. When goethite prepared from orthoferric hydroxide (I) is heated at 300° it becomes almost completely sol. in  $1.4N-H_2SO_4$ . Further heating either of this product or of (I) at 800° greatly reduces the solubility. It is inferred that a sol. amorphous product is formed as an intermediate stage in the conversion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. F. L. U.

 $[\alpha-\mathrm{Fe}_2\mathrm{O}_3,\mathrm{H}_2\mathrm{O},\mathrm{goethite}\mathrm{or}\mathrm{needle}\mathrm{ironstone},$ and the conversion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.] R. FRICKE (Z. Elektrochem., 1935, 41, 340; cf. A., 1934, 1083, and preceding abstract).-X-Ray examination of partly converted  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O indicates, not a mixture of amorphous and cryst. oxide, but a broken lattice with normal distance between the lattice planes. F. L. U.

Complex iron thiocyanates with pyridine. O. BINDER and P. SPACU (Compt. rend., 1935, 200, 1405-1407).--[Fe(C<sub>5</sub>H<sub>5</sub>N)<sub>3</sub>(CNS)<sub>3</sub>] (I) and the black and yellow forms of  $[Fe(C_5H_5N)_4(CNS)_2]$  (II) all have characteristic X-ray spectra. It is suggested that the yellow form of (II) is the trans- and the black form the *cis*-modification. Rosenheim's salt (A., 1932, 1009) is a mixture of (I) and small quantities of (II). J. W. S.

Cobalto-complexes. J. V. DUBSKY (Z. anorg. Chem., 1935, 223, 197-198).-The action of piperazine on CoCl<sub>2</sub> affords a blue cryst. compound which is not a tetrahalogen salt, as previously supposed, but is [CoCl<sub>6</sub>]H<sub>4</sub>, piperazine. The compound with piperazinodiethyleneamine is similar. M. S. B.

Complex ammines of fluoboric acid. G. SPACU and L. DIMA (Z. anorg. Chem., 1935, 223, 185-191).--The following cryst. compounds have been prepared :

 $\begin{array}{l} [\mathrm{Mn}(\mathrm{C}_{5}\mathrm{H}_{5}\mathrm{N})_{2}](\mathrm{BF}_{4})_{2}, \ [\mathrm{Cd} \ \mathrm{bzd}_{3}](\mathrm{BF}_{4})_{3}. \\ [\mathrm{en} = (\mathrm{CH}_{2}\cdot\mathrm{NH}_{2})_{2}; \ \ \mathrm{bzd} = (\mathrm{C}_{6}\mathrm{H}_{4}\cdot\mathrm{NH}_{2})_{2}]. \\ [\mathrm{last \ are \ sol. \ in \ H}_{2}\mathrm{O}. \end{array}$ All but the M. S. B.

Triethylenediaminecobaltic salts with mixed anions. K. HOEHNE (J. pr. Chem., 1935, [ii], 143, 90-93).-The following compounds have been [Co en<sub>3</sub>]Cl<sub>3</sub>,CoCl<sub>2</sub>,H<sub>2</sub>O, green crystals; prepared : [Co en<sub>3</sub>]NO<sub>2</sub>Cl<sub>2</sub>,CoCl<sub>2</sub>,H<sub>2</sub>O, reddish grey-brown plates, which give the dihydrate on exposure to the atm.;  $[Co\ en_3]NO_2Cl_2, H_2O$ , reddish-yellow crystals. R. S.

Rhodium hydroxopentammines. B. E. DIXON (J.C.S., 1935, 779-781).-Rh forms the complex salts  $[Rh(NH_3)_5OH]Br_2, H_2O, [Rh(NH_3)_5OH](NO_3)_2,$ and [Rh(NH<sub>3</sub>)<sub>5</sub>OH]SO<sub>4</sub>,2H<sub>2</sub>O, which strongly resemble the corresponding Ir compounds (cf. A., 1934, 267). They resemble the pentammine rather than the hexammine type in their behaviour towards sp. ammine reagents. O. J. W.

Trichlorides of iridium<sup>III</sup>-aquo-dipyridines. M. DELÉPINE (Compt. rend., 1935, 200, 1373-1375).—On heating an aq. solution of cis-pyridino- $[Ir(C_5H_5N)_2Cl_4]M$  (M=metal) at 130° for 1 hr. considerable decomp. occurs into the compound  $[Ir(H_2O)(C_5H_5N)_2Cl_3), 1.5H_2O$  (I). trans-

 $[Ir(C_5H_5N)_2Cl_4]M$  gives the compounds  $[Ir(C_5H_5N)_2Cl_3]$ and  $[Ir(H_2O)(C_5H_5N)_2Cl_3],H_2O$  (II), forming an orange-red aq. solution. (I) and (II) dissolve easily in NH<sub>3</sub>. NaOH and KOH solutions containing excess of alkali deposit salts of  $[Ir(C_5H_5N)_2(OH)Cl_3]H$ , but addition of acid reproduces the original complexes. On dehydration at 140—145°, (I) and (II) lose their  $H_2O$  of crystallisation and composition and are no longer sol.

in alkali. They combine with  $AgNO_3$  in neutral or alkaline solution to form the sparingly sol. *compounds*  $[Ir(C_5H_5N)_2(OH)Cl_3)_2HAg$ , and in acid solution to form the *compounds*  $[Ir(C_5H_5N)_2Cl_3NO_3]Ag,H_2O$ , of which the product from (I) loses its  $H_2O$  on drying at 105—110°. The product from (II), on treatment with KCl, yields (II) and KNO<sub>3</sub>. (II) on oxidation with HCl-HNO<sub>3</sub> gives  $Ir^{IV}(C_5H_5N)_2Cl_4$ , which on reduction regenerates  $[Ir(C_5H_5N)_2Cl_4]C_5H_5NH$ .

J. W. S. Constitution of the heteropoly-acids. G. ELST-NER (Angew. Chem., 1935, 48, 343-347).—A review. E. S. H.

Identification of artificial radioactive elements produced by neutron bombardment, and their application in chemistry as indicators. O. ERBACHER and K. PHILIPP (Angew. Chem., 1935, 48, 409-414).—Chemical and physical methods of identifying artificial radioactive elements are summarised. A. J. M.

Rapid spectroscopic determination of metals. II. Comparator for the intensity of spectrum lines. A. P. SNESSAREV, N. N. ROSANOV, and P. J. Assoskov (J. pr. Chem., 1935, [ii], 142, 237—242).— The background is illuminated by means of a separate source, the intensity of which is varied until the line becomes invisible. Data with NaF and  $BaCl_2$ indicate that the concn. of metal can be determined to within a few %. D. R. D.

Quantitative flame spectrum analysis. F. WAIBEL (Wiss. Veröff. Siemens-Werken, 1935, 14, 32—40).—The applications are discussed and technique is recommended. Two solution sprays are described. E. S. H.

Microchemical spectral analysis in the highfrequency spark. A. SCHLEICHER and N. BRECHT-BERGEN (Z. anal. Chem., 1935, 101, 321-338).-The spectra are excited by a high-frequency Tesla discharge between a Cu, Ag, or Au wire and a tilted glass plate carrying the specimen, and resting on the lower (plate) electrode. The ppt., or 1-2 microdrops of the solution under analysis, is applied to a 1cm. filter, which is then embedded in a thin layer of hot agar-gelatin jelly (electrodialysed until spectrally pure). For detection of constituents of glass (Na, K, Si) Au foil is interposed between the specimen and the glass plate. Spectra are taken progressively during the ashing of the gelatin carrier. For complete qual. analysis, a group separation is made into (I) oxides insol. in HCl (Si, Ta, W, Ti, +AgCl); (II) metals pptd. by  $H_2S$ ; (III) metals pptd. by aq.  $NH_3$ or by  $(NH_4)_2CO_3$ ; (IV) remaining elements. Ppts. are best purified by electrodialysis before sparking. J. S. A.

Sampling analyses and sample size.—See B., 1935, 609.

Recent development of colorimetric technique and allied processes of measurement. A. THIEL (Ber., 1935, 68, [B], 1015-1023).—A lecture.

H. W.

Personal error in colorimetry. R. A. HOUSTOUN and A. J. YOUNGER (Phil. Mag., 1935, [vii], **19**, 1107— 1115).—A discussion, based on statistical data, of anomalies in visual observations. N. M. B. Conductometry. W. BÖTTGER and J. PIEPER (Z. Elektrochem., 1935, 41, 453-457).-Polemical (cf. this vol., 598). E. S. H.

Conductometry. G. JANDER, J. HARMS, and K. F. JAHR (Z. Elektrochem., 1935, 41, 457).—A reply (cf. preceding abstract). E. S. H.

 $p_{\rm H}$  determination (indicator papers). K. Höll (Chem. Fabr., 1935, 8, 218–219).—Colorimetric  $p_{\rm H}$  determination may be carried out by a drop method on indicator papers covering the full  $p_{\rm H}$  range. The method is advantageous for viscous or turbid solutions. J. S. A.

Use of brilliant-yellow and Poirrier-blue C<sub>4</sub>B as indicators of  $p_{\rm H}$ . M. B. DE LA ROCHE (Bull. Soc. chim., 1935, [v], 2, 1148-1151).-With brilliantyellow (I) the limit of transmission on the red side occurs at 7500 Å. for all vals. of  $p_{\rm H}$ , but on the violet side at 5025-5800 Å. for  $p_{\rm H}$  4.5-13.  $p_{\rm H}$  may be determined by the transmission limit of (I) in the violet, or by the use of a series of standard papers, the colour changes being :  $p_{\rm R}$  3.5-6 citron-yellow, 6.2-6.8 Cd-yellow, 7-8 orange-yellow, 8.2-9.5 appearance of carmine, 9.7-10.1 carmine-orange, 10.4—13 carmine. With blue  $C_4B$  (II) the transmission spectrum occurs at 4100—5150 Å. for  $p_{\rm H} < 10$ . At  $p_{\rm H} = 10.4$  ( $p_{\rm H}$  of dil. Na<sub>3</sub>PO<sub>4</sub>) the absorption increases considerably, and a feeble red band is transmitted at 6000-7500 Å., becoming intense at  $p_{\rm H}$ 13. (II) may be used for titration of  $H_3PO_4$ , the neutral point being given by the appearance in a spectroscope of the red band, but visual observation is inexact. R. S. B.

Volumetric determination of free acid in solutions of iron salts.—See B., 1935, 628.

Extraction method for the determination of acids and its application to p-hydroxybenzoic acid. V. K. LAMER and J. GREENSPAN (J. Amer. Chem. Soc., 1935, 57, 969—973).—The principle of the procedure is to determine an acid (HA) in aq. solution by adding a measured, excess vol. of standard alkali, and determine the excess alkali by adding a measured, excess vol. of a second acid (HE), extracting the excess of HE with a solvent in which HA is insol., and subsequently determining the extracted excess of HE by the usual methods. E. S. H.

Spectrographic determination of minor chemical constituents in water supplies.—See B., 1935, 608.

Rapid potentiometric determination of minute quantities of chlorides. S. V. BRUEVITSCH and F. E. VARFOLOMEEVA (J. Appl. Chem. Russ., 1935, 8,366—373).—0.5 mg. of Cl per litre can be determined by electro-titration (AgCl electrode), with a max. error of 4%, and 2.5 mg. with a max. error of 1.2%. The method is applicable to direct Cl determination in natural waters. R. T.

Theory of potentiometric precipitation titrations using electrodes of the second kind. A. RINGBOM (Z. physikal. Chem., 1935, 173, 198—206).— Expressions for the concn. of the pptg. ion at the equiv. point and the turning point of the potential curve have been derived. The concn. and excess or deficiency of this ion at the latter point when the two solid phases are binary or ternary electrolytes are tabulated for various solubility products. R. C.

Potentiometric titrations with electrodes of the second kind. A. RINGBOM (Z. physikal. Chem., 1935, 173, 207–215).—The titration of  $IO_3'$  with Pb(NO<sub>3</sub>)<sub>2</sub>, using a K<sub>3</sub>Fe(CN)<sub>6</sub>-Pb<sub>2</sub>Fe(CN)<sub>6</sub> electrode, and of Ca<sup>\*\*</sup> with Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, using a Ag-Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> electrode, are described and the results compared with the theory (cf. preceding abstract). The former titration is of little practical significance, whilst the second is practicable, but not very exact, at not too high dilutions and salt content. R. C.

Rapid determination of hydrogen sulphide in gaseous mixtures. P. Woog, R. SIGWALT, and J. DE SAINT-MARS (Bull. Soc. chim., 1935, [v], 2, 1214—1216).—Paper dipped in aq. Pb(OAc)<sub>2</sub> containing glycerol is pressed between filter-paper and placed in a tube which is evacuated and opened in the gaseous sample. Colorimetric examination of the stain permits the determination of as little as 1 in 80,000. R.S.B.

Nephelometric determination of sulphur dioxide in air. I. I. PLETNIK, A. V. VELITSCHKOVSKI, and I. O. FRIDMAN (Ukrain. Chem. J., 1935, 10, 7-14).-30 litres of air are bubbled through 50 c.c. of 0.1N-NaOH, 2 c.e. of 25% HCl and 5 c.e. of 0.1N-KMnO<sub>4</sub> are added, the solution is decolorised with 5% NaNO<sub>2</sub>, BaCl<sub>2</sub> is added, and SO<sub>4</sub>" is determined nephelometrically. 0.1 mg. of SO<sub>2</sub> can be determined with a mean error of 10-15%. R. T.

Determination of small quantities of sulphur dioxide and hydrogen sulphide. L. E. KARLSON (Ukrain. Chem. J., 1934, 9, 312-316).-Gorodetzki's method, consisting in leaving a known vol. of air containing SO<sub>2</sub> or H<sub>2</sub>S in contact with aq.  $NH_3$  containing H<sub>2</sub>O<sub>2</sub>, and determining ( $NH_4$ )<sub>2</sub>SO<sub>4</sub> after 24 hr., is untrustworthy when < 0.5 mg. of SO<sub>2</sub> is present; satisfactory results are obtained when the bottle is paraffin-coated, and when the solution, after evaporation, is heated for 15 min. at 100°, and not 135°, as suggested by Gorodetzki. Gurevitsch's method, depending on oxidation with aq. KClO3 and determination of SO4" colorimetrically (as  $PbCrO_4$ ), gives high results; substitution, in the case of  $SO_2$  of aq.  $NH_3$ , and in that of  $H_2S$  of ammoniacal  $H_2O_2$ , for aq. KClO<sub>3</sub> gives good results. R. T.

Use of lead nitrate for precipitation-titration of anions. I. Potentiometric titrations. II. Hydrolytic precipitation titrations. A. RINGBOM (Acta Acad. Aboensis, 1934, 8, No. 5, 142 pp.; Chem. Zentr., 1935, i, 754—755).—I. SO<sub>4</sub>", WO<sub>4</sub>", MoO<sub>4</sub>", and SO<sub>3</sub>" at  $p_{II} > 6$  may be titrated potentiometrically with Pb(NO<sub>3</sub>)<sub>2</sub> using a K<sub>3</sub>Fe(CN)<sub>6</sub>-Pb<sub>2</sub>Fe(CN)<sub>6</sub> electrode. CO<sub>3</sub>", HCO<sub>3</sub>', and C<sub>2</sub>O<sub>4</sub>" may be determined in hot solution, or by back titration.

II. Pb(NO<sub>3</sub>)<sub>2</sub> may be titrated in dil. solution with Na<sub>2</sub>CO<sub>3</sub>, using phenol-red (I) as indicator. The following anions may be determined similarly:  $C_2O_4''$  at  $p_{\pi}$  8, with (I); SO<sub>4</sub>'' at  $p_{\pi}$  9, with bromocresol-purple (II); CrO<sub>4</sub>'' at  $p_{\pi}$  9, with (II); WO<sub>4</sub>'' with (II) or bromothymol-blue; MoO<sub>4</sub>'', with (I). J. S. A.

"Depolarimetry" by thermo-electricity. J. GUZMÁN and A. RANCAÑO (Anal. Fís. Quím., 1934, 32, 590-601).—A modified form of dead-stop endpoint electrometric titration which employs a single Cu-constantan thermocouple heated by a Bunsen burner, and uses a small titration vessel mechanically stirred, is described. The method has been applied to the determination of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with I, CuSO<sub>4</sub>, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KIO<sub>3</sub>, Ce(SO<sub>4</sub>)<sub>2</sub>, and ZnCl<sub>2</sub> and KIO<sub>3</sub>, of Fe<sup>II</sup> salts with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and of KMnO<sub>4</sub> with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. J. W. S.

Separation of selenium from cadmium, lead, bismuth, antimony, molybdenum, tungsten, and vanadium. V. HOVORKA (Coll. Czech. Chem. Comm., 1935, 7, 182—197).—The determination of Se in a solution of  $H_2SeO_3$  by reduction with  $N_2H_4$  has been studied. In presence of the above metals a direct separation of Se by this method is possible only under certain conditions, which depend on the particular metals present. O. J. W.

Measurement of small volumes of nitrogen obtained by micro-Dumas method. H. C. GULL (Analyst, 1935, 60, 401–403).—The vol. of  $N_2$ is calc. from the wt. of  $H_2O$  displaced from a flask of special construction. E. C. S.

Physiological arsenic and the use of the Kjeldahl flask in its detection. W. DECKERT (Z. anal. Chem., 1935, 101, 338-339).—Dissolution of As from the glass of the flask (cf. this vol., 554) is appreciable only on the first occasion a flask is used. J. S. A.

Physiological arsenic and the use of the Kjeldahl flask in its detection. G. LOCKEMANN (Z. anal. Chem., 1935, 101, 340-341).—A reply to Deckert (see preceding abstract). J. S. A.

Detection of nitrate ions. P. G. POPOV (Ukrain. Chem. J., 1934, 9, 310—311).—1 c.c. of solution and 1 c.c. of saturated aq.  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> are stratified on conc. H<sub>2</sub>SO<sub>4</sub>, when a violet-red ring indicates  $\leq 0.025$ mg. of KNO<sub>3</sub>. Other oxidising agents do not interfere. R. T.

Potentiometric determination of hypophosphoric acid in presence of phosphoric acid and phosphorous acid. W. GRUNDMANN and R. HELL-MICH (J. pr. Chem., 1935, [ii], 143, 100–105).—The determination of  $H_2PO_3$  as Ag salt is unsatisfactory in presence of  $H_3PO_4$ .  $H_2PO_3$  can be determined in presence of  $H_3PO_4$  and  $H_3PO_3$  by potentiometric titration of a NaOAc-buffered solution with AgNO<sub>3</sub>, using a AgI indicator electrode. Cl', Br', I', CN', and CNS' can be separately determined in presence of  $H_2PO_3$ . R. S.

Colorimetric determination of arsenic. D. B. JOCHELSON (Ukrain. Chem. J., 1934, 9, 344-347).--Na<sub>2</sub>S is added to the acid solution, the As<sub>2</sub>S<sub>3</sub> is washed and dissolved in 2% aq. NH<sub>3</sub>, aq. AgNO<sub>3</sub> is added to the solution, and the brown coloration is compared with that given by standard As solution under the same conditions. The method is rapid and accurate, and may be applied to the determination of As in concns. of  $\leq 0.0001\%$ , in presence of org. substances. R. T. Volumetric determination of minimal amounts of arsenic. J. H. KŘEPELKA and B. RAKUŠAN (Lékárn., 1934, 14, 290–301; Chem. Zentr., 1935, i, 757).—AsH<sub>3</sub> is passed through 0·1N-I and the excess titrated back. J. S. A.

Boric acid-alcohol flame reaction. W. STAHL (Z. anal. Chem., 1935, 101, 342–347; cf. A., 1931, 587).—The optimum amount of  $H_2SO_4$  is 3 c.c. in 15 c.c. of MeOH. For detection of small amounts of B, the substance is mixed in a Rosenbladt apparatus with 0.5 c.c. of fresh MeOH+ $H_2SO_4$ , and kept for 15 min. The tube is warmed to 65°, and a current of air passed through it into a non-luminous gas flame. 0.00076 mg. of B may be detected. J. S. A.

Rapid determination of small amounts of boron through the intensity of the flame coloration. W. STAHL (Z. anal. Chem., 1935, 101, 348—356; cf. A., 1931, 587).—Equal currents of air are passed simultaneously through an unknown and a standard B solution in apparatus of identical dimensions into non-luminous gas flames, and the flame colorations compared. The concn. of the standard solution is varied to give the same intensity of flame coloration. Suitable apparatus is described. J. S. A.

Photo-colorimetric determination of silicic acid in presence of phosphoric acid. M. ČERNÝ (Chem. Obzor, 1934, 9, 121–122, 138–140; Chem. Zentr., 1935, i, 600).—SiO<sub>2</sub> is converted by HCl+ (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> into silicomolybdate, which is reduced with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and examined in a colorimeter. Interference by P<sub>2</sub>O<sub>5</sub> is inhibited by addition of KMnO<sub>4</sub> and then NH<sub>4</sub> citrate. J. S. A.

Organic carbon in sea-water. L. ESPIL (Bull. Soc. chim., 1935, [v], 2, 1007—1012).—A method for the determination of org. C in sea-water is described. The org. C, which is partly due to the dissolution of marine algæ, is greatest in coastal waters, and is subject to seasonal variation. R. S.

Determination of carbon monoxide with various cuprous chloride solutions.—See B., 1935, 509.

Gas-analytical methods for determination of carbon suboxide in presence of carbon dioxide, carbon monoxide, and oxygen. A. KLEMENC, R. WECHSBERG, and G. WAGNER (Monatsh., 1935, 65, 405–410).—Mixtures of  $C_3O_2+CO_2$  are treated with  $H_2O$ , and the  $CO_2$  is pumped off. The  $CH_2(CO_2H)_2$ formed is titrated with 0.01N-Ba(OH)<sub>2</sub>, and CO<sub>2</sub> is determined nephelometrically (or in larger amounts by titration) with  $Ba(OH)_2$ .  $C_3O_2$  and  $CO_2$  are separated from CO and  $O_2$  by condensation at  $-180^\circ$ .  $O_2$  is absorbed by P, and  $C_3O_2$  and  $CO_2$  in the nonvolatile portion are determined as above. Very small amounts of CO2 are better determined manometrically by pumping off at  $-40^{\circ}$ . When recovery of  $C_3O_2$  is desired,  $CO_2$  may be fractionally pumped off from solid (but not liquid) mixtures at  $-125^{\circ}$  to  $-130^{\circ}$ . A suitable semi-micro gas analysis apparatus for 1 c.c. of gas is described. J. S. A.

Determination of traces of cyanides in water.— See B., 1935, 656. Determination of small concentrations. IX. Hydrogen cyanide. E. M. JOFINOVA-GOLDFEIN and S. S. GURVITZ. X. Microalkalimetry. S. L. KAGAN (J. Gen. Chem. Russ., 1935, 5, 34–38, 179–181).—IX. The methods of Kolthoff (A., 1918, ii, 138), Smith (A., 1929, 686), and Anderson (A., 1916, ii, 585) serve for determining  $\leq 0.003$  mg. of HCN.

X. The most uniform results in the microtitration of aq.  $Ba(OH)_2$  are given by 0.01-0.02N-HCl.

R. T. Determination of anions with benzidine. Oxalates and selenates. A. DEL CAMPO and F. SIERRA (Anal. Fís. Quím., 1934, 32, 451-473).— The solubility of benzidine (I) salts increases with decrease of  $p_{\rm H}$ , whilst the salts have a marked power of adsorption. Means of obviating errors arising from these factors have been studied. The best reagent for determination of oxalate contains 2.7 g. of (I) and 130 c.c. of 0.1N-HCl per litre; the sample should contain 0.1-0.15 g. of oxalate, and 150-200 c.c. of reagent should be employed. With a more conc. reagent [0.5% (I)], and under the conditions described, selenate may be determined to within 1%; the error of published methods is 5-6%.

H. F. G.

Determination of potassium in oilfield water.— See B., 1935, 608.

Characterisation of metallic ions by microchemical tests with picric acid. C. FRANGOPOL (Bul. Chim. Soc. Romane, 1934. **37**, 259–261).— Addition of 1% picric acid to salts of Na, K, NH<sub>4</sub>, Be, Ag, Ba, Ca, Fe<sup>\*\*\*</sup>, Mg, Mn, and Pb on a microscope slides affords characteristic crystals of the picrates : K, NH<sub>4</sub>, and Pb triclinic prisms, Ba slender prisms with an inclined base, Ca stout triclinic prisms, Mg and Mn Y-shaped crystals, Ag sheaves of fine needles, Al aborescent growths, Na radiating clusters of fine needles. A. R. P.

Determination of sodium in potassium salts by the uranyl acetate method.—See B., 1935, 627.

Electro-analysis of silver with three electrodes. J. GUZMAN and L. QUINTERO (Anal. Fís. Quím., 1934, 32, 602—610; cf. A., 1916, ii, 114).—The Pt cathodes normally used in the Guzman method have been replaced successfully by Ag wire nets, Ag foil, and in some cases by Ag-plated brass, and the Pt anodes by stainless steel for acid solutions and by Fe (in some cases passified) for alkaline solutions. Data are given for solutions containing  $(NH_4)_2SO_4$ and  $NH_3$ ,  $(NH_4)_2SO_4$  and NaOH. KCN and NaOH,  $NH_4OAc$  and AcOH in presence of EtOH, and HNO<sub>3</sub> and EtOH. The process is also applied to the largescale determination of Ag. J. W. S.

Detection of barium, strontium, and calcium present together. N. A. TANANAEV (Ukrain. Chem. J., 1935, **10**, 15—18).—10 drops of saturated aq. K<sub>4</sub>Fe(CN)<sub>6</sub> are added to 1 drop of the solution, the mixture is evaporated to dryness, and the residue warmed with 40 drops of H<sub>2</sub>O, when an opalescent solution is obtained in presence of < 0.07 mg. Ca; Mg interferes, Ba and Sr do not. Sr is detected by adding HNO<sub>3</sub> to the solution, evaporating to dryness, and warming, when  $Sr(NO_3)_2$ , sputtering into the flame, gives a red coloration. Ba is detected as  $BaCrO_4$ . R. T.

Enrichment process for the detection of small quantities of chemical constituents in minerals. H. ROSE and R. BÖSE (Naturwiss., 1935, 23, 354— 355).—For the detection of small quantities of substances in beryl and other minerals the arc method of Mannkopff and Peters (A., 1931, 991) is used. For the detection of small quantities of volatile substances, the mineral is heated in vac. to 1200° in a quartz tube open at one side. Ring-like deposits of metals are formed on the cooler parts of the tubes, which can be separated by cutting the tube. The deposits are separately dissolved, and the solutions examined by the spark spectrum. Elements not indicated by the arc method can thus be detected. A. J. M.

**Reaction for cadmium.** P. G. Porov (Ukrain. Chem. J., 1934, 9, 307–309).—1 c.c. of solution is heated with 0.5 g. of  $NH_4Br$  and 1.5 c.c. of conc.  $H_2SO_4$  to evolution of  $SO_3$ ,  $H_2O$  is added to 8 c.c., 0.5 g. of Fe powder is added, the suspension is filtered after 30 sec., an equal vol. of  $H_3PO_4$  added to the filtrate, and  $H_2S$  is passed, when a yellow ppt. is obtained with < 0.9 mg. of Cd. Other metals do not interfere. R. T.

Determination of small amounts of lead. K. SEELKOPF and H. TAEGER (Z. ges. exp. Med., 1933, 94, 539–548; Chem. Zentr., 1935, i, 757).—The electrolytic method of Schmidt does not give quant. results. A colorimetric method using dithizone is described. J. S. A.

Determination of small amounts of lead. P. SCHMIDT, F. WEYRAUCH, A. NECKE, and H. MÜLLER (Z. ges. exp. Med., 1934, 94, 1-6; Chem. Zentr., 1935, i, 757).—A reply to Seelkopf and Taeger (cf. preceding abstract). J. S. A.

Application of diphenylcarbazone to determination of metals. E. S. VASSERMAN and I. B. SUPRUNOVITSCH (Ukrain. Chem. J., 1934, 9, 330— 340).—Many cations are quantitatively pptd. as complexes (I) insol. in  $H_2O$ , but sol. in org. solvents; the application of such solutions to the colorimetric determination of the metals gives untrustworthy results. Pb, Hg, and Zn may be determined gravimetrically as (I). R. T.

Determination of traces of thallium in presence of other metals. A. L. HADDOCK (Analyst, 1935, 60, 394—399).—TI, together with Pb and Bi, is separated from other metals by extraction with dithizone in CHCl<sub>3</sub>, and determined in the form of TlCl<sub>3</sub> by liberation of I from KI. 0.005-0.200mg. of Tl may be determined in presence of 1 g. of many metals and their salts, but 0.5 mg. of Bi and Pb or 0.1 g. of Hg, Ni, and Zn interfere. E. C. S.

Alkaloidal reagents. VII. Detection of thallium. J. C. MUNCH and J. C. WARD (J. Amer. Pharm. Assoc., 1935, 24, 351–358).—Numerous pptn. reactions for the detection of Tl have been tested and their sensitivities recorded. M. T.

Sensitive detection of metals with "thionalid" [thioglycol-β-naphthylamide]. II. R. BERG and W. ROEBLING (Angew. Chem., 1935, 48, 430–432).– "Thionalid" gives ppts. with the following metals in EtOH or AcOH solution (limiting dilution×10<sup>6</sup> given in parentheses) Cu (10), Ag (5), Au (2·5), Hg (15), Sn (12·5), As (100), Sb (40), Bi (10), Pt (10), Pd (10). In alkaline tartrate solution the series is Cu (2), Au (0·2), Hg (1), Cd (2·5), Tl (10); Ag is reduced, Mn gives MnO<sub>2</sub>, and Fe<sup>\*\*</sup> is not sensitive. In tartrate solution containing KCN, it is Au (0·2), Tl (10), Sn (0·25), Pb (10), Sb (2), Bi (2·5) and in presence of NaOH–KCN it is reduced to Tl (10), Hg, Pb, Bi (not sensitive), which allows the reagent to be used for the detection of very small amounts of Tl (details given). S. C.

Fractional reaction for mercury. M. SCHTSCHIG-OL (J. Appl. Chem. Russ., 1935, 8, 158—159).— An equal vol. of 10% KI is added to the solution, followed by 30% aq. KOH, and the mixture is heated and filtered. 1 ml. of glycerol and 2—3 ml. of aq. NaOH are added to the filtrate, and the mixture is boiled for several min., when a black ppt. of Hg forms, or, in presence of very small amounts of Hg, the liquid darkens. < 0.35-3.25 mg. of Hg can be detected in presence of other ions. R. T.

Volumetric determination of mercury. M. SCHTSCHIGOL (J. Appl. Chem. Russ., 1935, 8, 160– 164).—0.2—0.4 g. of substance is dissolved in H<sub>2</sub>O, 20—30 ml. of 30% aq. NaOH and 5—10 ml. of glycerol are added, the mixture is boiled for 5 min., diluted to 100 ml., and filtered. The washed ppt. (Hg) is dissolved in 10—15 ml. of HNO<sub>3</sub>, the solution is diluted, oxides of N are removed by KMnO<sub>4</sub>, excess of which is removed by FeSO<sub>4</sub>, and Hg is titrated with 0.1N-NH<sub>4</sub>CNS. The reactions involved are : HgX<sub>2</sub>+ 2NaOH  $\longrightarrow$  HgO+2NaX; HgO+OH·CH(CH<sub>2</sub>·OH)<sub>2</sub>  $\longrightarrow$  Hg+OH·CH<sub>2</sub>·CH(OH)·CHO. R. T.

Fractional detection of mercury. (A) N. A. TANANAEV. (B) N. A. TANANAEV and N. V. JUNITZ-KAJA (J. Appl. Chem. Russ., 1935, 8, 356—358, 359—360).—(A) Br is added to 1—2 ml. of neutral solution to appearance of a yellow coloration, the solution is boiled and added to 5 ml. of a solution of 10 g. of KI in 100 ml. of 10% NaOH, the mixture is boiled and filtered, and SnCl<sub>2</sub> added to the filtrate, when a black ppt. indicates Hg ( $\leq 0.001N$  in absence of other cations, and  $\leq 0.005N$  in their presence).

(B) Wet  $Ag_2S$  is added to a few ml. of the neutral solution, the suspension is heated for 10-20 sec., allowed to settle, and the sediment is treated with boiling 50% HNO<sub>3</sub>, when HgS, if present, remains undissolved. Other cations do not interfere. R. T.

Rapid determination of mercury. F. I. TRISCHIN (Ukrain. Chem. J., 1934, 9, 341-343).--Ag, KI, NaOH, and Br-H<sub>2</sub>O are added to the solution, which is shaken, Na<sub>2</sub>S is added, and the filtrate is made acid with HCl, when a black ppt. indicates the presence of Hg. Other cations do not interfere. R. T.

Volumetric determination of mercuric chloride with lead sulphide.—See B., 1935, 628.

Separation of rare earths. P. W. SELWOOD (J. Amer. Chem. Soc., 1935, 57, 1145).—Separation of Eu is facilitated by co-pptn. with  $BaSO_4$ , which is then washed repeatedly with hot, conc.  $HNO_3$ . Partial separation of Nd and Sm is effected by treating the anhyd. chlorides with  $H_2$  at 700°, and treating the product with  $H_2O$ . E. S. H.

Precipitation of aluminium with ammonium hydrogen carbonate. T. KOZU (Mem. Coll. Sci. Kyoto, 1934, A, 17, 17–26).—The pptn. is quant.; procedure for the determination of Al is given. The ppt. is  $4Al(OH)CO_3,6Al(OH)_3,9H_2O$ , which is fairly stable in a solution at  $p_{\rm H}$  7.6 and has a solubility in H<sub>2</sub>O of 0.00242 g. per 1000 c.c. at 20°.

E. S. H.

Colour reaction between manganese and formaldoxime. E. KAHANE (Ann. Chim. Analyt., 1935, [iii], 17, 175—178; cf. A., 1932, 491).—The reaction is sensitive, is positive whatever the state of oxidation of Mn, and is suitable for colorimetry. Fc, which interferes, is removed with  $Zn(OH)_2$ . E. C. S.

Determination of cobalt as a new complex compound. A. TAURINS (Z. anal. Chem., 1935, 101, 357-359).—Co is pptd. by an excess of 10% aq. K<sub>2</sub>HgI<sub>4</sub> from strongly ammoniacal solution as [Co(NH<sub>3</sub>)<sub>6</sub>][HgI<sub>3</sub>]<sub>2</sub> (I). The ppt. is washed with EtOH and Et<sub>2</sub>O, and dried at room temp. (I) is decomposed by H<sub>2</sub>O, and must be pptd. in a CO<sub>2</sub> atm. to avoid oxidation. J. S. A.

Quantitative separation of nickel and cobalt. E. RAYMOND (Compt. rend., 1935, 200, 1850– 1852).—To the solution of Ni and Co salts is added excess of 20% N(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>3</sub> and then excess of aq. NaOH. Both metals form complex salts, that of Ni being decomposed quantitatively by boiling, with pptn. of Ni(OH)<sub>2</sub>. The ppt. is washed with 0·01*N*-NaOH, dissolved in H<sub>2</sub>SO<sub>4</sub>, and Ni determined electrolytically. The filtrate containing Co is neutralised with H<sub>2</sub>SO<sub>4</sub>, excess of CO(NH<sub>2</sub>)<sub>2</sub> is added, and the Co determined electrolytically. Fe must be absent. The method may be used in qual. analysis. H. J. E.

Detection and determination of nickel by means of dimethylglyoxime in presence of copper. J. RANEDO (Anal. Fís. Quím., 1934, **32**, 611—613).— Ni can be determined in presence of Cu by means of dimethylglyoxime (I) if excess of  $Na_2S_2O_4$  is added before addition of (I). The method is particularly applicable to the analysis of Ni-Cu alloys. J. W. S.

Rapid determination of tungsten. C. RAJCHIN-SCHTEIN and N. KOROBOV (J. Appl. Chem. Russ., 1935, 8, 154—157).—WO<sub>4</sub>" is determined by titration with standard aq. Pb(OAc)<sub>2</sub>, with diamine-scarlet 6BS as adsorption indicator. The method is also applicable to the determination of Pb. R. T.

Iodometric determination of titanium, uranium, molybdenum, and vanadium in presence of iron by the method of liquid amalgams. G. N. PANTSCHENKO (J. Appl. Chem. Russ., 1935, 8, 361— 365).—Ti<sup>IV</sup>, U<sup>VI</sup>, Mo<sup>VI</sup>, and V<sup>V</sup> are reduced by Zn-Hg in HCl and H<sub>2</sub>SO<sub>4</sub> to Ti<sup>III</sup>, U<sup>III</sup>, Mo<sup>II</sup>, and V<sup>II</sup>, and the solution is titrated with 0·1*N*-I. The method is suitable for determination of these elements in presence of Fe, as Fe<sup>II</sup> is not oxidised by I. R. T. Organic compounds as analytical reagents. III. Pyrocatechol as reagent for the identification of titanium. N. R. PIKE, J. B. FICKLEN, and I. L. NEWELL (Ber., 1935, 68. [B], 1023-1026).— The pyrocatechol test is not sp. for Ti and can scarcely be used for the detection of the latter when unknown substances are present. Its sensitiveness (1 in  $5 \times 10^6$ ) makes it very serviceable for the identification of Ti which has been separated by a standard process. H. W.

Sources of errors in the assaying of gold and platinum.—See B., 1935, 595.

Separation of metals of the platinum group by hydrogen under pressure. V. V. IPATIEV and V. G. TRONEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 29—35).—Separation of metals in the Pt group from binary mixtures depends on the oxidationreduction potentials of the components. Pd is separated from a mixture of PdCl<sub>2</sub> and CuCl<sub>2</sub>, leaving the CuCl<sub>2</sub> unchanged; replacement of the CuCl<sub>2</sub> by FeCl<sub>3</sub> gives reduction of the FeCl<sub>2</sub> before deposition of the Pd-black. A mixture of PdCl<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub> gives reduction of Pt<sup>IV</sup> to Pt<sup>II</sup>, separation of Pd, and finally Pt-black from Pt<sup>II</sup>; by adjustment of this mixture rapid separation of Pd from Pt may be effected. Similar methods may be applied to Ir and Rh. A. B. D. C.

High-temperature hydrogen furnace. J. A. V. FAIRBROTHER (J. Sci. Instr., 1935, **12**, 200–201).— The furnace consists of concentric  $SiO_2$  tubes, the inner one being wound with W or Mo wire. A temp. of 1300° may be maintained for many hrs., and may be raised if the inner tube is of  $Al_2O_3$ . C. W. G.

Production of high temperatures. A. N. SISOEV (Ukrain. Chem. J., 1934, 9, 405-409).-Temp. of 2000° can be obtained using a laboratory furnace in which the resistance consists of tubes of refractory material ( $Al_2O_3$ ,  $Fe_3O_4$ , etc.) coated with graphite. The material is practically non-conductive at lower temp., but its resistance falls rapidly at >500°. The furnace is economical (12,000 volts, 0.03 amp.), and can be used in an oxidising atm.

R. T. Laboratory furnace working at 1550°. K. KUMANIN (J. Appl. Chem. Russ., 1935, 8, 177–183).— An electrically heated oven is described. R. T.

Union calorimeter. Optimum volume of gas. W. C. Moss (J. Sci. Instr., 1935, **12**, 188—191).— Graphs of optimum vol. of gas against calorific val. are given. C. W. G.

Exact measurement of isotherms. J. J. M. VAN SANTEN (Comm. Kamerlingh Onnes Lab., 1934, No. 227, 1—10; Chem. Zentr., 1935, i, 677).—The calibration of a closed manometer, the construction of an electric thermostat, and the measurement of the expansion coeff. of glass are described. H. J. E.

Recording microphotometer. N. B. BHATT and S. K. K. JATKAR (J. Sci. Instr., 1935, 12, 185–188).— A photo-electric cell, a bridge amplifier, and a directly coupled recording camera are used.

C. W. G.

Magnesium oxychloride for photometer screens and test plates. J. S. PRESTON (J. Sci. Instr., 1935, **12**, 197–198).—MgO is added to an equal wt. of  $MgCl_2, 6H_2O$  dissolved in the min. quantity of  $H_2O$ , to the consistency of plaster. The cement is translucent in thicknesses of a few mm. and does not shrink or expand appreciably on setting.

C. W. G.

Measuring the optical constants of small crystals. R. G. WOOD and S. H. AYLIFFE (J. Sci. Instr., 1935, 12, 194—196).—A single-circle goniometer is mounted on a microscope stage with its axis of rotation horizontal. The crystal is immersed in a very shallow cell and the interference figure observed through the microscope. C. W. G.

Method of taking stereoscopic radio-micrographs. U. YOSHIDA and H. TANAKA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 401-404).—X-Ray apparatus, provided with two separate targets, is described. E. S. H.

Photo-electric cell in the study of phosphorescence. W. H. BYLER and A. C. KRUEGER (J. Physical Chem., 1935, **39**, 695—699).—The use of a photo-electric cell for the measurement of luminous intensity of phosphorescence is recommended in preference to the usual photometric method.

F. L. U.

Valve voltmeter. H. POLLATSOHEK (Z. Elektrochem., 1935, 41, 340—344).—The instrument described works without zero drift, with a grid current of  $< 10^{-11}$  amp., and is accurate to  $\pm 1$  mv. F. L. U.

Measurements with the glass electrode. G. KILDE (Dansk Tidsskr. Farm., 1935, 9, 129–152).— Chiefly a summary of the theory and use of the glass electrode. Data are given for the deviation of this from the H electrode at  $p_{\rm H}$  2—9. Above  $p_{\rm H}$  9, the glass electrode does not behave reproducibly, but is dependent on the presence of neutral salts. Its resistance increases greatly in alkaline solutions containing Na, owing to the transport of Na<sup>\*</sup> through the glass. J. S. A.

Moving mercury cathode apparatus. B. S. EVANS (Analyst, 1935, 60, 389–393).—The cathode consists of a thread of Hg issuing from a jet. The Hg is kept in continuous circulation by means of an air-lift, and the metal dissolved in it is partly removed by washing before again issuing from the jet. E. C. S.

Measurements of dielectric constants. P. C. HENRIQUEZ (Physica, 1935, 2, 434-437).—A precision variable condenser and a small liquid condenser suitable for use in determination of the dielectric consts. of liquids are described. The vol. of liquid required is 0.5 c.c. J. W. S.

General system of bimetallic electrodes for potentiometric analysis. I. A. ATANASIU and A. K. VELCULESCU (Bul. Chim. Soc. Romane, 1934, 37, 165—172).—The electrode system Pt-Ni can be used advantageously in all potentiometric titrations, in which it behaves as a completely polarised system; the potential jump at the end-point is usually > with the Pt-Hg<sub>2</sub>Cl<sub>2</sub> system. Examples of its use in the titration of Pb" with K<sub>4</sub>Fe(CN)<sub>6</sub>, benzidine with KNO<sub>2</sub>, and 8-hydroxyquinoline with KBrO<sub>3</sub> are given. A. R. P. Micro-burette with a changeable tip. J. KHOURI (J. Pharm. Chim., 1935, [viii], 21, 607).

Apparatus for determination of carbon dioxide. M. H. HEY (Min. Mag., 1935, 24, 76-83).— An apparatus for the absorption of  $CO_2$  in  $Ba(OH)_2$ solution, and the filtration and washing of the  $BaCO_3$ with exclusion of atm.  $CO_2$  is described. L. J. S.

Automatic device for recording drop numbers in interfacial tension measurements. C. W. GIBBY and C. C. ADDISON (J. Sci. Instr., 1935, 12, 198—199).—Rising drops of the lighter liquid strike a vane on a balanced arm and actuate a relay which is coupled directly to the escapement of a clock. The dial is altered to read directly in drops. C. W. G.

Lead jointing of metals. H. G. JONES, G. E. ROWLAND, and A. WILLIAMS (J. Sci. Instr., 1935, 12, 201).—Pb is cast around the joint in a cardboard mould. C. W. G.

Measurement of thickness of thin transparent crystalline plates. K. S. SUNDARARAJAN (Phil. Mag., 1935, [vii], **19**, 1076—1079).—For measurements with plates of small area ( $>1.0\times0.5$  mm.) a modified form of Darbyshire's method is described (cf. Proc. Physical Soc., 1934, **46**, 626). Results for chrysene are given. N. M. B.

Vacuum filter for drop analysis. L. KULBERG (J. Appl. Chem. Russ., 1935, 8, 387–388). R. T.

Silver absorber for gaseous halogen compounds. A. D. PELSCH (J. Appl. Chem. Russ., 1935, 8, 184—185).—AgCl is reduced with Zn, the powder is washed, dried, and heated at the sintering point of AgCl, when Ag is obtained in grains. The product is a satisfactory absorbent of Cl compounds formed during microanalytical combustions. R. T.

Micropyknometric method for the determination of the specific gravities of minerals. F. V. SYROMYATNIKOV (Amer. Min., 1935, 20, 364– 370). L. S. T.

Acoustic interferometer for a wide temperature range. H. L. ANDREWS (Rev. Sci. Instr., 1935, [ii], 6, 167—168).—The Pierce acoustic interferometer is modified to measure velocities at a frequency of 4 megacycles from  $-63^{\circ}$  to  $150^{\circ}$  to about  $2^{\circ}_{0}$ . C. W. G.

Improved absolute manometer for pressures from 0.001 micron to one atmosphere. E. B. BAKER and H. A. BOLTZ (Rev. Sci. Instr., 1935, [ii], 6, 173—174).—Two McLeod gauges with bulbs of different sizes are connected together. C. W. G.

Liebig condenser [modification]. H. SCHANZ (Chem.-Ztg., 1935, 59, 458).—A Liebig condenser having two right-angle bends 10—15 cm. apart between the inlet end and the condenser jacket is described. Increased turbulence of the vapours causes more efficient condensation and fewer fractures occur. G. M.

Linear mineralogical arithmetic. A. L. PAR-SONS (Amer. Min., 1935, 20, 388-392).—A graphic method of determining mol. proportions and the calculation of mineral percentages is illustrated.

L. S. T.

History of chemical catalysis. A. PASSAGEZ (Bull. Soc. chim., 1935, [v], 2, 1000-1002).—The discovery of the catalysis of org. reactions has been erroneously attributed to Kirchoff (1811).  $C_2H_4$ was prepared by Bondt, Deimann, Van Troostwyck, and Lauwerenburg (1795) by passing EtOH or Et<sub>2</sub>O over Al<sub>2</sub>O<sub>3</sub> etc. R. S.

## Geochemistry.

Composition of air from the stratosphere. A. LEFAPE and G. COLANGE (Compt. rend., 1935, 200, 1871—1873).—Analytical data  $(O_2, N_2, \text{ total rare}$ gases) are recorded for samples from altitudes up to 16.8 km. The proportions are the same as in ordinary air, indicating complete mixing. He was detected spectroscopically. H. J. E.

Water vapour and carbon dioxide in the air of the stratosphere. A. LEPAPE and G. COLANGE (Compt. rend., 1935, 200, 2108—2110; cf. preceding abstract).—The quantities of  $H_2O$  vapour found were many times > the saturation pressure at  $-50^\circ$ , the approx. stratosphere temp. The CO<sub>2</sub> was also abnormally high. H. J. E.

Origin of combined nitrogen in the atmosphere. Analysis of tropical rain and its importance in agriculture. A. RAM (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 147—158).— The mean NH<sub>3</sub>-N (I) and NO<sub>3</sub>'-N (II) in freshly collected rain-water at Allahabad is 0.469 and 0.881 mg. per litre, respectively. The NH<sub>3</sub> is derived chiefly from the soil and the decomp. of org. matter. There is no correlation between the incidence of thunderstorms and the (II) in the atm., and these oxides are possibly produced by photochemical oxidation of NH<sub>3</sub> and N<sub>2</sub>. In general, the (II) and the ratio (II)/(I) in the tropics are > in other regions. J. G. A. G.

Partition coefficient of radon between gases and water from springs. M. GESLIN (Compt. rend., 1935, 200, 1423—1425).—The partition coeff. of Rn between  $H_2O$  and air at various temp. is compared with the ratio of the radioactivities of the  $H_2O$ and natural gases. The relatively high amounts found in the gases of hotter springs are attributed to the liberation of gas from cooler water on meeting hotter water. In cooler springs the dissolved gases liberated are < the amounts corresponding with equilibrium. J. W. S.

Ionic ratios in sea-water. L. ESPIL (Bull. Soc. chim., 1935, [v], 2, 1012-1015).—The concess. of common anions and cations in the water of the Arcachon basin have been determined and compared with the vals. for ocean water. The variations are attributed to the presence of marine organisms.

R. S.

Concentration of  $D_2O$  in natural ice. E. BARONI and A. FINK (Monatsh., 1935, 65, 386—390). —The concn. of  $D_2O$  in high-altitude ice from Alpine glaciers and ice caves was derived from pyknometric determination of *d*. All samples deviated from the normal [ $D_2O$ ], most showing an increase of 50—100%. J. S. A.

Heavy water in Czechoslovakian mineral waters. J. Z. SCHNEIDER and J. SLEZÁK (Chem.

Obzor, 1934, 9, 160—161; Chem. Zentr., 1935, i, 510). —No enrichment in  $D_2O$  was detected in 4 springs. H. J. E.

Isotopic composition of rain-water and snow. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 206).—During a rainfall the  $H_2O$  was initially slightly heavier than normal  $H_2O$ , and subsequently slightly lighter. This may be due to fractional condensation or vaporisation.  $H_2O$  from melted snow is 0.5—3.3 p.p.m. lighter than normal  $H_2O$ . This is attributed to the action of gravity on atm.  $H_2O$ . J. W. S.

Radioactivity of spring water from Hot Springs, Arkansas. H. SCHLUNDT (Amer. J. Sci., 1935, [v], 30, 45–50).—Radioactivity varies for the water and tufa of different springs. The mixed water contains 0.46 millimicrogram of Rn, corresponding with  $0.46 \times 10^{-9}$  g. Ra, whilst the amount of Ra found is only  $1.38 \times 10^{-12}$  g. per litre. L. J. S.

Isothermic evaporation at 25° of Lake Kutschuk water, with determination of the vapour pressure in relation to the concentration. M. N. JAKIMOV and E. I. KUMINOVA (J. Appl. Chem. Russ., 1935, 8, 221—226).—The v.p. and composition of the summer and the winter brines, at various conens., have been determined. The solid phases are NaCl and MgSO<sub>4</sub>,6H<sub>2</sub>O in winter, and NaCl, MgSO<sub>4</sub>,7H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>,10H<sub>2</sub>O, and astrakhanite in summer brine. The mother-liquors contain  $2\cdot3$ —3 kg. of Br per cu.m., and may be used for the prep. of MgCl<sub>2</sub>,6H<sub>2</sub>O, for the cement industry, and for Br production.

R. T. Hydrogeology of the springs of the Ilmen district and of Lake Turgoyak (South Urals). M. O. KLER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2,52-54).—Conditions at the Lake are not favourable for radioactivity. Rare-earth elements and U compounds give the springs high activity, but the deposits are unlikely to be of industrial val. A. B. D. C.

Radioactivity of the springs of the Ilmen district and of Lake Turgoyak (South Urals). P. R. BORODIN and M. G. GADD (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 47—51).—The highest radioactivity was shown by a spring located in the Ilmen mineralogical preserve. A. B. D. C.

Size of crystals. C. FRONDEL (Amer. Min., 1935, 20, 469–473).—Factors which influence the size of crystals are discussed. Large crystals of numerous minerals with their localities are cited. L. S. T.

Rational classification of silicates. A. J. MIKEI (Ukrain. Chem. J., 1934, 9, 472–474).—A classification is proposed. R. T.

Dilatometric study of natural silicates. I. J. MIKEI and I. A. BRODSKA (Ukrain. Chem. J., 1935, 10, 66—75).—The temp.-vol. diagrams of serpentine, tremolite, pelicanite, chloropal, and obsidian have been constructed. R. T.

Celadonite from Koktebel (Crimea). S. D. TSOHETVERIKOV and A. F. FIOLETOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 269-272).— $V_2O_5$  is reported in the celadonite which otherwise closely approximates to the composition of celadonite from Beskid. W. R. A.

Greenalite. F. JOLLIFFE (Amer. Min., 1935, 20, 405-425).-The typical greenalite (I) from the Mesabi iron range, Minnesota, is a green hydrated Fe<sup>II</sup> silicate, probably  $3FeO, 4SiO_2, 2H_2O$ , occurring in rounded granules, d 2.85-3.15,  $n_F 1.686\pm0.001$ ,  $n_{\rm D}$  1.674 ±0.001,  $n_{\rm c}$  1.670 ±0.002, which are moderately magnetic. On heating, it loses H<sub>2</sub>O readily and becomes black in colour and strongly magnetic. (I) is probably a definite mineral varying only slightly in composition and properties because of its colloidal origin. It has probably been deposited as a ppt. from H<sub>2</sub>O which received Fe and SiO<sub>2</sub> directly from igneous sources. Alteration yields (i) Fe oxides and hydroxides by the action of surface waters, (ii) an aggregate of minute green crystals associated with small, opaque green masses (metagreenalite) by crystallisation, (iii) a light-coloured fibrous mineral, a hydrated metasilicate of Fe<sup>II</sup>, Fe<sup>III</sup>, and Mg, by the action of Mg-bearing H<sub>2</sub>O not of surface origin, and (iv) an intergrowth of magnetite and amphiboles in the neighbourhood of heated igneous bodies. The greenalite rock has SiO, 49.43, Fe<sub>2</sub>O<sub>3</sub> 8.16, FeO 30.52,  $MgO 4.77, CaO 0.18, MnO 0.17, H_2O + 6.24, H_2O - 0.51,$ CO<sub>2</sub> 0.43, and Cl, S, SO<sub>3</sub> trace, total 100.41%.

L. S. T.

Crystallography of herderite from Topsham, Maine. G. M. YATSEVITCH (Amer. Min., 1935, 20, 426-437).—Novelties exhibited by crystals of herderite (I), CaBe(OH,F)PO<sub>4</sub>, are described. (I) is abundant in this locality and is attached to quartz, cleavelandite, lepidolite, topaz, and sericite. The crystallography of the species is revised and referred to new parameters, a:b:c=0.6307:1:1.2822,  $\beta$  $90^{\circ}$  6'. L. S. T.

Dickite from Pennsylvania. A. P. HONESS and F. J. WILLIAMS (Amer. Min., 1935, 20, 462-466).--Dickite has been discovered in two new localities, at the Pine Knot Colliery, Schuykill Co., and at Natalie, Pennsylvania. Optical, chemical, and X-ray data are summarised. L. S. T.

U-Galena and uraninite in Bedford, New York, cyrtolite. P. F. KERR (Amer. Min., 1935, 20, 443– 450).—An unusual occurrence of galena (I) in the Bedford cyrtolite (II) which contains Pb 0.33 and S 0.05% is described. (I) must be made up essentially of Pb isotopes derived from U and is named "Ugalena." Radiograms of (II) show a lack of uniformity in the distribution of the strongly radioactive areas. Microscopic and X-ray data indicate that much of the U is present as finely-divided uraninite (III) scattered throughout (II). The uneven distribution of (III) makes it doubtful that different specimens of (II) would give the same U content, and this may affect age determinations of the mineral. L. S. T. Origin of cyanite. J. L. STUCKEY (Econ. Geol., 1935, 30, 444-450).—The cyanite deposits of N. Carolina appear to have been formed by metasomatic replacement by hot solutions given off by the quartz veins, pegmatite dykes, and their parent magmas. L. S. T.

Structure of the schönites. A. GARRIDO and E. MOLES (Anal. Fís. Quím., 1934, 32, 432—445).— The dehydration of compounds of the type  $M^{II}SO_4, M^{IS}O_4, 6H_2O$ , where  $M^{II}$  and  $M^{I}$  are respectively Zn and K, Cu and K, Mn and  $NH_4$ , Fe and  $NH_4$ , and Mn and K, has been studied. Dihydrates, but no tetra- or penta-hydrates, are formed in each case (except that of the Mn salts, which yield monoand tri-hydrates), whilst when K is present a hemihydrate is also formed. Corresponding hydrates have approx. the same v.p. There is no evidence that 1 mol. of  $H_2O$  is associated with the anions and 5 mols. with the cations. The results accord with Werner's formula for schönites, viz.,  $[M^{II}(H_2O)_6]SO_4,SO_4M_2$ . H. F. G.

Petrology of Barnavave, Carlingford, Irish Free State. I. The junction hybrids. S. R. NOCKOLDS (Geol. Mag., 1935, 72, 289-315).—The basic hybrids and xenoliths, and the contaminated granites are described. Reciprocal reaction is discussed on the basis of the chemical analyses given, and the mineral transformations which have occurred are discussed. L. S. T.

Origin of basic xenoliths in plutonic rocks, with special reference to their grain-size. G. A. JOPLIN (Geol. Mag., 1935, 72, 227-234).—The formation of a fine-grained xenolith from a coarse- or medium-grained basic plutonic rock is discussed. Grain-size may be reduced (i) if the temp. of the invading magma be sufficient, by the formation of a granoblastic structure, (ii) by the development of highly poikilitic crystals of hornblende or biotite and their final disruption, and (iii) by the formation of granular masses of pyroxene or by criss-cross flakes of biotite during hybridisation. L. S. T.

Petrography of the Blea Wyke Series. R. H. RASTALL and J. E. HEMINGWAY (Geol. Mag., 1935, 72, 125-138). L. S. T.

Diorite-limestone reaction at Ben Bullen, New South Wales. G. A. JOPLIN (Geol. Mag., 1935, 72, 97—116).—Diorite tongues invading limestone are shown to have given rise to a series of contaminated rocks in which definite mineral assemblages are recognised. The petrography of the parent rocks and the contaminated zones are discussed and chemical analyses are given. The mineralogical changes brought about by assimilation of CaO are illustrated. A reciprocal reaction is shown to have occurred. Concn. is concluded to be the most important factor in contamination, and assimilation has occurred at a low temp. in presence of abundant volatiles, of which  $H_2O$  is the most important. L. S. T.

Structural relations of southern Appalachian zinc deposits. L. W. CURRIER (Econ. Geol., 1935, 30, 260—286).—The general geology of the various districts is described. The Zn deposits were accumulated in breccias of tectonic origin by ascending hypogene solutions. L. S. T.

Primary silver mineralisation at Sabinal, Chihuahua, Mexico. P. KRIEGER (Econ. Geol., 1935, 30, 242-259).-Mineralisation in the Florencia-Magda vein is described. Barite, SiO<sub>2</sub>, calcite, and siderite are abundant gangue minerals of the vein, and some fluorite and Fe oxide are present. Ag occurs chiefly as masses of nodular grains intimately associated with Co and Ni arsenides. The presence and mode of occurrence of the arsenides provide strong evidence for the primary origin of the Ag, which is supported by the galena, sphalerite, barite, calcite, and small amounts of chalcopyrite and tetrahedrite with which the Ag is also associated. Pyrargyrite and polybasite occur most abundantly along the contact of the vein material and the wall rock, and argentite forms fine intergrowths with many of the metallic minerals. The mineralisation in the Florencia-Magda vein is of a low-temp., epithermal character and the apparent source of mineralising solutions is an alaskite intrusive. Some supergene mineralisation has also occurred, and wires and plates of Ag of such origin are occasionally found.

L. S. T.

Revision of structure and stratigraphy of the Aspen district, Colorado, and its bearing on the ore deposits. J. W. VANDERWILT (Econ. Geol., 1935, 30, 223—241).—The general geology, structure, breccia, dolomitisation, and silicification are discussed. L. S. T.

High-temperature mineral associations at shallow to moderate depths. A. F. BUDDINGTON (Econ. Geol., 1935, 30, 205-222).—Mineral associations formed at 300-500° and at depths >2000-3000 ft. are termed xenothermal, and the xenothermal deposits of Pt, magnetite (martite)-apatite-pyroxene, cassiterite and cassiterite-wolframite, molybdeniteorthoclase-quartz, scheelite, tourmaline-cherty quartz or jasperoid, and tourmaline-chalcopyrite of different localities are discussed. L. S.

Differentiation in traps and ore deposition. T. M. BRODERICK and C. D. HOHL (Econ. Geol., 1935, 30, 301—312).—Differentiation in Keweenawan lava flows of the Michigan Cu district has been investigated. The Cu and S contents of twelve basaltic rocks, three quartz porphyries, and three phases of the Mt. Bohemia gabbro are recorded. The average Cu content selected for the Keweenawan traps is 0.01%, and the Cu is mainly in the form of Cu Fe sulphides. The distribution of the Cu, volatile transfer of elements, and ore deposition are discussed. The ascending magmatic  $H_2O$  theory best explains the occurrence of Cu in the Michigan deposits. L. S. T.

Dumortierite-andalusite mineralisation at Oreana, Nevada. P. F. KERR and P. JENNEY (Econ. Geol., 1935, 30, 287-300).—Considerable quantities of andalusite (I) are associated with the dumortierite (II). Quartz (III), albite, and sericite also occur, together with minor amounts of titanite, rutile, leucoxene, zircon, magnetite, limonite, tourmaline, biotite, and vein carbonate in various parts of the mineralised zone. The history of the deposit appears to be (i) deposition of a series of rhyolitic and trachytic tuffs with intercalated flows, (ii) intrusion of an adjacent igneous mass accompanied by shearing, devitrification and alteration of the tuff series, (iii) invasion of volcanics by quartz-albite endstage material from the igneous source, accompanied or followed by a conen. of (I) and (III) along restricted zones in the tuffs, and (iv) hydrothermal mineralisation involving replacement of (I) by (II), resulting in the formation in three stages of coarse euhedral crystals of blue (I), matted lavender or pink masses, and fibrous veins or isolated crystals. L. S. T.

Marginal and contact phenomena of the Dorback granite. F. WALKER and C. F. DAVIDSON (Geol. Mag., 1935, 72, 49-63). L. S. T.

"Limonite" of molybdenite derivation. R. BLANCHARD and P. F. BOSWELL (Econ. Geol., 1935, 30, 313—319).—When massive, molybdenite (I) normally oxidises to molybdic ochre, but when disseminated, Mo compounds frequently undergo complete leaching yielding an indigenous limonite (II) which, on account of its colour and frequent occurrence in Cu areas, may be confused with that of chalcocite origin. Two (II) products of (I) derivation, foliated boxwork and granular structure, have been identified, and serve as a means of differentiation from limonite of Cu derivation. (II) of (I) derivation occurs at many places in the South-western States, Mexico, and Australia. L. S. T.

Comparison of three Scottish magmas. S. ELDER (Geol. Mag., 1935, 72, 80-85).—The percentages of  $FeO+Fc_2O_3$ , MgO, CaO, and  $Na_2O+K_2O$ are each plotted against those of SiO<sub>2</sub> for the Devonian, Carboniferous, and Tertiary igneous rocks of Scotland. The curves show the calc-alkali character of the Devonian and Tertiary as compared with the Carboniferous magma, and indicate a magnesian tendency in the Devonian and a ferriferous in the Tertiary magma. L. S. T.

Spectrographic examination of smoky and ordinary quartz from Rincon, California. T. G. KENNARD (Amer. Min., 1935, 20, 392—399).—The colourless and the pale smoky quartz samples contain more Li than the dark smoky quartz. Al, V, Ti, Ca, and Mg are also present, but there is no significant difference in content between the various samples examined. L. S. T.

Sericite of unusual composition. D. B. MEYER (Amer. Min., 1935, 20, 384–388).—Sericite (I) from Pilot Knob, Ironton, Missouri, SiO<sub>2</sub> 47·30, Al<sub>2</sub>O<sub>3</sub>  $36\cdot31$ , Fc<sub>2</sub>O<sub>3</sub> 2·17, Na<sub>2</sub>O 5·27, K<sub>2</sub>O 2·70, H<sub>2</sub>O 5·80, total 99·55%, has d 2·69 and  $\mu$  1·580±0·003. The dehydration curve of (I) is so distinctive that it should be used in determinations of the mineral. There is a slight loss of H<sub>2</sub>O between 85° and 450° and between 600° and 1080° and a rapid loss at 450–600°. A mixture of albite and orthoclase may have been the original source of the mineral. L. S. T.

Minerals of the White Raven Mine, Ward, Colorado. E. E. WAHLSTROM (Amer. Min., 1935, 20, 377–383).—The occurrence and origin of these minerals are described. Horn quartz, massive galena with small amounts of pyrite and sphalerite, manganiferous siderite, and native wire Ag, formed probably in this order, occur in important amounts in the ore shoots of the Pb-Ag vein. Secondary minerals are calcite, and hydrated Fe and Mn oxides. L. S. T.

Adamite from Gold Hill, Tooele Co., Utah. L. W. STAPLES (Amer. Min., 1935, 20, 371–376).— This adamite occurs as individual pale yellow crystals and as colourless rosettes; a:b:c=0.9742:1:0.7095;  $n_a$  1.711 $\pm$ 0.003,  $n_{\beta}$  1.732 $\pm$ 0.003,  $n_{\gamma}$  1.756 $\pm$ 0.003. L. S. T.

Topaz from Devil's Head, Colorado. M. A. PEACOCK [with A. MONTGOMERY and E. OVER, jun.] (Amer. Min., 1935, 20, 354—363).—Topaz crystals of unusual size and regular development and smaller crystals of unusually distorted habits are described. The topaz is associated with quartz, microcline, albite, muscovite, fluorite, and cassiterite in pegmatite.

L. S. T. Distribution of the heavy minerals in the clays of Middlesex County, New Jersey. A. C. HAW-KINS (Amer. Min., 1935, 20, 334-353).—The residues obtained by elutriation of Cretaceous clays have been studied in detail. The percentages of ilmenite, tournaline, and zircon have been used for the correlation of the clay beds. Total org. C has also been determined. The areal distribution of the heavy minerals and C has been plotted. Ilmenite is plentiful and rutile scarce. L. S. T.

Tetradymite from Inyo Mountains, California. R. W. WEBB (Amer. Min., 1935, 20, 399-400).— Tetradymite occurs as numerous brilliant tabular crystals embedded in bismutite in a brecciated quartz vein in the quartz monzonite of the Inyo Mountains. A trace of S, but no Se, is present. L. S. T.

Plasticity of crystals of sylvine. E. W. ZEHNO-WITZER (Nature, 1935, 135, 1076).—Crystals of sylvine (I) become plastic after treatment with  $H_2O$ . At 700—780°, (I) possesses considerable plasticity. Crystals removed from their mother-liquor and wiped with filter-paper are at first very plastic, but become fragile on keeping in air for a few hr. The plasticity of crystals of (I) when formed from a melt or a solution may explain the frequent occurrence of bent and twisted crystals. L. S. T.

Amphibolites from Zlatibor (West Serbia). S. PAVLOVITCH (Compt. rend., 1935, 200, 2094— 2096).—Analytical data are recorded and discussed. H. J. E.

Recrystallisation of diorites and quartzite diorites in the Manson plateau (Puy-de-Dôme) under the influence of granitic contact metamorphism. J. JUNG (Compt. rend., 1935, 200, 2091—2093).—A review and discussion of the minerals of the region. H. J. E.

Petrographical study of Zlatibor peridotites (W. Serbia). S. PAVLOVITCH (Compt. rend., 1935, 200, 1864—1866).—Petrographical and analytical data are recorded. H. J. E.

Hydroclastic elements of the Czeremosz district. H. TOKARSKI (Bull. Acad. Polonaise, 1935, A, 79-84).—Petrographical and analytical data for a no. of specimens are recorded and discussed. H. J. E.

Mylonites from the San Andreas fault zone. A. C. WALTERS and C. D. CAMPBELL (Amer. J. Sci., 1935, [v], 29, 473-503).—Description of crushed rocks from California are given. Analysis of an ultramylonite suggests that the original rock was an arkose. L. J. S.

Rôle of kyanite in the "hornfels zone" of the Carn Chuinneag granite (Ross-shire). C. E. TILLEY (Min. Mag., 1935, 24, 92—97).—The hornfelses in the metamorphic zone surrounding the granite contain almandine (FeO 32.40, MnO 0.72%) and kyanite. The latter occurs as replacements of chiastolite and cordierite, as fine needles associated with biotite, and as larger crystals in quartz-kyanite veinlets. Kyanite is typically a stress mineral, and its occurrence as a transient mineral phase in the formation of cryst. schists is unusual. L. J. S.

Chondrodite in the Glenelg limestone, Inverness-shire. H. H. READ and I. S. DOUBLE (Min. Mag., 1935, 24, 84—89).—Small grains of chondrodite (previously mistaken for fosterite) occur in the cryst. limestone, usually forming rims around crystals of fosterite. It has probably been formed by the introduction of F-bearing solutions. L. J. S.

Ankerites from the Northumberland coalfield. L. HAWKES and J. A. SMYTHE (Min. Mag., 1935, 24, 65—75).—Several analyses, with determinations of d and n, are given of ankerite and calcite occurring as veinlets in the coal. The ankerites are members of an isomorphous series consisting of dolomite MgCO<sub>3</sub>, CaCO<sub>3</sub> and ferrodolomite FeCO<sub>3</sub>, CaCO<sub>3</sub>, with small amounts of mangandolomite MnCO<sub>3</sub>, CaCO<sub>3</sub>, and they may hold up to 20% CaCO<sub>3</sub> in solid solution.  $n(\omega)$  for FeCO<sub>3</sub>, CaCO<sub>3</sub> is deduced as 1.765. The calcite is of later deposition. L. J. S.

Two new bismuth minerals from South Africa. E. D. MOUNTAIN (Min. Mag., 1935, 24, 59–64).—Bismoclite was found as a pale grey nodule with Bi ores in pegmatite at Steinkopf in Namaqualand. Analysis corresponds closely with BiOCl; d 7.36. It differs from daubreelite (BiO[OH,Cl]) from Bolivia in containing more Cl (13%). Boksputite from pegmatite at Boksput in Gordonia is pale yellow to greyishbrown and massive. Analysis corresponds with 6PbO,Bi<sub>2</sub>O<sub>3</sub>,3CO<sub>2</sub>; d 7.29. L. J. S.

Chironomide tufa. J. WALLNER (Bot. Arch., 1935, 37, 128–134).—The tufa result from an association of  $CaCO_3$ -depositing fresh-water algæ and incrusted larva tubes of *Chironomidæ*. A. G. P.

Differentiation of Hawaiian lavas. H. A. POWERS (Amer. J. Sci., 1935, [v], **30**, 57-71).—A field study of the crystallisation of basalt suggests conditions other than those obtained in the laboratory. L. J. S.

Occurrence of petroleum, natural gas, iodised and sulphurated waters in South Bavaria. K. A. WEITHOFER (Petroleum, 1935, 31, No. 22, 1—8; No. 27, 5—8).—A survey is given of recorded observations of the occurrence of the above products. C. C.

Radioactivity of Kuznietzk basin coals. E. S. BURKSER, V. V. KONDOGURI, N. P. KAPUSTIN, and P. P. POTAPOV (Ukrain. Chem. J., 1934, 9, 441–445). —The mean Ra content of 20 samples is  $0.5 \times 10^{-12}$ %, and of Th  $0.17 \times 10^{-3}$ %, as compared with  $28 \times 10^{-12}$ % and  $0.37 \times 10^{-3}$ % for Donetz basin coals. It is concluded that concn. of radioactive substances is not involved in the growth of plants. R. T.

Classification of coals. M. C. STOPES (Nature, 1935, 136, 33).—A reply to criticism (this vol., 843). L. S. T.

# Organic Chemistry.

Internal energy relationships of organic compounds. VII. Laws of coupling of paired and unpaired *B* electrons. O. SCHMIDT (Ber., 1935, 68, [*B*], 1026—1028; cf. this vol., 480).—The double linking rule is qualitatively deduced from the course of the potential curve between paired *B* electrons and *A* electrons. Considerations of unpaired *B* electrons lead directly to Criegee's rule that when 2 atoms or groups in the  $\alpha$ 8 position in a mol. are removed the remainder becomes ruptured between the  $\beta$  and  $\gamma$ atoms. H. W.

Catalytic influence of mercury vapour on the cracking of methane by the glow discharge.—See this vol., 943.

Straight-chain- and the many-membered  $CH_2$ ring-molecule. A. MÜLLER (Nature, 1935, 135, 994).—At low-temp. X-ray data show that the vols. occupied by a  $CH_2$  group in  $n \cdot C_{12}H_{26}$  and in the corresponding cyclohydrocarbon are identical. As the temp. rises the  $CH_2$  in the straight-chain compound occupies more space than that of the ring compound, probably owing to its greater mobility. L. S. T.

Mechanism of catalytic hydrogenation.—See this vol., 940.

Action of hydrogen peroxide on olefines. A. P. BARCHASCH (J. Gen. Chem. Russ., 1935, 5, 254-255).  $-H_2O_2$  does not react with  $C_2H_4$  and amylene at room temp. In presence of FeSO<sub>4</sub> amylene and  $H_2O_2$ yielded a mixture of products, amongst which COMe<sub>2</sub>, CO<sub>2</sub>, HCO<sub>2</sub>H, and AcOH were identified; aldehydes, homologues of COMe<sub>2</sub>, EtCO<sub>2</sub>H, and glycols were absent. R. T.

Absorption of ethylene by solid cuprous chloride. H. TROPSCH and W. J. MATTOX (J. Amer. Chem. Soc., 1935, 57, 1102—1103).—CuCl<sub>2</sub> absorbs 1 mol. of  $C_2H_4$  at 60—62 atm. The dissociation pressure at 0°, 16·S°, 30°, and 40° is 2·14, 5·95, 11·7, and 19·49 atm., respectively. The rate of absorption is increased by previous use of the CuCl<sub>2</sub> or addition of < 10% of infusorial earth or a little H<sub>2</sub>O. No polymerisation occurs at 100—200°/65—80 atm. C<sub>3</sub>H<sub>6</sub> is not absorbed, but C<sub>3</sub>H<sub>6</sub>-C<sub>2</sub>H<sub>4</sub> mixtures cannot be quantitatively separated by CuCl<sub>2</sub>. Aq. CuCl<sub>2</sub> does not absorb C<sub>2</sub>H<sub>4</sub>. R. S. C.

Isomerisation of allene hydrocarbons by silicates. II. Isomerisation of  $\Delta^{a\beta}$ -butadiene in presence of floridin. J. M. SLOBODIN (J. Gen. Chem. Russ., 1935, 5, 48—52).—The light hydrocarbon fraction obtained when CHMe:C:CH<sub>2</sub> (I) is passed over floridin at 245° contains (I) 96.6, CEt:CH 3.4%, divinyl traces; at 330° the corresponding yields are 75.5, 3.9, and 20.6%. The % of (I) converted into polymerides [the dimerides of (I) and (II) are absent] is 22 and 25. (I) is conveniently prepared from crotyl alcohol (a by-product of the synthetic rubber industry) by conversion into CHMeBr·CHBr·CH<sub>2</sub>Br, from which HBr is eliminated (KOH at 120°) to yield CHMeBr·CBr:CH<sub>2</sub>, and this gives (I) when boiled with Zn in EtOH. R. T.

Raman effect and organic chemistry. cistrans-Isomerism of ethylenic compounds CHMe:CHR. Classification of the radicals R. (MLLE.) B. GREDY (Bull. Soc. chim., 1935, [v], 2, 1029-1037).—The Raman spectra of the following substances are given: cis-CHR:CHMe [R = Et, Pr<sup>a</sup>, Bu<sup>a</sup> (I), n-C<sub>5</sub>H<sub>11</sub>, n-C<sub>6</sub>H<sub>13</sub>, Ph (II)], cis-δ-cyclo-pentyl- $\Delta^{\beta}$ -butene, b.p. 156–158°, cis-ζ-cyclohexyl- $\Delta^{\beta}$ -hexene, trans-crotyl chloride (III), trans- $\delta$ -methyl- $\Delta^{\beta}$ -pentene, and the *trans*-isomerides of (I) and (II). The cis-compounds were prepared by hydrogenation (colloidal Pd) of the corresponding acetylenic compounds (cf. A., 1928, 28; 1930, 79). Some were converted into mixtures (IV) of the cis- and transisomerides by successive treatment with Br and Zn, or by the dehydration of the appropriate alcohol. The Raman spectra of (IV) have also been examined. The frequency (near 1600 cm.<sup>-1</sup>) characteristic of the ethylenic linking is higher for the trans- than for the corresponding cis-compounds (cf. A., 1932, 897). Radicals R are classified according to their effect on this line. A close parallelism exists between this classification and that based on the compounds CHR:CH2 (cf. A., 1932, 676). (III) and MgPrBr do not give  $\Delta^{\beta}$ -heptene. H. G. M.

Raman effect and organic chemistry. Trisubstituted ethylenes. (MLLE.) B. GREDY (Bull. Soc. chim., 1935, [v], 2, 1038-1044).-The Raman spectra of the following compounds have been measured:  $\gamma$ -methyl- $\Delta^{\beta}$ -nonene, b.p.  $64 \cdot 5 - 65^{\circ}/14 \text{ mm.}$ , CMeBr:CHMe, CHMe:CMe·CHO, CHEt:CMe·CHO, CHMe:CEt·CHO,  $\beta$ -methyl- $\Delta^{\beta}$ -octene, b.p. 145—146°,  $n_{\rm p}^{21}$  1.4240, and CHMe:CBr·CH<sub>2</sub>Br. Only one line (near 1600 cm.-1) characteristic of the ethylenic linking has been observed. The classification of R and R' in CHMe:CRR' according to their effect on this line resembles that for the compounds CHMe:CHR (see preceding abstract). The effects on this line of conjugation (cf. A., 1932, 897) and of changes in the relative positions of Me, R, and R' in CHMe:CRR' are discussed. a-Methoxy-B-methyln-octane, b.p. 76°/16 mm., and HBr afford β-methyln-octyl bromide, b.p.  $92^{\circ}/16 \text{ mm.}$ , which with quinoline gives a mixture of  $\beta$ -methyl- $\Delta^{a}$ - and  $-\Delta^{\beta}$ -octene. Dehydration of  $\gamma$ -methylnonan- $\gamma$ -ol, b.p.  $91^{\circ}/13 \text{ mm.}$ (prepared by the Grignard reaction from Me hexyl ketone), affords mainly C<sub>5</sub>H<sub>11</sub>·CH:CMeEt.

H. G. M.

New trimeric compound of acetylene. Acetylenyldivinyl. A. L. KLEBANSKI, C. A. DRANITZINA, and I. M. DOBROMILSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 229–236).— $\Delta^{ayc}$ -Hexadieneinene (acetylenyldivinyl), b.p.  $32^{\circ}/100$  mm. (Cu derivative), is isolated from the products of the polymerisation of C<sub>2</sub>H<sub>2</sub> in presence of CuCl-NH<sub>4</sub>Cl-H<sub>2</sub>O. It is very sensitive towards air, yields (?)  $\beta$ -chloro- $\Delta^{a\gamma\epsilon}$ -hexatriene with HCl, gives a ketone (semicarbazone) with dil. H<sub>2</sub>SO<sub>4</sub>, and slowly affords non-cryst. substances with p-C<sub>6</sub>H<sub>4</sub>Me·SH. H. W.

Reaction for differentiating chloroform and carbon tetrachloride. J. ROZEBOOM (Pharm. Weekblad, 1935, 72, 689).—1 c.c. (free from EtOH) containing a crystal of I is treated with papaverine hydrochloride (10 mg.) or other alkaloid salt insol. in CHCl<sub>3</sub> but sol. in CCl<sub>4</sub>. The violet colour disappears in CHCl<sub>3</sub> but not in CCl<sub>4</sub>. S. C.

Differentiation of chloroform and carbon tetrachloride. N. SCHOORL (Pharm. Weekblad, 1935, 72, 751).—CHCl<sub>2</sub> reduces boiling Fehling's solution. CCl<sub>4</sub> gives COCl<sub>2</sub> and Cl<sub>2</sub> (detected with starch-KI) when one drop is heated in a loosely corked test-tube (flameless combustion). The tests are sp. S. C.

Reactions of bromo- and dibromo-olefines. G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 1088-1090).— $\alpha\alpha$ -Dibromo-olefines do not react with hot aq. Na<sub>2</sub>CO<sub>3</sub>, anhyd. C<sub>5</sub>H<sub>5</sub>N, or NH<sub>2</sub>Ph. Me·[CH<sub>2</sub>]<sub>4</sub>·CH:CBr<sub>2</sub> and NaOEt-EtOH give a 70% vield of heptinene and some AcOH. CHMe:CBr<sub>2</sub> and NaEtS give Et<sub>2</sub>S<sub>2</sub> and CMe·CH. CHMe:CHBr, Me·[CH<sub>2</sub>]<sub>5</sub>·CH:CHBr, CHMe:CBr<sub>2</sub>, and Me·[CH<sub>2</sub>]<sub>5</sub>·CH:CBr<sub>2</sub> with Na in liquid NH<sub>3</sub> give

Me·[CH<sub>2</sub>]<sub>5</sub>·CH:CBr<sub>2</sub> with Na in liquid NH<sub>3</sub> give acetylenes and olefines, the ratio of these products formed being 0·012, 0·45, 0·71, and 1·8, respectively; the Br<sub>2</sub>-compounds give also some polymeric compounds. By addition of Cl<sub>2</sub> or Br in CCl<sub>4</sub> at  $-5^{\circ}$ are obtained  $\alpha\beta$ -dichloro- $\alpha$ -bromo-, b.p. 154·5°,  $\alpha\beta$ -dichloro- $\alpha\alpha$ -dibromo-, b.p. 84°/16 mm., and  $\alpha\alpha\alpha\beta$ -tetrabromo-propane (I), b.p. 122°/15 mm. CHMe:CBr<sub>2</sub> does not react with O<sub>2</sub> in EtOH or NH<sub>2</sub>Ph, but when homogeneous or in hydrocarbon solvents (best dry) affords CHMeBr·COBr, and, by partial hydrolysis and reaction of the liberated HBr, some (I). CH<sub>2</sub>N<sub>2</sub>, NOCl, CH<sub>2</sub>Ph·SH, and H<sub>2</sub>-Pt do not react.

R. S. C.

o-Nitro-, m-nitro-, and 3:5-dinitro-phenylcarbimides as reagents for alcohols. F. HOEKE (Rec. trav. chim., 1935, 54, 505-517).—The carbimide and alcohol are heated in light petroleum. Reaction occurs readily except with benzoin derivatives. m-Nitro- and 3:5-dinitro-phenylcarbimides fulfil all conditions required for a reagent for identification of alcohols. The following are described. m-Nitrophenylcarbamates:  $Pr^a$ , m.p. 76°;  $Bu^a$ , m.p. 51°; n-amyl, m.p. 62°; n-hexyl, m.p. 52°; n-heptyl, m.p. 57°; n-octyl, m.p. 63°; n-nonyl, m.p. 66°; n-decyl, m.p. 67°; n-undecyl, m.p. 56°; n-dodecyl, m.p. 76°; cetyl, m.p. 78°; n-octadecyl, m.p. 77°;  $Pr^3$ , m.p. 91°;  $Bu^{\beta}$ , m.p. 62°;  $Bu^{\gamma}$ , m.p. 95°; secbutyl, m.p. 86°; benzyl, m.p. 118°;  $\beta$ -phenylethyl, m.p. 80°;  $\gamma$ -phenyl-n-propyl, m.p. 57°; benzoin, m.p. 112°; allyl, m.p. 51°; cholesteryl, m.p. 184°. o-Nitrophenylcarbamates:  $Pr^a$ , m.p. 15°;  $Bu^a$ , m.p. -10° and +7°, n-hexyl, m.p. 33°; n-heptyl, m.p. 17°; n-octyl, m.p. 44°; n-nonyl, m.p. 34°; n-decyl, m.p. 52°;

64°; sec-butyl, m.p. 26°;  $Bu^{\gamma}$ , m.p. 90°; benzyl, m.p. 65°;  $\beta$ -phenylethyl, m.p. 58°; benzoin, m.p. 161°; allyl, m.p. 20°; cholesteryl, m.p. 169°. 3:5-Dinitrophenylcarbamates :  $Pr^{a}$ , m.p. 97°;  $Bu^{a}$ , m.p. 70°; n-amyl, m.p. 58°; n-hexyl, m.p. 75°; n-heptyl, m.p. 61°; n-octyl, m.p. 69°; n-nonyl, m.p. 66°; n-decyl, m.p. 70°; n-undecyl, m.p. 62°; n-dodecyl, m.p. 81°; cetyl, m.p. 86°; n-octadecyl, m.p. 88°;  $Pr^{\beta}$ , m.p. 112°;  $Bu^{\beta}$ , m.p. 119°, sec-butyl, m.p. 120°;  $Bu^{\gamma}$  m.p. 166° (decomp.); benzyl, m.p. 181°;  $\beta$ -phenylethyl, m.p. 139°;  $\gamma$ -phenyl-n-propyl, m.p. 71°; benzoin, m.p. 220° (decomp.); allyl, m.p. 114°; cholesteryl, m.p. 198°. n-Dodecyl phenylcarbamate, m.p. 74°. p-Nitrophenylcarbamates:  $\beta$ -phenylethyl, m.p. 135°;  $\gamma$ -phenyl-npropyl, m.p. 104°; allyl, m.p. 108°. P. G. C.

Odd-membered *n*-primary alcohols.  $(\alpha \rightarrow \beta$ -transition).—See this vol., 921.

Catalytic dehydration of butyl alcohol by alumina. I. Isomerisation of butenes. II. Determination and preparation of butenes. C. MATIGNON, H. MOUREU, and M. DODÉ (Bull. Soc. chim., 1935, [v], 2, 1169—1181, 1181—1187).—I. Bu<sup>a</sup>OH and pure Al<sub>2</sub>O<sub>3</sub> (from the sulphate or nitrate) at 380° gives  $\Delta^{a}$ -n-butene, but presence of a trace of acid, e.g., SO<sub>4</sub>", causes complete or partial isomerisation to  $\Delta^{\beta}$ -n-butene, increased slightly by previous heating of the Al<sub>2</sub>O<sub>3</sub> to 450° or by details of its prep. which could not be precisely defined. Al<sub>2</sub>O<sub>3</sub> prepared from the carbonate is less liable to cause isomerisation.

II. Details are given for the prep. (above method) of pure  $\Delta^{\alpha_2}$  or  $\Delta^{\beta_2}$ -*n*-butene; the proportions of each in a mixture may be determined either by the b.-p. curve of the mixed dibromides or by transformation thereof into the diacetates, hydrolysis to the glycols, oxidation of the  $\beta_{\gamma}$ -glycol in the mixture to Ac<sub>2</sub>, and determination of the Ac<sub>2</sub> by NH<sub>2</sub>OH. R. S. C.

Action of calcium hypochlorite on organic compounds with hydroxyl and carbonyl groups. I. Calcium hypochlorite and the higher primary alcohols. J. SUKNEVITSCH and A. TSCHILINGARJAN (Ber., 1935, 68, [B], 1210—1216).—The hypothesis that EtOCl is the primary product in the action of OCl' on EtOH is strengthened by the observation that much less CHCl<sub>3</sub> is formed by the action of NaOCl on EtOH in presence of Na oleate, undecenoate, or cinnamate than in control experiments. The presence of OEt and Cl in the fatty acid layer establishes the addition to oleic acid. CHPh:CH·CO,Na in absence of EtOH is oxidised to BzOH, whereas CHPh:CHCl is produced in its presence. The following schemes: MeCHO  $\implies$  CH<sub>2</sub>:CH·OH  $\rightarrow$ (+EtOCl) CH<sub>2</sub>Cl·CH(OH)·OEt etc. and CH<sub>2</sub>:CH·OH  $\rightarrow$  CH<sub>2</sub>:CH·OCl  $\rightarrow$  CH<sub>2</sub>Cl·CHO  $\rightarrow$  CHCl:CH·OH are suggested, the former being regarded as the more probable, since EtCHO and Pr<sup>g</sup>CHO do not give CHCl<sub>3</sub>, but only the corresponding acids, and McOH yields only HCO<sub>2</sub>H, CO<sub>2</sub>, and MeOCl. If reaction between one of these aldehydes and Ca(OCl)<sub>2</sub> takes place in presence of MeOH, CHCl, is formed good vield:  $Pr^{\beta}CHO = CMe_{\beta}:CH \cdot OH \rightarrow$ in (+MeOCl) CMe<sub>2</sub>Cl·CH(OH)·OMe  $\rightarrow$  CMe<sub>2</sub>Cl·CHO  $\rightarrow$ CMe<sub>2</sub>Cl·CO<sub>2</sub>H. Salts of CMe<sub>2</sub>Cl·CO<sub>2</sub>H and CH2Cl·CH(OH)·OEt readily afford CHCl3, whereas CH<sub>2</sub>Cl·CH(OEt)<sub>2</sub> does not. The yield of CHCl<sub>3</sub>

from MeCHO and Ca(OCl)<sub>2</sub> is increased by the presence of EtOH; the impossibility of isolation of intermediates is probably due to the fact that CH<sub>2</sub>Cl·CHO is more readily enolised than MeCHO. CCl<sub>3</sub>·CHO is readily oxidised by Ca(OCl)<sub>2</sub> to CCl<sub>3</sub>·CO<sub>2</sub>H and CaCO<sub>3</sub> formed during the usual prep. of CHCl<sub>3</sub> is due to the decomp. of (CCl<sub>3</sub>·CO<sub>2</sub>)<sub>2</sub>Ca as well as to the oxidation of (HCO<sub>2</sub>)<sub>2</sub>Ca. Higher alcohols R·CH<sub>2</sub>·OH react thus: CH<sub>2</sub>R·CH<sub>2</sub>·OH  $\rightarrow$ CH<sub>2</sub>R·CHO  $\rightarrow$  CRCl<sub>2</sub>·CHO  $\rightarrow$  CRCl<sub>2</sub>·CO<sub>2</sub>H  $\rightarrow$ 

R·CO·CO<sub>2</sub>H. Thus Pr<sup>a</sup>OH affords AcCO<sub>2</sub>H and thence by oxidation or enolisation AcOH, CO2,  $H_2C_2O_4$ , and CHCl<sub>3</sub>. Bu<sup>a</sup>OH gives EtCO<sub>2</sub>H and CO<sub>2</sub> with little CHCl<sub>3</sub>. Alcohols CHRR'•CH<sub>2</sub>•OH react : CHRR'•CH<sub>2</sub>•OH → CHRR'•CHO → CCIRR'•CHO →  $CCIRR' \cdot CO_2H \rightarrow OH \cdot CRR' \cdot CO_2H \rightarrow CORR' + CO_2 +$ H<sub>2</sub>O, and therefore yield the same products as obtained from the ketone CORR' with, in addition, the acid produced by direct oxidation. Thus Bu<sup>2</sup>OH yields Pr<sup>\$CO2</sup>H, AcOH, CO2, and CHCl3, whilst COMe2 gives AcOH and CHCl3. CHMeEt OH affords CHMeEt CO2H, EtCO2H, AcOH (very little),  $CO_2$ , and  $CHCl_3$ ; the same products, except CHMeEt·CO<sub>2</sub>H, are derived from COMeEt. Aldehydes, in which all H atoms attached to C united with CHO are replaced, are oxidised by OCl' to acids (CCl<sub>3</sub>·CHO; BurCHO). sec.-Alcohols are transformed by Ca(OCl)<sub>2</sub> into ketones, whereas tert.-alcohols yield only small amounts of the corresponding alkyl hypochlorite. The lengthening of the C chain of a primary alcohol is accompanied by an increase in the amount of acid with the same no. of C atoms; this is ascribed to increasing difficulty of enolisation of the corresponding aldehyde. H. W.

Preparation of glycerol trichlorohydrin from propylene chloride. A. L. KLEBANSKI and A. S. VOLKENSCHTEIN (J. Appl. Chem. Russ., 1935, 8, 106— 116).—CHMeCl·CH<sub>2</sub>Cl (1) is obtained in 80% yield from Cl<sub>2</sub> and CHMe:CH<sub>2</sub>; the further chlorination of (I) to CHCl(CH<sub>2</sub>Cl)<sub>2</sub> (II), in presence or absence of catalysts, yields a mixture of products, chieffy CHMeCl·CHCl<sub>2</sub>, with very small yields of (II). (I), when heated with CaCl<sub>2</sub>, BaCl<sub>2</sub>, CaO, Ca(OH)<sub>2</sub>, MgO, or soda-lime, affords  $\alpha$ -chloropropene and allene, but no allyl chloride. The synthesis of glycerol from (I) is not commercially realisable. R. T.

**Existence of carbon monoxide acetals. II.** F. ADICKES and P. P. PECKELHOFF (Ber., 1935, 68, [B], 1138—1140).—If, in accordance with Scheibler, the ppt. obtained by the action of  $HCO_2Et$  on  $CNaPh_3$  contains  $ONa \cdot C \cdot OEt$  in addition to  $HCO_2Na$  addition of anhyd. EtOH must produce NaOEt and  $HCO_2Et$  and the amount of  $HCO_2H$  in the filtrate must exceed that due to the solubility of  $HCO_2Na$ . Since this is not the case, the existence of  $ONa \cdot C \cdot OEt$  is denied. The only possible cause of formation of  $HCO_2Na$  appears to be in fission of  $HCO_2Et$  by  $CNaPh_3$  into  $C_2H_4$  and  $HCO_2Na$ . H. W.

Rotational contribution of chromophoric groups in compounds of analogous structure. W. KUHN and H. BILLER (Z. physikal. Chem., 1935, B. 29, 1-41).—The validity of the vicinal rule (A., 1933, 211) has been examined. The optical absorp-

tion, rotatory dispersion, and circular dichroism of the nitrites of methyl-n-hexyl-, methylcyclohexyl-, and phenylmethyl-carbinol show that ring closure at the *n*-hexyl group and the replacement of hexyl by Ph are to be regarded as small chemical changes in the sense of the vicinal rule. With rotatory dispersion and circular dichroism the absorption region is divided into discrete bands, which are absent or only faintly indicated in optical absorption. The replacement of cyclohexyl by Ph in hexahydromandelic acid is a small change, whilst the replacement of CO2Et in OH CHPh CO2Et by CN or Me is a large change. Replacement by Me of the H attached to the asymmetric C of OH·CHPh·CO2H is a large change in relation to the rotational contribution of the Ph absorption band, but only a small change for the contributions of the other substituents. This leads to the formulation of the rule that if a chemical change occurs in a mol., then of absorption bands with chromophoric centres equidistant from the point of change strong bands undergo less change in their active properties than weaker bands. The rule is valid even when there are large chemical changes lying outside the scope of the vicinal rule. Both rules are related to physical considerations. R. C.

Thermal analysis of binary mixtures of organic nitrates. III. T. URBANSKI (Rocz. Chem., 1935, 15, 191—197).—The m.-p. diagrams do not suggest formation of compounds in the systems mannitol hexanitrate (I)-camphor; pentaerythritol tetranitrate-phthalide,  $-\text{NHPh}\cdot\text{CO}_2\text{Et}$ , and -dinitro-dimethyloxamide; erythritol tetranitrate (II)-1:2:4-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub>,  $-1:3:5\text{-C}_6\text{H}_3(\text{NO}_2)_3$ ,  $-\text{CO}(\text{NPhEt})_2$ . 1:2-Compounds are found in the systems (I)-m-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub>, transition point 58·1°, and (II)-trinitro-anisole, m.p. 61·6°. R. T.

Mannitol-dimolybdic acid. (MME.) Z. SOU-BAREV-CHATELAIN (Compt. rend., 1935, 200, 1942— 1944).—The conclusions of Honnelaître (A., 1925, i, 509) have been confirmed by the isolation of the substance  $C_6H_{14}O_6,H_2Mo_2O_7,H_2O$  (I) by cooling an aq. solution of  $H_2Mo_2O_7$  and mannitol (1:1). (I) loses  $1H_2O$  above  $120^\circ$  giving a product freely sol. in  $H_2O$ . (I) gives no coloration with  $K_4$ Fe(CN)<sub>6</sub>, and with AgNO<sub>3</sub> gives a yellow ppt. only after some time or when the solution is heated. H. G. M.

Simple alkaneseleninic acids. H. J. BACKER and W. VAN DAM (Rec. trav. chim., 1935, 54, 531— 538).—Simple alkaneseleninic acids (I) are obtained by oxidation of dialkyl diselenides with the theoretical quantity of dil. HNO<sub>3</sub>. They are weaker than the corresponding carboxylic acids (dissociation consts. are given) and form mol. compounds (II) with strong acids. The m.p. of (I) and (II) show the same regularities.  $Me_2$  diselenide, b.p. 155—157°, 57°/21 mm., and  $Me_2$ Se, b.p. 58°, are obtained from  $Me_2$ SO<sub>4</sub> and  $K_2$ Se<sub>2</sub>.  $Pr^a_2$  diselenide, b.p. 103—104°/15 mm., from Pr<sup>a</sup>Br and  $K_2$ Se<sub>2</sub>, and  $Bu^a_2$  diselenide, b.p. 129—130°/13 mm., are described. Methaneseleninic acid (III), m.p. 134° (decomp.) (Pb and Ba salts), ethaneseleninic acid (IV), n-propaneseleninic acid (V), m.p. 75° (Pb and Ba salts), and n-butaneseleninic acid (VI), m.p. 68° (Pb salt), are described. The following mol. compounds were obtained. Of (III): hydrochloride, decomp. 100°; nitrate, m.p. 103° (decomp.); sulphate, m.p. 130° (decomp.); methanesulphonate, m.p. 142°; ethanesulphonate, m.p. 105°; benzenesulphonate, m.p. 150° (decomp.); methionate. Of (IV): hydrochloride, m.p. 106° (decomp.); methionate. at 103°); nitrate, m.p. 73°; sulphate, m.p. 98°; methanesulphonate, m.p. 115°; ethanesulphonate, m.p. 86°; benzenesulphonate, m.p. 130° (decomp.); methionate, m.p. 113°. Of (V): hydrochloride, decomp. 101— 102°; nitrate, m.p. 101°; sulphate, m.p. 119°; methanesulphonate, m.p. 122°; ethanesulphonate, m.p. 103°; benzenesulphonate, m.p. 136° (decomp.); methionate, m.p. 115°. Of (VI): hydrochloride, decomp. 99°; nitrate, m.p. 96°; sulphate, m.p. 117°; methanesulphonate, m.p. 99°; ethanesulphonate, m.p. 98°; benzenesulphonate, m.p. 121°; methionate, m.p. 111°. P. G. C.

Ester hydrolysis in pure water.—See this vol., 938.

Highly unsaturated acids in sardine oil. II. Constitution of hiragonic acid,  $C_{16}H_{26}O_2$ . Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, **10**, 192—199).—Oxidation of Me hiragonate with KMnO<sub>4</sub> gives AcOH, (CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, and Me H adipate, whilst ozonolysis affords also McCHO,

CHO·[CH<sub>2</sub>]<sub>4</sub>·CO<sub>2</sub>Me, CHO·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H, and

 $(^{\circ}CH_2 \cdot CHO)_2$ . Hiragonic acid is  $\Delta^{av}$ -hexadecatrienoic acid. F. R. S.

**Preparation of pure elaidic acid and the elaidin** reaction. C. LUTENBERG (Fettchem. Umschau, 1935, 42, 89—91).—The yield of elaidic acid (I) obtained by the Holde and Rietz-Rankoff method (cf. B., 1924, 264; A., 1931, 1271) depends on the time and temp. of the reaction and on the mount of NaNO<sub>2</sub> used. (I), prepared by a modified method (details given) from the "liquid" fatty acids separated from arachis oil fatty acids by Twitchell's method and recryst. from Et<sub>2</sub>O and EtOH, had m.p. 44·4—44·6°, I val. 89·95, SCN val. 89, mol. wt. 278, and contained 0.5% of saturated acids. HCN is demonstrable in the volatile products of the elaidinisation reaction.

**E**. L.

New stereoisomeride of elæostearic acid in pomegranate seed oil. Y. TOYAMA and T. TSU-CHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 182— 185B).—Punicic acid (I), m.p. 43·5—44°, has been obtained from the oil extracted by Et<sub>2</sub>O from pomegranate seeds. When dissolved in light petroleum and kept during a week under CO<sub>2</sub> (but not H<sub>2</sub>) (I) is converted into  $\beta$ -elæostearic acid (II), m.p. 70·5—71°. (I) with Br in light petroleum affords a tetrabromide, m.p. 113·5—114°, identical with that obtained from (II). (I) is regarded as a stereoisomeride of (II) of the structure, Me·[CH<sub>2</sub>]<sub>3</sub>·[CH:CH]<sub>3</sub>·[CH<sub>2</sub>]<sub>7</sub>·CO<sub>2</sub>H. This has been confirmed by ozonolysis of (I) and its Me ester. H. G. M.

Another new stereoisomeride of elæostearic acid in the seed oil of karasu-uri, *Trichosanthes* cucumeroides. Y. TOMAYA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 185—1878).—*Tri*chosanic acid (I), m.p. 35—35.5°, has been isolated from the seed oil of karasu-uri. In petroleum under  $CO_2$  or with a trace of I it passes readily into its isomeride,  $\beta$ -elæostearic acid (II). (I) with Br in light petroleum affords a tetrabromide, m.p. 113—113.5°, identical with that obtained from (II). H. G. M.

Synthetic fats. I. Preparation of trinonadecylin. D. W. WOOLLEY and R. B. SANDIN (J. Amer. Chem. Soc., 1935, 57, 1078–1079).—*Tri*nonadecylin,  $\alpha$ -, m.p. 66.5–67°,  $\beta$ -, m.p. 70.5°, and  $\gamma$ - (a glass), m.p. 60°, forms, is prepared. A form of Me'[CH<sub>2</sub>]<sub>17</sub>°CN (modified prep. and hydrolysis) has m.p. 34–34.5°. R. S. C.

Anodic reactions during the electrolysis of  $\alpha$ -hydroxy-acids. E. TOMMILA (Suomen Kem., 1935, 8, B, 25; cf. A., 1934, 739).—Electrolysis of lactic acid in 5*N*-NaOH (conditions described) gives at the anode a mixture of O<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, AcOH, HCO<sub>2</sub>H, MeCHO, and CO<sub>2</sub>. The reaction mechanisms are described. J. L. D.

Acetone [isopropylidene] compounds of  $\alpha$ -hydroxy-acids and their Raman spectra. H. OEDA (Bull. Chem. Soc. Japan, 1935, 10, 187— 192).—Lactic acid and COMe<sub>2</sub> give (H<sub>2</sub>SO<sub>4</sub> under anhyd. conditions) the *ether-anhydride* CHMe·O>CMe<sub>2</sub> (I), b.p. 49—49·5°/11 mm.; the *anhydrides* 

 $CO = 10 CMe_2$  (II), b.p.  $84.5 = 85.5^{\circ}/13$  mm., and CO = 0

CO O CMe<sub>2</sub>, m.p. 63 64°, are similarly ob-CH(CH<sub>2</sub>Ph)·O CMe<sub>2</sub>, m.p. 63 64°, are similarly obtained. The Raman spectra of (I) and (II) correspond with those of a 5-membered saturated ring. F. R. S.

Kinetic studies of the cyclisation problem, with regard to the preparation of lactones with musk and amber odours. M. STOLL and A. ROUVÉ (Rev. Marques Parfum. Savonn., 1934, 12, 328—334; Chem. Zentr., 1935, i, 810).—The influence of the catalyst on the lactonisation of  $\omega$ -OH-acids is limited, since the frequency of cyclising collisions is independent of the catalyst.  $\xi$ -Hydroxypentadecoic acid is best lactonised by means of PhSO<sub>3</sub>H in C<sub>6</sub>H<sub>6</sub>. Higher lactones, such as "exaltolide" (94% yield by the above process), are valuable in perfumery.

H. N. R.

Pyrolysis. II. Pyrolysis of derivatives of  $\alpha$ -acetoxyisobutyric acid, and related substances. R. BURNS, D. T. JONES, and P. D. RITCHIE (J.C.S., 1935, 714—717; cf. this vol., 607).—Me  $\alpha$ -acetoxyisobutyrate, b.p. 76—77°/18 mm. [obtained from Me  $\alpha$ -hydroxyisobutyrate (I)], affords on pyrolysis AcOH and Me  $\alpha$ -methylacrylate (II). Similarly  $\beta$ -methoxyethyl  $\alpha$ -acetoxyisobutyrate, b.p. 105°/12 mm. [obtained from acetone cyanohydrin (III),  $\beta$ -methoxyethyl alcohol, and H<sub>2</sub>SO<sub>4</sub>, followed by acetylation], affords AcOH and  $\beta$ -methoxyethyl  $\alpha$ -methylacrylate, b.p. 88—89°/20 mm.; and  $\beta$ -phenoxyethyl  $\alpha$ -acetoxyisobutyrate, b.p. 166°/4 mm. (obtained similarly through  $\beta$ -phenoxyethyl  $\alpha$ -hydroxyisobutyrate, b.p. 156— 157°/5 mm.), affords  $\beta$ -phenoxyethyl  $\alpha$ -methylacrylate, b.p. 138°/7 mm. The polymerisation of the methylacrylic esters is described.

(III) with Ac<sub>2</sub>O and AcCl (or  $H_2SO_4$ ) gives  $\alpha$ acetoxyisobutyronitrile (IV), but with  $HClO_4$  as catalyst (IV) and N-acetyl- $\alpha$ -acetoxyisobutyramide (V), m.p. 81—82°, b.p. 120—130°/13 mm., are formed. On pyrolysis (IV) gives  $\alpha$ -methylacrylonitrile (VI) and some COMe<sub>2</sub> and HCN (the proportion of these two products increases with rise in temp.), whilst (V) gives AcOH and (VI). Me  $\alpha$ -benzoyloxyisobutyrate, b.p. 156°/19 mm., is pyrolysed to (II) and BzOH, whilst Me  $\alpha$ -chloroisobutyrate, b.p. 133—135°/760 mm., gives some HCl and (II). On pyrolysis (III) gives COMe<sub>2</sub> and HCN, and (I) gives some COMe<sub>2</sub> and (II). H. G. M.

Preparation of oxalic acid from sodium formate. V. M. SEMENOV, A. J. SCHAGALOV, and P. I. ASTRACHANTZEV (J. Appl. Chem. Russ., 1935, 8, 99—105).—The method of Merz and Weitz (A., 1881, 18) gives 83%, and that of Koepp (A., 1906, i, 4) 95%, yields. The latter method is studied in detail. R. T.

Reaction between sodium sulphate and oxalic acid. K. TANEMURA and S. MIYOSHI (J. Soc. Chem. Ind. Japan, 1935, 38, 188B).— $H_2C_2O_4$  reacts with conc. aq. Na<sub>2</sub>SO<sub>4</sub> solutions containing  $H_2SO_4$ , giving NaHC<sub>2</sub>O<sub>4</sub>, $H_2O$  as solid phase. MgSO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> remains in solution, but ZnSO<sub>4</sub> interferes. J. S. A.

Condensation of aldehydes with malonic acid in presence of organic bases. III. Condensation of salicylaldehyde with ethyl malonate. P. N. KURIEN, C. J. PETER, and K. C. PANDYA (Proc. Indian Acad. Sci., 1935, **1**, **A**, 775—779).—Using  $C_5H_5N$  as catalyst, the max. yield (55%) of Et coumarincarboxylate is secured when equimol. proportions of  $CH_2(CO_2Et)_2$  and o-OH·C<sub>6</sub>H<sub>4</sub>·CHO are treated with 0·15 mol. of  $C_5H_5N$  at 100° for 18 hr. and then kept at room temp. for 3 days. Quinoline, *iso*quinoline, lutidine,  $\alpha$ -naphthaquinoline, and quinaldine are somewhat less efficient, whereas cinchonidine (0·14 mol.) gives equally good results. H. W.

Reactivity of alkylmalonic esters. M. GRUN-FELD (Bull. Soc. chim., 1935, [v], 2, 994—996).— The velocity of reaction between  $CR'R''(CO_2Et)_2$  (I)  $(R'R''=H_2, PrH, Pr_2, BuH, and Bu_2)$  and *n*-octylamine in EtOH under seal at 100° has been studied. The reactivity of (I) decreases as its absorption in the ultra-violet diminishes (cf. A., 1930, 452; 1932, 365). H. G. M.

Structure of glutaryl chloride. S. G. P. PLANT and (MISS) M. E. TOMLINSON (J.C.S., 1935, 856).—Both forms of glutaryl chloride (I) are involved in its interaction with AlCl<sub>3</sub> and anisole, since a mixture of  $\alpha\gamma$ -dianisoylpropane, m.p. 99°, and  $\delta\delta$ -di-panisylvalerolactone, m.p. 111—113°, is obtained. Similarly, (I) with AlCl<sub>3</sub> and phenetole gives a mixture of  $\alpha\gamma$ -diphenetoylpropane, m.p. 133°, and  $\delta\delta$ -di-pphenetylvalerolactone, m.p. 82°. Glutaric anhydride and AlCl<sub>3</sub> with anisole gives  $\gamma$ -anisoylbutyric acid, m.p. 137°, and with phenetole  $\gamma$ -phenetoylbutyric acid, m.p. 114°, is obtained. P. G. C.

New reaction of tartaric acid. M. PESEZ (J. Pharm. Chim., 1935, [viii], 21, 542—546).—Addition of 0·1 c.c. of a solution containing 2 g. of resorcinol (I) and 10 g. of KBr in 100 c.c. of  $H_2O+1$  c.c. of  $H_2SO_4$  to 0·1 c.c. of a tartrate solution in 2 c.c. of  $H_2SO_4$  (d 1·84) and warming to 100° (2—5 min.) affords an intense blue colour, changed to currant-red by addition of 1 c.c. of  $H_2O$ , and giving a fugitive violet coloration when neutralised. The reaction is sp. for tartaric acid (sensitivity 0.1 mg.) and for (I) (other phenols give different colours), is unaffected by  $\text{BrO}_3'$ ,  $\text{NO}_2'$ , or Fe<sup>...</sup>, but is negative in presence of OCl',  $\text{ClO}_3'$ ,  $\text{NO}_3'$ ,  $\text{MnO}_4''$  (all eliminated by Zn-Cu couple), I',  $\text{IO}_3'$ , or  $\text{CrO}_4''$ .  $\text{CCl}_3$ ·CHO gives the same blue colour, but is easily removed by previous alkaline hydrolysis. J. W. B.

Complex formation between manganese or aluminium with tartaric acid in alkaline medium. S. P. GOVEL and B. L. VAISHYA (J. Indian Chem. Soc., 1935, 12, 193—196; cf. A., 1934, 615).— From polarimetric and potentiometric measurements of solutions of K tartrate (I), alkali, and MnCl<sub>2</sub> or  $Al_2(SO_4)_3$  it is inferred that complexes containing Mn and (I) in the mol. ratio 1:1, and Al and (I) in the ratio 2:3 (cf. A., 1933, 240), are formed.

H. G. M.

Cyclisation of aβ-ethanedimalonic esters by sodium ethoxide. E. R. MEINCKE, R. F. B. Cox, and S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1133-1135).-(CH<sub>2</sub>Br)<sub>2</sub> and Et<sub>2</sub> magnesiomalonate give  $[CH_2 \cdot CH(CO_2Et)_2]_2$  and  $Et_4$  1:1:4:4-cyclo-hexanetetracarboxylate, b.p. 195-207°/15 mm., m.p. 76-77° [giving the acid, m.p. 249-250° (decomp.), and thence hexahydroterephthalic acid, m.p. 172-173°]. The former ester with NaOEt, first at 85°/760 mm. and then at 120°/200 mm., gives Et<sub>2</sub> cyclopentanone-2: 5-dicarboxylate (31%), Et cyclopentanone-2-carboxylate (15%), Et<sub>2</sub>CO<sub>3</sub>, and a trace of EtOH.  $Et_4$  n-hexane-aadd-tetracarboxylate from NaOEt, CH2(CO2Et)2, and (CO2Et)2CEt·CH2·CH2Br], b.p. 192-195°/8 mm., with NaOEt at 115° gives 74.3% of Et2 2-ethylcyclopentanone-2: 5-dicarboxylate, m.p. 147-154°/8 mm. (hydrolysed to 2-ethylcyclopentanone), Et<sub>2</sub>CO<sub>2</sub>, and a little EtOH. Et<sub>4</sub> noctane-yy ( -tetracarboxylate is largely unchanged by NaOEt even at  $250^{\circ}$  (gives a little Et<sub>2</sub>CO<sub>3</sub> and EtOH). Cyclisation, therefore, requires presence of an a-H and probably proceeds by way of

 $CH_2 - C(CO_2 Et)_2 > C(OH) \cdot OEt$  (R=H or Et) with  $CH_2 \cdot CR(CO_2 Et) > C(OH) \cdot OEt$  (R=H or Et) with subsequent elimination of  $CO_2 Et$  and the ketal OEt to form  $Et_2 CO_3$ . R. S. C.

The two  $\beta$ -sulphoacrylic acids. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 54, 523— 530).—(NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> converts cis- $\beta$ -chloroacrylic acid into trans- $\beta$ -sulphoacrylic acid (I), also obtained from propiolic acid. The Ba, K, Tl, and NH<sub>3</sub>Ph, m.p. 117—118° (decomp.), salts are described. Similarly, trans- $\beta$ -chloroacrylic acid affords cis- $\beta$ -sulphoacrylic acid (II) (+1H<sub>2</sub>O), m.p. 82—84°, (+2H<sub>2</sub>O) m.p. about 87—88° (Ba and NH<sub>3</sub>Ph, decomp. 155—158° after becoming discoloured at 120—130°, salts). Hydrogenation of (I) or (II) gives  $\beta$ -sulphopropionic acid. P. G. C.

β-Sulphocrotonic acid. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 54, 551-560).— The action of HSO<sub>3</sub>' on salts of α-bromo- (I), αbromoiso- (II), β-chloro-, or β-chloroiso-crotonic acid gives the same β-sulphocrotonic acid (III), m.p. 94-95° [Ba,  $K_2$ , and  $NH_3Ph$ , m.p. 191-192° (decomp.), salts], hydrogenated to β-sulphobutyric acid, which can be resolved into its optical antipodes by brucine. Treatment of (III) with the requisite halogen affords  $\alpha$ -bromo- $\beta$ -sulphocrotonic acid (*Ba* and *quinine*, m.p. 157—158°, salts) and  $\alpha$ -chloro- $\beta$ sulphocrotonic acid [*quinine* salt, m.p. 176° (decomp.)]. (I) or (II) yield *Et*  $\alpha$ -bromocrotonate, b.p. 192°/760 mm., when esterified with EtOH and H<sub>2</sub>SO<sub>4</sub> or when their Ag salts are treated with EtI. P. G. C.

 $\beta\beta$ -Disulphoglutaric acid. J. M. VAN DER ZANDEN (Rec. trav. chim., 1935, 54, 561-565).-- $\beta\beta$ -Disulphoglutaric acid, m.p. 162° (decomp.), has been obtained from H sulphite and sulphoglutaconic acid,  $\beta$ -chloroglutaconic acid, or glutinic acid. The Ba, K, Pb, Tl, Sr, Ca, Ag, tri-aniline, and di- and tristrychnine salts are described. The Na salts from either of the strychnine salts were optically inactive. P. G. C.

Disproportionation reaction of diselenides. A. FREDGA (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 46, 1-6).—An aq. solution of  $\alpha\alpha$ -diselenodipropionic acid (I) with Ag<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>O and NaOH, or AgCl and NaOH (but not Ag metal) undergoes disproportionation and affords a mixture of AgSe·CHMe·CO<sub>2</sub>H and AgSe·CHMe·CO<sub>2</sub>Ag, whilst the solution contains  $\alpha$ -seleninopropionic acid. Hg salts and (I) give a complex white ppt. It is possible that the following equilibrium obtains : 2(SeR)<sub>2</sub>+ 2H<sub>2</sub>O = 3R·SeH+R·SeO<sub>2</sub>H (R=·CHMe·CO<sub>2</sub>H); the equilibrium lies to the left, but on the addition of a Ag salt, one of the products is removed as an insol. Ag salt. An alternative mechanism involving oxidation of (I) by Ag' is not, however, excluded.

#### H. G. M.

Configurative relationship between optically active selenodipropionic acid and  $\alpha$ -thiodipropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1935, **11**, B, No. 43, 1-6).—Se(CHMe·CO<sub>2</sub>H)<sub>2</sub>, m.p. 147°, has been resolved into its optical antipodes (I), m.p. 124°,  $[\alpha]_{\rm b}$  +234·5°, and (II)  $[\alpha]_{\rm b}$  -235° in 0·4N-HCl. The fusion diagrams of (I) and (II), (I) and (+)-thiodipropionic acid (III), (I) and (-)-thiodipropionic acid (IV), and (III) and (IV) are given. (I) and (III) form a continuous series of mixed crystals, whilst (I) and (IV) form a 1:1 mol. compound [optically active racemate (cf. A., 1921, ii, 598)]. It is concluded that (I) and (III) have the same configuration. The respective S and Se acids are regarded as isomorphous. H. G. M.

Interaction of diselenodicarboxylic acids with mercury. A. FREDGA (Arkiv Kemi, Min., Geol., 1935, **11**, **B**, No. 44, 1-4).—The compound Hg(Se·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> (I), decomp. 120°, or its alkali salts, is obtained when a solution of (Se·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> (II) (A., 1929, 1285), or its alkali salts, respectively, is shaken with Hg. Hg(S·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> could not be prepared in a similar way. (I) suspended in dil. H<sub>2</sub>SO<sub>4</sub> may be titrated : Hg(Se·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>+2I'+  $2KI=(Se·CH_2·CO_2H)_2+K_2HgI_4$ . Homologues of (II) also react readily with Hg. Neutralised solutions of (II) dissolve Cu (but not Ag) and the resulting Cu compound is pptd. by addition of H<sub>2</sub>SO<sub>4</sub> as an amorphous yellow ppt. The Hg in (I) is not pptd. by alkali or KI, or by H<sub>2</sub>S except after a long time. The salts of (I) give a black ppt. with (NH<sub>4</sub>)<sub>2</sub>S. (I) is sol. in aq. KCN and is repptd. unchanged by the addition of HCl. The alkali, Pb, Ba, Ca, Sr, Mn, Zn, Cu, Cr, Ag,  $Fe^{II}$ ,  $Te^{III}$ , Ni, Co, Bi, and Hg salts are described. H. G. M.

Schiff colour reaction of aldehydes. P. RUMPF (Ann. Chim., 1935, [xi], 3, 327-442).—An historical account of the application and theory of the Schiff colour reaction is given. Reagents other than fuchsin,  $H_2O$ , and  $SO_2$  fail to give the colour, whilst O does not enter into the reaction. The influence of different concns. of SO2, aldehydes, etc. has been studied spectrographically. The reaction is not due to fuchsin or Schiff's bases, and is produced only by the combined action of SO<sub>2</sub> and a substance containing free CHO on aq. fuchsin. Aldoses liberate fuchsin. The absorption max. (5600-5850 Å.) is sp. for a given aldehyde only under strictly defined conditions. In buffer experiments, reaction is independent of the type of buffer used and is governed only by the  $p_{\rm H}$ . The spectrographic data indicate that the no. of acid substituents in the  $NH_2$  groups of the coloured complex (I) is variable. The rate of formation of (I), determined by a photo-electric cell, is initially  $\propto$  $t^2$  and approx.  $\propto$  [SO<sub>3</sub>']<sup>2</sup>, but decreases with increasing [H']. Electrometric titrations with the glass electrode indicate the formation of strong monobasic acids in solutions containing SO<sub>2</sub> and aldehydes, but the titration curve of  $H_2SeO_3$  is unaffected. Compounds of the type NHR·SO<sub>2</sub>H could not be detected in dil. solutions of amines and SO<sub>2</sub>. Addition of an aldehyde to SO<sub>3</sub>" solutions of aromatic amines produces strong complex acids containing one mol. of each constituent. Dissociation consts. of NH2derivatives of  $C_6H_6$  and  $CHPh_3$  indicate that (I) is a carbonium ion (II), basicity being conferred on the central C by the p-NH<sub>2</sub> groups. The decolorisation of various  $\tilde{C}HPh_3$  dyes has been studied. The concn. of colourless  $-NH_3$  relative to coloured (II)  $\propto [H^{-}]^n$ , where n is the no. of p-NH<sub>3</sub> groups. In the Schiff reagent, the H<sub>2</sub>SO<sub>3</sub> may combine further with (II) itself. It is suggested that (I) consists of a univalent (II) containing a variable no. of ionisable CHR·SO<sub>3</sub>H substituents in the NH<sub>2</sub> groups. R. S.

Separation of formaldehyde from hexamethylenetetramine at different hydrogen-ion concentrations and constant temperature. E. PHILIPPI and J. LOBERING (Biochem. Z., 1935, 277, 365– 375).—The kinetics of the breakdown of  $(CH_2)_6N_4$ into  $CH_2O$  and  $NH_3$  in various buffer solutions of different  $p_{\rm H}$  are investigated and a series of curves and velocity coeffs. summarise the results. P. W. C.

Limits of aldol condensation of acetaldehyde. E. A. SCHILOV (J. Appl. Chem. Russ., 1935, 8, 93– 98).—Aldol and MeCHO afford a readily dissociable additive compound, CHMe  $< \begin{array}{c} O & --CHMe \\ CH_2 \cdot CH(OH) > O$ , to the formation of which is ascribed the spurious equilibrium found in the aldol condensation. R. T.

Constitution of aldols. M. BACKÈS (Compt. rend., 1935, 200, 1669—1671; cf. A., 1933, 1050).— Acetaldol (I) in H<sub>2</sub>O or aq. HCl (but not in C<sub>5</sub>H<sub>5</sub>N) shows a strong absorption band at 2800 Å., characteristic of CO:, which shows that the cyclic structure for (I) is favoured in non-aq. solutions. The ring is opened easily by many aldehydic reagents, but its presence explains the thermal decomp. of (I) mainly to give 2 mols. of MeCHO, and not predominantly an unsaturated aldehyde. Propion-, *iso*- and *n*-butan-, and heptan-aldol, when heated, also decompose to give 30-60% of saturated and some unsaturated aldehyde, also polymerides. In presence of H<sub>2</sub>O, the open-chain decomp. occurs almost exclusively. J. L. D.

Action of organomagnesium halides on  $\alpha\beta$ unsaturated aldehydes. P. G. STEVENS (J. Amer. Chem. Soc., 1935, 57, 1112—1117).—Only traces of 1:4-addition of MgRCl to CHMe:CH·CHO (I) occur when R=Ph, Et, Pr<sup>a</sup>, allyl, or Pr<sup>β</sup>, but considerable amounts (> 20%) when R=Bu<sup>γ</sup> or tert.-amyl. MgBu<sup>γ</sup>Br gives 11% of 1:4-addition. MgBu<sup>γ</sup>Cl gives also a substance, C<sub>16</sub>H<sub>30</sub>O, b.p. 96·3—97·9°/1 mm., unstable, and ?  $\alpha\alpha$ -dimethyl- $\delta$ -( $\alpha'\beta'\beta'$ -trimethylpropyl)- $\Delta$ <sup>ζ</sup>-octene- $\gamma$ z-diol (II), m.p. 128—129°, probably formed thus: (I)+MgBu<sup>γ</sup>Br $\rightarrow$ 

CHMeBur·CH:CH·OMgCl $\rightarrow$ [+(I)]

 $CHO \cdot CHEtBu^{\gamma} \cdot CH(OMgCl) \cdot CH: CHMe \rightarrow (+MgBu^{\gamma}Cl;$  $+H_2O$  (II). The amount of 1:4-addition may thus be considerably > estimated for MgBu<sup>y</sup>Cl and also for Mg tert.-amyl chloride (which gives substances, b.p. 84-89°/3 mm. and 120-121°/2 mm., respectively) and MgPr<sup> $\beta$ </sup>Cl, which all give > 34% of complex products. Mesityl oxide and MgBu<sup> $\gamma$ </sup>Cl give no 1:4-addition, but this occurs to the extent of 41.4 and 54% with CHMe:CH·COMe and MgEtCl and MgBuvCl, respectively. The results are inexplicable. The following are described. Byy-Trimethylvaleraldehyde, b.p. 56-57°/19 mm. (semicarbazone, m.p. 166°), oxidised by Ag<sub>2</sub>O to the acid, b.p. 124-124.5°/19 mm. (amide, m.p. 163-164°), which yields (P, Br, MeOH) Me a-bromo-Byy-trimethylvalerate, b.p. 90.5-91°/8 mm., converted by NPhEt2 at 190-200° into Me Byytrimethyl-Aª-pentenoate, b.p. 184-186°/765 mm., which with O3 in AcOH affords CHO·CO2Me and COMeBu<sup> $\gamma$ </sup>. a  $\alpha$ -Dimethyl- $\Delta^{\delta}$ -hexen- $\gamma$ -ol, b.p. 75-76°/ 36 mm., the H phthalate of which with strychnine affords the d-form,  $[\alpha]_{D}^{25}$  +15°.  $\beta\gamma\gamma$ -Trimethylhex-aldehyde semicarbazone, m.p. 172°.  $\beta$ -Methyl- and βy-dimethyl-valeraldehyde semicarbazones, m.p. 128py-active logitiditerial english semicative discrete discre  $146 - 15\bar{3}^{\circ}$ . R. S. C.

Hydrogenation of a mixture of two  $\alpha$ -ethylenic aldehydes. General method of synthesis of glycols, OH·CHR·CHR'OH. J. WIEMANN (Bull. Soc. chim., 1935, [v], 2, 1209—1214).—Reduction of a mixture of two  $\alpha\beta$ -unsaturated aldehydes by a Zn–Cu couple gives most mixed glycol if the rate of reduction of the two aldehydes is similar and if the nature of the aldehydes is diverse. Reduction proceeds by formation of ·CHR·OH and coupling of two such residues. It leads to both stereoisomerides. Citral, which alone gives an *oxide*, C<sub>20</sub>H<sub>32</sub>O, b.p. 181—182°/9 mm., with CH<sub>2</sub>·CH·CHO (I) or CHMe:CH·CHO (II) in aq. EtOH gives the products previously described (this vol., 608) as formed in AcOH. A mixture of (I) and (II) gives Griner's  $[CH_2:CH\cdot CH(OH)\cdot]_2$  (III), Charon's  $[CHMe:CH\cdot CH(OH)\cdot]_2$  (IV), and a mixture of isomeric  $\gamma\delta$ -dihydroxy-Δ<sup>αε</sup>-heptadienes, b.p. 111°/12 mm., hydrogenated (colloidal Pd) to heptane- $\gamma\delta$ -diol, b.p. 109°/15 mm., m.p. 103—104° (lit., 98—99°). (I) (4 mols.) and furfuraldehyde (V) (3 mols.) give (1II) (15%) and a mixture of 2-αβ-dihydroxy-Δ*x*-butenylfurans (40%), b.p. 115—116°/3 mm. (stereoisomeric phenylurethanes, m.p. 189° and 116—118°, respectively). (II) and (V) yield (IV) (10%) and mixed 2-αβ-dihydroxy-Δ*x*-pentenylfurans [stereoisomeric phenylurethanes, m.p. 222—223° (block) and  $\gg$  220°, respectively]. (I) and PhCHO give stereoisomeric α-phenyl-Δ*x*-butene-αβ-diols (cf. this vol., 750). R. S. C.

Successive reactions in heterogenous catalysis. III. Mechanism of the formation of acetone from acetaldehyde and water. M. J. KAGAN, I. A. SOBOLEV, and G. D. LUBARSKI (Ber., 1935. 68, [B], 1140-1146).—When the vapours of anhyd. EtOH or MeCHO are passed over Cu, Cu+Cr<sub>2</sub>O<sub>3</sub>, ZnO, or  $ZnO+Cr_2O_3$  at  $300-350^\circ$  ester is produced in definite amount. If the reactants are previously mixed with steam the content of ester decreases, whilst that of AcOH increases. At temp.  $> 400^{\circ}$  COMe<sub>2</sub> is obtained in place of AcOH. The intermediate production of EtOAc in the prep. of  $COMe_2$  from MeCHO and  $H_2O$ is therefore regarded as established. At  $300-600^{\circ}$ MeCHO yields CO and  $CH_4$ ; formation of H and keten is not observed. Anhyd. EtOAc is converted at 400° in presence of ZnO+Cr<sub>2</sub>O<sub>3</sub> into COMe<sub>2</sub>, EtOH, C2H4, and CO2. Anhyd. EtOH similarly affords COMe<sub>2</sub> through decomp. of the intermediate EtOAc. Aq. EtOAc at 450° also affords COMe2, but the process involves hydrolysis of the ester. H. W.

Influence of hydrogen sulphite solutions on mono- and di-hydroxyacetone at raised temperature. G. MENZINSKY (Ber., 1935, 68, [B], 1154— 1159).—Acetol is partly resinified and partly oxidised to  $HCO_2H$  and AcOH when heated with aq. NaHSO<sub>3</sub> at 130°. Since it is little affected when heated with  $H_2O$  or  $H_2SO_4$  the change is not due to  $H^+$ , but is a sp. action of NaHSO<sub>3</sub>. Under similar conditions  $CO(CH_2 \cdot OH)_2$  affords  $HCO_2H$  and  $OH \cdot CH_2 \cdot CO_2H$ .

H. W.

Hydrazone and osazone reactions. E. G. R. ARDAGH and F. C. RUTHERFORD (J. Amer. Chem. Soc., 1935, 57, 1085—1088; cf. A., 1932, 377).—The formation of d-glucose-, fructose-, and d-galactose-phenylhydrazone is very slow in unbuffered solutions, increases tenfold as the buffer conen. rises to 0.3M, is much greater with PO<sub>4</sub><sup>'''</sup> than with OAc' buffers, and rises with change of  $p_{\rm H}$  from 7.5 to 4.0. The reaction is bimol. (cf. lit.). Osazone formation is similar. Only that portion of the NHPh·NH<sub>2</sub> present as salt reacts (cf. lit.). R. S. C.

Transformation of glucose into galactose and gulose by simple optical inversion. J. W. H. OLDHAM and G. J. ROBERTSON (J.C.S., 1935, 685— 689).—The following experiments support the view (cf. A., 1934, 871) that anhydro-formation is the necessary precursor of the inversion of glucose into gulose and galactose (this vol., 329). Dissopropylideneglucose 3-p-toluenesulphonate affords dissopropyl-

ideneglucose, m.p. 107-108°, on boiling with KOH-EtOH. 6 - Triphenylmethyl - 2 : 3 - dimethyl -  $\alpha$  - methyl glucoside 4-p-toluenesulphonate, m.p. 146-147°, [a]<sub>D</sub>  $+66\cdot3^{\circ}$  in CHCl<sub>3</sub>, is hydrolysed by NaOMe to (I), and after removal of CPh<sub>a</sub> is hydrolysed (NaOMe-MeOH- $H_2O$ ) to 2: 3-dimethyl- $\alpha$ -methylglucoside and a trace of an unsaturated substance (probably a derivative of glucoseen). 6-Triphenylmethyl-a-methylglucoside 2:3dibenzoate 4-p-toluenesulphonate, m.p. 163-164°, [a]<sub>D</sub>  $+66\cdot3^{\circ}$  in CHCl<sub>3</sub>, is converted by NaOH, H<sub>2</sub>O, and COMe<sub>2</sub>, and then Ac<sub>2</sub>O and C<sub>5</sub>H<sub>5</sub>N, into an amorphous compound considered to be 6-triphenylmethyl-3:4anhydro-a-methylgalactoside 2-acetate. This with HCl and COMe2 gives a mixture containing isopropylidene- $\alpha$ -methylguloside acetate (II), m.p. 176—178°,  $[\alpha]_D$  $+76.8^{\circ}$  in CHCl<sub>3</sub>, and isopropylidene- $\alpha$ -methylgalactoside acetate (III), m.p.  $101-102^{\circ}$ ,  $[\alpha]_{\mathbb{D}} + 127\cdot3^{\circ}$  in CHCl<sub>3</sub>. (II) is deacetylated to isopropylidene- $\alpha$ -methylguloside (IV), m.p.  $132-133^{\circ}$ ,  $[\alpha]_{\mathbb{D}} + 88\cdot5^{\circ}$  in CHCl<sub>3</sub>, hydrolysed by 0.02N-H<sub>2</sub>SO<sub>4</sub> to the free sugar. (IV) with 0.002N-H<sub>2</sub>SO<sub>4</sub> affords  $\alpha$ -methylguloside, m.p. 77-79°,  $[\alpha]_p$  +109.7° in H<sub>2</sub>O. (III) is deacetylated to *iso*propylidene- $\alpha$ -methylgalactoside, m.p. 102– 104° (cf. this vol., 329),  $[\alpha]_{\rm D}$  +147.9° in CHCl<sub>3</sub>, +168.6° in  $H_2O$ , hydrolysed (dil. AcOH) to  $\alpha$ -methylgalactoside. Further 4: 6-benzylidene- $\alpha$ -methylglucoside 3-benzoate 2-p-toluenesulphonate affords on alkaline hydrolysis a 4: 6-benzylidene-2: 3-anhydro- $\alpha$ -methylhexoside, converted by NaOMe into a methyl-4: 6-benzylidene- $\alpha$ methylhexoside, which is not a derivative of glucose.

H. G. M.

Walden inversion in the sugar group. I. Fission of 3:4-anhydro- $\beta$ -methylhexoside. A. MÜLLER (Ber., 1935, 68, [B], 1094-1097).-Treatment of the anhydro- $\beta$ -methylhexoside (I) (obtained by hydrolysis of  $\beta$ -methylglucoside triacetate 4-ptoluenesulphonate (A., 1930, 1411; 1934, 513) with  $N-H_2SO_4$  leads to a non-cryst. mixture of sugars from which *d*-glucosazone and *d*-gulosazone are isolated. (I) is either an anhydroglucoside or, if Walden inversion occurs during elimination of  $p-C_6H_4Me$ ·SO<sub>2</sub>, an anhydrogalactoside. The balance of evidence favours the latter supposition, since the product does not appear to contain the oxide ring in the trans position, as it is stable towards boiling Ac<sub>2</sub>O. The formation of galactosazone could not be established. The presence of gulose among the products of hydrolysis confirms the 3:4-position of the ring and its (*ll*)-cis configuration. H. W.

Reagent for eliminating interference due to calcium in volumetric Fehling's titration for invert sugar. J. G. N. GASKIN (Analyst, 1935, 60, 318—319).—Ca<sup>\*\*</sup> is rendered inert by addition of Na hexametaphosphate (Calgon). E. C. S.

Additive compounds of the carbohydrates. II. Potassium hydroxide-sucrose. E.G. V. PERCIVAL (J.C.S., 1935, 648—653; cf. A., 1934, 1092).—Sucrose (1) (or its octa-acetate), EtOH, and KOH afford the compound (II),  $C_{12}H_{22}O_{11}$ ,3KOH, which with dry  $Me_2SO_4$  yields much (I) and a trimethylsucrose, acetylated to a penta-acetate which is hydrolysed to 6-methylglucopyranose and 1:6-dimethylfructofuranose. In (II), therefore, one KOH is associated (by co-ordination) with each of the three primary alcohol groups of (I). H. G. M.

Disaccharides in "hydrol." G. H. COLEMAN, (MISS) M. A. BUCHANAN, and P. T. PAUL (J. Amer. Chem. Soc., 1935, 57, 1119—1121).—Methylation (Me<sub>2</sub>SO<sub>4</sub>-NaOH and Ag<sub>2</sub>O-MeI) of the non-fermentable portion of "hydrol" (I) (the residue from the commercial hydrolysis of maize-starch) gives 20% of heptamethyl- $\beta$ -methylgentiobioside and 80% of an oily octamethyldisaccharide,  $[\alpha]_{D}^{20}$  +80° in EtOH, hydrolysed to 2:3:4-trimethyl- and 2:3:4:6tetramethyl-glucose. (I) may, therefore, contain  $6-\alpha$ -glucosidoglucose. R. S. C.

Polysaccharides. IX. Hydrolysis of "xyloglucuronide" and the isolation of the new disaccharide "barium xyloglucuronate." K. NISHIDA and H. HASHIMA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 66—69).—Hydrolysis of xyloglucuronide yields xylose, glucuronic acid, and xyloglucuronic acid isolated and purified as the *Ba* salt  $C_{22}H_{34}O_{22}Ba$ , decomp. 180°,  $[\alpha]_D^{20} + 54\cdot8°$  in  $H_2O$ . No other hexoses or pentoses could be detected.

J. N. A. Emulsin. XXI. Influence of substitution in the benzene nucleus of phenol-\u00b3-d-glucosides on their ease of fission with enzymes. В. HELFERICH, H. E. SCHEIBER, R. STREECK, and F. VORSATZ (Annalen, 1935, 518, 211-225).-With aq. EtOH-KCN w-bromo-o- and -p-cresol-β-d-glucosaq. EtOH-KCN  $\omega$ -bromo-o- and -p-cresol- $\beta$ -d-glucos-ide tetra-acetate afford, respectively, the  $Ac_4$  deriv-ative, m.p. 143—145°,  $[\alpha]_{2^4}^{p_4} - 15 \cdot 17°$  in CHCl<sub>3</sub>, of o-(I), m.p. 170—175° (corr.),  $[\alpha]_{2^0}^{p_0} - 66 \cdot 6°$  in H<sub>2</sub>O (deacetylation by NH<sub>3</sub>-MeOH), and p-cyanomethyl-phenol- $\beta$ -d-glucoside (II), m.p. 159·5—161·5° (corr.),  $[\alpha]_{2^0}^{p_0} - 71 \cdot 4°$  in H<sub>2</sub>O ( $Ac_4$  derivative, m.p. 134—136°,  $[\alpha]_{2^0}^{p_2} - 19°$  in CHCl<sub>3</sub>). Hydrolysis of (I) and (II) with 2N-NaOH affords, respectively, o- (only as its Na salt, decomp. above 207°,  $[\alpha]_{2^0}^{p_0} - 52°$  in H<sub>2</sub>O) and p-carboxymethylphenol- $\beta$ -d-glucoside, m.p. 190—193° (corr.),  $[\alpha]_{2^0}^{p_0} - 63°$  in H<sub>2</sub>O {Na salt,  $[\alpha]_{2^0}^{p_0} - 54 \cdot 9°$  in H<sub>2</sub>O; Me ester, sinters 106°, m.p. 121—124° (corr.)}. By heating the appropriate phenol with  $\beta$ -glucose By heating the appropriate phenol with  $\beta$ -glucose penta-acetate and a dehydrating agent (ZnCl<sub>2</sub>, p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H) at 100°, or with tetra-acetylglucosidyl bromide and NaOH-aq. COMe<sub>2</sub>, and subsequent deacetylation are obtained 2:4-dimethylphenol-, m.p. 181—183.5° (corr.),  $[\alpha]_{D}^{20}$ —65° in H<sub>2</sub>O (Ac<sub>4</sub> derivative, m.p. 171–173°,  $[\alpha]_{D}^{20}$  –24° in CHCl<sub>3</sub>), o-, m.p. 157– 158° (corr.),  $[\alpha]_{D}^{20}$  –24° in CHCl<sub>3</sub>), o-, m.p. 157– 158° (corr.),  $[\alpha]_{D}^{21}$  –65° in H<sub>2</sub>O [Ac<sub>4</sub> derivative, m.p. 152–154° (corr.),  $[\alpha]_{D}^{22}$  –28° in CHCl<sub>3</sub>], and p-ethyl-phenol-, m.p. 164–166° (corr.),  $[\alpha]_{D}^{20}$  –65·4° in H<sub>2</sub>O [Ac<sub>4</sub> derivative, m.p. 146–147° (corr.)  $[\alpha]_{D}^{23}$  –16° m CHCl<sub>3</sub>; o-hydroxyacetophenone-, m.p. 152-154° (corr.),  $[\alpha]_{D}^{20} - 66.5^{\circ}$  in  $H_2O$ ; protocatechualdehyde, m.p. 172—174°,  $[\alpha]_{D}^{24} - 93^{\circ}$  in  $H_2O$  (Glaser *et al.*, A., 1923, i, 820, give m.p. 73—74°,  $[\alpha]_{D}^{14} - 36.2^{\circ}$  in H<sub>2</sub>O) [Ac<sub>4</sub> derivative, m.p. 180° (corr.),  $[\alpha]_{D}^{18} - 53^{\circ}$ in EtOH] (glucose residue is in the 4-position, since methylation gives the vanillin compound); iso-vanillin-, m.p. 174—175° (corr.),  $[\alpha]_{D}^{\otimes 0}$ —108.4° in H<sub>2</sub>O [Ac<sub>4</sub> derivative, m.p. 141—142° (corr.),  $[\alpha]_{D}^{\otimes 0}$ -28° in CHCl<sub>3</sub>]; 3-hydroxy-4-ethoxyphenol-, m.p. 169.5° (corr.),  $[\alpha]_{D}^{\otimes 0}$ —90° in H<sub>2</sub>O buffered to  $p_{\rm H}$  5.0 [Ac<sub>4</sub> derivative, m.p. 164° (corr.),  $[\alpha]_{D}^{\otimes 0}$ —33° in

CHCl<sub>3</sub>], -β-d-glucoside; protocatechualdehyde-β-d-diglucoside, m.p. 202–203° (corr.),  $[\alpha]_D^{\circ 0} -109\cdot4^{\circ}$  in H<sub>2</sub>O [Ac<sub>8</sub> derivative, dimorphous, m.p. 180° (corr.) and 168.5°,  $[\alpha]_D^{\circ 0} -72^{\circ}$  in CHCl<sub>3</sub>], o-cresol- $\alpha$ -d-, +H<sub>2</sub>O and anhyd., polymorphous, m.p. varies between 75° and 121°,  $[\alpha]_D^{\circ 0} +188^{\circ}$  in H<sub>2</sub>O (Ac<sub>4</sub> derivative, m.p. 86-88.5°,  $[\alpha]_D^{\circ 0} +173^{\circ}$  in CHCl<sub>3</sub>), and vanillin-β-dgalactoside, m.p. 203–205° (corr.),  $[\alpha]_D^{\circ 0} -65^{\circ}$  in H<sub>2</sub>O [Ac<sub>4</sub> derivative, m.p. 126–127° (corr.),  $[\alpha]_D^{\circ n} -28^{\circ}$ in CHCl<sub>3</sub>], are similarly prepared. Ease of fission of the above with emulsin at  $p_H$  5.0 does not run parallel to HCl-hydrolysis. Fission is promoted by o-Me or -Et (Me  $\gg$  Et), and retarded by p-Me or -Et. Unlike NH<sub>2</sub> a p-CO<sub>2</sub>H (or CO<sub>2</sub>Et) has no retarding action. The most effective substituents for accelerating fission are CH<sub>2</sub>·CN<COMe<CHO. Parallel results are obtained with β-d-glucosides and β-dgalactosides. J. W. B.

Hydrolysis and oxidation of salicoside.—See this vol., 1042.

Amyloses. Corn  $\alpha$ -amylose and retrograded β-amylose. T. C. TAYLOR and S. G. MORRIS (J. Amer. Chem. Soc., 1935, 57, 1070-1072).-When a 3% clear dispersion of maize  $\beta$ -amylose (I) (the sol. portion of the whole starch) is frozen, then warmed to room temp., and finally boiled for 10 min., retrograded β-amylose (II) remains insol. Prolonged boiling of (II) in H<sub>2</sub>O gives some material in solution indistinguishable from (I). (II) is readily dissolved by cold 2.5% NaOH and is not pptd. by cold dil. HCl.  $\alpha$ -Amylose (III) (the portion of the whole starch originally insol.) is also dissolved by 2.5% NaOH, but is pptd. nearly quantitatively by HCl. Mixtures of (III) and (II) may be thus determined. The repptd. (III) contains the same amount (4.8%) of combined fatty acid as did the original (III). (III) is thus different from (II), and maize contains very little, if any, (II). (I) consists probably of single chains of glucose units, hydrated in solution, which are converted by freezing into partly dehydrated " bundles " of these chains. R. S. C.

Sakurada's publications [on cellulose]. H. STAUDINGER (Ber., 1935, 68, [B], 1234—1238).— Mainly a refutation of criticisms of the author's work. H. W.

Highly-polymerised compounds. CXIII. Cellulose in Schweitzer's reagent. H. STAUDINGER and B. RITZENTHALER [with, in part, S. KAUTZ] (Ber., 1935, 68, [B], 1225-1233).-When, under usual conditions, various types of cellulose are dissolved in Schweitzer's reagent and pptd. from the solution, the properties of the ppts. differ from those of the original material. If air and light are completely excluded during dissolution and pptn. is effected by dil. AcOH or in completely neutral Na K tartrate solution, the properties of the original and repptd. materials are identical. Since, however, the apparent mean degree of polymerisation of ramie cellulose decreases from 1300 to about 900 and then remains const., this is true only for cellulose mols. of mean degree of polymerisation about 900. Since cellulose thus behaves like a substance of low mol. wt., there 16 no reason to doubt its macro-mol. structure.

H. W.

Osmometric investigations of dilute solutions of polymeric carbohydrates. VIII. State of technical cellulose acetate (cellit) in solution. M. ULMANN (Ber., 1935, 68, [B], 1217-1224; cf. this vol., 231) .- The solution relationships of the highly viscous fraction I of technical cellit are more complicated than those of fractions II and III (loc. cit.). The observed mol. wts. are not integral multiples of  $(C_6)_2$ , vals. intermediate between  $(C_6)_2$ ,  $(C_6)_4$ ,  $(C_6)_8$ ,  $(C_6)_{16}$ , and  $(C_6)_{32}$  being obtained. Further dilution of the solution after reaching approx. the  $(C_6)_2$  stage causes appearance of mols.  $(C_6)_8$ . The magnitude of the change in osmotic pressure during the transitions of the different types of mol. is explained by the hypothesis that the fraction contains two components one of which undergoes stepwise degradation on dilution, whereas the mols. of the other component remain stable. The most probable ratio of the two types is 1:1. H. W.

Compounds of high mol. wt. IV. Mol. wts. of esters of cellulose with higher aliphatic acids. A. NOWAKOWSKI (Rocz. Chem., 1935, 15, 234—248).— The HOI, cryoscopic, and viscosimetric methods of determining the mol. wt. of esters of cellulose with  $EtCO_2H$ ,  $PrCO_2H$ , and  $C_5H_{11}$ ·CO<sub>2</sub>H yield comparable results. R. T.

Interaction of amines with heavy water. P. GOLDFINGER and V. LASAREV (Compt. rend., 1935, 200, 1671—1673).—The hydrochlorides of  $NH_2Me$  and  $NHMe_2$  react with  $D_2O$  in  $H_2O$  at room temp., the N functioning as ter- (cf. A., 1933, 1020; this vol., 563) and not quinque-valent as in the form  $CH_2$ : $NH_3$  which is present only in minute amounts. NaOAc reacts with  $D_2O$  after 6 months (cf. A., 1934, 497).

J. L. D.

Quaternary ammonium salts from bromopropyldialkylamines. V. Conversion of cyclic ammonium salts into linear polymerides. C. F. GIBBS and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 1137—1139; cf. A., 1934, 515).—When

Br·[CH<sub>2</sub>]<sub>3</sub>·NMe<sub>2</sub> is kept in much EtOH at room temp. for 40 hr., it gives NN-dimethyltrimethyleneammonium bromide, cryst., which at room temp. (2 weeks) or 200° (3 min.) gives the linear polymeride, decomp. 240— 250°, probably owing to dissociation to the Br-amine. Cyclic salts with radicals other than Me do not thus polymerise. The following are described. NN-Diisobutyl-, b.p. 149—150°/5 mm. (platinichloride, m.p. 119—120°), -isoamyl-, b.p. 159—160°/5 mm., -allyl-, b.p. 129—130°/5 mm., and -benzyl-γ-phenoxypropylamine, b.p. 215—217°/2 mm. (hydrobromide, m.p. 163—164°): NN-di-ethyl-, b.p. 165—167°/1 mm., and -n-butyl-γ-phenoxydecylamine, b.p. 171—173°/0·5 mm.; diisoamyl-γ-bromopropylamine, b.p. 109—111° 3 mm. (platinichloride, m.p. 159—160°); diisoamyltrimethyleneammonium bromide, m.p. 71—73°. Other γ-OPh-bases were not cleaved by HI. R. S. C.

Synthesis of *d*-arginine anhydride and *d*-lysine anhydride and their ring fission by pepsin. Y. TAZAWA (Acta Phytochim., 1935, 8, 331–336).— Treatment of arginine Me ester dihydrochloride with MeOH-NH<sub>a</sub> at 30° gives d-arginine anhydride tetrahydrochloride (I), decomp. 240°,  $[\alpha]_{\rm p}$  +6.28°, which is stable towards boiling H<sub>2</sub>O, whereas the corresponding base undergoes auto-hydrolysis due to its proper alkalinity. d-Lysine anhydride dihydrochloride (II), decomp. 225°,  $[\alpha]_{\text{D}}$  +8.25°, is obtained similarly. (I) and (II) are smoothly hydrolysed by pepsin, but are indifferent towards trypsin and papain. H. W.

Combination of certain fatty acids with lysine, arginine, and salmine. T. H. JUKES and C. L. A. SCHMIDT (J. Biol. Chem., 1935, **110**, 9–16).—The  $p_K$ of 10 straight-chain fatty acids in EtOH-H<sub>2</sub>O mixtures were determined and vals. of  $p_K$ , between 4.9 and 5.0 were deduced for them all in H<sub>2</sub>O. Lysine and arginine combine with lauric and oleic acids in 72% EtOH giving salts hydrolysed to < 1%. Salmine combines with HCl, octoic and lauric acids. Lysine and arginine laurate and stearate, arginine and lysine erucate were prepared.  $p_K$  of salmine is 11.1 in H<sub>2</sub>O and 12.3 in 72% EtOH. H. D.

Canavanine. J. M. GULLAND and C. J. O. R. MORRIS (J.C.S., 1935, 763-766).—The structure  $NH_2 \cdot C(:NH) \cdot NH \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2 H (cf. Kita$ waga, A., 1930, 121) is established for canavanine byits conversion by chloramine-T into a mixture of(CHO), and tartronic semialdehyde (isolated as pnitrophenylhydrazones), and by hot conc. HBr into a $mixture of <math>\alpha$ -amino- $\gamma$ -butyrolactone hydrobromide (I),  $NH_2$ , and guanidine. (I) and HBr gave optically inactive  $\gamma$ -bromo- $\alpha$ -aminobutyric acid hydrobromide, m.p. 164°, also obtained from synthetic  $\alpha$ -aminobutyrolactone. P. G. C.

Djenkolic acid, a new amino-acid containing sulphur. A. G. VAN VEEN and A. J. HYMAN (Rec. trav. chim., 1935, 54, 493—501),—Djenkolic acid,  $CH_2[S \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H]_2$  (I), decomp. 300—350°,  $[\alpha]_D^{00} - 25^{\circ}$  in 1% HCl, is obtained in 1.6% yield from the djenkol bean (*Pithecolobium lobatum*). It gives a  $Bz_2$  derivative (+1H<sub>2</sub>O), m.p. 85° (decomp.), hydrochloride, m.p. 250°, unstable  $Et_2$  ester hydrochloride, m.p. 60°, and dihydantoin derivative,  $C_9H_{12}O_4N_4S_2$ , m.p. 200°. (I) yields  $CH_2O$  when treated with  $H_2SO_4$  and is hydrolysed by conc.  $H_2SO_4$  to S,  $SO_2$ ,  $NH_3$ , and cystine. P. G. C.

Preparation of carbamide from carbon dioxide and ammonia. III. M. TOKUOKA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 41-44).—Thermodynamical considerations and experimental data show that the optimal temp. for the prep. of  $CO(NH_2)_2$ from  $NH_2 \cdot CO_2 NH_4$  or  $CO_2 + NH_3$  is > the m.p. of  $NH_2 \cdot CO_2 NH_4$ , but  $\Rightarrow 19^\circ$ . A catalyst is unnecessary but up to 2% of  $H_2O$  causes acceleration. The presence of a little EtOH is immaterial. 35% conversion can be obtained in 30 min. E. A. H. R.

Hydrogen cyanide. V. Reactions of iminoformylcarbylamine. L. E. HINKEL, E. E. AYLING, and J. H. BEYNON (J.C.S., 1935, 674—679).—Iminoformylcarbylamine (I) is hydrolysed in cold H<sub>2</sub>O to  $HCO_2NH_4$  (cf. A., 1896, i, 71). (I) with AgNO<sub>3</sub> in H<sub>2</sub>O gives an indefinite compound probably owing to the hydrolysis of (I), but with AgNO<sub>3</sub> in EtOH the *compound* 2AgNO<sub>3</sub>,5HCN is formed. (I) with HgCl<sub>2</sub> in Et<sub>2</sub>O affords the *compound* HgCl<sub>2</sub>,3HCN, converted by HCl into the *compound* 2HgCl<sub>2</sub>,3(2HCN,HCl). (I) and AlCl<sub>3</sub> afford AlCl<sub>3</sub>,2HCN (II), m.p. 125°, identical with the compound obtained from AlCl<sub>3</sub> and HCN (A.,

1932, 132). (I) is not formed when (II) is heated alone or with quinoline. AlCl<sub>3</sub> and NH:CH·N:CHCl (III) [from (I) and HCl] give the compound AlCl<sub>3</sub>,2HCN,HCl (IV), m.p. 80°, identical with that obtained from (II) and HCl at 80°, and by the decomp. of the compound AlCl<sub>3</sub>,2HCN.3HCl (V), m.p. 62°, prepared by the action of AlCl<sub>3</sub> on the sesquihydrochloride (VI) of HCN. (IV) at 100° yields (III), and with PhMe and AlCl<sub>3</sub> affords p-C<sub>6</sub>H<sub>4</sub>Me·CHO, also obtained together with tolylhydrylamine (VII) by heating (V) with PhMe. (V) with PhMe and  $AlCl_3$  at 50—55° affords only (VII). (I) heated with 2 mols. of a primary aromatic amine  $(\mathrm{NH}_{2}\mathrm{Ph}, p \cdot \mathrm{C}_{6}\mathrm{H}_{4}\mathrm{Me} \cdot \mathrm{NH}_{2}, p \cdot \mathrm{C}_{6}\mathrm{H}_{4}\mathrm{Br} \cdot \mathrm{NH}_{2}, p \cdot \mathrm{C}_{6}\mathrm{H}_{4}\mathrm{Cl} \cdot \mathrm{NH}_{2},$ and p-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>,  $\alpha$ - and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, but not o- and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, 3:1:4-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·NH<sub>2</sub>, or p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH) affords the corresponding NN'-diarylformamidine obtained by Dains (A., 1902, i, 602) from these amines and (VI) or (III). This supports the view that the first step in the latter reactions is the removal by the base of HCl from (VI) or (III) with the formation of (I), which then reacts with the amine. NHPhMe and (III) [or (VI) but not (I)] at 100° afford N-phenyl-N-methylformamidine hydrochloride, m.p. 192°, which with  $H_2O$  at 100° gives form-methylanilide, m.p. 8-10°, b.p. 244-245° (lit. b.p. 243-244°), and with 4N-NaOH gives NHPhMe. (III) and EtOH (dry) yield CH(OEt)<sub>3</sub> and formamidine hydrochloride, m.p. 81°, and these products were also obtained from (I), HCl, and EtOH. They are also obtained (Claisen et al., Ber., 1883, 16, 309) together with EtCl from EtOH and (VI), which must therefore readily decompose into (III) and HCl. H. G. M.

Saturation pressure of mustard oils and sulphides. H. BAUER and K. BURSCHKIES (Ber., 1935, 68, [B]. 1238—1243).—In connexion with the physiological activities of vapours measurements are recorded of v.p. and temp. of PhNCS, MeNCS,  $Et_2S$ ,  $(CH_2:CH:CH_2)_2S$ ,  $Bu^a_2S$ ,  $Bu^a_2S_2$ , dissoamyl sulphide, thiodiglycol, and  $CH_2:CH:CH_2:OH$ . H. W.

Magnesium methoxides. (MLLE.) M. L. QUINET (Bull. Soc. chim., 1935, [v], 2, 1201-1205).--Mg reacts smoothly with MeOH in presence of a little Mg(OMe)<sub>2</sub> to give at -20° a compound,

 $Mg(OMe)_{2,4}MeOH$  (I), at 20° a compound, Mg(OMe)\_{2,2}MeOH, and at 66° MgCO<sub>3</sub> and other decomp. products. (I) in air gives (II) and over  $H_2SO_4$ , more rapidly in vac. or at 110°, a compound

 $3Mg(OMe)_{2,}MgCO_3$ ,  $H_2$ , and  $C_2H_6$ . (I) in moist air at room temp. gives  $Mg(OH)_{2,}4MgCO_3$ , and a solution of (I) in MeOH, faintly alkaline to phenolphthalein, is unchanged by  $CO_2$ , but with a few drops of  $H_2O$  gives a gel. (I) with N- $H_2SO_4$  or N-HCl gives first this gel and then the Mg salt. MgCl<sub>2</sub> gives a ppt.,  $xMgCl_2,yMg(OMe)_{2,}zMeOH$ . R. S. C.

Interchange of heavy atoms in organo-metallic compounds. I. NORVICK (Nature, 1935, 135, 1038—1039; cf. this vol., 851).—Bi amyl dichloride and MgEtBr yield  $BiEt_3$  and tri-*n*-amyl- and diethyl*n*-amyl-bismuthine, indicating some looseness of linking between the Bi and the alkyl residues.

L. S. T.

Organic compounds of tin. M. LESBRE (Bull. Soc. chim., 1935, [v], 2, 1189—1201).—Mainly a comparison of known org. compounds of Sn with those of C, Pb, Ge, etc. If SnCl<sub>2</sub> (1 mol.) is added to 10% aq. NaOH (7 mols.), the NaHSnO<sub>2</sub> formed decomposes at >20° to Sn and Na<sub>2</sub>[Sn(OH)<sub>6</sub>], but at < 20° with RBr or RI (less well with RCl) gives alkyl- or arylstannonic acids, RSnO<sub>2</sub>H, in which R=Ph, CH<sub>2</sub>Ph, allyl,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>, CH<sub>2</sub>Br-CH<sub>2</sub>, CHCl<sub>2</sub>, and CH<sub>2</sub>Ac, which give hydrates, +H<sub>2</sub>O, Na, and K salts, a basic salt, RSnO<sub>2</sub>Ag,Ag<sub>2</sub>O, and complex acids, [RSnCl<sub>5</sub>]H<sub>2</sub> and [RSnBr<sub>5</sub>]H<sub>2</sub> [K<sub>2</sub>, (C<sub>5</sub>H<sub>6</sub>N,H)<sub>2</sub>, and (NH<sub>4</sub>)<sub>2</sub>, decomp. > 200°, salts], and decompose, when heated, partly into SnO and ROH, and partly into SnO<sub>2</sub> and RH, but, if R=aryl, some SnR<sub>4</sub> and H<sub>2</sub>O are also obtained.

R. S. C.

Metallo-organic compounds of tin. S. N. NAUMOV and Z. M. MANULKIN (J. Gen. Chem. Russ., 1935, 5, 281–287).—SnMe<sub>4</sub> is obtained in 85% yield by boiling an Et<sub>2</sub>O solution of MgMeI with SnCl<sub>4</sub> for 5 hr., distilling off the Et<sub>2</sub>O, and heating the residue at 120–140° for 8 hr. SnMe<sub>4</sub> and I in Et<sub>2</sub>O yield SnMe<sub>3</sub>I, which with MgEtBr in Et<sub>2</sub>O affords SnMe<sub>3</sub>Et; this, in turn, is converted into SnMe<sub>2</sub>EtI, SnMe<sub>2</sub>EtPr, and SnMeEtPrI, separation of which into its optical antipodes was unsuccessful. R. T.

Synthesis of mixed dihalogen derivatives of compounds of tin with aliphatic radicals. K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1935, 5, 211-215).—The reactions  $\text{SnR}_4+\text{SnX}_4\rightarrow 2\text{R}_2\text{SnX}_2$ (R=Me, Et, Pr; X=Cl, Br) take place with considerable heat evolution. The following reactions are described:  $\text{SnMeBr}_3+\text{SnMe}_4\rightarrow 3\text{SnMe}_2\text{Br}_2$ ;  $\text{SnEt}_3\text{X}+\text{SnX}_4\rightarrow 3\text{SnEt}_2\text{X}_2$ ;  $\text{SnMe}_3\text{Br}+\text{SnMeBr}_3\rightarrow 2\text{SnMe}_2\text{Br}_2$ . R. T.

**Preparation of mercury di***iso***butyl.** A. MÜLLER (J. Amer. Chem. Soc., 1935, 57, 1142–1143).—  $HgBu\beta_2$ , b.p. 85°/11 mm., is prepared in 27% yield from Bu<sup>g</sup>Br and 0.5—1% Na-Hg in EtOAc.

R. S. C. Hexadeuterobenzene. I. G. R. CLEMO and A. McQUILLEN (J.C.S., 1935, 851—855).—Apparatus and conditions are described for optimum conversion of  $C_2H_2$  into  $C_6H_6$  over a Te catalyst, and the method is applied to the conversion of  $C_2D_2$  into hexadeuterobenzene (I), b.p. 82.5°, m.p. -1.0°. Nitration of (I) using HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> gave a (NO<sub>2</sub>)<sub>2</sub>-compound, m.p. 89° not lowered when mixed with m- $C_6H_4(NO_2)_2$ . Nitration using DNO<sub>3</sub> and D<sub>2</sub>SO<sub>4</sub> gave m-dinitrohexadeuterobenzene, m.p. 78°, mixed m.p. with m- $C_6H_4(NO_2)_2$  87°. P. G. C.

Function of sulphuric acid in nitration. D. I. JAMES (J.C.S., 1935, 785—787).—The conclusions of Hetherington *et al.* (A., 1933, 267) concerning the effect of  $H_2SO_4$  on mononitration of PhNO<sub>2</sub> and  $C_6H_4Me\cdotNO_2$  are extended to nitration of 1:2:4- $C_6H_3Me(NO_2)_2$ . Up to a point, represented approx. by 95° and an excess of 4 mols. of  $H_2SO_4$  beyond that required to form the monohydrate, the action of the excess of  $H_2SO_4$  is sufficiently explained by its promoting the miscibility of the reagents. Beyond this point, rise of temp. and increase of  $H_2SO_4$ conen. diminish the amount of  $HNO_3$  available for nitration. P. G. C.

Dealkylation of aromatic hydrocarbons. Reversibility of the Friedel-Crafts reaction. N.N. ORLOV and L. S. SOLODAR (J. Appl. Chem. Russ., 1935, 8, 117—127).—PhMe is obtained in 25% yield from xylene and AlCl<sub>3</sub> (4%) at the b.p., by a continuous process. No advantage is gained by passing HCl during the process, in disagreement with Dougherty's view as to the mechanism of the Friedel-Crafts reaction (A., 1929, 421). R. T.

Condensation of alcohols with aromatic hydrocarbons in presence of anhydrous aluminium chloride. I. Condensation of *tert*.-aliphatic alcohols with benzene and toluene. I. TZUKKER-VANIK (J. Gen. Chem. Russ., 1935, 5, 117—120). *tert*.-C<sub>5</sub>H<sub>11</sub>·OH and AlCl<sub>3</sub> yield CMe<sub>2</sub>·CHMe and *tertl*.-C<sub>5</sub>H<sub>11</sub>·OH and AlCl<sub>3</sub> yield CMe<sub>2</sub>·CHMe and *tertl*.-C<sub>5</sub>H<sub>11</sub>Cl, whilst Bu<sup>v</sup>OH affords only Bu<sup>v</sup>Cl; in presence of C<sub>6</sub>H<sub>6</sub> or PhMe a Friedel-Crafts reaction takes place, to give C<sub>5</sub>H<sub>11</sub>Ph, b.p. 189—191°, and m-amyltoluene, b.p. 208—210°, and PhBu<sup>v</sup> or m-C<sub>6</sub>H<sub>4</sub>MeBu<sup>v</sup>. R. T.

Constitution and reactivity. IX. Sulphonation of benzylidene chloride and benzotrichloride. K. LAUER (J. pr. Chem., 1935, [ii], 142, 252-257).—CPhCl<sub>3</sub> treated with gaseous SO<sub>3</sub> yields almost exclusively *m*-sulphobenzoic acid. Similar treatment of CH<sub>2</sub>PhCl and CHPhCl<sub>2</sub> gives unsatisfactory results. CHPhCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O at 35° yield mixed sulphobenzylidene chlorides, which with CaCO<sub>3</sub> form sulphobenzaldehydes, oxidised to a product which is mainly *p*-sulphobenzoic acid. E. W. W.

Sulphonation of mesitylene. H. J. BACKER (Rec. trav. chim., 1935, 54, 544-551).—Mesitylene is converted by ClSO<sub>3</sub>H into the 2:4-disulphonyl chloride, m.p. 123·5—124°, which with oleum at 105° (16 hr.) gives mesitylenetrisulphonic acid (Ba and  $NH_4$  salts). The following derivatives and salts of mesitylenedisulphonic acid are described: distrychnine, Ba, K, and Tl salts;  $Ph_2$  ester, m.p. 110— 111°; di-amide, m.p. 240°; di-methylamide (I), m.p. 171—171·5°; di-methylnitrosoamide, m.p. 183°; di-dimethylamide, m.p. 137·5—138°; di-tert.-butyl amide, m.p. 223° (decomp.); di-anilide, m.p. 150— 151°; di-o-toluidide, m.p. 178°. Nitromesitylenedisulphomethylnitroamide, NO<sub>2</sub>·C<sub>6</sub>Me<sub>3</sub>(SO<sub>2</sub>·NMe·NO<sub>2</sub>)<sub>2</sub> [from (I) and HNO<sub>3</sub> at -10°], m.p. 181° (explodes). P. G. C.

Structure of tolan. A. WEISSBERGER (J.C.S., 1935, 855-856; cf. A., 1933, 339).—Catalytic hydrogenation of tolan (I) gives a  $99\cdot3\%$  yield of (·CH<sub>2</sub>Ph)<sub>2</sub>, m.p.  $52\cdot5-53\cdot2^\circ$ ; since rearrangement under these conditions is unlikely and CHPh<sub>2</sub>Me is liquid at room temp., it is considered that (I) is CPh;CPh not CPh<sub>2</sub>:C (Smyth *et al.*, A., 1931, 669; Berger, this vol., 431). P. G. C.

Highly arylated aromatic compounds. V. W. DILTHEY, W. SCHOMMER, W. HÖSCHEN, and H. DIERICHS (Ber., 1935, 68, [B], 1159—1162; cf. this vol., 213).—Gradual addition of diphenyldiacetylene to 2:3:4:5-tetraphenyl- $\Delta^{2:4}$ -cyclopentadien-1-one (I) at 240—250° yields CO and 2:3:4:5:6-pentaphenyltolan, m.p. 258°, which slowly decolorises Br and is oxidised by CrO<sub>3</sub> in AcOH to 2:3:4:5:6pentaphenylbenzil, m.p. 276—277°. Replacement of acetylenes by olefines in the above reaction does not affect the elimination of CO, but the additional H causes reduction of (I). Nevertheless, (I) and  $(\cdot CH:CH_2)_2$  at 260—290° afford 2:3:4:5:2':3':4':5'-octaphenyldiphenyl, m.p. 318—319°, which does not add Br, whilst (I) and cyclohexene at 280° slowly yield 5:6:7:8-tetraphenyl-1:2:3:4-tetrahydronaphthalene, m.p. 271—272°. (I) and CPh:CBr at 160° give bromopentaphenylbenzene, m.p. 281—282°. Pentaphenylpyridine, m.p. 241—242° (perchlorate, m.p. 299°), is slowly produced when a mixture of (I) and PhCN is boiled, but is best obtained in a sealed tube at 275—300°. 2:3:4:5-Tetraphenylthiophen, m.p. 184—185°, is obtained from (I) and S at 270—350°. H. W.

Experimental demonstration of the allene asymmetry. P. MAITLAND and W. H. MILLS (Nature, 1935, 135, 994).—van 't Hoff's prediction that unsymmetrically substituted allenes would show enantiomorphism has been verified. With the usual dehydrating agents  $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-t-naphthylallyl alcohol is converted into r-diphenyldi-1-naphthylallene, m.p. 242—244°. If dehydration is effected with d- or l-camphorsulphonic acid in C<sub>6</sub>H<sub>6</sub> an optically active product is obtained from which d-, m.p. 158—159°,  $[\alpha]_{5461}+437°$ , and l-,  $[\alpha]_{5461}$ -438°, -diphenyldi-1-naphthylallene are isolated. L. S. T.

Bromo-derivatives of naphthalene. J. SALKIND and Z. STETZURO (J. Gen. Chem. Russ., 1935, 5, 94–99).–1:  $4 \cdot C_{10}H_6Br_2$  and Br in CS<sub>2</sub> at 0° afford  $C_{10}H_6Br_2,Br_4$  (I) and  $1: 4: 6 \cdot C_{10}H_5Br_3$  (II); at S0° the chief product is  $1: 4: 6: x: x \cdot C_{10}H_3Br_5$ , m.p. 179–183°. (I) in  $C_6H_6$  and NaOEt (at the b.p.) yield 1: 4: 6: 7- and  $1: 2(3?): 4: 6 \cdot C_{10}H_4Br_4$ , m.p. 116–120°, both of which afford (II) when reduced (Zn in AcOH).  $2: 6 \cdot C_{10}H_6Br_2$  and Br in CHCl<sub>3</sub> (in presence of Fe) give a mixture of  $2: 6: x \cdot C_{10}H_5Br_3$ , m.p. 171–173°, and  $2: 6: x: x \cdot C_{10}H_4Br_4$ , m.p. 100–101°. Bromination of  $1: 2: 6 \cdot C_{10}H_5Br_3$  affords  $C_{10}H_3Br_5$ , m.p. 274–279°. (I) and Mg in Et<sub>2</sub>O give MgBr<sub>2</sub> and  $C_{10}H_6(MgBr)_2$ .

Action of selenium on compounds containing angular methyl groups. G. R. CLEMO and H. G. DICKENSON (J.C.S., 1935, 735-738).-An attempt to obtain simple examples of the structural changes which occur when, e.g., sterols are dehydrogenated with Se (cf. A., 1933, 610). 9-Methyldccahydro-naphthalene (A., 1931, 1302), 8-methylhydrindane, b.p. 159-160°/760 mm. [from 2-acetyl-1-methyl-Δ<sup>1</sup>cyclopentene and CHNa(CO<sub>2</sub>Et)<sub>2</sub>, followed by hydro-lysis and reduction], and 2-carboxy-1-methylcyclohexane-1-acetic acid were not attacked by Se, Pt, S, S+Se, or SeO<sub>2</sub>. 1:1:6-Trimethyltetrahydro-naphthalene gave 1:6-C<sub>10</sub>H<sub>6</sub>Me<sub>2</sub>. The  $Cl_2$ -compound, b.p. 150—155°/13 mm., from 2:4-diketo-9-methyldecahydronaphthalene and  $PCl_5$  was converted by Se (280-300°; 60 hr.) into  $1-C_{10}H_7Me$ ; migration of the Me may have resulted from the action of the PCl<sub>5</sub> or Se. 2:4-Diketo-8-methylhydrindane, b.p. 143°/0·3 mm., m.p. 91—92°, was converted by PCl<sub>5</sub> into a  $Cl_2$ -compound, b.p. 109-110°/12 mm., which gave a small quantity of non-picrate-forming oil when heated with Se. P. G. C.

Anthracene-9:10-disulphonic acid. C. MAR-SCHALK and N. OUROUSSOV (Bull. Soc. chim., 1935, [v], 2, 1216—1218).—9:10-Dichloroanthracene and 5% aq. Na<sub>2</sub>SO<sub>3</sub> in PhOH at 170—180° give Na<sub>2</sub> anthracene-9:10-disulphonate, cryst., readily hydrolysed by acid to anthracene and very readily oxidised to anthraquinone. R. S. C.

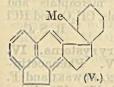
Synthesis of carcinogenic 1:2-benzpyrene. A. WINTERSTEIN, H. VETTER, and K. SCHÖN (Ber., 1935, 68, [B], 1079—1085).—Improvements in Cook's method of preparing 1:2-benzpyrene from

(•CH<sub>2</sub>·CO)<sub>2</sub>O and pyrene (I) (A., 1934, 601) coupled with chromatographic purification at two stages of the operations increase the yield of the hydrocarbon to 35—40%. (I) and methylsuccinic anhydride afford  $\gamma$ -pyrenoyl- $\alpha$ (or  $\beta$ )-methylpropionic acid, m.p. 204—205° (corr.; Berl), whence  $\gamma$ -1-pyrenyl- $\alpha$ (or  $\beta$ )methylbutyric acid, m.p. 176° (corr.; Berl), transformed by SnCl<sub>4</sub> into 4'-keto-2'(3')-methyl-1': 2': 3': 4'-tetrahydro-1: 2-benzpyrene, m.p. 176—177° (corr.; Berl). The ketone is converted by Se into 2'(3')-methyl-1: 2benzpyrene, m.p. 143—144° (corr.; Berl). H. W.

Syntheses of polycyclic compounds related to the sterols. IV. Identification of 3'-methyl-1:2-cyclopentenophenanthrene and its preparation from cholesterol. D. J. C. GAMBLE, G. A. R. KON, and B. SAUNDERS (J.C.S., 1935, 644-646; cf. this vol., 741).—When carefully purified, 3'-methyl-1: 2-cyclopentenophenanthrene (I) (A., 1934, 288) is identical with the hydrocarbon  $C_{18}H_{16}$  (II) prepared by the method of Bergmann et al., (A., 1933, 1154). The  $C_6H_3(NO_2)_3$  (III) and  $C_6H_2Me(NO_2)_3$  compounds and the styphnate (IV) of (I) and (II), respectively, have the same m.p., but the picrate of (I) melts 1° < that of (II). They are not fluorescent in daylight, but show a violet fluorescence in ultraviolet light. A hydrocarbon of identical properties was isolated from the dehydrogenation product of cholesterol, except that the picrate melted 4° too low. This is due to the presence of a second form (this vol., 286). (III) and (IV) (ibid., 741), but not the picrate, are suitable for the identification of the H. G. M. hydrocarbon.

Synthesis of cholanthrene. J. W. COOK, G. A. D. HASLEWOOD, and (MRS.) A. M. ROBINSON (J.C.S., 1935, 667-671).-1-Iodoacenaphthene (A., 1931, 81), Mg, Et<sub>2</sub>O, EtBr, and  $(CH_2)_2O$  afford  $\beta$ -1-acenaphthyl-ethyl alcohol, m.p. 94—95°, b.p. 179—180°/0·3 mm. [3:5-dinitrobenzoate, m.p. 233—234·5°; chloride (I), m.p. 54-55°, b.p. 145-150°/0.1 mm.; bromide (II), m.p. 66°, b.p.  $165^{\circ}/0.4$  mm.]. (II) heated with K dissolved in Et *cyclo*hexanone-2-carboxylate and  $C_6H_6$  affords Et 2-( $\beta$ -1'-acenaphthylethyl)cyclohexanone-2-carboxylate (III), m.p. 76-77°, b.p. 210-220°/ 0.4 mm., hydrolysed (MeOH-KOH) to  $\alpha$ -( $\beta$ '-1-acenaphthylethyl)pimelic acid, m.p. 165°. (III) is cyclised by  $H_2SO_4$  to Et hexahydrocholanthrenecarboxylate, m.p. 150° (solutions of this have an intense violet fluorescence), hydrolysed to the acid, m.p. 241-242° (with evolution of gas). This on heating with Pt-black at 295-305° during 1<sup>1</sup>/<sub>4</sub> hr. yields cholanthrene, m.p. 170-171° (sublimes 170-190°/0.05 mm.) (picrate, m.p. 167-168°). This on oxidation (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-AcOH) and subsequent decarboxylation yields 5-methyl-1: 2-benzanthraquinone (A., 1934, 180). (I), Mg, Et<sub>2</sub>O, and 2-methylcyclohexanone

afford 1-ethylacenaphthene, m.p. 30°, b.p.  $120-125^{\circ}/$ 0·4 mm. (picrate, m.p.  $102-102\cdot5^{\circ}$ ), and an oil, b.p.  $210/0\cdot7$  mm., which on heating with KHSO<sub>4</sub> gives 2-methyl-( $\beta$ -1'-acenaphthylethyl)- $\Delta^1$ -cyclohexene (IV), b.p.  $182-185^{\circ}/0\cdot2-0\cdot3$  mm. (picrate, m.p.  $107-108^{\circ}$ ); this on treatment with AlCl<sub>3</sub> gives a mixture which on purification had m.p.  $178-182^{\circ}$  (picrate,  $157-158^{\circ}$ ) and gave the same product after treatment



with Se at  $320-30^{\circ}$  for 32 hr. This is believed to be the spiran (V). The cyclisation of (IV) is therefore anomalous. 2-Methylcyclohexanone and  $\beta$ -1-naphthylethyl chloride, Mg, and Et<sub>2</sub>O afford 2 - methyl-1-( $\beta$ -1'-naphthylethyl)-

cyclohexanol, b.p.  $185-195^{\circ}/0.5$  mm. (3:5-dinitro $benzoate, m.p. 136^{\circ})$ , dehydrated by KHSO<sub>4</sub> to 2-methyl-( $\beta$ -1'-naphthylethyl)- $\Delta^1$ -cyclohexene, b.p. 135°/0.1 mm. This is cyclised by AlCl<sub>3</sub> to the anticipated methyloctahydrochrysene (VI), b.p. 145°/0.1 mm. (picrate, m.p. 105-106°), and a heavy oil. (VI) was dehydrogenated to chrysene by Se at 295-305°, but not by Pt-black. H. G. M.

Dissociable organic oxides. 1:1'-Diphenylrubene,  $C_{30}H_{20}$ ; thermal decomposition of its photo-oxide,  $C_{30}H_{20}O_2$ . C. DUFRAISSE and M. LOURY (Compt. rend., 1935, 200, 1673—1675; cf. A., 1931, 1151).—Hydrolysis of Et 1:1'-diphenylrubene-3:3'-dicarboxylate (cf. this vol., 213) gives 1:1'diphenylrubene (I), m.p.  $301-302^\circ$ , and another product. The absorption spectrum of (I) resembles those of other rubenes, but is displaced towards the violet. Photo-oxidation of (I) affords an oxide, m.p.  $234-235^\circ$ , which is converted at 170°, without evolution of gas, into a resin; some rubene is also formed. J. L. D.

Boranilide. C. R. KINNEY and D. F. PONTZ (J. Amer. Chem. Soc., 1935, 57, 1128—1129).—Chaudhuri's directions (J.C.S., 1920, 117, 1081) for the prep. of boranilide give  $(NH_2Ph)_2$ ,  $ZnCl_2$ ; some of the reactions described for the product could not be duplicated, but BzCl gives NHBzPh and Br  $p-C_6H_4Br\cdot NH_2$ . R. S. C.

Hydrolysis of substituted benzanilides. F. ASINGER (J. pr. Chem., 1935, [ii], 142, 291-300).— The times of half-hydrolysis by about 12.5% KOH-EtOH under reflux of benz-3:4:5-, m.p. 210°, and -2:4:6-tribromoanilide, m.p. 204°, 3:4:5-, m.p. 220°, and 2:4:6-tribromobenzanilide, m.p. 237°, and NHBzPh are 2, 215, 5,  $\infty$ , and 16 hr., respectively, showing the effect of steric hindrance. The prep. of the necessary acids and bases and of 3:4:5-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·NO<sub>2</sub> is modified. 3:4:5-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>Me gives C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·CBr<sub>3</sub> at 200-220°, but 2:4:6-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>Me gives at this temp. gives only 2:4:6-tribromobenzyl bromide, m.p. 75°, b.p. 202°/18 mm., the CBr<sub>3</sub>-compound being obtained at 250-260°. R. S. C.

Reaction between chloral hydrate and phenylhydrazine. I. C. TORRES and S. BROSA (Anal. Fis. Quim., 1934, 32. 509-518).—CCl<sub>3</sub>·CH(OH)<sub>2</sub> with  $2:4-(NO_2)_2C_6H_3\cdot NH\cdot NH_2$  (I) in dil.  $H_2SO_4$  yields  $2:4-(NO_2)_2C_6H_3\cdot NH\cdot NH\cdot CH(OH)\cdot CO_2H$  (cf. Brady, A., 1931, 937) and chloroglyoxalbis-2:4-dinitrophenylhydrazone, decomp. 278° (Ac derivative, decomp. 228°), which with NaOAc and  $Ac_2O$  yields the  $Ac_3$  derivative of (I), m.p. 207° (decomp.), also given by (I), NaOAc, and  $Ac_2O$ . F. R. G.

Interaction of ethylene oxide with *m*-phenylenediamine. J. O. GABEL and R. M. MATZKEVITSCH (Ukrain. Chem. J., 1935, **10**, 4–6).–(CH<sub>2</sub>)<sub>2</sub>O and  $m \cdot C_6 H_4(NH_2)_2$  (30°; 8 hr.) yield  $\beta$ -p-aminophenylaminoethyl alcohol, m.p. 52–53° [picrate, m.p. 106– 108° (decomp.); benzoate]. R. T.

Complex compounds of 2:4:6-triaminotoluene.—See this vol., 944.

Reactions of diazotised p-sulphanilic acid and formation of an azoxybenzene. E. JUSTIN-MUELLER (Bull. Soc. chim., 1935, [v], 2, 1024— 1028).—Diazotised p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H (I) is adsorbed by wool fibres in an acid medium. In an alkaline medium a reddish-brown coloration appears both on the fibres and in the solution. This is due not to the presence of tyrosine in the fibres (cf. A., 1905, i, 75), but to the formation of azoxybenzene-pp'-disulphonic acid (II). This occurs in alkaline solutions of diazotised (I), and also, but more slowly, in an AcOH medium. (II) is readily split into (I) by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. H. G. M.

Coloured local anæsthetics. J.H. GARDNER and L. JOSEPH (J. Amer. Chem. Soc., 1935, 57, 901).— Diazotised procaine (I) gives dyes with H-acid, o-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, and m-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, decomp. 250°, o-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me, m.p. 196·5°, o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me, m.p. 216—219°, p-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>, m.p. 109—110°, and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, m.p. 190° (decomp.). Bisazo-dyes are obtained from (I) and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>+ $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, decomp. 250°, (I) and Me anthranilate + $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, decomp. 250°, and (I) and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>+procaine, m.p. 169—172°. The acid and OH-compounds have no anæsthetic action. R.S.C.

Preparation of a fat-soluble azo-dye. I. Dye from stearic acid. O. ROUTALA and A. ARHO (Suomen Kem., 1935, 8, B, 25-26).—Stearo- $\beta$ naphthylamide affords a  $(NO_2)_1$ -derivative (45%), reduced to 3-aminostearo- $\beta$ -naphthylamide (45%), the diazonium derivative of which couples with  $\alpha$ - and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> to give dyes, the latter of which when diazotised couples again with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>. These dyes are sol. in fats and fatty acids. J. L. D.

[Metallic salts of] diazoamino-compounds. II. III. Unsaturated chromophores. I. A. MANGINI (Gazzetta, 1935, 65, 298-308, 308-317).— II. The following derivatives of diazoaminobenzene yield Hg and Ag salts which are (I) yellow, (II) red, or (III) orange (mixed) (cf. A., 1934, 68) : p-bromo-, Hg(I and II or III) and Ag (II and III) salts; o-nitro-(new prep. from o-NO<sub>2</sub>·C<sub>0</sub>H<sub>4</sub>·NH<sub>2</sub>), Hg (I, II, and III) and Ag (II) salts; 4-bromo-2'-nitro-, Hg (I and III) and Ag (II and III) salts; 4-bromo-3'-nitro-, Hg (I) and Ag (I, III, and unstable II) salts; 4-bromo-4'nitro-, Hg (I, II, and III) and Ag (I, II, and III) salts.  $\beta$ -Naphthyldiazoaminobenzene yields Hg (I, II, and III) and Ag (II) salts. 4-Bromo-2'-nitrodiazoaminobenzene, m.p. 149-150°, is obtained from diazotised o-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> and p-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>.

III. The Na and K salts of o-nitro- and 4-bromo-2'nitro- and -4'-nitro-, and the K salts of m-nitro- and 4-bromo-3'-nitro-diazoaminobenzene, are all intensely coloured. Since m-compounds are included, the coloration is not due to a quinonoid structure. It is suggested that the NO<sub>2</sub>-group acts as a negative auxochrome, promoting a dipole structure in the diazoamino-system, and that the Na and K salts are formed with the latter, and are not nitronic.

Action of aromatic hydroxysulphonic acids on hippuricacid. I. G. MACHEK (Monatsh., 1935, 65, 433-442).-The product from PhOH and hippuric acid (I) in presence of H<sub>o</sub>SO<sub>4</sub> gives, not sulphophenylglycine,  $C_8H_9O_5NS+H_2O$  (A., 1885, 55, 1235), but a salt, glycine phenylsulphonate, C<sub>8</sub>H<sub>11</sub>O<sub>6</sub>NS, new m.p. 185-186°, which is also obtained using glycine instead of (I). Similarly are obtained glycine o., m., and pcresolsulphonates, m.p. 161-162°, 175-176°, and 180-181° (all corr.), respectively. The last gives a Ag salt. These substances all give a strong FeCl<sub>3</sub> reaction. E. W. W.

Constitution and reactivity. XI. Oxidation of o- and m-dinitrobenzene. K. LAUER (J. pr. Chem., 1935, [ii], 142, 310–312).—o-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> and 30% oleum at 120–134° give 12% of 2:3-dinitrophenol. m-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> and 35% oleum at 140-150° give 2:4- (6 parts) and 2:6-dinitrophenol (1 part). R. S. C.

Two optically active diastereomeric forms of a-phenylsulphoxypropionic acid. L. RAMBERG and I. HEDLUND (Arkiv Kemi, Min., Geol., 1935, 11, and I. HEDLUND (Arkiv Kemi, sim., Geol., 1959, 11, B, No. 55, 1-5).—d- $\alpha$ -Phenylthiolpropionic acid (I),  $[\alpha]_{D}^{-} + 123 \cdot 0^{\circ}$  in 0.03N aq. solution, with H<sub>2</sub>O<sub>2</sub> in COMe, at 0° affords after 5 days two optically active phenylsulphoxypropionic acids A+, m.p. > 180° (depends on mode of heating),  $[\alpha]_{D}^{25} + 190^{\circ}$  in 0.01N aq. solution, and B-, m.p. 98·3-98·6°,  $[\alpha]_{D}^{25} - 112^{\circ}$  in 0.03N aq. solution. These are readily separated on account of their different solubilities in C.H. and on account of their different solubilities in C6H6, and on further oxidation both give d-a-phenylsulphonylpropionic acid (II). This oxidation is accompanied by slight racemisation, although (I) is oxidised directly to (II) by KMnO<sub>4</sub> without any racemisation. The solubility of A + and B - in H<sub>2</sub>O at 15° and  $[\alpha]_{p}^{p}$  at various concns. are given. H. G. M.

Thiophenols. II. Reaction between aromatic mercaptals and formaldehyde. W. H. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 1065-1068; cf. A., 1934, 69).—PhSH, excess of CH<sub>2</sub>O, and HCl in AcOH at room temp. give CH2(SPh)2 (I), m.p. 36°, but after several months at room temp. or a few hr. when heated the product is a mixture of mono- to tetra-merides, double m.p. 140-145° and 245-250°. The appropriate aldehyde, thiophenol, and HCl in AcOH give mnitrobenzaldehyde diphenyl- (III), m.p. 65.5°, and di-ptolyl-mercaptal (III), m.p. 85.5°, p-tolualdehyde di-ptolylmercaptal, m.p. 72°, o-nitrobenzaldehyde diphenyl-mercaptal, m.p. 101°, and 2-bromo-5-hydroxybenzaldehyde di-p-tolylmercaptal (IV), m.p. 97°. (II), (III), and (IV) with CH<sub>2</sub>O and HCl in hot AcOH give products (V), m.p. (double)  $192-195^{\circ}$  and  $250^{\circ}$ ,  $180-181^{\circ}$ , and  $179^{\circ}$ . (I). CHPh(SPh)<sub>2</sub>, CHPh(S·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>-p)<sub>2</sub>, CHPh(S·C<sub>6</sub>H<sub>4</sub>Me-p)<sub>2</sub>. and

 $CH_2(S \cdot C_6H_4Me \cdot p)_2$  give similar products ( $\tilde{V}$ ), m.p. (double) 181-184° and 250°, (double) 192-195° and

250°, 183°, 183-184°, and 186°, respectively. CPh<sub>2</sub>(SPh)<sub>2</sub> does not react. (V) appear to be formed by replacement of the aldehyde by CH<sub>2</sub>O and to be



(VI) or its substitution products; for the products with double m.p. condensation may have occurred in the *p*-position with formation of large rings. (V) are not formed from the formaldehyde mercaptals and HCl in AcOH or from the thiophenols, CH<sub>2</sub>O, and HCl in AcOH. M.p. are corr. R. S. C.

Thermal equilibrium in ternary systems. IV. Antipyrine-phenacetin-salol. V. Phenacetin-Anterpyrine phenotal. K. HRYNAKOWSKI and F. ADAMANIS (Rocz. Chem., 1935, 15, 173—179, 184— 190).—IV. The eutectic, m.p. 32.5°, contains antipyrine 13.5%, phenacetin 4%, and salol 82.5%. V. The eutectic, m.p. 69.5°, contains phenacetin

22%, NHPhAc 44%, and sulphonal 34%. **R**. **T**.

Thermal equilibrium in the system  $\beta$ -naphtholβ-naphthylamine. K. HRYNAKOWSKI and M. SZMYTÓWNA (Rocz. Chem., 1935, 15, 180-183).-The m.-p. diagram corresponds with Roozeboom's third type. R. T.

Preparation of 1-alkyl- $\beta$ -naphthols. K. DZIEwoński and C. Dragan (Rocz. Chem., 1935, 15, 198-201).— $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH, anhyd. NPhMe<sub>2</sub>, and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·ONa yield 1-methyl-β-naphthol (300°; 8 hr.) (picrate, m.p. 163—164°). The corresponding 1-Et compound, m.p. 105° (benzoate, m.p. 75°), is prepared analogously. R. T.

Action of hydroxylamine on the hydrogen sulphite compounds of 1-nitroso-β-naphthol-6- and -7-sulphonic acids. S. V. BOGDANOV and I. I. LEVKOEV [with V. V. DURMASCHKINA] (J. Gen. Chem. Russ., 1935, 5, 18–27).—NaHSO<sub>3</sub> is added to an aq. suspension of Na 1-nitroso-β-naphthol-6-sulphonate (I) to complete dissolution of the latter, when HCl and NH<sub>2</sub>OH,HCl (II) are added, to yield a ppt. of Na 2-nitroso-a-naphthol-4: 6-disulphonate (III) (75% yield). (III) is also obtained by the action of HCl on the dioxime of 1:2-diketo-1:2:3:4-tetrahydronaphthalene-4: 6-disulphonicacid, prepared from (I), NaHSO3, and (II) in presence of NaOAc in neutral aq. solution, and converted by NaOH into the Na salt of the dioxime of 1:2-naphthaquinone-6-sulphonic acid, the anhydride of which is described. Under analogous conditions, the -7-sulphonic acid corresponding with (I) affords the -4 : 7-disulphonic acid analogue (IV) of (III). The constitutions of (III) and (IV) are established by comparing the products of reduction with the corresponding synthetically prepared aminonaphtholdisulphonic acids. R. T.

Purification of benzonaphthol. G. A. KIRCH-GOF and A. D. STEPANOV (Khim. Farm. Prom., 1934. No. 3, 16-17).-Washing with dil. alkali is followed by crystallisation from petroleum. CH. ABS. (r)

Purification of benzonaphthol. T. I. ZACHA-ROVA and F. PALEI (Khim. Farm. Prom., 1934, No. 3, 19-20).-Addition of PhCl to the reaction mixture hinders resin formation. The crude product meets CH. ABS. (r)pharmaceutical requirements.

E. W. W.

nonohydroxychrysene —See trans-cyclo

Manufacture of monohydroxychrysene.—See B., 1935, 585.

Rearrangement of *y*-nitrosites of propenylphenyl ethers. Synthesis of β-nitro-a-alkoxyphenylpropanols and their methyl ethers. BRUCKNER and E. VINKLER (J. pr. Chem., 1935, [ii], 142, 277-290).—The decomp. of propenylbenzene- $\psi$ -nitrosites and  $\beta$ -nitro- $\alpha$ -acetoxypropyl-benzenes varies inexplicably with the nature of the substituents in the Ph nucleus. Asarone- $\psi$ -nitrosite with hot MeOH gives 2:4:5-trimethoxy- $\alpha\beta$ -dioximinopropylbenzene peroxide,  $0 < \stackrel{\text{N:CAr}}{O-N} > CMe$ , m.p. 155° (lit. 149°), and 2:4:5-trimethoxy-β-nitroa-methoxypropylbenzene (I), m.p. 118°, also obtained with MeOH-HCl at 65°. Methylisoeugenol- $\psi$ -nitrosite with hot MeOH gives β-nitro-3: 4-dimethoxypropiophenoneoxime, m.p. 91° (decomp.), and the (impure) glyoxime peroxide, but with HCl-MeOH at 70° 3: 4-dimethoxy- $\beta$ -nitro- $\alpha$ -methoxy-n-propylaffords benzene (II), m.p. 119°, also obtained from the corresponding a-OAc-compound (III) and HCl in MeOH or aq. MeOH. (III) and HCl-COMe2 give, however, 3: 4-dimethoxy-β-nitro-α-hydroxy-n-propylbenzene, m.p. 124-133° (decomp.), which is unchanged by HCl-MeOH and with AcCl-C5H5N re-forms (III). iso-Safrole- $\psi$ -nitrosite with hot MeOH gives  $\beta$ -nitro-3:4methylenedioxypropiophenoneoxime, m.p. 122° (decomp.) (with alkali gives the glyoxime peroxide), and with HCl-MeOH affords 3:4-methylenedioxy- $\alpha\beta$ -dioximino-n-propylbenzene, m.p. 206-207° (decomp.), stable to alkali but hydrolysed by hot dil. H<sub>2</sub>SO<sub>4</sub>. 3:4-Methylenedioxy- $\beta$ -nitro- $\alpha$ -acetoxy-n-propyl-benzene is unchanged by 7% HCl-COMe<sub>2</sub>, but with HCl-MeOH gives the  $\alpha$ -OH-compound, an oil (decomposed when distilled), which is reduced electrolytic-ally to 3:4-methylenedioxy- $\beta$ -amino- $\alpha$ -hydroxy-n-propylbenzene hydrochloride, m.p. 195–196° (decomp.). (II) gives similarly electrolytically 3:4-dimethoxy-βamino- $\alpha$ -methoxy-n-propylbenzene hydrochloride, m.p. 180°, but (I) affords 2:4:5-trimethoxy- $\beta$ -hydroxylamino-a-methoxy-n-propylbenzene, m.p. 128

### R. S. C.

Thermal analysis of binary systems of antipyrine and resorcinol with certain organic compounds. K. HRYNAKOWSKI and F. ADAMANIS (Rocz. Chem., 1935, 15, 163—172).—The m.-p. diagrams of the systems antipyrine with o-, m-, and p-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, salicylic and benzoic acids, and salipyrine, also of resorcinol with pyrocatechol, quinol, and phenacetin, indicate complete miscibility of the fused components. The existence of a no. of compounds previously described by other authors is confirmed. Resorcinol and phenacetin form a 3:2compound, m.p. 76.5°. R. T.

2:4:5-Trimethoxy-1-allylbenzene.—See this vol., 1041.

Stereochemistry of dicyclic ring systems. XI. Stereoisomerism of hexahydrohydrindenes and their derivatives. III. Hexahydrohydrindenes substituted in the five-membered ring. W. HUCKEL, M. SACHS, J. YANTSCHULEWITSCH, and F. NERDEL (Annalen, 1935, 518, 155-183; cf. A., 1927, 238).-Both Et<sub>2</sub> cis-, b.p. 176°/21 mm., and

3т

trans-cyclohexane-1-propionate-2-carboxylate, b.p. 164°/13 mm. [from the cis-, m.p. 103°, and trans- (1) -acid, which are prepared by catalytic reduction of o-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H], give with Na-EtOH, Et hexahydro. a-hydrindone-2-carboxylate, hydrolysed (KOH) to (I) and hexahydro- $\alpha$ -hydrindone, the oxime, m.p. 80°, of which is separated by crystallisation from ligroin (or by benzoylation) into the cis-oxime (II), m.p. 100° (Bz derivative, m.p. 96°), and trans-oxime (III), m.p. 146° (Bz derivative, m.p. 153°) (ratio 10:1). Reduction (Na-EtOH) of (II) gives a mixture of two cis-amines, separated as the Bz derivative, m.p. 180°, and Bz derivative, m.p. 131°, of cis-hexahydro-a-hydrindylamine-I (Ac derivative, m.p. 126°) and -II: similar reduction of (III) gives only trans-hexahydro-a-hydrindylamine (Ac derivative, m.p. 110°) as its Bz derivative, m.p. 153°. Reduction (Adams) of  $\alpha$ -hydrindone (improved prep.) affords first a-hydrindol, and finally a mixture of cis-hexahydro-a-hydrindols, separated (through various esters) into a form, m.p. 18° (*H phthalate*, m.p. 127°; *H succinate*, m.p. 63°; p-nitrobenzoate, m.p. 72°; *phenylurethane*, m.p. 115°) [oxidised to the ketone which gives only (II)], and a liquid form (*H phthalate*, when gives only (11), and a riquid form (in principal  $\alpha$ , m.p. 140°; *H* succinate, liquid; p-nitrobenzoate, m.p. 89°; phenylurethane, m.p. 100°). Similar reduction of  $\beta$ -hydrindone affords first  $\beta$ -hydrindol, m.p. 70° (*H* phthalate, m.p. 133—134°; *Ac* derivative, m.p. 32°; phenylurethane, m.p. 130°), and finally a mixture of cis-hexahydro- $\beta$ -hydrindols, from which is isolated a pure form, m.p. 5°, b.p. 110°/12 mm. (cf. loc. cit.) (p-nitrobenzoate, m.p. 115°; oxalate, m.p. 94°). The other form, m.p. 10°, b.p. 108°/11 mm. (H phthalate, m.p. 103·5—105°; H succinate, m.p. 65·5°; phenylurethane, m.p. 102°), cannot be isolated pure from the mother-liquor, but is obtained by the action of  $HNO_2$  on the amine (IV) below. Reduction (Na-EtOH) of cis-hexahydro-\beta-hydrindoxime affords a mixture of amines (IV), separated after benzoylation into the Bz derivative, m.p. 144° (main product; also obtained by catalytic reduction), and the Bz derivative, m.p. 133° (dimorphous), of cis-hexahydro-B-hydrindylamine. Similar reduction of the trans-β-oxime, m.p. 161° (Bz derivative, m.p. 123°), gives trans-hexahydro-β-hydrindylamine (Bz, m.p. 140°, and Ac, m.p. 94°, derivatives), converted by HNO<sub>2</sub> into (V) (below). Reduction (Skita or Na-EtOH) of trans-hexahydro-\beta-hydrindono affords only transhexahydro-\beta-hydrindol (V), m.p. 23°, b.p. 102°/11 mm. (H phthalate, m.p. 87°; H succinate, m.p. 58°; oxalate, m.p. 70°). Reduction (Adams) of β-hydrindoxime affords only di-(\(\beta-hydrindyl\)amine, m.p. 102°. When heated with KHSO<sub>4</sub> at 180° (V) gives mainly di-(transhexahydro-3-hydrindyl) ether, m.p. 38°, and a little trans-hexahydrindene, b.p. 154-155° (oxidised by KOH-KMnO<sub>4</sub> to trans-cyclohexane-1-acetic-2-carb-oxylic acid). dl-trans-cycloHexane-1: 2-diacetic acid is resolved (cinchonine and brucine salts) into the d-,  $[\alpha]_{D}^{19.5} + 48.28^{\circ}$ , and l-,  $[\alpha]_{D}^{19.5} - 48.28^{\circ}$  in EtOH, *a.*,  $[\alpha]_{\rm B}^{\rm op} \rightarrow 10\ 20$ , and 1,  $[\alpha]_{\rm B}^{\rm op} \rightarrow 20\ {\rm m}$  Bioli, *-acids*, converted by Ac<sub>2</sub>O at 250°, respectively, into 1-, b.p. 92°/13 mm.,  $[\alpha]_{\rm B}^{\rm op} \rightarrow -297\cdot3°$  in EtOH [*oxime*, m.p. 160°,  $[\alpha]_{\rm D}^{\rm op} \rightarrow -97\cdot74°$  in EtOH (*Bz* derivative, m.p. 130°,  $[\alpha]_{\rm B}^{\rm op} \rightarrow -60\cdot50°$  in COMe<sub>2</sub>)], and d-transhexahydro- $\beta$ -hydrindone, b.p. 88°/11 mm.,  $[\alpha]_{D}^{18-5}$  + 297.4° in EtOH. cis-Hexahydrohydrindene, b.p. 166°/

760 mm., has a heat of combustion 1347.5 kg.-cal. per mol., the *trans*-compound, b.p.  $159^{\circ}/760$  mm. (by Clemmensen reduction of *trans*-hexahydro- $\beta$ -hydrind-one), has 1345.7 kg.-cal. per mol. Comparisons with the various decalone derivatives are made. J. W. B.

Asymmetric reactions. IV. Causes of optical selectivity in reactions with optically active catalysts. R. WEGLER and A. RÜBER (Ber., 1935, 68, [B], 1055-1059; cf. A., 1934, 771).-The selectivity of the catalytic action of nicotine, benzylpipecoline, a-phenylethyl-dimethyl- or -methylpropylamine on the partial esterification of CHPhMe OH by  $Ac_2O$  or the partial conversion of *r*-hydratropyl chloride into amide is very slight in comparison with that of brucine; a relationship between selectivity and constitution of catalyst is not obvious. In the presence of cinchonine (as Ac derivative) an esteralcohol mixture is obtained with  $\alpha_p + 3.9^\circ$ , whereas in that of the isomeric cinchonidine the product has  $\alpha_p = -2 \cdot 2^\circ$ . Apparently in the first case a predominating portion of the centres of asymmetry has a positive selective influence, whereas in the second instance the configurative alteration at two centres causes a more pronounced selectivity in the opposite sense. The possibility of obtaining catalysts of high selectivity by choice of isomerides obtained by accumulating asymmetric centres in a given compound is examined by converting camphor into the corresponding N-dimethylbornylamines, one of which gives an alcohol-ester mixture with  $\alpha_{\rm p}^{20} + 1.6^{\circ}$ , whereas the other affords a product with  $\alpha_{\rm D}^{20} + 12.8^{\circ}$ .

H. W.

Preparation of aromatic alcohols by the crossed Cannizzaro reaction with formaldehyde. D. DAVIDSON and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 905).—Aromatic aldehydes and  $CH_2O$  in hot MeOH give 85—90% yields of  $HCO_2H$  and the aromatic alcohol with 2—5% of aromatic acid. Anisyl, piperonyl, and veratryl alcohols are conveniently prepared thus. R. S. C.

Sensitivity of  $\beta$ -amino- and  $\beta$ -hydroxylamino- $\alpha$ alkoxyphenylpropyl alcohols to alkali. V. BRUCK-NER [with A. KRÁMLI and E. VINKLER] (J. pr. Chem., 1935, [ii], 142, 301-309).-3: 4-Dimethoxy-β-vera $trylideneamino - \alpha - hydroxy - n - propylbenzene$  (I), m.p.  $(+H_2O)$  151° after sintering at 90–100° or (anhyd.) 151° (sharp), is obtained (a) from 3:4-dimethoxy-3-acetamido-a-hydroxypropylbenzene and KOH-aq. MeOH at room temp. (several weeks), or from 3: 4-dimethoxy- $\beta$ -amino- $\alpha$ -hydroxypropylbenzene and (b) hot 10% H<sub>2</sub>SO<sub>4</sub> or (c) veratraldehyde (II) and cold NaOH. 3: 4-Methylenedioxy- $\beta$ -piperonylideneamino- $\alpha$ -hydroxypropylbenzene (III), m.p. 119°, is obtained by methods (a) and (b). The nitrone, m.p. 150-151°, corresponding with (I) is obtained from 3: 4-dimethoxy-β-hydroxylamino- (IV) or -B-N-acetylhydroxylamino-a-hydroxy-*n*-propylbenzene and 5% KOH-aq. MeOH (1:1) at room temp. (2-3 weeks) and from (III) and (II). The nitrone, m.p. 179°, corresponding with (III) is similarly obtained. The reactions involved are :  $OH \cdot CHAr \cdot CHMe \cdot NRAc$  (R=H or OH)  $\rightarrow KOAc +$ OH-CHAr-CHMe-NHR or  $\rightarrow$  NHEtAc+ (V) ArCHO;  $(V) \rightarrow NHEt_2 + ArCHO;$ ArCHO+(V) $\rightarrow$  (I) and (III) or their nitrones. R. S. C.

Use of the  $\psi$ -nitrosites of propenylphenol ethers for the synthesis of β-hydroxylamino- and β-amino-*α*-arylpropanols. Wandering of acyl groups. Methylisoeugenol and isosafrole deriva-tives. V. BRUCKNER and (in part) V. KARDOS (Annalen, 1935, 518, 226–244). Methylisoeugenol- $\psi$ -nitrosite (improved prep. in 75% yield) is converted by Ac<sub>2</sub>Oconc.  $H_{0}SO_{4}$  into  $\beta$ -nitro- $\alpha$ -3: 4-dimethoxyphenylpropyl acetate (I), m.p. 98°, hydrolysed (dil. KOH-EtOH) to  $C_6H_3(OMe)_2$ ·CH:CMe·NO<sub>2</sub>. Electrolytic reduction (conditions prescribed) of (I) affords (III) (below) and  $\beta$ -acetamido- $\alpha$ -3: 4-dimethoxyphenylpropan- $\alpha$ -ol (II), m.p. 130-131° (additive compound with CHCl<sub>3</sub> and with  $C_6H_6$ ), the structure of which is proved by its conversion by POCl<sub>3</sub> in boiling CHCl<sub>3</sub> into 6:7-di-methoxy-1:3-dimethylisoquinoline, m.p. 121.5°. The formation of (II) involves Ac migration from O to N. The reverse migration (N to O) also occurs since (II) with 4.66% MeOH-HCl affords the hydrochloride, m.p. 174—175° (decomp.), of  $\beta$ -amino- $\alpha$ -3:4-dimethoxy phenylpropyl acetate [reconverted by basification into (II)], and, by refluxing with 1% MeOH-HCl, is converted into the hydrochloride, m.p. 184° (decomp.), of  $\beta$ -amino- $\alpha$ -3: 4-dimethoxyphenylpropan- $\alpha$ -ol (Bz derivative of Me ether, m.p. 121°). Under different conditions in the electrolytic reduction of (I) the main product is the N-Ac derivative (III), m.p. 176° (decomp.), of  $\beta$ -hydroxylamino- $\alpha$ -3: 4-dimethoxyphenylpropan-a-ol (also formed by Ac migration from O to N), converted by N-MeOH-HCl at room temp. into the hydrochloride, m.p. 138°, of  $\beta$ -hydroxylamino- $\alpha$ -3:4-dimethoxyphenylpropyl acetate [converted by 40% CH<sub>2</sub>O into the methylene nitrone, m.p. 197° (decomp.)], reconverted into (III) by aq.  $Na_2CO_3$ . Similar derivatives are prepared from *iso*safrole- $\psi$ nitrosite. This with  $Ac_2O-H_2SO_4$  gives  $\beta$ -nitro- $\alpha$ -3: 4-methylenedioxyphenylpropyl acetate (IV), m.p. 85°, hydrolysed to  $\beta$ -nitroisosafrole, reduced electrolytically to the hydrochloride, m.p.  $188^{\circ}$ , of  $\beta$ -amino- $\alpha$ -3:4-methylenedioxyphenylpropane. Electrolytic reduction of (IV) affords the N-Ac derivative (V), m.p. 162°, of  $\beta$ -hydroxylamino- $\alpha$ -3: 4-methylenedioxyphenylpropan-a-ol [converted by HCl-MeOH into the hydrochloride, m.p. 159°, of  $\beta$ -hydroxylamino- $\alpha$ -3 : 4-methylenedioxyphenylpropyl acetate (methylene nitrone, m.p. 218°), which is reconverted into (V) by NaOH], and  $\beta$ -acetamido -  $\alpha$  - 3 : 4 - methylenedioxyphenylpropan -  $\alpha$  - ol (VI), m.p. 124°, converted by MeOH-HCl into the hydrochloride, m.p. 176°, of the isomeric O-Ac deriv-ative (reconverted by NaOH). (VI) with POCl<sub>3</sub>-CHCl3 affords 6:7-methylenedioxy-1:3-dimethylisoquinoline, m.p. 147°. (VI) is hydrolysed (10%  $H_2SO_4$ ) to the corresponding  $\beta$ - $NH_2$ -compound, m.p. 96.5° [hydrochloride, m.p. 195—196° (decomp.)]. J. W. B.

Amino-alcohols. X. Ring-substituted propadrines. W. H. HARTUNG, H. C. MUNCH, and F. S. CROSSLEY (J. Amer. Chem. Soc., 1935, 57, 1091– 1093; cf. A., 1933, 746).—Five ephedrine analogues are less useful than ephedrine. The relation of structure to pharmacological activity in this group is discussed. The following Et ketones are prepared: (a) from MgEtBr and the nitrile: *m*-tolyl (76.6%), b.p. 134—135°/30—33 mm. (semicarbazone, m.p. 172°);  $\alpha$ - (68%), b.p. 166—169°/8 mm., and  $\beta$ -C<sub>10</sub>H<sub>7</sub>

(67%), b.p. 180—190°/8—10 mm., m.p. 56° (oxime, m.p. 133—133·5°; semicarbazone, m.p. 199°); (b) from EtCOCI: p-C<sub>6</sub>H<sub>4</sub>Cl (81%), b.p. 115°/3 mm.; p-C<sub>6</sub>H<sub>4</sub>Ph (90%), m.p. 102° (oxime, m.p. 162°). These give oximino-derivatives, m.p. 69·5—70°, 130°, 157°, 122—123° (gives the dioxime, m.p. 217° after decomp. from 208°), and 180° (dioxime, m.p. 235°), respectively. Hydrogenation (Pd-black; EtOH-HCl) then affords the hydrochlorides, m.p. 147°, 267° (uncorr.), 230—231°, 245°, and 228° (decomp.), respectively, of the corresponding  $\beta$ -amino-a-aryl-n-propyl alcohols. By analogy with ephedrine the following names are proposed : OH·CHPh·CHR·NH<sub>2</sub> alkaldrine;

Phenanthrene series. VIII. Amino-alcohols 1:2:3:4:5:6:7:8-octaderived from hydrophenanthrene. J. VAN DE KAMP and E. MOSETTIG (J. Amer. Chem. Soc., 1935, 57, 1107-1110; cf. A., 1934, 1104).—β-Amino-α-hydroxyderivatives are made for pharmacological examination. 1:2:3:4:5:6:7:8-Octahydrophenanthrene (prep. by H<sub>2</sub>-Raney Ni at 120°/1600-2100 lb.; 70-85% yield), b.p. 179-180°/20 mm., cryst., gives (Friedel-Crafts;  $-15^{\circ}$ ; CS<sub>2</sub>) good yields of the 9-CO·CH<sub>2</sub>Cl (I), -CO<sub>2</sub>H (II), m.p. 241-242° (*Me* ester, m.p. 45°), -*Ac* (III), m.p. 58-59° (*oxime*, m.p. 158·5-159·5°; *semicarbazone*, m.p. 191·5-193°), and -*COEt* (IV) derivatives, m.p. 52·5-53° (*oxime*, m.p. 146-147°). (I) does not react smoothly with sec. bases. The position 9 of the substituent is proved by prep. of (II) by hydrogenation of phenanthrene-9-carboxylic acid. (III) and (IV) give oximino-derivatives, reduced by SnCl<sub>2</sub> to 9-glycyl- [hydrochloride, m.p. 232-234° (decomp. from 225°); picrate, m.p. 215-216° (decomp.)] and 9-a-amino-propionyl-1:2:3:4:5:6:7:8-octahydrophenanthrene [hydrochloride, m.p. 231-233° (decomp.); picrate, m.p. 181-182° (decomp.)], and with Br afford the 9-CO·CH<sub>2</sub>Br, m.p. 55-56° (does not react with NH<sub>2</sub>Me or NH<sub>2</sub>Et), and 9-CO·CHBrMe derivative, an oil. These yield the following

1:2:3:4:5:6:7:8-octahydrophenanthrene derivatives by condensation with the appropriate base and/ or hydrogenation (PtO<sub>2</sub>; best in EtOH-HCl): 9dimethylamino- [hydrochloride, m.p. 236-237.5° (decomp.) after sintering at 226°; picrate, m.p. 116-117°], -diethylamino- (perchlorate, m.p. 165–166°; picrate, m.p. 144.5—145.5°), and -piperidino-acetyl-(perchlorate, m.p. 220.5—222°; picrate, m.p. 116.5— 117°). 117°); 9-α-dimethylamino- [perchlorate, m.p. 198.5— 200°; picrate, m.p. 185—186° (decomp.) after sintering at 180°], -diethylamino- (perchlorate, m.p. 209-210°), -piperidino- (hydrochloride, m.p. 181-182°), -methylamino-, an oil [hydrochloride, m.p. 223-224.5°; picrate, m.p. 192-193° (decomp.) after sintering at 189°], and -ethylamino-propionyl-, an oil (hydrochloride, m.p. 226—228°; picrate, m.p. 163—164°); 9-β-amino-, m.p. 103—104° [hydrochloride, m.p. 253·5—254°; picrate, m.p. 208.5-209.5° (decomp.)], -dimethylamino-, m.p. 80-80.5° (hydrochloride, m.p. 217-218°; picrate, m.p. 193-194°), -diethylamino-, m.p. 72.5-73° (hydrochloride, m.p. 148-149°; picrate, m.p. 159-160°), and -piperidino-a-hydroxyethyl-, m.p. 86-86.5° (hydrochloride, m.p. 227-227.5°; picrate, m.p. 164.5-165.5°);

9-β-amino-, m.p.  $164-165 \cdot 5^{\circ}$  [hydrochloride, m.p. 278-279°; picrate, m.p.  $224-224 \cdot 5^{\circ}$  (decomp.) after sintering at 223°], -dimethylamino-, an oil (hydrochloride, m.p. 227-228°; picrate, m.p.  $174-174 \cdot 5^{\circ}$ ), -diethylamino-, an oil (hydrochloride, m.p. 210-211°), -piperidino-, m.p.  $126 \cdot 5-127 \cdot 5^{\circ}$  (hydrochloride, m.p. 235-236°), -methylamino-, m.p.  $129 \cdot 5-130^{\circ}$  (hydrochloride, m.p. 218-219°; picrate, m.p.  $179-180^{\circ}$ ), and -ethylamino- $\alpha$ -hydroxy-n-propyl-, m.p.  $124 \cdot 5-125^{\circ}$  (hydrochloride, m.p.  $118-119^{\circ}$ ). R. S. C.

Pinacol-pinacolone rearrangement. VII. Rearrangement of 9:10-diaryldihydrophenanthrenediols. W. E. BACHMANN and (MISS) J. H. Сни (J. Amer. Chem. Soc., 1935, 57, 1095-1098; сf. A., 1934, 1355).—Six 9: 10-dihydroxy-9: 10-dihydro-9:10-diarylphenanthrenes are prepared (a) from phenanthrenequinone by the Grignard reaction and (b) by Na-Hg reduction of 2 : 2-diacyldiphenyls (prep. from o-C<sub>6</sub>H<sub>4</sub>Br aryl ketones and Cu at 200–250°). In each case (a) and (b) give stereoisometric pairs of compounds, both of which with I-AcOH lose H<sub>2</sub>O to form the same 10-keto-9:9-diaryl compound, exclusively, which with KOH at 200-300° gives 2-diarylmethyldiphenyl-2-carboxylic acids. The reverse of reaction (b) is effected by CrO3-AcOH. The following are 9:10-Dihydroxy-9:10-dihydro-9:10-didescribed. arylphenanthrenes, m.p. referring to the products of aryiphenanthrenes, m.p. reterring to the products of reactions (a) and (b), respectively : phenetyl- (I), m.p.  $140.5-141^{\circ}$ ,  $155.5^{\circ}$ ,  $\alpha \cdot C_{10}H_{7^{\circ}}$  (II), m.p.  $263-264^{\circ}$ ,  $204-204.5^{\circ}$ ,  $p \cdot C_{6}H_{4}Ph$ - (III), m.p.  $192-192.5^{\circ}$ ,  $159-160^{\circ}$ ,  $p \cdot C_{6}H_{4}Ph$ - (III), m.p.  $187-188^{\circ}$ ,  $223^{\circ}$ ,  $p \cdot C_{6}H_{4}F$ - (V), m.p.  $180-181.5^{\circ}$ ,  $210-211^{\circ}$ , and  $m \cdot C_{6}H_{4}Me$ - (VI), m.p.  $148.5-149^{\circ}$ , an oil. 9:9- $Diarylphenanthr-9-ones : (I), m.p. <math>136-137^{\circ}$ , (II), m.p.  $258.5-259^{\circ}$ , (III), m.p.  $253-253.5^{\circ}$ , (IV), m.p.  $138-139^{\circ}$ , (V), m.p.  $170-170.5^{\circ}$ , (VI), m.p.  $197-170.5^{\circ}$ , 138-139°, (V), m.p. 170-170.5°, (VI), m.p. 197-138–139, (V), fil.p. 170–170.9, (V1), fil.p. 177– 198°. 2-Diarylmethyldiphenyl-2'-carboxylic acids: (I), m.p. 97–98°, (II), m.p. 215°, (III), m.p. 197–198°, (IV), m.p. 205–206°, (V), m.p. 162°, (VI), m.p. 90°. o- $C_6H_4Br$  m-tolyl, m.p. 54·4°, b.p. 180–181°/5 mm., p- $C_6H_4Cl$ , m.p. 81°, p- $C_6H_4Ph$ , m.p. 90°5–91°, p- $C_6H_4Cl$ , m.p. 81°, p- $C_6H_4Ph$ , m.p. 49·5–91°, and  $\alpha$ - $C_{10}H_7$ , m.p. 87°, ketones. 2: 2'-Diacyldiphenyls: m- $CH_MeCQ$  m.p. 105–106° n- $OEtrC_2H_2CQ$  m.p. m- $C_6H_4Me^{\circ}CO$ , m.p. 105—106°, p- $OEt^{\circ}C_6H_4^{\circ}CO$ , m.p. 137—138°,  $\alpha \cdot C_{10}H_7^{\circ}CO$ , m.p. 200°, p- $C_6H_4Ph^{\circ}CO$ , m.p. 2095—210°, p- $C_6H_4Cl^{\circ}CO$ , m.p. 139—140°, p-C.H.F.CO, m.p. 136.5-137.5°. R. S. C.

Heteropolarity. XXV. Constitution and colour. W. DILTHEY and R. WIZINGER (Ber., 1935, 68, [B], 1037—1040).—In reply to Hantzsch *et al.* (A., 1933, 1158) it is pointed out that the absorption spectra of aminated CHPh<sub>3</sub> dyes do not afford any experimental evidence of the new views of the action of auxochromes or of the presence of special conjugated systems. H. W.

Magenta series. I. Preparation and spectrography of the lower basic members. J. T. SCANLAN (J. Amer. Chem. Soc., 1935, 57, 887— 892).—The following names are given: 4:4'diaminofuchsonimonium chloride, magenta O; its 3-Me, 3:3'-Me<sub>2</sub>, and 3:3':3''-Me<sub>3</sub> derivatives magenta I, II, and III, respectively [termed below (0), (I), (II), and (III), respectively]. The "old" (Coupier) process (modified) gives these products in a nearly pure form when the amines and nitrocompound are properly selected. The "new" (CH<sub>2</sub>O) process gives anomalous results, as the 4:4'-diaminodiphenylmethane derivative apparently reacts by oxidation to the benzhydrol and fission to the aldehyde and hydrocarbon, thus providing only I Ph of the product. In accordance with this mechanism CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>·p)<sub>2</sub> (IV) with NH<sub>2</sub>Ph, HCl, PhNO<sub>2</sub>, and FeCl<sub>2</sub> gives (0) and with o-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> and o-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub> mainly (II), whilst the 3:3'-Me<sub>2</sub> derivative of (IV) with NH<sub>2</sub>Ph and PhNO<sub>2</sub> gives mainly (I) and with o-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> and o-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub> gives (III). (0), (I), (II), and (III) are characterised by absorption spectra. R. S. C.

Surface films of sterols and their derivatives. N. K. ADAM, F. A. ASKEW, and J. F. DANIELLI (Biochem. J., 1935, 29, 1786-1801; cf. A., 1934, 1067).—Surface pressure and potential measurements of sterols and their derivatives confirm the generally accepted view of sterol constitution; differentiation between epi and normal configuration is sometimes possible. Sterols with OH at position 3 and with > one double linking stand practically vertical in the surface and occupy an area of 37-44 sq. A. Tilting is produced by CO in the 3 and, to a great extent, CO or OH in the 6 or 7 position. Factors involved in tilting include H2O-attraction and position in ring of the groups. apoCholic acids form gaseous films with flat-lying mols. F. O. H.

Synthesis of the carbon skeleton present in sterols etc. P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 95—107).—Theoretically possible methods are outlined. R. S. C.

 $\Delta^3$ -Tetrahydro-*p*-toluic acid. E. LEHMANN and W. PAASCHE (Ber., 1935, 68, [B], 1068-1072).-The product of the condensation of isoprene and acraldehyde is identified as  $\Delta^3$ -tetrahydro-p-tolualdehyde, since it is oxidised by CrO<sub>3</sub> in AcOH or by Ag<sub>2</sub>O in 50% EtOH to ∆3-tetrahydro-p-toluic acid (I), m.p. 99°, also obtained from isoprene and acrylic acid and dehydrogenated by Se at 270° to p-C6H4Me CO2H. (I) yields an Et ester, b.p. 105-108°/12 mm., and chloride, b.p. 90°/19 mm., which yields the amide, m.p. 182°, and sec.-amide, m.p. 203°. 4(3)-Hydroxy-3(4)-methylcyclohexanecarboxylactone, m.p. 69°, converted by boiling 15% NaOH into 4(3)-hydroxy-3(4)were de by bohing 13% NaOH into 4(3)-hydroxy-3(4)-methyleyclohexane-1-carboxylic acid, m.p. 156°, is obtained as by-product in the prep. of (I). Addition of Cl<sub>2</sub> to (I) in CCl<sub>4</sub> at 0° is accompanied by evolution of HCl and formation of 3-chloro- $\Delta^{3(4)}$ -tetrahydro-p-tolwic acid, m.p. 121°. Br and (I) in CCl<sub>4</sub> afford 3:4-dibromohexahydro-p-tolwic acid, m.p. 108° (Me, h p. 136-137°/4 mm and Et h p. 128°/0.8 mm b.p. 136—137°/4 mm., and Et, b.p. 128°/0.8 mm., esters), converted by CH<sub>2</sub>Br·CO<sub>2</sub>Me and Cu powder at 180° into  $Me_2 2: 2'$ -dimethyl- $\Delta^{1:1'(2:2')}$ -octahydrodiphenyl-5:5'-dicarboxylate, b.p. 164-165°/1.5 mm. (corresponding acid, m.p. 227°). H. W.

Derivatives of  $\alpha\alpha$ -dibenzamidopropionic acid. B. H. NICOLET (J. Amer. Chem. Soc., 1935, 57, 1073).—AcCO<sub>2</sub>H and NH<sub>2</sub>Bz at 110—120°/20—30 mm.give  $\alpha\alpha$ -dibenzamidopropionic acid, m.p. 181—186° (decomp.) [*Et* ester, m.p. 132—133°; amide, m.p. 212—213° (slight decomp.), stable to hot Ac<sub>2</sub>O], converted by hot AcOH into  $\alpha$ -benzamidoacrylic acid, m.p. 137–138°, and by hot Ac<sub>2</sub>O into the azlactone, m.p. 203–205°, which with glycine gives  $\alpha\alpha$ -dibenzamidopropionylglycine, m.p. 197° (decomp.). R. S. C.

Catalytic action of platinum and manganese dioxide on benzoyl peroxide and perbenzoic acid. —See this vol., 941.

Ring-systems with para-linkings. II. G. HELLER and R. EBELING (J. pr. Chem., 1935, [ii], 142, 274—276; cf. A., 1926, 286).—p-Nitrobenzhydrazide (modified prep.) gives Et acetoacetate-pnitrobenzoylhydrazone, m.p. 115°, which at 170— 175° yields s-di-p-nitrobenzoylhydrazine, m.p. 283°, reduced (Zn dust and HCl-AcOH) to the di-p-aminocompound, m.p. 303—304° ( $Ac_2$  derivative, m.p. 335°), identical with the compound previously considered to be p-benzisopyrazolone. R. S. C.

M.p. of sulphosalicylic acid. HORKHEIMER (Pharm. Ztg., 1935, 80, 660).—Sulphosalicylic acid (I) is usually stated to have m.p.  $108-113^{\circ}$ . If a finely-powdered sample is kept for 24 hr. over  $H_2SO_4$  in a desiccator and the m.p. determined immediately it is opened, figures as high as 200° are obtained. Keeping for a few min. in the open allows sufficient  $H_2O$  to be absorbed to give results about  $108-113^{\circ}$ . The divergence is not due to loss of  $H_2O$  of crystallisation. C. I.

Stereochemical studies. V. Optical isomerism of  $\alpha$ -phenylsulphinylphenylacetic acids. W. PIECHULEK and J. SUSZKO (Rocz. Chem., 1935, 15, 221-233).-Racemic SPh·CHPh·CO<sub>2</sub>H (I), m.p. 103–104°, and brucine yield a salt (II),  $+C_6H_6$ , m.p. 97° (decomp.),  $[\alpha]_D +55°$ , from which the d-acid (III), m.p. 129–130°,  $[\alpha]_D^{18} +216°$ , is regenerated; cinchonidine (IV) and dl-(I) yield a mixture of d- and l-salt (chiefly d-), from which pure (III) is obtained by hydrolysis and fractional crystallisation. The salt obtained from (III) and (IV) has m.p. 176–178° (decomp.),  $[\alpha]_{D}^{19}$  +38.6°. The acid (V) regenerated from the mother-liquors from (II) has m.p. 129-130°,  $[\alpha]_{\rm D}^{*0} = -215 \cdot 6^{\circ}$ ; a 1 : 1 mixture of (III) and (V) has m.p. 103-104°. (V) and *l*-menthylamine afford a salt, m.p. 157-158°,  $[\alpha]_{\rm D}^{20} = -170 \cdot 2^{\circ}$ . (III) yields PhSO·CHPh·CO<sub>2</sub>H (VI), m.p. 149-150°, [α]<sup>20</sup>+419.4°, when treated with H2O2 in AcOH; the filtrate contains PhSO·CHPh·CO<sub>2</sub>H, m.p. 139° (decomp.), [a]<sup>20</sup> tails 1 not offit  $(-)_{s}$ ,  $(-)_{c}$ , m.p. 135 (decomp.),  $[\alpha]_{p}^{p_{0}}$  $+195^{\circ}$ . The  $(-)_{s}$ ,  $(-)_{c}$ , m.p. 148—149° (decomp.),  $[\alpha]_{p}^{p_{0}}$   $-420.4^{\circ}$ , and  $(+)_{s}$ ,  $(-)_{c}$ , m.p. 139° (decomp.),  $[\alpha]_{p}^{p_{0}}$   $-191.2^{\circ}$ , acids are obtained analogously from (V). 1:1 Mixtures of the  $(-)_{s}$ ,  $(-)_{c}$ , and  $(-)_{s}$ ,  $(+)_{c}$ acids, and of the  $(+)_{s}$ , $(-)_{c}$  and  $(+)_{s}$ , $(+)_{c}$ -acids have m.p. 135—137°,  $[\alpha]_{\rm D} \pm 116°$ . (III), on pro-tracted treatment with  $\rm H_2O_2$  in AcOH, affords PhSO<sub>2</sub>·CHPh·CO<sub>2</sub>H, m.p. 180—187° (decomp.),  $[\alpha]_{\rm P}^{19}$  $+107.6^{\circ}$  (both diminished on repeated crystallisation), which represents a mixture of unstable optical isomerides. The above findings for the diastereomerides of (VI) are in agreement with the principle of optical superposition. All vals. of  $[\alpha]$  are in 1:1 R. T. EtOH-CHCl<sub>3</sub>.

cis-Cinnamic acids.—See this vol., 916.

Modes of addition to conjugated unsaturated systems. VIII. Reduction of a-vinylcinnamic acid. C. K. INGOLD and M. A. T. ROGERS (J.C.S., 1935, 717-721).-Reduction of a-vinylcinnamic acid (I) by Na-Hg in alkaline and acid solution and by Al-Hg in neutral solution affords a mixture of  $\alpha$ benzylcrotonic acid (II) and varying amounts of a liquid product (III), b.p. 119-122°/2 mm., 174°/19 mm., shown, contrary to the conclusions of Kuhn et al. (A., 1932, 739), to be essentially  $\beta$ -phenyl- $\alpha$ vinylpropionic acid, the theoretically expected product (A., 1929, 1270). This result was established by ozonolytic degradation by the methods of Burton and Ingold (A., 1929, 1270) and Fischer et al. (A., 1932, 1113). (III), however, is converted quantitatively into (II) by 2N-NaOH at 100° during 15 min., or at room temp. during a longer time. Et benzylmalonate with K in Et<sub>2</sub>O and dibromoethylene afford Et benzyl-β-bromovinylmalonate, b.p. 130-140°/0.05-0.07 mm., reduced by Zn-EtOH to ethyl benzylvinylmalonate, b.p. 100-110°/0.14 mm. (cf. A., 1933, 51). This on hydrolysis by KOH– EtOH, NaOH–EtOH–H<sub>2</sub>O, and HCl–AcOH gave only (II). Et  $\alpha$ -vinylcinnamate, b.p. 106–108°/1 mm. [obtained from the Ag salt of (I) and EtI], affords on reduction (Al-Hg in moist ether) a  $H_2$ -derivative, b.p. 134—144°/13—14 mm. Reduction of a-styrylcinnamic acid by Na-Hg in EtOH-AcOH (cf. A., 1899, i, 614) and in NaOH-H<sub>2</sub>O affords  $\beta$ -phenyl- $\alpha$ -styrylpropionic acid, unchanged when refluxed with 5N aq. NaOH during 2 hr.

The theory of Burton and Ingold is in agreement with all the known facts. It cannot, however, be applied to the reduction of  $\beta$ -phenylsorbic acid (Å., 1933, 1159), as this case is too complicated (cf. A., 1929, 1270). Contrary to the views of Kuhn *et al.* (Å., 1933, 1159), the theory readily accommodates the occurrence of pinacol-like reduction and the known effects of the purity of amalgams. Further, it can be linked to current views on over-potential.

H.G.M.

Synthesis of hydrogenated derivatives of phenanthrene and of phenanthrenic hydrocarbons. G. DARZENS and A. LÉVY (Compt. rend., 1935, 200, 2187—2189).— $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>Cl (modified prep.) gives Et<sub>2</sub> 1-naphthylmethylmalonate, m.p. 32° (lit. an oil), and thence Et<sub>2</sub> 1-naphthylmethylallylmalonate ( $\alpha$ -1naphthyl- $\Delta^3$ -pentene- $\beta\beta$ -dicarboxylate), m.p. 28°, b.p. 209°/2 mm., which yields the corresponding acid, an oil, decomp. at about 185—190° into  $\alpha$ -1-naphthylmethyl- $\Delta^{\gamma}$ -pentenoic acid, m.p. 73·5°. With H<sub>2</sub>SO<sub>4</sub>-AcOH (1:1) at 50° this gives the lactone, m.p. 98°, and 1-methyl-1:2:3:4-tetrahydrophenanthrene-2carboxylic acid, m.p. 157°, converted by S at 265° into 1-methylphenanthrene. Yields are excellent. R. S. C.

Synthesis of pinononic acid. P. C. GUHA and K. GANAPATHI (Current Sci., 1935, 3, 484—485). trans-Norpinic acid (A., 1929, 445) with Ac<sub>2</sub>O at 190—200° gives the *cis*-anhydride, which with NaOMe-MeOH (equimol. amount) affords Me H cis-norpinate; *cis*-norpinyl chloride with ZnMeI is converted into Me<sub>2</sub> pinononate, b.p. 130—135°/14 mm., hydrolysed to pinononic acid (cf. A., 1913, i, 495). J. L. D. **2-Iodo-3-hydroxybenzoic acid.** T. A. HENRY and T. M. SHARP (J.C.S., 1935, 856-857).—The compound, m.p. 133° (J.C.S., 1922, 121, 1059, m.p. incorrectly given there as 233°), obtained by the oxidation of 2-iodo-3-hydroxybenzaldehyde (I) (cf. A., 1924, i, 738) in COMe<sub>2</sub> with KMnO<sub>4</sub> is impure (I). Oxidation of the Ac derivative of (I) in COMe<sub>2</sub> with KMnO<sub>4</sub> affords 2-iodo-3-acetoxybenzoic acid, m.p. 179-180° (corr.), from which the desired 2-iodo-3-hydroxybenzoic acid, m.p. 158-159° (corr.), is obtained by hydrolysis. H. G. M.

Action of thionyl chloride on phenylglycollic acid. P. CARRÉ and D. LIBERMANN (Bull. Soc. chim., 1935, [v], 2, 1166—1168).—OH·CHPh·CO<sub>2</sub>H (I) and  $SOCl_2$  (1·2 mols.) in Et<sub>2</sub>O at room temp. give CHPhCl·COCl and the sulphite anhydride,

O < CHPh > CO, which decomposes at 29-30° into PhCHO, SO<sub>2</sub>, and CO, or with H<sub>2</sub>O or EtOH affords SO<sub>2</sub> and (I) or its Et ester, respectively. Explanations in the lit. are fallacious. CHPhCl<sub>2</sub> arises by reaction of PhCHO with excess of SOCl<sub>2</sub>. OH·CPh<sub>2</sub>·CO<sub>2</sub>H and SOCl<sub>2</sub> (3 mols.) in CCl<sub>4</sub> at room temp. give an excellent yield of CPh.Cl·CO<sub>2</sub>H and a

temp. give an excellent yield of  $CPh_2Cl \cdot CO_2H$  and a little  $COPh_2$ , probably formed from a sulphite anhydride (cf. lit.). R. S. C.

Phenylpyruvic acid; product of its condensation with phenylacetonitrile. P. CORDIER (Compt. rend., 1935, 200, 1412—1413).—In EtOH-H<sub>2</sub>O containing KOH or, preferably,  $K_2CO_3$ ,  $CH_2Ph\cdot CO\cdot CO_2H$ and  $CH_2Ph\cdot CN$  afford  $\alpha$ -hydroxy- $\beta$ -phenyl- $\alpha$ - $\alpha$ '-cyanobenzylpropionic acid, slow decomp. > 160°, which decomposes into its components in presence of conc. alkali, and is transformed by AcOH at 100° into  $\beta$ -phenyl- $\alpha$ -benzylmaleic anhydride, m.p. 76°, converted by KOH and MeI into its  $Me_2$  ester, m.p. 68°. H. W.

Addition of mercaptans to ethylenic linkings. B. H. NICOLET (J. Amer. Chem. Soc., 1935, 57, 1098—1099).— $\alpha\beta$ -Unsaturated kctones, in which the C:C linking is reactive, condense with mercaptans without addition of alkali. CHPh:CH·COPh (I) at 100° thus yields in 5 min.  $\beta$ -benzyl-, m.p. 71°, and -p-tolyl-thiol- $\beta$ -phenylpropiophenone. CHPh:CH·CO·CO<sub>2</sub>H in 10 min. gives  $\alpha$ -keto- $\gamma$ -p-tolyl-, m.p. 97—98° (oxime, m.p. 160°), and -benzylthiol- $\gamma$ -phenylbutyric acid, an oil (oxime, m.p. 95—97°). CHPh:CH·CO<sub>2</sub>Me with (not without) a little piperidine gives (2 hr.) Me  $\beta$ -p-tolyl-, m.p. 59—60°, and -benzyl-thiol- $\beta$ -phenylpropionate, m.p. 119—120°. H<sub>2</sub>S adds to such ketones in EtOH in presence of a little Na<sub>2</sub>CO<sub>3</sub> and to (I) in neutral EtOH. R. S. C.

Asymmetric syntheses. XII. Asymmetric synthesis of phenyl-p-tolylglycollic and p-tolylmethylglycollic acids. A. McKENZIE and E. W. CHRISTIE (Biochem. Z., 1935, 277, 426–436).—The prep. is described of (-)menthyl p-toluoylformate (I),  $C_{19}H_{26}O_3$ , an oil, b.p. 217—220°/11 mm.,  $n_D^{15}$  1·5069, and of (-)bornyl p-toluoylformate (II),  $C_{19}H_{24}O_3$ , an oil b.p. 215—217°/10 mm.,  $n_D$  1·5195, and the mutarotation of these compounds examined. (I) with MgPhBr gave an acid, m.p. 128—130°,  $[\alpha]_{20}^{20}H_1 + 1°$ . *d*-Phenyl-p-tolylglycollic acid, prepared by resolution with quinine of the r-acid, has  $[\alpha]_{20}^{20}H_2 + 2\cdot 5°$  and m.p. 125—127°, whereas the r-acid has m.p. 133— 134°. (I) with MgMeI gave (-)p-tolylmethylglycollic acid, m.p. 139—142°,  $[\alpha]_{5,61}^{20}$ —47° in EtOH, which is practically optically pure, since the corresponding acid (by resolution with quinine of the r-acid) has m.p. 140—142°,  $[\alpha]_{5,61}^{20}$ —51°. (II) with MgMeI gave r-p-tolyltrimethylethylene glycol, m.p. 79·5—80·5°, together with r-p-tolylmethylglycollic acid, m.p. 102—104°. P. W. C.

β-3-Hydroxycholanic acid. F. REINDEL and K. NIEDERLÄNDER (Ber., 1935, 68, [B], 1243— 1246).—Lithocholic [α-3-hydroxycholanic] acid (I) is oxidised by CrO<sub>3</sub> to dehydrolithocholic acid (II) [semicarbazone, m.p. 231—232° (decomp.)], which is hydrogenated (PtO<sub>2</sub>) in acid solution to β-3-hydroxycholanic acid (III), leaflets (+1H<sub>2</sub>O) or anhyd. needles, m.p. 176—177°,  $[\alpha]_{\rm D}$  +25·83° in abs. EtOH [Me ester (III), m.p. 113—114·5°; Ac derivative, m.p. 183—185°]. The main product of the hydrogenation of (II) in alkaline medium is (I). (III) is partly isomerised to (I) by NaOEt at 180°. (III) and (IV) give ppts. with digitonin in 90% EtOH; these are more freely sol. than the digitonides of the sterols and do not appear in 95% EtOH. H. W.

Optical properties of some bile acids. B. JOSEPHSON (Biochem. J., 1935, 29, 1484—1489).— Sp. rotations and rotatory dispersions are given for cholic (I), deoxycholic (II), glycocholic, and taurocholic acids and their alkali salts. (I) and (II) have  $[\alpha]_{1}^{\infty}$  $+35.07^{\circ}$  and  $55.56^{\circ}$  in EtOH, respectively. For the other acids the rotation is dependent on the concn. of the solution. The alkali salts of all the acids showed increasing  $\alpha_p$  with decreasing concn. J. N. A.

Constitution of caryophyllene. H. N. RYDON (Chem. and Ind., 1935, 557).—3:3-Dimethylcyclobutane-1:2-dicarboxylic and 3:3-dimethyl- $\Delta^1$ -cyclobutene-1:2-dicarboxylic acids, synthesised from  $\beta\beta$ dimethyladipic acid by the application of the method of Fuson and Kao (A., 1929, 794), show no depression of m.p. on admixture with racemic norearyophyllenic and with dehydronorcaryophyllenic acids, respectively. The structures assigned to the latter acids (this vol., 351, 489) are thus confirmed. H. N. R.

Orientation in the benzene ring. Preparation of 5-chloro- $\beta$ -resorcylic acid. R. B. SANDIN and R. A. MCKEE (J. Amer. Chem. Soc., 1935, 57, 1077— 1078).—5-Chloro- $\beta$ -resorcylic acid, dimorphic, m.p. 224—225° (corr.) (after several months, 211—213°), best identified by the *Ac* derivative, m.p. 169° (corr.), is obtained from 4-chlororesorcinol and KHCO<sub>3</sub> or from  $\beta$ -resorcylic acid and SO<sub>2</sub>Cl<sub>2</sub> or Cl<sub>2</sub> in AcOH (cf. lit.). R. S. C.

Homoamines and homoacids. P. L. JULIAN and B. M. STURGIS (J. Amer. Chem. Soc., 1935, 57, 1126—1128).—An improved prep. of rhodanine, m.p. 170°, renders practicable the large-scale prep. of arylacetonitriles and thence of aryl-ethylamines and -acetic acids from aromatic aldehydes. Veratrylidenerhodanine, m.p. 232°, with 15% NaOH at 100° gives  $\alpha$ -thio-3 : 4-dimethoxyphenylacetic acid.

gives  $\alpha$ -thio-3: 4-dimethoxyphenylacetic acid, CH<sub>2</sub>R·CS·CO<sub>2</sub>H, m.p. 179°, which with NH<sub>2</sub>OH-EtOH affords 3: 4-dimethoxyphenylpyruvic acid oxime, dehydrated by warm Ac<sub>2</sub>O to veratryl cyanide. All the yields are excellent. Piperonal and anisaldehyde give similar results. R. S. C.

Ketonic acid analogues with thyroxine. A. CANZANELLI, R. GUILD, and C. R. HARINGTON (Biochem. J., 1935, 29, 1617—1619).—The synthesis of 3:5-di-iodo-4-(3':5'-di-iodo-4'-hydroxyphenoxy)-

phenylpyruvic acid (I), the ketonic acid analogous with thyroxine, is described. The azlactone from acetylglycine and 3:5-di-iodo-4-(4'-methoxyphenoxy)benzaldehyde, m.p. 227° (decomp.), on boiling with 30% KOH and saturating with SO<sub>2</sub>, give 3:5di-iodo-4-(4'-methoxyphenoxy)phenylpyruvic acid, m.p. 205° (decomp.), dark green FeCl<sub>3</sub> colour in EtOH solution, demethylated with HI-AcOH to 3:5-diiodo-4-(4'-hydroxyphenoxy)phenylpyruvic acid, m.p. 156°, which with I-KI gave (I), m.p. 173°, intense reaction with HNO<sub>2</sub>+NH<sub>3</sub>. The ratio of the activities of thyroxine and of (I) on the metabolism of an adult female dog on const. maintenance diet was about 11:3. P. W. C.

Formation of unsymmetrical acid amides. B. H. NICOLET (J. Amer. Chem. Soc., 1935, 57, 1064– 1065).—An as-acid anhydride,  $X \cdot CO > O$ , may react with NH<sub>3</sub> first by addition, to yield

CO<sub>2</sub>H·Y·X·CO·NH<sub>2</sub>. If the imide,  $X \cdot CO_{Y}$  NH, reacts with NaOH first by addition at the same CO, it will yield the isomeric amide, NH<sub>2</sub>·CO·Y·X·CO<sub>2</sub>H. This is true for *d*-camphoric anhydride [gives mainly  $\alpha$ -amide (I)] and imide [gives very little (I)] and for the following cases. 3-Nitrophthalic anhydride and NH<sub>2</sub>Ph at room temp. give 3-nitrophthal-2-anilic acid, m.p. (+0·5H<sub>2</sub>O) 172°, (anhyd.) 154°, not identical with the 1-anilide, m.p. 181°, prepared from the phenylimide, which with NH<sub>3</sub> at 150° gives 3-nitrophthal-1-anilide-2-amide, m.p. 200—204° (decomp.). 3-Nitrophthalimide with NH<sub>2</sub>Ph at 100° gives the 2-anilide-1-amide, m.p. 228—230°. R. S. C.

Dipole moment and structure of organic compounds. XIV. Direction of the electric moment of the NiC group. A. WEISSBERGER and R. SANGE-WALD (J.C.S., 1935, 855).—The moment of p-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub> is indistinguishable from zero. The CN group therefore shows axial symmetry about the direction of the bond of attachment to the benzene ring. 4:4'-Dicyanodiphenyl is not sufficiently sol. in C<sub>6</sub>H<sub>6</sub> at 25° and in decalin at 70° to make a determination of the moment possible, but it is considered that the moment is zero and that the reported val. 1·1D (A., 1930, 399) is erroneous. H. G. M.

Modes of addition to conjugated unsaturated systems. VII. Addition of hydrogen cyanide and methyl malonate to methyl cinnamylidenemalonate. D. A. DUFF and C. K. INGOLD (J.C.S., 1934, 87—93).—Condensation of Et atropate with Et ethanetricarboxylate affords Et  $\delta$ -phenyl-n-butane- $\alpha\beta\beta\delta$ -tetracarboxylate, b.p. 165°/0.03 mm., hydrolysed and decarboxylated to  $\delta$ -phenyl-n-butane- $\alpha\beta\delta$ -tricarboxylic acid, m.p. 210—212°. Et benzylmalonate (I) with Et fumarate yields Et  $\delta$ -phenyl-n-butane- $\alpha\beta\gamma\gamma$ tetracarboxylate, b.p. 204—208°/0.09 mm., hydrolysed and decarboxylated to a  $\delta$ -phenyl-n-butane- $\alpha\beta\gamma\gamma$ tetracarboxylate, b.p. 204—208°/0.09 mm., hydrolysed and decarboxylated to a  $\delta$ -phenyl-n-butane- $\alpha\beta\gamma\gamma$ -tricarboxylic acid, m.p. 168°. (I) and Et bromosuccinate yield Et 8-phenyl-n-butane-abyy-tetracarboxylate, b.p. 184-186°/0.6 mm., hydrolysed and decarboxylated to a  $\delta$ -phenyl-n-butane- $\alpha\beta\gamma$ -tricarboxylic acid, m.p. 187-190° (decomp.) (Me3 ester, m.p. 60°; Me2 ester, m.p. 112°; anhydro-acid, m.p. 114°), identical with that obtained by hydrolysis of the additive product (II) from HCN and Me cinnamylidenemalonate (III). (II) is therefore Me  $\beta\gamma$ -dicyano- $\delta$ -phenyl-*n*-butane- $\alpha\alpha$ dicarboxylate, and not the  $\alpha\delta$ -dicyano-isomeride as supposed by Thiele and Meisenheimer (A., 1899, i, 603), initial  $\alpha\beta$ -addition being followed by prototropic change and subsequent  $\beta_{\gamma}$ -addition. The additive product of  $CH_2(CO_2Me)_2$  (IV) and (III) is hydrolysed to  $\beta$ -phenylisohexane-aze-tricarboxylic acid, m.p. 140°, esterified and the Me<sub>3</sub> ester, b.p.  $250^{\circ}/0.2$  mm., cyclised to the cyclic ketonic ester (V), m.p.  $139^{\circ}$ , described by Meerwein (A., 1908, i, 545), accompanied by a stereoisomeride, m.p. 64°, converted into (V) on keeping or on treatment with HCl-MeOH. (V), on hydrolysis, yields 3phenylcyclohexanone-5-acetic acid, m.p. 118-119°, reduced (Clemmensen) to 3-phenylcyclohexane-1-acetic acid (VI), m.p. 52—54°. Ét cyclopentanone-2-carboxylate, with  $CH_2PhCl$  in NaOEt-EtOH, affords Et  $\alpha$ -benzyladipate, b.p. 208°/16 mm., hydrolysed to  $\alpha$ -benzyladipic acid, m.p. 116—118°. With Ac<sub>2</sub>O this yields 2-benzylcyclopentanone (VII), b.p. 144-146°/16 mm. (semicarbazone, m.p. 198-200°). (VII) condenses (piperidine) with CN·CH<sub>2</sub>·CO<sub>2</sub>Et, yielding Et a-cyano-2-benzylcyclopentylidene-1-acetate, m.p. 81-83°, which cannot satisfactorily be hydrolysed; conc. H<sub>2</sub>SO<sub>4</sub> affords Et 2-sulphobenzylcyclopentylidene-1-malonamate, m.p. 120°. (VII), on reduction (Namoist Et<sub>2</sub>O), affords 2-benzylcyclopentanol, b.p. 154°/ 16 mm., converted by HBr-AcOH into 2-bromo-1benzylcyclopentane, b.p. 150-155°/15 mm. This with  $CH_2(CO_2Et)_2$  affords Et 2-benzylcyclopentane-1-malon-ate, b.p. 142–150°/1 mm., hydrolysed to 2-benzylcyclopentanemalonic acid, m.p. 137°, which, when heated, yields 2-benzylcyclopentaneacetic acid, m.p.  $53-54^{\circ}$ . 3-Phenylcyclohexanol, with HBr-AcOH, yields 3-bromo-1-phenylcyclohexane, b.p.  $126^{\circ}/0.5$  mm., which, with CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, affords Et 3-phenyl-cyclohexane-1-malonate, b.p.  $160-165^{\circ}/0.5$  mm. hydrolysed to 3-phenylcyclohexane-1-malonic acid, m.p. 166°, decarboxylated to (VI), m.p. and mixed m.p. 52°. The structures assigned by Meerwein (loc. cit.) are thus confirmed. It is considered that, in the addition of (IV) to (III), both  $\alpha\beta$ - and  $\alpha\delta$ -additive products are formed, but only the latter can undergo further addition; hence, although it is thermodynamically the less stable, the excess of (IV) continuously displaces the equilibrium in its favour.

H. N. R.

Michael reaction. I. Condensation of ethyl benzylmalonate with ethyl fumarate. H. N. RYDON (J.C.S., 1935, 420–425; cf. preceding abstract).—Condensation of Et bromosuccinate with Et benzylmalonate (I) affords Et  $\delta$ -phenyl-*n*-butane- $\alpha\beta\gamma\gamma$ tetracarboxylate (II), b.p. 203–209°/2·5 mm., which is hydrolysed and decarboxylated to a  $\delta$ -phenyl-*n*butane- $\alpha\beta\gamma$ -tricarboxylic acid (III), m.p. 190–191°. (II) does not contain H directly replaceable by Na, since attempted methylation in C<sub>6</sub>H<sub>6</sub> affords only decomp. products yielding, on hydrolysis, a mixture containing benzylmethylmalonic acid, identified by conversion into  $\beta$ -phenyl- $\alpha$ -methylpropionamide, m.p. 106°. (II) is readily methylated in EtOH, yielding Et  $\delta$ -phenyl- $\alpha$ -methyl-n-butane- $\alpha\alpha$ -trans- $\beta\gamma$ -tetracarboxylate (IV), b.p. 175—195°/1.5 mm., hydrolysed and decarboxylated to  $\delta$ -phenyl- $\alpha$ -methyl- $\alpha$ -trans- $\beta\gamma$ -tricarboxylic acid (V), m.p. 181—183°. (I) with Et fumarate (VI) affords Et  $\delta$ -phenyl-n-butane- $\alpha\alpha$ -trans- $\beta\gamma$ -tetracarboxylate (VII), b.p. 215—220°/1.5 mm., hydrolysed and decarboxylated to  $\delta$ -phenyl-n-butane- $\alpha$ -trans- $\beta\gamma$ tricarboxylic acid (VIII), m.p. 175°. (VII) differs from (II) in possessing a H directly replaceable by Na, since methylation proceeds readily in both C<sub>6</sub>H<sub>6</sub> and EtOH, yielding (IV). (III) and (VIII) are stereoisomeric, since, when heated, both yield  $\beta$ -carboxy- $\alpha$ benzylglutaric anhydride, m.p. 111—113°, reconverted into (VIII) by H<sub>2</sub>O. It is concluded that the condensation of (I) with (VI) proceeds mainly in accordance with Thorpe's mechanism (J.C.S., 1900, 77, 923). H. N. R.

Validity of Holden and Lapworth's theory of the mechanism of abnormal Michael additions. C. K. INGOLD and H. N. RYDON (J.C.S., 1935, 857— 858).—The observations of Rydon (see above) on the addition of Et fumarate to Et sodiobenzylmalonate are accommodated to Holden and Lapworth's theory (A., 1931, 1272), and do not require Michael's hypothesis for their explanation. When the steric relations between the CO<sub>2</sub>Et groups of  $CH_2Ph \cdot C(CO_2Et)_2 \cdot CH(CO_2Et) \cdot CH_2 \cdot CO_2Et$  (I), re-

 $CH_2Ph \cdot C(CO_2Et)_2 \cdot CH(CO_2Et) \cdot CH_2 \cdot CO_2Et$  (I), required as an intermediate compound by Holden and Lapworth's theory, and the no. of Walden inversions which occur in the subsequent transformation of (I) and in the direct hydrolysis of (I) are considered, it is possible to account for the formation of a product which hydrolyses to a stereoisomeride of the compound,  $CH_2Ph \cdot CH(CO_2H) \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$ , obtained directly by hydrolysis of (I). H. G. M.

Lichen substances. LII. Methanolysis of lichen depsides and synthesis of divaric acid. Y. ASAHINA and H. AKAGI. LIII. Synthesis of hydroxydivaricatic acid and of sekikaic acid. Y. ASAHINA and M. YASUE (Ber., 1935, 68, [B], 1130-1132, 1133-1137).-LII. Fission of depsides is conveniently effected by gentle warming with KOH-MeOH, the method being particularly suitable for those of the evernic acid type which afford free acids of the orsellinic variety and Me esters of the everninic acid class. Thus divaricatic acid affords divaric acid (I), m.p. 179° (decomp.) (Me ester, m.p. 78°), and Me divaricatate, hydrolysed to divaricatic acid, m.p. 151°. Similar methanolysis of sekikaic, evernic, and lecanoric acids is recorded, whilst for gyrophoric, barbatic, and obtusatic acids a somewhat

modified procedure is necessary. [With T. WAKE.] Divarin is transformed by  $Zn(CN)_2$  and HCl in Et<sub>2</sub>O followed by boiling H<sub>2</sub>O into divarinal dehyde, which with  $ClCO_2Me$  and N-NaOH gives dicarbomethoxy divarinal dehyde. The latter substance is oxidised by KMnO<sub>4</sub> to dicarbomethoxy divaric acid, hydrolysed to (I), m.p. 179°.

LIII. 2-Aldehydo-1-propylpyrogallol 3:5-Me<sub>2</sub> ether (II) and NH<sub>2</sub>Ph yield the corresponding and (III), m.p. 86—87°, slowly converted by warm MeI into the anil of 2-aldehydo-1-propylpyrogallol 5-Me ether (IV),

m.p. 135-136° [hydrolysed by HCl to NH<sub>2</sub>Ph,HCl and 2-aldehydo-1-propylpyrogallol 5-Me ether (V)  $(+0.5H_2O)$ , m.p. 98°, which re-forms (IV) with NH2Ph], and 3-hydroxy-2: 4-dimethoxy-6-propylbenzylideneaniline methiodide (VI), m.p. 163-165°, hydrolysed by dil. HCl to (II) and NHPhMe, HCl. Loss of Me in the Freund-Becker reaction is therefore not due to MeI, but to a trace of HI. Treatment of (III) with NH, Ph, HI in absence of MeI gives (IV) almost quantitatively, whilst (VI) yields (IV) when warmed with NH2Ph. Addition of ClCO2Et to (V) in  $C_5H_5N$  at  $-15^{\circ}$  affords 3:4-dicarbethoxy-2aldehydo-1-propylpyrogallol 5-Me ether, m.p. 67-68°, oxidised by  $KMnO_4$  in  $COMe_2$  to hydroxydicarbethoxy-divaricatic acid, m.p. anhyd. 124—125°, m.p. (+1H<sub>2</sub>O), 128—129°, hydrolysed by N-NH<sub>3</sub> to hydroxy-divaricatic acid, m.p. 163—164°. Carbethoxydivaricatic acid, m.p.  $101^{\circ}$ , from the acid and ClCO<sub>2</sub>Et in C<sub>5</sub>H<sub>5</sub>N at  $-15^{\circ}$ , is transformed by SOCl<sub>2</sub> into the corresponding chloride, which is converted by successive treatments with (V) and ClCO2Et in C5H5N into dicarbethoxysekika-aldehyde, m.p. 136-137°; oxidation of the latter with KMnO4 in COMe2 at 40-50° leads to dicarbethoxysekikaic acid, m.p. 147-148° (decomp.), hydrolysed to sekikaic acid, m.p. 143-144°, identical with the natural product. H. W.

#### Benzoin reaction.—See this vol., 938.

Mixed magnesium alcoholates, and their molecular compounds. II. Molecular compounds formed from magnesium alcoholate iodides, aldehydes, and certain diketones. III. Existence of equilibrium systems in ethereal solutions of magnesium alcoholate iodides. V. M. TOL-STOPJATOV (J. Gen. Chem. Russ., 1935, 5, 73–82, 83–93).—II [with B. N. SVERDLOVA]. Cryst. 1:1 and 1:2 compounds are obtained from PhCHO or CHPh:CH·CHO and OR·MgI (R=Et, Bu<sup>°</sup>, Bu<sup>°</sup>) in Et<sub>2</sub>O. OBu<sup>°</sup>·MgI and (PhCO·)<sub>2</sub> (I) afford a 1:1 compound.

IÎI [with A. T. RISKALTSCHUK]. OR·MgI (R=cetyl,  $\alpha$ - and  $\beta$ -octyl, Bu<sup>a</sup>, Pr) and COPh<sub>2</sub> in Et<sub>2</sub>O afford the compound MgI<sub>2</sub>,3COPh<sub>2</sub>, whilst with (I) mol. compounds of the above type are formed. It is concluded that the equilibrium 2OR·MgI = Mg(OR)<sub>2</sub>+MgI<sub>2</sub> exists in Et<sub>2</sub>O. R. T.

Enamine form of Schiff's bases. R. WEGLER and A. RUZICKA (Ber., 1935, 68, [B], 1059—1062).— Treatment of d-valeraldehyde,  $\alpha +10^{\circ}$  to  $+11^{\circ}$ , with CH<sub>2</sub>Ph·NH<sub>2</sub>, NH<sub>2</sub>Ph, or NHPh·NH<sub>2</sub> in wellcooled Et<sub>2</sub>O and removal of the solvent at 20° after contact with much anhyd. Na<sub>2</sub>SO<sub>4</sub> at > 5° for 3 hr. gives Schiff's bases with  $\alpha +4\cdot30^{\circ}$ ,  $+5\cdot4^{\circ}$ , and  $+12\cdot7^{\circ}$ , respectively. These bases, and also those obtained with NH<sub>3</sub>, NH<sub>2</sub>Me, or CHPhMe·NH<sub>2</sub>, are completely racemised in 10 hr. at 50°; the phenylhydrazone and semicarbazone, m.p. 105°, are exceptions. Racemisation is retarded greatly by the presence of a little free amine. The probability that racemisation is due to the transformation CHR<sub>2</sub>·CH:N·CHR<sub>2</sub> == CR<sub>2</sub>·CH·NH·CHR<sub>2</sub> is strengthened by the apparent non-existence of optically active Schiff's bases from optically active hydratropaldehyde. H. W.

New diene syntheses. E. LEHMANN and W. PAASCHE (Ber., 1935, 68, [B], 1146-1149).-Acraldehyde (I) and  $\alpha$ -phenylbutadiene at 100° afford 2-phenyl- $\Delta^3$ -tetrahydrobenzaldehyde (II), b.p. 144°/12 mm. (additive compound with NaHSO<sub>3</sub>), reduced by Zn-Hg and conc. HCl to 2-phenyl- $\Delta^3$ . tetrahydrotoluene, b.p. 110-113°/12 mm., dehydro-genated by Se at 270-300° to o-C<sub>6</sub>H.PhMe, b.p. 255—258° (whence o-C<sub>6</sub>H<sub>4</sub>Ph·CO<sub>2</sub>H, m.p. 112·5°), and oxidised by CrO<sub>3</sub> in AcOH to 2-phenyl- $\Delta^3$ -tetrahydrobenzoic acid, m.p. 105°. Addition of (II) to acrylic acid gives 3-phenyl-∆4-tetrahydrobenzoic acid, m.p. 122°. Addition of HCN to (II) in presence or absence of KCN does not appear to give the corresponding cyanohydrin, the sole isolable product being 2: 2'-diphenyl-Δ<sup>3:3'</sup>-octahydrobenzoin, m.p. 167°. (I) and  $\beta$ -2:4-dimethylphenylpentadiene at 100-110° afford 2-2': 4'-dimethylphenyl-2-methyl- $\Delta^3$ -tetrahydrobenzaldehyde, b.p. 179-181°/12 mm. (NaHSO, compound). Condensation of the aldehydes to phenanthrene derivatives could not be effected. H. W.

Studies in the synthesis of vitamin-A. I. W. H. DAVIES, I. M. HEILBRON, W. E. JONES, and A. LOWE (J.C.S., 1935, 584-587).-Et β-hydroxy-δ-(2:2:6-trimethylcyclohexyl)-β-methylvalerate, obtained from tetrahydroionone and CH, Br CO, Et (Reformatsky), is converted by PBr, in ligroin into the corresponding  $\beta$ -Br-ester, reduced (Zn-HCl-AcOH) Et  $\delta$ -(2:2:6-trimethylcyclohexyl)- $\beta$ -methylto This is further reduced (Na-C<sub>5</sub>H<sub>11</sub>·OH) valerate.  $\varepsilon$ -(2:2:6-trimethylcyclohexyl)- $\gamma$ -methyl-n-amyl to alcohol, b.p. 136°/1.5 mm. (lit. b.p. 150-156°/7 mm.), which with PBr<sub>3</sub> in petroleum affords the bromide, b.p. 140-145°/4 mm. (cf. Karrer et al., A., 1932, 852). This with CHNaAc CO2Et in EtOH or C6H6 affords an unsaturated hydrocarbon  $C_{15}H_{28}$ , b.p. 112—115°/2 mm. [probably  $\varepsilon$ -(2:2:6-trimethyl-cyclohexyl)- $\gamma$ -methyl- $\Delta^{a}$ -pentene].  $\beta$ -Ionone, NaNH<sub>2</sub> in Et<sub>2</sub>O, and C<sub>2</sub>H<sub>2</sub> afford  $\varepsilon$ -(2:2:6-trimethyl- $\Delta^{6}$ -cyclohexenyl)- $\gamma$ -methylpent- $\delta$ -en- $\alpha$ -inen- $\gamma$ -ol, b.p. 112— 115°/3 mm. (cf. A., 1935, 492) (gives blue colour with SbCl<sub>3</sub>; Ag salt), which could not be isomerised to  $\alpha$ -aldehydo-δ-(2:2:6-trimethyl-Δ<sup>6</sup>-cyclohexenyl)-β-methyl-Δ<sup>α</sup>/-butadiene (I), b.p. 92-93°/1·8 mm. (phenylsemicarbazone, m.p. 182-183°). This was obtained by dry distillation of the Ba salt of the corresponding  $\alpha$ -carboxylic acid with (HCO<sub>2</sub>)<sub>2</sub>Ba, and was reduced by  $Al(OPr^{\beta})_{3}$  in  $Pr^{\beta}OH$  to the alcohol, b.p. 99—100°/2 mm. (possesses no growth-promoting activity). (I) with  $CH_2Br\cdot CO_2Et$  and Zn in  $C_6H_6$  affords  $Et \beta$ -hydroxy- $\zeta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl) -  $\delta$  - methyl -  $\Delta^{\gamma_{\epsilon}}$  - hexadiene -  $\alpha$  - carboxylate, b.p. 138-140°, which on hydrolysis and distillation of the Ba salt of the acid with  $(HCO_2)_2$ Ba regenerates (I). (I) with COMe<sub>2</sub> and C<sub>5</sub>H<sub>11</sub>N affords β-keto-δ-hydroxy-θ- $(2:2:6-trimethyl-\Delta^{6}-cyclohexenyl)-\zeta-methyl-\Delta^{en}-octa$ diene, b.p. 104—105°/1·5 mm. (phenylsemicarbazone, m.p. 171—172°). H. G. M.

Jute-lignin. VI. Isolated lignin and lignin native in jute. P. B. SARKAR (J. Indian Chem. Soc., 1935, 12, 168—172).—Lignin, whether isolated or native in jute, contains no Ac groups and no alkoxygroups other than OMe. From the OMe content of raw jute, delignified jute, and isolated (HCl) lignin it is calc. that the theoretical OMe content of lignin is 18.37%, in agreement with the assumed mol. wt. 830 (cf. A., 1934, 1355; this vol., 214) and the presence of 5 OMe. During isolation by means of HCl lignin loses 1.96% OMe. The amounts of CO<sub>2</sub> obtained from jute, delignified jute, and lignin by boiling with 12% HCl have been determined. H. G. M.

Action of 2-chlorocyclopentanone on organomagnesium halides. V. M. MITCHOVITCH (Compt. rend., 1935, 200, 1601—1603).—The reaction yields 2-alkyl- or -aryl-cyclopentanones, without change in the ring structure (cf. A., 1934, 654). In this way, 2-methyl-, -ethyl-, and -isopropyl-cyclopentanones are obtained, and 2-phenylcyclopentanone, m.p. 126—127° [oxime, m.p. 146°; semicarbazone, m.p. 228° (each decomp.)]. E. W. W.

cycloHexanone. C. L. WILSON (Chem. and Ind., 1935, 558).—The condensation of cyclohexanone with  $CH_2Br\cdot CO_2Et$  is described in detail. H. N. R.

Synthesis of 2-methyldicyclo-[1:2:2]-heptan-3-one. G. KOMPPA (Ber., 1935, 68, [B], 1127-1129).-Reduction of santene ketone with Na and EtOH affords mainly 2-methyldicyclo-[1:2:3]-octan-4-ol (I), b.p. 97-99°/13 mm., accompanied by a stereoisomeride, C9H16O2, m.p. 194-195°, of santene glycol which does not give a cryst. product with OBr' or a solid diphenylurethane. (I) is oxidised by  $HNO_3$  (d 1.27) at 100° to  $\alpha$ -methylhomonorcamphoric  $CH_2 \cdot CH(CHMe \cdot CO_2H) > CH_2, m.p. 130-131^{\circ}$ acid, CH2.CH(CO2H)-(Ca salt; dianilide, m.p. 241.5°), the Pb salt of which passes when heated into 2-methyldicyclo-[1:2:2]heptan-3-one (6-methylnorcamphor), b.p. 180-182°/ 761 mm. (semicarbazone, m.p. 184-185°). H. W.

Autoxidation of  $\alpha\beta$ -unsaturated ketones. VIII. Function of peroxides as intermediate products. W. TREIBS (Ber., 1935, 68, [B], 1049— 1050).—The hypothesis that autoxidation of  $\alpha\beta$ -unsaturated ketones in alcoholic alkaline solution involves loss of H<sub>2</sub>O<sub>2</sub> from the primary additive product of ketone and O<sub>2</sub> and transformation of unchanged ketone by H<sub>2</sub>O<sub>2</sub> into the oxide is supported by the observation that 3:5-dimethyl- $\Delta^2$ -cyclohexenone (I) is converted by H<sub>2</sub>O<sub>2</sub> in presence of NH<sub>3</sub> into the substance (II), C<sub>8</sub>H<sub>12</sub>O,O<sub>2</sub>,NH<sub>3</sub>, m.p. 88° (decomp.). Both added O atoms of the peroxide can be titrated with KI. Treatment of (I) with (II) in EtOH yields the oxide, C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>, b.p. 212—214°. H.W.

Synthesism of Tiemann's irone. A. VERLEY (Bull. Soc. chim., 1935, [v], 2, 1205—1209).— Rhodinal and aq. HOCl give  $\zeta$ -chloro- $\eta$ -hydroxy- $\beta\eta$ dimethyloctaldehyde, which with COMe<sub>2</sub> and alkali affords  $\iota$ -chloro- $\kappa$ -hydroxy- $\zeta\kappa$ -dimethyl- $\Delta^{\gamma}$ -undecen- $\beta$ one, dehydrated by H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, or SiO<sub>2</sub> to 1-chloro-2:2:4-trimethyl-3- $\gamma$ -keto- $\Delta^{a}$ -butenylcyclohexane ("irone" hydrochloride), from which HCl is removed by KOH, NaNH<sub>2</sub>, NR<sub>3</sub>, etc., to give l-1:1:3trimethyl-2- $\gamma$ -keto- $\Delta^{a}$ -butenyl- $\Delta^{5}$ -cyclohexene, b.p. 140°/ l<sup>2</sup> mm.,  $[\alpha]_{D}$  -21° (phenylhydrazone), which possesses Tiemann's formula for irone and has high val. as a commercial perfume. R. S. C.

Synthesis of vitamin-A. I. Action of magnesium on a mixture of ionone and  $\alpha\delta$ -dibromo $\Delta^{\circ}$ -butene. V. TETERIN and A. IVANOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 259–262).—The action of Mg and (:CH·CH<sub>2</sub>Br)<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> on ionone causes reduction to the corresponding glycol (·CMe(OH)·CH:CH·C $\langle CMe_2 \cdot CH_2 \rangle$  which contains 2 OH (Zerevitinov) and absorbs 8 H (Pd-CaCO<sub>3</sub>) giving a product oxidised to tetrahydroionone (semicarbazone, m.p. 163–165°). Divinyl is simultaneously produced. H. W.

α-Halogenated ketones. G. RICHARD (Compt. rend., 1935, 200, 1944—1946).—CHPhCl·COMe and powdered dry KOH in Et<sub>2</sub>O afford CH<sub>2</sub>Ph·COMe, Bz<sub>2</sub>, and CH<sub>2</sub>Ph·CH<sub>2</sub>·CO<sub>2</sub>H. Similarly Ph·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>H is obtained from CH<sub>2</sub>Ph·CHCl·COMe,

Ph·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>H is obtained from CH<sub>2</sub>Ph·CHCl·COMe, and CHPh<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H from CPh<sub>2</sub>Cl·COMe. These results are explained by tautomeric change of CHCIR·COMe into CH<sub>2</sub>R·CO·CH<sub>2</sub>Cl, which with KOH is converted, probably through CH<sub>2</sub>R·CH<sub>2</sub>·CO, into CH<sub>2</sub>R·CH<sub>2</sub>·CO<sub>2</sub>H (cf. A., 1934, 191).

H. G. M. Haloform reaction. XVI. Action of hypoiodite on hindered ketones. R. JOHNSON and R. C. FUSON (J. Amer. Chem. Soc., 1935, 57, 919— 920; cf. this vol., 751).—With a limited amount of NaOI acetomesitylene gives mesityl  $CH_2I$  ketone, m.p.  $34\cdot5-35\cdot5^\circ$ , but with an excess mesityl  $CHI_2$  ketone, m.p.  $98-99^\circ$ . By use of an excess of NaOI are prepared di(di-iodoacetyl)mesitylene, m.p. 160° (decomp.), di- $\beta$ -isoduroyliodomethane, m.p. 191—192°, and 3-diiodoacetyl-2:4:6-trimethylbenzoic acid, m.p. 132— 133° (decomp.). No I<sub>3</sub>-compounds could be prepared, nor could CHI<sub>3</sub> be obtained from these ketones. Pinacolone gives the mono- or di-iodo-compounds or CHI<sub>3</sub> according to the amount of NaOI used. These effects are steric. R. S. C.

Steric hindrance in a-diketones : mesitylbenzylglyoxal [ $\alpha\beta$ -diketo- $\gamma$ -phenyl- $\alpha$ -mesityl-propane]. R. P. BARNES (J. Amer. Chem. Soc., 1935, 57, 937-940).-Mesityl styryl ketone (I) and 30% H2O2 in 6N-NaOH give the oxide (80% yield), b.p. 195°/8 mm., rearranged by hot an. NaOH to  $\alpha\beta$ -diketo- $\gamma$ -phenyl- $\alpha$ -mesitylpropane (II), m.p. 100°, shown by MgMeI to be 100% enolic when solid, but only 81–90% in various solvents (by Br). (II) is oxidised by  $Na_2O_2$  to  $CH_2Ph \cdot CO_2H$  and  $C_6H_2Me_3 \cdot CO_2H$ , and is, therefore, an  $\alpha$ -diketone. It gives an O-allyl, m.p. 55°, b.p. 230°/30 mm. (unchanged), O-Me, m.p. 75°, b.p. 157°/2 mm., and O-CPh<sub>3</sub> ether, m.p. 195— 198°, an O-Ac, m.p. 109°, and O-Bz derivative, m.p. 81°. It resists catalytic hydrogenation, but with SnCl<sub>2</sub> gives β-keto-α-phenyl-γ-mesitylpropane, m.p. 72°, the constitution of which is proved because the benzoate, m.p. 86°, of its oxime decomposes above the m.p., 85°, into BzOH and CH<sub>2</sub>Ph·CN. (II) does not give a quinoxaline or dioxime, but yields a  $\beta$ -oxime, m.p. 88°, identical with the oximino-derivative obtained from nitrite and mesityl  $\beta$ -phenylethyl ketone, b.p. 163-165°/3 mm. [obtained by hydrogenation (PtO2; EtOH) of (I)]. The configuration of the oxime is shown by decomp. of the benzoate, m.p. 95°, above the m.p. into BzOH, (II), and CH<sub>2</sub>Ph·CN. (I) affords a semicarbazone, m.p. 227°, assumed by analogy to be a  $\beta$ -C-derivative. R. S. C.

Oxidation of benzophenoneoxime. K. VON AUWERS and H. WUNDERLING (Ber., 1935, 68, [B], 1072-1078; cf. A., 1933, 505; 1934, 654).-The blue compound (I) obtained by the oxidation of  $CPh_2$ :N·OH with  $K_3Fe(CN)_6$ , to which the structure  $CPh_2$ :N·O or  $CPh_2$ :N·O has been tentatively ascribed, liberates from acidified HI 45-57% of the amount of I which would be expected if it evolves 1 O. Attempts to obtain additive products with CPh<sub>3</sub>, CH<sub>2</sub>N<sub>2</sub>, NO, or NO<sub>2</sub> failed. (I) is converted by cautious treatment with Zn dust and AcOH into CPh<sub>2</sub>:N·OH. Reduction with H<sub>2</sub>S immediately affords CSPh<sub>2</sub>, possibly through intermediate pro-duction of CPh<sub>2</sub>:NH. Free halogens and halogen acids rapidly transform (I) into a mixture mainly of COPh, and the corresponding salts of CPh, NH sometimes containing diphenylketazine oxide (II). COPh<sub>2</sub> and usually (II) are obtained by the action of I on CPh<sub>2</sub>:N·ONa, but the formation of (I) is never observed. The oxidised product from the Na salt is further distinguished from (I) by its greater stability towards heat, but its behaviour towards acidified KI resembles that of (I). It appears therefore that an unstable blue and a stable colourless compound are formed during the oxidation of CPh2:N.OH with  $K_3Fe(CN)_6$ . More or less deeply coloured products are obtained by the action of K3Fe(CN)6 on p-methyl-, o-methyl-, and p-chloro-benzophenoneoxime, aceto-phenoneoxime, Ph  $Bu^{\gamma}$  ketoxime, and  $(CH_2Ph)_2$ ketoxime. H. W.

Synthesis of naphthyl methyl ketone. Mechanism of the Friedel-Crafts reaction. S. M. RIVKIN (J. Gen. Chem. Russ., 1935, 5, 277–280).— A mixture of  $\alpha$ - and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·COMe is obtained in 90% yield from AcCl, C<sub>10</sub>H<sub>8</sub>, and AlCl<sub>3</sub> in PhNO<sub>2</sub> at  $\geq 10^{\circ}$ , and in 58% yield when benzine is substituted for PhNO<sub>2</sub>. R. T.

Phenanthrene derivatives. III. o-Toluoyland  $\beta$ -methylnaphthoyl-phenanthrene. W. E. BACHMANN and L. H. PENCE (J. Amer. Chem. Soc., 1935, 57, 1130—1131; cf. this vol., 622).—Phenanthrene, o-C<sub>6</sub>H<sub>4</sub>Me·COCl, and AlCl<sub>3</sub> in PhNO<sub>2</sub> give 3- (24%), m.p. 89—90°, and 2-o-toluoylphenanthrene (3·4%), m.p. 115—116°, also obtained (Grignard and subsequent hydrolysis with conc. HCl at 200°; dil. HCl has no effect) in good yield from the cyanophenanthrenes and o-C<sub>6</sub>H<sub>4</sub>Me·MgBr. Similar Grignard reactions give good yields of 9-o-toluoyl-, 3-, m.p. 148·5—149·5° (lit. 145—146°), 9-, m.p. 176— 177° (lit. 170°), and 2-2'-methyl-1'-naphthoylphenanthrene, m.p. 184—185° (slow heating), or double m.p. (sudden heating) 168—170° and 184—185°.

R. S. C. Planar configuration of diamagnetic nickel complexes. II. H. J. CAVELL and S. SUGDEN (J.C.S., 1935, 621-624; cf. A., 1932, 272).—Methyl*n*-propylglyoxime, m.p. 175° (lit. m.p. 168°), affords a Ni derivative from which the  $\alpha$ - (I), m.p. 165° (lit. m.p. 144° and 160°), and  $\beta$ -form (II), m.p. 133°, were obtained. Similarly methyl-n-butylglyoxime, m.p. 173°, prepared from Et *n*-butylacetoacetate through the intermediate oximinoketone, m.p. 60°, affords a Ni derivative,  $\alpha$ - (III), m.p. 150°,  $\beta$ -form (IV), m.p. 86°. p-C<sub>6</sub>H<sub>4</sub>Cl·COEt was converted through its oximino-derivative, m.p. 119°, into p-chlorophenylmethylglyoxime, m.p. 223°, the Ni derivative, m.p. 283°, of which is unsuitable for separation into isomerides. p-Chlorophenyl n-amyl ketone, m.p. 64°, b.p. 165°/20 mm., prepared from n-hexoyl chloride, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub>, was converted through the oximinoderivative, m.p. 42°, into p-chlorophenyl-n-bulylglyoxime, m.p. 206°, which gives a Ni derivative,  $\alpha$ -form (V), m.p. 266°; indications of the existence of a lower-melting form were obtained. The  $\alpha$ - and βforms of these Ni derivatives are interconvertible by fusion; m.p. are therefore taken in a special way. The dipole moments of the Ni derivative were measured in C<sub>6</sub>H<sub>6</sub> and are as follows (all in Debye units): (I) 1·4, (II) 1·5, (III) 1·3, (IV) 1·3, (V) 1·8, Ni benzylmethylglyoxime,  $\alpha$ - 1·3, β-form 1·6. The small effect of the C·CI linkings in (V) on the observed moment strongly supports the view that the Ni glyoximes have a planar configuration (cf. Pauling, A., 1931, 670) and that the higher-melting forms have the trans-configuration.

Ni NN-di-n-propyldithiocarbamate, m.p. 135°, and Ni NN-di-n-butyldithiocarbamate, m.p. 91°, prepared from CS<sub>2</sub>, KOH, aq. NiCl<sub>2</sub>, and the corresponding dialkylamine, are diamagnetic, and on fusion and fractional crystallisation gave only one form. H. G. M.

α-Benzoylbutyrolactone, δ-keto-δ-phenyl-*n*butyl alcohol, and δ-keto-δ-phenyl-*n*-butyl bromide. G. V. TSCHELINCEV and E. D. OSETROVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 251– 254).—The interaction of  $(CH_2)_2O$  with CHNaBz·CO<sub>2</sub>Et in EtOH gives α-benzoylbutyrolactone, b.p. 193—195°/8 mm., transformed by boiling 10% K<sub>2</sub>CO<sub>3</sub> into δ-keto-δ-phenyl-*n*-butyl alcohol, b.p. 165—166°/10 mm., m.p. 32—33°, whence δ-keto-δphenyl-*n*-butyl bromide, m.p. 36°. H. W.

3-Methylindan-1: 2-dione and its oxime; isocoumarin synthesis. G. HELLER [with R. EBELING] (Ber., 1935, 68, [B], 1085-1090; cf. von Braun et al., A., 1913, i, 1363).-3-Methylindan-1:2-dioneoxime (I) and  $CH_2O$  in AcOH-conc. HCl gave the substance  $C_{21}H_{18}O_5$ , m.p. about 167° (slight decomp.) after softening at 160°, which like the simplest indandione does not immediately give a coloured solution in NaOH, showing thus that a preliminary transformation is necessary. (I) and NH<sub>2</sub>OH in AcOH-H<sub>2</sub>O give 3-methylindan-1:2-dionedioxime, the alkaline solution of which does not become coloured until heated. Acetyl-3-methylindandione-2-oxime, m.p. 134-135° (decomp.), from (I) and Ac2O (corresponding Bz derivative, m.p. 131-132°), is transformed by prolonged contact with 10% NaOH into 0-a'hydroxyethylphenylglyoxylic acid (II), m.p. 144°, and an amorphous substance, C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>N, m.p. 173°. The formation of the blue colour is not due to salt formation, as in the case of isatin, but to absorption of O and transformation. (II) is converted by  $Ac_2O$ and NaOAc into 3:4-dimethylisocoumarin, m.p. 129°, transformed by conc. alkali into  $0-\beta$ -keto- $\alpha$ methyl-n-propylbenzoic acid, m.p. 119°. (I) is transformed by NaOEt and EtI into methylindandioneoxime Et ether, m.p. 94°; the corresponding Me ether,

m.p. 138°, is too sensitive to alkali to be prepared in this manner or by  $Me_2SO_4$ , but is obtained with  $CH_2N_2$ . When treated with Zn dust and AcOH (I) gives a non-cryst. carmine-red Zn salt. Treatment of (I) with 10% NaOH and  $Na_2S_2O_4$  followed by  $Ac_2O$ leads to 2-ketacetimido-1-hydroxy-3-methyldihydroindene, m.p. 127—128°. H. W.

Aldol condensation between aldehydes and  $\beta$ -keto-acids, and their importance in the biosynthesis of natural products. C. SCHÖPF and K. THIERFELDER (Annalen, 1935, 518, 127-155).-Optimum yields (in parentheses) of the condensation products of aldehydes and  $\beta$ -keto-acids are obtained in neutral solution, the yield decreasing in either acid or alkaline medium. Thus at  $p_{\rm H}$  7 PhCHO and CH<sub>2</sub>Ac·CO<sub>2</sub>H (I) afford (90%) β-hydroxy-β-phenyl-ethyl Me ketone (II), m.p. 38–39° (Kubota *et al.*, A., 1926, 520) (semicarbazone, m.p. 172°), converted by NHPh·NH<sub>2</sub> not into its phenylhydrazone (loc. cit.) but into benzylideneacetonephenylhydrazone, m.p.  $153-154^{\circ}$ . The yield of (II) is reduced to  $10^{\circ}_{10}$ at  $p_{\rm ff}$  1, and to 0 at  $p_{\rm ff}$  13. Introduction of p-OH or OMe into the aldehyde greatly reduces the condensation yields with both (I) and (IV) (below). Thus (I) with anisaldehyde (III) gives only a trace of a compound which affords anisylideneacetonesemicarbazone, veratraldehyde affords  $(5\%)\beta$ -hydroxyβ-3: 4-dimethoxyphenyl Me ketone, m.p. 93-95°, but vanillin and COPhMe give no condensation products. Similar condensation of CH<sub>2</sub>Bz·CO<sub>2</sub>H (IV) with PhCHO (74%), (III) (8%), and MeCHO (27%) gives, respectively Ph  $\beta$ -hydroxy- $\beta$ -phenylethyl ketone, m.p. 53-54° (semicarbazone, m.p. 180°), Ph  $\beta$ -hydroxy- $\beta$ -p-methoxyphenylethyl ketone (as its semicarbazone, m.p. 183-184°), and Ph B-hydroxy-npropyl ketone (as its semicarbazone, m.p. 153—154°, sinters 149°). Condensation of PhCHO with  $CO(CH_2 \cdot CO_2H)_2$  (in N<sub>2</sub>) gives  $di \cdot (\beta \cdot hydroxy - \beta \cdot phenyl-$ ethyl) ketone, m.p. 163—165°, sinters 159°, and  $\beta \cdot keto - \delta \cdot phenyl - \Delta^{\gamma} - n \cdot pentenoic acid, m.p. 136—141°$ (decarboxylated to CHPh:CHAc).

CO<sub>2</sub>H·CO·CH<sub>2</sub>·CO<sub>2</sub>H with PhCHO affords (42%), CHPh:CH·CO·CO<sub>2</sub>H, p-OMe·C<sub>6</sub>H<sub>4</sub>·CHO gives (19%) p-OMe·C<sub>6</sub>H<sub>4</sub>·CH:CH·CO·CO<sub>2</sub>H, vanillin (V) and 3:4-(OH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>·CHO give, respectively, 4-hydroxy-3-methoxy-, m.p. 145—147°[alsofrom (V) and AcCO<sub>2</sub>H], and 3:4-dihydroxy- +H<sub>2</sub>O (yellow and red forms), sinters 196°, m.p. 202—204° (decomp.), -benzylidenepyruvic acid. The role of aldehyde- $\beta$ -keto-acid condensations in biosynthesis is discussed, especially in relation to gingerol, alkaloids of angostura bark, and muscone. Such condensations probably play no important part in the biosynthesis of fatty acids. J. W. B.

Reduction of deoxybenzoin and benzoin.—See this vol., 937.

Compounds of  $\alpha$ -benzoinoxime with bivalent metals. J. S. JENNINGS, E. SHARRATT, and W. WARDLAW (J.C.S., 1935, 818—822).—Cu benzoinoxime (I) [from aq. CuCl<sub>2</sub> and benzoinoxime (II) in EtOH (cf. A., 1923, ii, 880)] with hot EtOH-HCl affords *Cu benzoinoxime dichloride* (III),

(C<sub>14</sub>H<sub>13</sub>O<sub>2</sub>N)CuCl<sub>2</sub>,EtOH (EtOH is lost on keeping),

sol. in EtOH and COMe2, but decomposed by H2O into (I) and HCl. This confirms Feigl's structure CHPh-O CPh=NO>Cu for (I). (II) also forms compounds with Ni, Pd, and Pt (a ppt., but no pure compound, could be obtained with Co) [cf. A., 1923, ii, 880; "Organic Reagents for Metals" (1934)]. These compounds (structures given) exist in two forms which are interconvertible by means of solvents (e.g., EtOH, CCl<sub>4</sub>, and CHCl<sub>3</sub>). Their m.p. vary with the rate of heating. The second form of Ni dibenzoinoxime (IV) (obtained from the first by treatment with CCl<sub>4</sub>) contains 1 mol. of CCl<sub>4</sub> of crystallisation lost on keeping or more readily at 90°. When (II) in EtOH is added to NiSO<sub>4</sub> and NH<sub>4</sub>OAc in H<sub>2</sub>O and the mixture heated at  $40^{\circ}$  during 1 hr., Ni dibenzoinoxime diacetate (V) is obtained (structure proposed). (VI) is also obtained from (IV) and AcOH. (II) functions as a chelate group in three ways : (a) with two principal valencies as in (I), (b) with one principal valency and one co-ordinate linking, (c) with two co-ordinate links as in (III) and (V). The Ni compounds of (II) are paramagnetic, but the corresponding Pd compounds are diamagnetic. The configurations of these compounds are discussed.

H. G. M. **Michael condensation.** III. Addition of simple **ketones**. D. B. ANDREWS and R. CONNOR (J. Amer. Chem. Soc., 1935, 57, 895—898; cf. this vol., 215).— The reactivity of simple ketones with  $\alpha\beta$ -unsaturated ketones is decreased by substitution in the reactive CH<sub>2</sub>, the effect of Et being > that of Me. CHPh'CH-COPh with COPh Me gives 27% of binol

CHPh:CH:COPh with COPhMe gives 27% of bimol. and 56% of termol. product, with COPhEt  $\alpha\gamma$ -dibenzoyl- $\beta$ -phenylbutane, m.p. 102—103.5° (54%), and 27% of termol. compound, m.p. 231—235°, with COPhPr<sup>a</sup>  $\alpha\gamma$ -dibenzoyl- $\beta$ -phenyl-n-pentane, m.p. 91— 92° (corr.) (19%), and 58% of termol. compound, m.p. 219.3—219.6° (corr.), with COPhBu<sup>g</sup> 5% of termol. compound, m.p. 308.2—308.7° (corr.), only [when catalysed, 30% of termol., much probably quadrimol., m.p. > 360°, and a trace of possibly bimol. compound, m.p. 139.6—139.9° (corr.)], with COEt<sub>2</sub> a mixture (giving as only pure product the termol. compound), and with COMeBu<sup>y</sup> the termol., C<sub>36</sub>H<sub>36</sub>O<sub>3</sub>, m.p. 244.6—246° (corr.), and no bimol. compound. CHPh:CH·COBu<sup>y</sup> with COPhMe gives  $\alpha$ -benzoyl- $\gamma$ pivalyl- $\beta$ -phenylpropane, m.p. 59—59.5° (39%), and with COPhMe the bimol. (25%) and termol. (51%) compounds, but does not react with COMeBu<sup>y</sup>.

R. S. C.

Constitution of dehydroandrosterone. W. SCHOELLER, A. SERINI, and M. GEHRKE (Naturwiss., 1935, 23, 337).—Dehydroandrosterone has a *trans*configuration. With digitonin it affords a sparingly sol. additive product, whereas androsterone does not. This difference in behaviour affords a simple means of separating the two substances, which are present in the urine of men in approx. equal amounts.

H. G. M.

Synthesis of dehydroandrosterone by the decomposition of  $\gamma$ -sitosterol from soya beans. R. V. OPPENAUER (Nature, 1935, 135, 1039).— Acetylated sitosterol from soya beans was chlorinated in the 5:6-position to protect the double linking, and the side-chain removed by  $\text{CrO}_3$ . The sparingly-sol. semicarbazone obtained from the dichlorinated and saponified reaction mixture gave, on hydrolysis, a hydroxyketone, m.p. 147—148° (corr.), chemically and physiologically identical with dehydroandrosterone (I) from urine [oxime, m.p. 190° (corr.); benzoate, m.p. 252—253° (corr.), [ $\alpha$ ] +13.5° in EtOH]. (I) is therefore 3-hydroxy- $\Delta^{5:6}$ -ætiocholenone-(17). L. S. T.

Derivatives of 2-methylcyclopentan-one and -ol. M. GODCHOT and M. MOUSSERON (Compt. rend., 1935, 200, 2189-2192).-2-Methylcyclopentanone with Cl<sub>2</sub> and CaCO<sub>3</sub> gives a mixture of cis- and trans-5-chloro-ketone (I), b.p. 87°/14 mm. and 98-99°/14 mm., with a little methylcyclopentenone. Both forms of (I) with hot H.O give the same 1-methylcyclopentan-2-one-3-ol, b.p. 110°/14 mm., m.p. 100-101° (phenylhydrazone, m.p. 104-105°), and with hot quinoline 2-methyl-14-cyclopentenone (II), b.p. 140° (semicarbazone, m.p. 175-176°). 3-Methylcyclopentene gives a mixture of steroisomeric 3-chloro-1methylcyclopentan-2-ols, b.p. 69-70°/31 mm. and 101-102°/31 mm., converted by oxidation and heating with quinoline into (II). R. S. C.

Hydroxypolyketones. I. Alkylation of benzoylformoin. A. H. BLATT (J. Amer. Chem. Soc., 1935, 57, 1103-1107) .- It is proved that benzoylformoin (I), OH CHBz COBz, with acid in EtOH gives the monoalkyl ether O < CPh = C OR' CPh = C OR'(II; R=H), which has glucosidic properties and with NaOR-RI affords the dialkyl ether (II; R=alkvl), hydrolysed to the isomeric monoalkyl ether (III), OH-CPh.C(OR)-COBz. (I) (modified prep.), m.p. 187° (decomp.), gives 2 mols. of BzOH with Na<sub>2</sub>O<sub>2</sub>, is decomposed by conc. H<sub>2</sub>SO<sub>4</sub>, cannot be methylated by CH2N2 or MeI-NaOMe, but with HCI-MeOH gives the Me ether (II; R=Me, R'=H), m.p. 182°, which does not react with NH2OH or o.C6H4(NH2)2, is decomposed by conc. H2SO4 owing to hydrolysis to (I), with HCl-EtOH gives the Et ether (R=Et) (from which it is re-formed by H<sub>2</sub>SO<sub>4</sub>-MeOH), and with MeI-NaOMe affords the  $Me_2$  ether (II; R=R'=Me) (4-keto-3:5-dimethoxy-2:5-diphenylfuran), m.p. 78-79°. This is unchanged by NHPh•NH, or

o-C<sub>0</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, gives with H<sub>2</sub>SO<sub>4</sub>-EtOH the Me Et ether (II; R=Et; R'=Me), and with hot NaOMe an S8% or with conc. H<sub>2</sub>SO<sub>4</sub> a lower yield of the Me ether (III; R=Me) ( $\alpha$ -hydroxy- $\beta$ -methoxy- $\alpha$ -diphenyl- $\Delta^{\alpha}$ -butene- $\gamma$ -dione), m.p. 126—127°, the structure of which is proved as follows. It is 85% enolic (Br titration), is also obtained from the Me Et ether by NaOMe, is reconverted into the Me<sub>2</sub> ether by HCl-MeOH, and gives 2-phenyl-3-benzoylmethoxymethylquinoxaline, m.p. 131—132°, converted by MgPhBr into 2-phenyl-3- $\beta$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -methoxyethylquinoxaline, m.p. 173—174°, which with CrO<sub>3</sub> affords COPh<sub>2</sub> and 3-phenylquinoxaline-2-carboxylic acid.

R. S. C.

Oxonium compounds. Acidic complexes of quinones and their chlorination and bromination. V. V. TSCHELINGEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 244-250).—Treatment of a solution of benzoquinone in cold conc. HCl with Cl<sub>2</sub> rapidly yields 2:3-dichloro- $\Delta^5$ -cyclohexene-1:4-dione,

m.p. 147° (decomp.), converted by further action of Cl<sub>2</sub> into 2:3:5:6-tetrachlorocyclohexane-1:4-dione, m.p. 226° (decomp.). 2:3-Dibromo- $\Delta^5$ -cyclohexene-1:4-dione, m.p. 170°, and 2:3:5:6-tetrabromocyclohexane-1:4-dione are obtained similarly. Thermochemical data and ketonic properties justify the structure A

for compounds of quinones with HCl and invalidate Graebe's formulation of the former. H. W.

Influence of the R·COO- and R- groups on the cationoid reactivity of the quinone nucleus. H. ERDTMAN and A. LEÓN (Anal. Fís. Quim., 1934, 32, 614-626; cf. A., 1934, 184).-The reactivities of mono- and di-alkyl- and -alkoxy-p-benzoquinones are in qual. agreement with the electronic theory of valency, but for more highly substituted quinones there is less agreement, probably owing to steric effects. Contrary to theory, hydroxy-p- and hydroxy-m-xyloquinones show about the same reactivity. p-Xyloquinone, on acetylation by Thiele's method, yields 2:3:5-triacetoxy-p-xylene, hydrolysed to 2:3:5-trihydroxy-p-xylene (I), m.p. 157-158°, and oxidised by FeCl<sub>3</sub> to hydroxy-p-xyloquinone (II), m.p. 145-146° after sublimation. (II) on acetylation gives 2:3:5:6-tetra-acetyl-p-xylene, m.p. 250-252°. 2:3:5-Trimethoxy-p-xylene, b.p. 143-145°/30 mm., from (I), with Br in CHCl<sub>3</sub> gives 6-bromo-2:3:5trimethoxy-p-xylene (III), b.p. 175-180°/40 mm. (slight decomp.). Oxidation of (III) with HNO<sub>3</sub> yields 6-bromo-3-methoxy-p-xyloquinone, m.p. 81.5-82°. Acetylation of m-xyloquinone similarly yields triacetoxy-m-xylene, hydrolysed to 2:4:5-trihydroxy-m-xylene (IV), m.p. 119-121°, and oxidised by FeCl<sub>3</sub> to hydroxy-m-xyloquinone (V) (m.p. 103-104°), which on acetylation yields 2:4:5:6-tetra-acetoxy-*m*-xylene, m.p. 161°, hydrolysed to dihydroxy-*m*xyloquinone, m.p. 168-169°. Methylation of (IV) gives 2:4:5-trimethoxy-m-xylene, which on oxidation with HNO3 gives (V) and with Br in CHCl3 yields 6-bromo-2:4:5-trimethoxy-m-xylene, b.p. 151-155°/ 23 mm., oxidised by HNO3 to a bromomethoxy-mxyloquinone, m.p. 74°. J. W. S.

Action of alkaline hydrogen peroxide on quinones and polyhydric phenols. E. WEITZ, H. SCHOBBERT, and H. SEIBERT (Ber., 1935, 68, [B], 1163-1168).- a-Naphthaquinone is smoothly oxidised by H<sub>2</sub>O<sub>2</sub> in alkaline solution to so-called diketotetrahydronaphthalene oxide, m.p. 136°, whilst βnaphthaquinone gives hydroxynaphthaquinone. Attempts to isolate a mono- or di-oxido-compound from benzoquinone were unsuccessful, but a vigorous action occurs when the alkali and H<sub>2</sub>O<sub>2</sub> are used in large excess giving as-oxidoethylenedicarboxylic acid, from the Ba salt of which r-tartaric acid or chloromalic acid II is obtained by the action of dil. HNO<sub>3</sub> or HCl, respectively. Toluquinone is very rapidly oxidised, whereas chloranil is merely converted into chloranilic acid. Pyrocatechol gives the same products as quinol or benzoquinone. Resorcinol and quinol yield much CO<sub>2</sub> and non-investigated products. PhOH does not appear to react. Phenanthraquinone

smoothly yields diphenic acid, whereas anthraquinone is not attacked. H. W.

Preparation and hydrolysis of some  $\alpha$ -hydroxyanthraquinone glucosides. J. H. GARDNER, T. F. McDONNELL, and C. J. W. WIEGAND (J. Amer. Chem. Soc., 1935, 57, 1074—1076).—1-Hydroxyanthraquinone- $\beta$ -d-glucoside (I), m.p. 232·2—232·8°, is obtained from the tetra-acetate, m.p. 212—212·5°, by KOH-EtOH. Acetobromo-d-arabinose, 1-hydroxyanthraquinone (II), and Ag<sub>2</sub>O in quinoline give the triacetate, m.p. 189·2—189·4° (hydrolysed by cold K<sub>2</sub>CO<sub>3</sub>-EtOH), of 1-hydroxyanthraquinone- $\beta$ -d-arabinoside (III), m.p. 203—203·5°. (I) and (III) are hydrolysed by KOH, HCl, or borax, with decreasing ease in the order given, to nearly pure (II), except that (III) and KOH give also an indefinite material probably formed by reduction of (II) by arabinose. These hydrolyses are not in accord for a glucosidic formula for barbaloin. R. S. C.

Synthesis of hydroaromatic compounds with "angular" methyl groups. I. E. ADLER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 49, 1—5). *p*-Xyloquinone when heated at 160—170° during 10 hr. with about 4 mols. of butadiene (in 20%  $C_{\rm q}H_{\rm 6}$  solution) affords 1:4:5:8:11:12:13:14-octahydro-



12:14-dimethylanthraquinone (I), m.p. 171°. A migration of the Me is excluded because the substance contains no OMe and because it is not oxidised to a quinone by atm.  $O_2$  even in the presence of alkali at 100°. It is not acetylated by  $Ac_2O$ and  $C_5H_5N$ , yet fails to give an

oxime, probably owing to steric hindrance. (I) heated with alkali gives a *compound*, m.p. 202°.

H. G. M.

Preparation of cyclic compounds [quinones from dienes].—See B., 1935, 621.

Manufacture of 1:2:2':1'-anthraquinonoanthraquinones.—See B., 1935, 585.

**Preparation of picrotoxin.** E. P. CLARK (J. Amer. Chem. Soc., 1935, 57, 1111).—The prep. (1.4%) yield) of picrotoxin from *Anamirta cocculus* berries is modified. Optical data are given for this and for picrotin and picrotoxinin. R. S. C.

X-Ray crystallography of bufagin, cinobufagin, and strophanthidin.—See this vol., 921.

Yellow pigment from yeast.—See this vol., 1027.

Carotenoid pigments of Actinia equina, Anemonia sulcata, Actinoloba dianthus, and Tealia felina.—See this vol., 1005.

New pigment with lycopene spectrum. L. ZECHMEISTER and L. VON CHOLNOKY (Naturwiss., 1935, 23, 407).—The *polyene* from *Solanum dulcamara* behaves like lycopene, and its absorption spectrum has max. at 547, 507, 474, and 444 mµ; it is, however, distinguished by having m.p. 151° (corr.), depressed by adding lycopene. E. W. W.

Constituents of roots of Ch'ai Hu.—See this vol., 905.

Syntheses in the vitamin-A field. J. SALKIND, S. ZONIS, and N. BLOCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 57-63).-Mg vinylacetylenyl bromide with  $\beta$ -ionone in N<sub>2</sub> gives  $\gamma$ -hydroxy- $\alpha$ -(2:2:6trimethyl- $\Delta^{1:6}$ -cyclohexenyl) -  $\gamma$ -methyl- $\Delta^{a\zeta}$ -heptadien- $\Delta^{\delta}$ -inene, b.p. 135-145°/0·1 mm., which readily polymerises in air and is reduced (H<sub>2</sub>-Pd; +10 H) to a compound (I), b.p. 125-129°/0·1 mm. (I) when oxidised (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>) gives tetrahydroionone, trimethylcyclohexylacetic acid, and Bu<sup>a</sup>OH. (I) has no curative action on xerophthalmia in rats. J. L. D.

Isomerisation of linalool to geraniol. S. M. RIVKIN and E. A. MEERZON (J. Gen. Chem. Russ., 1935, 5, 274–276).—Geraniol is obtained in 14%yield from linalool and  $H_2O$  in presence of  $H_3BO_3$  or ZnCl<sub>2</sub> (200°/19 atm.; 90 min.). R. T.

Recent progress in the chemistry of the terpenes. J. L. SIMONSEN (J.C.S., 1935, 781-785).-A lecture. F. R. S.

Configuration of borneol and isoborneol. P. LEPP (Ber., 1935, 68, [B], 1029—1031).—The arguments of Asahina *et al.* (this vol., 625) are not regarded as decisive and it is doubtful whether the borneol-*iso*borneol problem can be solved by purely chemical methods. H. W.

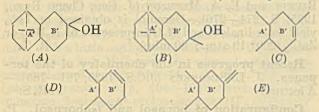
Tertiary 2:4-dimethylsantenol and 1:4-dimethylsantene. G. KOMPPA and G. A. NYMAN (Annalen, 1935, 518, 204—210).—4-Methylsantenone (this vol., 866) is converted by MgMeI into 2:4-dimethylsantenol (I), m.p. 55—58° (probably a mixture of stereoisomerides), dehydrated (KHSO<sub>4</sub> at 190— 200°) with rearrangement to 1:4-dimethylsantene (II), b.p. 161—162°, converted by ozonolysis into the diketone (III), b.p. 108—115°/7 mm. (disemicarbazone, m.p. 235—236°), showing that the double linking is between two tert.-C. Hydration of (II) with AcOH-60% H<sub>2</sub>SO<sub>4</sub> at 50—60° affords 4:6-dimethylsantenol (IV), b.p. 203—205° (Ac derivative, b.p. 97—98°/ 11.5 mm.), oxidised (CrO<sub>3</sub>-AcOH) to the corresponding

1 2 10	H. CMe-CH.	CH <sub>2</sub> ·CMe·CMe
	ĊHMe	CH <sub>2</sub> (II.)
ĊH <sub>2</sub> ·ĊMe—ĊMe•OH		CH <sub>2</sub> ·CMe·CMe
(III.)	CH. CMeAc	CH2. CMe-CH2
	CH,	CHMe (IV.)
	CH2.CMeAc	ĆH₂•ĆMe──ĆH•OH

ketone, 4:6-dimethylsantenone, b.p.  $202-205^{\circ}/760$  mm. (semicarbazone, m.p.  $177\cdot5-178\cdot5^{\circ}$ ), further oxidised (KMnO<sub>4</sub>-10% KOH) to cis-1:2:3:5-tetramethylcyclopentane-1:3-dicarboxylic acid, m.p. 191-192° (anhydride, m.p. 89-90°, by cold AcCl), which contains the same no. of C, thus proving the constitution of (IV). J. W. B.

Elucidation of the constitution of certain sesquiterpenes by powerful oxidative degradation. I. Cedrene and cedrol. W. TREIBS (Ber., 1935, 68, [B], 1041—1049).—Cedrene (I) is unaffected by Pd- or Pt-asbestos at 300°, but passes in presence of Ni-pumice at 420—450° into p-cymene. The change of refraction in the apparently unaltered portion points to the intermediate formation of amylcymene, which loses the thermally unstable amylene. Repeated drastic oxidation of artificial (I) with KMnO<sub>4</sub> in COMe<sub>2</sub> readily yields the ketone  $C_{14}H_{24}O$  and diketone

 $C_{15}H_{24}O_2$  obtained previously from natural (I); further oxidation of the salts thus obtained by  $KMnO_4$  in  $H_2O$  affords much  $CMe_2(CO_2H)_2$  and some  $CO_2H \cdot CH_2 \cdot CO_2H$ . The dicyclic system of (I) must therefore have the isopinane or camphane structure. Oxidation of the salts obtained from artificial (I) and  $\text{KMnO}_4$  in  $\text{COMe}_2$  with hot  $\text{HNO}_3$ (d 1.4) leads to little  $\text{CMe}_2(\text{CO}_2\text{H})_2$ , ( $\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , CO<sub>2</sub>H·CHMe·CMe<sub>2</sub>·CO<sub>2</sub>H, and a mixture of isomeric tricarboxylic acids,  $C_9H_{14}O_6$ , from which camphor-onic acid is obtained cryst. The dicyclic ring system



of (I) has the same structure as camphor, and cedrol (II) must have the structure A or  $\hat{B}$ . Loss of H<sub>2</sub>O during the conversion of (II) into (I) can occur in three directions. The constitution of cedrenedicarboxylic acid (III) proves that C is the predominant component of synthetic (I), whereas it is present in only small amount in natural (I).

Cedrene glycol (IV) is stable towards  $\text{KMnO}_4$ , but is readily oxidised by  $\text{CrO}_3$  to a *OH-ketone*,  $\text{C}_{15}\text{H}_{24}\text{O}_2$ , b.p. 180–185°/17 mm., which is converted by more



drastic oxidation into the ketonic acid,  $<_{\text{OH}} \begin{array}{c} C_{15}H_{24}O_3, \text{ m.p. } 82-83^{\circ} \text{ (semicarbazone,}\\ OH \text{ m.p. } 195^{\circ}\text{)}; \text{ since the latter can be}\\ <_{\text{H}}^{\text{OH}} \begin{array}{c} \text{degraded to (III) it is identical with the} \end{array}$ (non-cryst.) acid obtained by Semmler (F) by ozonisation of natural (I). (IV) has the structure F. When treated with  $30\% H_2SO_4$  it passes into the oxide, b.p. 148°/20 mm.

Contrary to Semmler, oxidation of (I) with KMnO<sub>4</sub> gives a mixture of acids, b.p. 200-230°/17 mm., from which a sparingly sol. semicarbazone, m.p. 240° (decomp.), is isolated. This when treated with  $H_2C_2O_4$  yields a non-cryst. *iso*keto-acid transformed by NaOBr into CBr<sub>4</sub> and *isocedrenedicarboxylic acid*, m.p. 210—211°. The acid is also obtained from (I) and HNO3 (d 1.4) in boiling AcOH. It does not afford an anhydride. Since its Me2 ester, b.p. 172°/ 17 mm., is converted by MgMeI into a hydrocarbon, b.p. 150-160°/17 mm., the acid and Semmler's acid, m.p. 182°, must be cis-trans-isomerides. Artificial (I) is racemised by conc. H<sub>2</sub>SO<sub>4</sub> with predominating production of an insol. stable and a sol., very readily autoxidised product. Natural (I) gives the same products in subsidiary amount, but 50% of it suffers polymerisation. H. W.

Gossypol. L.SCHMID and S. MARGULIES (Monatsh., 1935, **65**, 391–398).—Gossypol (formula  $C_{30}H_{30}O_8$  confirmed) yields (Pd, H<sub>2</sub>) hydrogossypol (I),  $C_{30}H_{36}O_8$ , decomp. 320° (evacuated tube), which forms no additive compound with AcOH, but which gives  $(C_5H_5N, Ac_2O)$  a  $Ac_6$  derivative, decomp. 235°. Zn- $H_2$  distillation of (I) furnishes a substance (II), identified with synthetic  $\beta$ -isoamylnaphthalene (III) [no picrate; the substance described as such (A., 1888, 1305; 1891, 730) is picric acid], with a sub-

stance containing O, m.p. 234-238°, b.p. 180°/12 mm. (II) or (III) with Br gives a substance, m.p. 70-72°, b.p. 135—140°/0·4 mm. (I) is oxidised by  $H_2O_2$ -NaOH to Pr<sup>a</sup>CO<sub>2</sub>H, with a substance,  $C_{25}H_{30}O_{10}(\hat{t})$ , decomp. about 170°, and a substance, b.p. 130°/12 mm. E. W. W.

β-Oxanols [ $\beta_{\gamma}$ -oxidopropan-α-ols]. Ε. Ρ. Кон-LER and C. L. BICKEL (J. Amer. Chem. Soc., 1935, 57, 1099-1101).-Cleavage of CHR>CH·CR'2·OH into CH2R·CHO and COR'2 is dependent on replacement of the H of the OH by a metal, since org. Mg or Li compounds or Na in liquid NH3 give metallic derivatives, which regenerate the oxide with acids, but, when heated, give the aldehyde and ketone. Rearrangement of the oxide to OH·CHR·CHCCHCCH

shown by the following reactions not to involve migration of R' or formation of a triol and to be an irreversible, catalytic reaction brought about by OH' or OMe', since it is effected by alkali hydroxides or carbonates, BaO, Mg(OEt)<sub>2</sub>, or NMe<sub>4</sub>·OH, but not by OAc', NH<sub>3</sub>,  $C_5H_5N$ , or piperidine. o- $C_6H_4$ Cl·CHO and COPhMe in NaOH-aq. EtOH give  $\beta$ -hydroxy- $\beta$ -ochlorophenylpropiophenone, m.p. 80°, hydrolysed to the aldehyde and ketone by aq. MeOH or heat, and stable to hot AcOH. In NaOMe-MeOH, however, o-C<sub>6</sub>H<sub>4</sub>Cl·CH:CH·COPh is formed, which with Na<sub>2</sub>O<sub>2</sub> gives  $\alpha\beta$ -oxido- $\beta$ -o-chlorophenylpropiophenone (84%) yield), m.p. 73-74°; MgPhBr yields By-oxido-aadiphenyl-y-o-chlorophenylpropan-a-ol, m.p. 107-108°, which with MgEtBr gives a Mg compound, decomposed by keeping into CPh<sub>2</sub>Et OH, with LiPh a Li compound, reconverted immediately by acid into the original oxide, but after 30 min. boiling in Et<sub>2</sub>O into  $(C_6H_4Cl CHO)_x$  (also obtained with COPh<sub>2</sub> by Na in NH<sub>3</sub>), and with bases affords  $\beta\gamma$ -oxido- $\gamma\gamma$ -diphenyl- $\alpha$ -o-chlorophenylpropan- $\alpha$ -ol, m.p. 114—115, the structure of which is of which is proved by oxidation  $(CrO_3)$  to  $COPh_2$ and  $o-C_8H_4Cl-CO_2H$ , whilst autoxidation gives o- $C_6H_4Cl\cdot CHO$ .  $\alpha$ -Hydroxy- $\beta$ -methoxy- $\beta$ -phenylpropiophenone is obtained cryst., m.p. 47-48°.  $\gamma$ -Methoxy- $\alpha\alpha\gamma$ -triphenylpropane- $\alpha\beta$ -diol does not yield an oxide with bases. R. S. C.

Extraction of furfuraldehyde from aqueous solutions. V. I. SHARKOV and I. BELJAEVSKI (Lesokhim. Prom., 1933, 2, No. 3, 15-19).-Salting-CH. ABS. (r)out effects are discussed.

Condensation of furan derivatives. IV. Nature of the coloured products of condensation of furfuraldehyde with acetone in aqueous sulphuric or hydrochloric acid, and the theory of reaction of alcohols and olefines with furfuraldehyde. V. Application of the furfurylidene test to the study of the process of condensation of acetone with formaldehyde. V. V. TSCHELINCEV (J. Gen. Chem. Russ., 1935, 5, 256—264, 265— 273).—IV [with E. K. NIKITIN]. The compounds  $C_4H_3O$ ·CH(CH<sub>2</sub>·COMe)<sub>2</sub>(I),  $C_4H_3O$ ·CH:CH·COMe (II), and CO(CH:CH·C<sub>4</sub>H<sub>3</sub>O)<sub>2</sub> (III) are obtained when  $C_4H_3O$ ·CHO (IV) and COMe<sub>2</sub> are condensed in aq. HCl or H<sub>2</sub>SO. (I) does not afford a coloured product  $HCl \text{ or } H_2SO_4$ . (I) does not afford a coloured product with acids, (II) gives an orange-red and (III) a violet-red coloration. (IV), when present in large

excess, undergoes polymerisation to yield a blue polymeride. The colorations obtained with fusel oil, pinene, and liquid olefines are due to the presence of  $COMe_2$  in these products, or to its formation under the conditions of condensation.

V [with M. N. TILITSCHENKO].  $CH_2O$  and  $COMe_2$ react in presence of KOH in two ways:  $COMe_2+CH_2O$  $\rightarrow CH_2$ : CH· $COMe+H_2O$ , and  $2CH_2O+H_2O \rightarrow HCO_2H$ +MeOH. The latter reaction is favoured by higher [KOH], and is catalysed by  $COMe_2$ , and the  $HCO_2H$ produced neutralises the KOH, thereby creating conditions unfavourable for the aldol condensation. R. T.

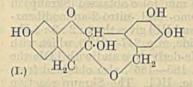
Orientation in the furan series. Hill's 3:5dibromo-2-furoic acid. H. GLMAN, R. J. V. WAL, R. A. FRANZ, and E. V. BROWN (J. Amer. Chem. Soc., 1935, 57, 1146).—Hill's "3:5-dibromo-2furoic acid" (A., 1886, 447) is really the 4:5-Br<sub>2</sub>-acid, because (a) replacement of the  $\alpha$ -Br by H, reaction with KCN–CuCN, and subsequent hydrolysis gives furan-2:4-dicarboxylic acid, (b) decarboxylation, interaction with KCN, and hydrolysis affords the 2:3-dicarboxylic acid, and (c) the Et ester with MgPhBr gives  $\alpha$ -bromo- $\delta\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadieno- $\gamma$ -lactone, hydrolysed by 5% NaOH to CHPh<sub>2</sub>·COMe. Hill's structures for 5-chloro- and -bromo-3-sulphoand 3:5-dichloro-furoic acid now need revision.

R. S. C.

Reactions of o-hydroxybenzylacetone. W. BAKER and J. WALKER (J.C.S., 1935, 646-648).-o-OH·C<sub>6</sub>H<sub>4</sub>·CH:CHAc is reduced by  $H_2/3$  atm. with Pd-SrCO<sub>3</sub> in MeOH to o-OH·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CH<sub>2</sub>Ac (I) in 80% yield, but with a PdCl<sub>4</sub> catalyst in EtOH to a mixture of (I) (NaOH-sol.) and 2-ethoxy-2-methylchroman (II), b.p. 105°/11 mm., 225°/760 mm., with some conversion into (III). The presence of (II) is due to HCl, since (I) is converted into (II) by EtOHtrace HCl at room temp. (II) is reconverted into (I) by hot dil. HCl. 2-Methoxy-2-methylchroman, b.p. 107°/14 mm., is similarly obtained. (I) dissolved in dry  $Et_2O$  over anhyd. Na<sub>2</sub>SO<sub>4</sub> is slowly (2 weeks) converted (probably by way of 2-hydroxy-2-methylchroman) into 2-methylchromene (III), b.p. 95-97°/10 mm., also obtained by boiling (II) with Ac<sub>2</sub>O. Reduction of (III) with  $H_2$ -Pt-SiO<sub>2</sub> gel in AcOH gives 2-methyl-chroman, b.p. 100-102°/11 mm.; specimens of this compound previously described in the lit. are probably mixtures. J. W. B.

Constitution of genisteïn. C. CHARAUX and J. RABATÉ (J. Pharm. Chim., 1935, [viii], 22, 32–33).— Genisteïn is an *iso*flavone, the formula  $C_{15}H_{10}O_5$ of Baker and Robinson (A., 1929, 192) being correct. Sophoricoside is a  $\beta$ -glucoside of formula  $C_{21}H_{20}O_{10}$ . H. G. R.

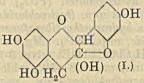
Leuco-anthocyanins and -anthocyanidins. I. Isolation of peltogynol and its molecular structure. (MRS.) G. M. ROBINSON and R. ROBINSON (J.C.S., 1935, 744—752).—Aq. extracts of the sawdust of *Peltogyne porphyrocardia* with EtOAc yield a leucoanthocyanidin, *peltogynol* (I),  $C_{16}H_{14}O_{6}$ ,  $[\alpha]_{p}^{D1}$ +273° in EtOAc (O- $Ac_4$ , m.p. 173°,  $[\alpha]_{p}^{D0}$  +125° in CHCl<sub>3</sub>, O- $Bz_4$ , m.p. 244°, O-tetra-anisoyl, m.p. 218°, O- $Me_4$ , m.p. 174°,  $[\alpha]_{p}^{20}$  +264° in CHCl<sub>3</sub>, and O- $Me_3$ derivatives, m.p. 198°,  $[\alpha]_{p}^{20}$  +254° in CHCl<sub>5</sub>; 2:4dinitrophenylhydrazone explodes 224°). Oxidation (HNO<sub>3</sub>) of (I) gives styphnic acid, whilst the O- $Me_3$  compound yields 4:5-dinitroveratrole and with KMnO<sub>4</sub> affords m-hemipinic acid and O-trimethylpeltogynic acid, C<sub>19</sub>H<sub>18</sub>O<sub>7</sub> (?). Optical and X-ray crystallographic examination of (I) confirm the constitution assigned. The dihydroanthocyanidin



Optical and X-ray of (I) confirm the dihydroanthocyanidin state of oxidation is stabilised by the ketose group, and it is suggested that the corresponding structure will be found in other leucoantho-

cyanins and that the formation of the anthocyanidins from these precursors is actually the result of oxidation. p-Methoxysalicylaldehyde and  $\omega$ -3:4-trimethoxyacetophenone (HCl) yield O-tetramethylfisetinidin chloride, which with CH<sub>2</sub>O gives a solution closely resembling that of trimethylpeltogynidin salts.

F. R. S. **Constitution of cyanomaclurin**. H. APPEL and R. ROBINSON (J.C.S., 1935, 752-755).—Cyanomaclurin (I) (Perkin, J.C.S., 1905, 87, 715) has  $[\alpha]_{B^0}^{-}$ +215° in EtOAc or +192° in H<sub>2</sub>O, neither solution showing mutarotation. The supposed Ac<sub>5</sub> and Bz<sub>5</sub>



derivatives are  $Ac_4$ ,  $[\alpha]_D^{\rm o}$ OH +95° in EtOAc, and  $Bz_4$ derivatives, respectively. (I) forms O-trimethylcyanomaclurin, m.p. 73-85° (Ac (I.) derivative), and is converted by Na<sub>2</sub>CO<sub>3</sub> into

morinidin chloride. Consideration of the reactions of (I) leads to the structure assigned. F. R. S.

Dibenzfuran [diphenylene oxide]. V. Dimetal-ation. H. GILMAN and R. V. YOUNG. VII. Aminoderivatives. W. H. KIRKPATRICK and P. T. PARKER (J. Amer. Chem. Soc., 1935, 57, 1121-1123, 1123-1126; cf. this vol., 867).-V. Substitution of dibenz furan by metals (" metalation ") occurs in the 1 and 8 positions, showing the great effect of the O. Monometalation is best effected by LiBua or NaBua in Et<sub>2</sub>O, and dimetalation by NaBu<sup>a</sup>, but NaEt, PbEt<sub>4</sub>, or Na-K and MgBu°Cl may also be used. Na 1-dibenzfuryl gives 1-methyl- (I) (45% yield) and 1-hydroxy-dibenzfuran (40%), m.p. 102° [Bz derivative, m.p. 91—92°; Me ether (II), m.p. 52°, b.p. 164—165°/5 mm.]. 1:8-Disodiodibenzfuran gives 1:8-dimethyl- (90%), -di-iodo- (19%), m.p. 160°, and -dihydroxy-dibenzfuran (III) (3%), m.p. 190°, and dibenzfuran-1: 8-dicarboxylic acid (IV) (77%), m.p. 325° (Me<sub>2</sub> ester, m.p. 161-162°), and -disul-phonic acid, decomp. 183-185°, oxidised to the  $(SO_3H)_2$ -derivative, decomp. about 300°. (I) and (II) yield 1-methyldibenzfuran-8-carboxylic acid, m.p. 238-240° [Me ester, m.p. 80-81°; with KMnO4 gives (IV)], and 1-hydroxy-8-methoxydibenzfuran, m.p. 109-110°, which with HI gives (III).

VI. NH<sub>2</sub>-derivatives are prepared for pharmacological examination. 2-Aminodibenzfuran (V) (modified prep.) yields the N-Me-, b.p.  $190^{\circ}/4$  mm., m.p. 48— 49° [hydrochloride, m.p.  $245-247^{\circ}$  (decomp.)], -Et-(hydrochloride, m.p. >  $315^{\circ}$ ), -Pr<sup>a</sup>-, b.p.  $203-205^{\circ}/1$ 

mm. (hydrochloride, m.p. 190°), -Me2-, b.p. 211-212°/ 4 mm., m.p. 96° (hydrochloride, m.p. 230-232°), and -Et2-, b.p. 205°/2-3 mm. [hydrochloride, m.p. 203-205° (decomp.)], derivatives, with Br·[CH<sub>2</sub>]<sub>5</sub>·Br 2-piperidinodibenzfuran, m.p. 111° (hydrochloride, m.p. 258-260°), by a Skraup reaction pyrido-[3:2-b]- (VI), m.p. 167.5—168.5°, and -[2:3-c]-dibenzfuran, m.p. 112°, b.p. 209—210°/3 mm. [also obtained (Skraup) in poor yield from 3-bromo- and -nitro-2-aminodibenz-furan]. (VI) with Sn and HCl gives the 1:2:3:4-H<sub>4</sub>derivative (hydrochloride, m.p. 247-248°), which with Me<sub>2</sub>SO<sub>4</sub> gives the N-Me-derivative and with LiMe the 3-Me-compound, m.p.  $185-186^{\circ}$ , also obtained from (V) and CH<sub>2</sub>O in conc. HCl. The Skraup reaction (As<sub>2</sub>O<sub>5</sub>) with 3-bromo-7-aminodibenzfuran affords a bromopyridodibenzfuran, m.p. 152°. 3-Aminodibenzfuran gives (Skraup) pyrido-[2:3-b]- and -[3:2-a]dibenzfuran and two isomerides, m.p. 185-186° [hydrochloride, m.p. 307-310° (decomp.)] and 160.5-161.5° [hydrochloride, m.p. 296-298° (decomp.)], respectively. 3-Bromo- (from the Ac derivative and Br in Et<sub>2</sub>O), m.p. 106-107°, and -chloro-acetyldibenzfuran (prep. by CH<sub>2</sub>Cl·COCl in CS<sub>2</sub>), b.p. 206-208°/ 1-2 mm., m.p. 109-110° (oxidised to the 3-carboxylic acid), give 3-diethylamino- (hydrochloride, m.p. 204-206°) and -piperidino-acetyldibenzfuran (hydrochloride, m.p. 270-271°), hydrogenated (PtO2) to 3-β-diethylamino-, b.p. 220°/2-3 mm. (hydrochloride, m.p. 137°), and -piperidino-a-hydroxyethyldibenzfuran, m.p. 103—104° (hydrochloride, m.p. 242°). Mg 3-dibenzfuryl bromide and CH2Cl·CHCl·OEt give 3-Bchloro-, b.p. 204-206°/6 mm., m.p. 58-59°, which yields 3-\$-piperidino-a-ethoxyethyldibenzfuran, m.p. 175°; epichlorohydrin yields similarly 3-y-chloro-, b.p. 205-206°/2 mm., and -diethylamino-β-hydroxypropyl-203–206 /2 mm., and -attethylamino-p-hylaroxypropyl-dibenzfuran (hydrochloride, m.p. 145°); (CH<sub>2</sub>)<sub>2</sub>O leads to 3-β-hydroxy-, m.p. 67–67.5°, -bromo-, b.p. 179–  $180^{\circ}/2$ —3 mm., m.p. 62–62.5°, and -diethylamino-ethyldibenzfuran, b.p. 169–170°/2 mm. (hydrochloride, m.p. 192–193°). Li 1-dibenzfuryl and (CH<sub>2</sub>)<sub>2</sub>O give 1-β-hydroxy-, m.p. 70–71°, b.p. 190–191°/4 mm., -bromo-, b.p. 165°/2 mm., m.p. 37–38°, and thence 1-diethylamino-ethyldibenzfuran (hydrochloride, m.p. 184-185°). 1-Hydroxydibenzfuran,

 $p-\dot{C}_6H_4Me\cdot SO_3\cdot\dot{C}H_2\cdot CH_2Cl$ , and aq. NaOH give 1- $\beta$ -chloro-, m.p. 64-65°, and thence 1- $\beta$ -diethylamino-(hydrochloride, m.p. 128.5-129.5°) and -piperidinoethoxydibenzfuran, b.p. 213°/2 mm. (hydrochloride, m.p. 210.5-212°). The 1-Li-derivative affords dibenzfuran-1-carboxyl chloride, m.p. 118°, which gives the amide, m.p. 181-182°, and thence 1-aminodibenzfuran, m.p. 84.5-85.5° (hydrochloride : Ac derivative, m.p. 172.5°), also obtained from the 1-OH-compound, ZnCl<sub>2</sub>, and NH<sub>4</sub>Cl at 275-280°. R. S. C.

Photochemical formation of diradicals. A. SCHONBERG (Annalen, 1935, 518, 299-302).-In part a priority claim (cf., inter alia, A., 1934, 643, 997).

OH-CPh 0

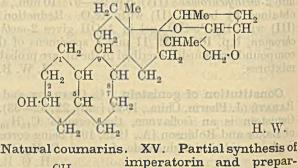
The compound formed by exposure of a chlorophyll solution to light in presence of an acceptor (Gaffron, A., 1927, CPh·OH 1225) has a diradical character similar to that obtained with

rubene (loc. cit.). Contrary to Liebermann et al. (A.,

1934, 531) the compound obtained by the action of HNO3 on chromorufen is not a diradical peroxide, but a glycol (formula annexed). J. W. B.

Synthesis of bergapten and its derivatives. I. Furocoumarins. J. N. RAY, S. S. SILOOJA, and V. R. VAID (J.C.S., 1935, 813-816).--7-Hydroxy-coumarin with CH<sub>2</sub>BrBz gives 7-*phenacyloxycoumarin*, m.p. 167° (with NaOEt forming 3'-*phenyl*-7:6-*furo*-*coumarin*, m.p. 200°), and with CH<sub>2</sub>ClAc yields 7-acetonyloxycoumarin, m.p. 167° (with NaOEt affording 3'-methyl-7 : 6-furocoumarin, m.p. 188°). β-Methylumbelliferone with CH2ClAc forms 7-acetonyloxy-4methylcoumarin, m.p. 157°, which with NaOEt gives 4:3'-dimethyl-7:6-furocoumarin, m.p. 220°. Acetyl-umbelliferone and AlCl<sub>3</sub> yield 7-hydroxy-8-acetyl-coumarin, m.p. 167°, the oxime, m.p. 223°, of which with POCl<sub>3</sub> affords the isooxazole and 8-acetamido-7-hydroxycoumarin, m.p. 251°, hydrolysed to the amine, m.p. 278°. Pyrogallaldehyde and  $CH_2(CO_2H)_2$ give daphnetin-3-carboxylic acid, m.p. 228°. Daphnetin and CH\_ClAc yield 8-hydroxy-7-acetonyloxycoumarin, m.p. 132-133°, methylated to the 8-OMe-compound, m.p. 81-82°, which with NaOEt forms 8-methoxy-3'-methyl-7:6-furocoumarin (+1H<sub>2</sub>O), m.p. 155°. The furocoumarins described have the linear structure. F. R. S.

Neutral saponins. Conversion of digitogenin, gitogenin, and tigogenin into identical derivatives. R. TSCHESCHE (Ber., 1935, 68, [B], 1090-1094).—Digitogenic acid semicarbazone is reduced by NaOEt at 160-170° to gitogenic acid (I). Digitogenin (II) and gitogenin (III) therefore differ only because of the presence of a third OH in the second ring of the former. Oxidation of tigogenin (IV) with Find of the former. Oxidation of tigggenin (17) with  $CrO_3$  affords (I) and an acid,  $C_{26}H_{35}O_8$ , m.p. 218–220° (Me ester, m.p. 85–86°), previously obtained from (III). (IV) is therefore a  $(OH)_1$ -compound with the same skeleton as (II) or (III). The annexed structure is suggested for (IV) whilst (III) is the 3:4-di- and (II) the 3:4:6-tri-hydroxy-compound of the same fundamental body.



CH **CH** CO Õ 0 (I.)

ation of oxyimperatorin. E. SPATH and H. HOLZEN (Ber., 1935, 68, [B], 1123-1125) .- Treatment of xanthotoxol as Na derivative with  $O \cdot CH_2 \cdot CH - CMe_2 \gamma$ -methyl- $\Delta^{\beta}$ -butenyl bromide in Et<sub>2</sub>O (not in MeOH) yields imperatorin, m.p. 101°, trans-

formed by BzO<sub>2</sub>H in CHCl<sub>2</sub> into oxyimperatorin (1), H. W. m.p. 115-116°.

Thiacyclopentane 1: 1-dioxides [tetramethylene sulphones]. H. J. BACKER and C. C. BOLT (Rec. trav. chim., 1935, 54, 538—544; cf. A., 1934, 662).— Catalytic hydrogenation of the unstable  $\Delta^3$ -thiacyclopentene 1: 1-dioxide (butadiene sulphone) (I) gave the stable thiacyclopentane 1: 1-dioxide (tetramethylene sulphone) (II). Rapidity of hydrogenation of substances of the type of (I) varies with structure. (II) has m.p. 20—21°, b.p. 149·5—150°/15 mm. (cf. A., 1917, i, 155). The following derivatives of (II) are described: 3-Me (m.p. 0—1°, b.p. 102—103°), from isoprene sulphone (cf. A., 1931, 1268); 3-Bu, m.p.  $42-42\cdot5°$ , b.p. 137—138°/2—3 mm.; 3-Ph, m.p. 96— 97°, b.p. 220—221°/15 mm., 351—354°/760 mm.; 3-cyclohexyl (by hydrogenation of the 3-Ph compound), m.p. 62·5—63°, b.p. 202—204°/14 mm.;  $3:4-Me_2$ , m.p. 50—51°, b.p. 136—137°/15 mm.;  $2:3:4:5-Me_4$ , b.p. 117°/2 mm., 152—154°/14 mm. The decomp. temp. of many substances of types (I) and (II) are compared. P. G. C.

Manufacture of hydroxydiphenylene compounds and derivatives.—See B., 1935, 585.

Relative reactivities of certain 2- and 2:6substituted piperidines. A. W. SINGER and S. M. MCELVAIN (J. Amer. Chem. Soc., 1935, 57, 1135— 1137).—The rate of reaction of piperidine with Bu<sup>a</sup>Br at 150—155° is depressed by 2- or 2:6-substituents; Me is a more effective substituent than Ph, CH<sub>2</sub>Ph, CH<sub>2</sub>Ph·CH<sub>2</sub>, or CO<sub>2</sub>Et. *Et*<sub>2</sub> pyridine-, b.p. 188— 188·5°/12 mm., m.p. 42—43°, and piperidine-2:6-dicarboxylate, b.p. 155—156°/11 mm., are described. 2:6-Di(phenylethyl)piperidine has b.p. 238—239°/11 mm. R. S. C.

Trichlorides of iridium<sup>III</sup>-aquodipyridines.— See this vol., 946.

Complex iron thiocyanates with pyridine.—See this vol., 946.

Phenacylpyridinium compounds. F. KROLL-PFEIFFER and A. MÜLLER (Ber., 1935, 68, [B], 1169-1177).-p-Anisyl CBrMe<sub>2</sub> ketone is slowly converted by boiling C5H5N into p-methoxy-ww-dimethylphenacylpyridinium bromide, m.p. 171-172°, transformed by NaOH immediately followed by acid into p-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and a little of the original salt and transformed in the usual manner into p-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and the N-isopropylpyridinium salt (picrate, m.p. 193-194°). 2-Bromo-1-ketotetrahydronaphthalene smoothly yields 1-keto-2-tetrahydronaphthylpyridinium bromide (I) decomp. 216—218°, or, from MeOH with much Et<sub>2</sub>O, a product, decomp. 246—248° (corresponding picrate, m.p. 187—188°). The action of alkali on (I) yields a substance, m.p. 75-80° (decomp.), which is certainly not the anhydro-base, reforms (I) when treated with acid or NH<sub>4</sub>Cl, and is transformed by further treatment with alkali into  $\gamma$ -o-carboxyphenylpropylpyridinium chloride (II) [CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·[CH<sub>2</sub>]<sub>3</sub>·NC<sub>5</sub>H<sub>5</sub>]+Cl<sup>-</sup>, m.p. 58—59° (corresponding picrate, m.p. 138-140°). When distilled in vac. (II) passes into the lactone, m.p. 54-56°, of 0-y-hydroxy-n-propylbenzoic acid, m.p. 70-71°, which is oxidised by  $KMnO_4$  to  $\beta$ -o-carboxyphenylpropionic acid.

1-Ketotetrahydronaphthalene and 4 Br in  $CS_2$ 3 U afford  $\beta\beta$ -dibromo-1-ketotetrahydronaphthalene, m.p. 59—60°, transformed by NPhMe<sub>2</sub> into  $\alpha$ -C<sub>10</sub>H<sub>7</sub>•OH and by C<sub>5</sub>H<sub>5</sub>N into 2-bromo- $\alpha$ -naphthol, m.p. 43—46°. The anhydro-base from 2-ethylthiol-5-methylphenacylpyridinium bromide and CS<sub>2</sub> in CHCl<sub>3</sub> yield the substance, C<sub>16</sub>H<sub>17</sub>ONS,CS<sub>2</sub>, m.p. 118—119° after softening, which is transformed by boiling AcOH into CS<sub>2</sub> and pyridinium salt and by conc. HCl or H<sub>2</sub>SO<sub>4</sub> into readily hydrolysed salts of the base C<sub>15</sub>H<sub>11</sub>ONS<sub>2</sub>, decomp. 285° when rapidly heated, best obtained in addition to 2-ethylthiol-5-methylbenzoic acid by the action of alkali. The same base and the corresponding benzoic acid are also produced by the action of alkali on the CS<sub>2</sub> compounds, decomp. 117—119°, 2-methoxy-5-methylphenacylpyridinium bromide, or the corresponding 2-OEt-derivative. H.W.

Enol-betaines. I. F. KRÖHNKE (Ber., 1935, 68, [B], 1177-1195).—The intermediate products formed by the action of alkali or, preferably, alkali carbonate

 $\begin{array}{c} & \text{on acal} \\ & \text{analogu} \\ \text{(cf. }A). \\ & \text{simply} \\ \text{HC=CPh} \\ & \text{co-ordin} \end{array}$ 

on acalkylpyridinium salts (I) and their analogues are regarded as enol-betaines (cf. A). Their intense colour is not due simply to the conjugated double linkings or the enol-betaine structure, but to co-ordinative unsaturation in conjunction

(.4.) with polarised double linking. The presence of the ethylenic linking is established by the occasional occurrence of cis-trans isomerism. The compounds react very readily with Bz<sub>2</sub>O giving C-Bz compounds and easily afford additive compounds. They give very marked colour reactions with chloranil, bromanil, and 2:3-dichloro- $\alpha$ -naphthaquinone, whereas those with p-O:C<sub>6</sub>H<sub>4</sub>:O, toluquinone, and  $\alpha$ -naphthaquinone are usually fugitive. Anthraquinone and its halogenated derivatives, o-quinones, and  $\alpha\beta$ -diketones do not react, whilst 2-keto-1:1:3:4tetrachloro-1:2:3:4-tetrahydronaphthalene behaves analogously to chloranil. Picryl chloride is a very sensitive reagent, followed by 1:2:4-C<sub>6</sub>H<sub>3</sub>Cl(NO<sub>2</sub>)<sub>2</sub>, C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>, mono-, di-, and tri-nitrobenzaldehyde. Similar colour changes, usually occurring only with (I), are given by compounds •CO•CRR'(Hal), in which at least R or R' is electronegative (e.g., CHBrPhBz, COPh·CHBr<sub>2</sub>, CHBrBz<sub>2</sub>, CBr<sub>3</sub>·CHO, CCl<sub>2</sub>Ph<sub>2</sub>) or by compounds with accumulated negative groups (CCl<sub>3</sub>·NO<sub>2</sub>, CHBr<sub>3</sub>, CHI<sub>3</sub>, C<sub>3</sub>HCl<sub>7</sub>, CPh<sub>3</sub>Cl). Non-cyclic NH<sub>4</sub> salts with an enolisable group and quaternary N give less intense colour reactions.

Phenacylpyridinium bromide and  $K_2CO_3$  give the additive compound  $C_{52}H_{45}O_4N_4Br$ , m.p. 74° (decomp.). Phenacylpyridiniumenol-betaine and Bz<sub>2</sub>O yield dibenzoylmethylpyridiniumenol-betaine (II) (cf. A), m.p. 220—222°, which does not immediately give the chloranil reaction and is transformed by 2N-HClO<sub>4</sub> into dibenzoylmethylpyridinium perchlorate, m.p. 149— 150° after softening at 148°. (II) is also obtained from CHBrBz<sub>2</sub> and  $C_5H_5N$ . The oxime, m.p. 158— 159°, of phenacylpyridinium perchlorate, the compound  $C_{76}H_{61}O_4N_4Br$ , m.p. 166° (decomp.), from p-phenylphenacylpyridinium bromide and  $K_2CO_3$ , and acetonylpyridinium bromide, m.p. 185°, are described. p-Bromophenacylpyridinium bromide, m.p. 241—242°), is transformed by  $K_2CO_3$  into the corresponding

enol-betaine, m.p. 135-136° (decomp.), which yields p-bromophenacylpyridinium benzoate, m.p. 95-96° (decomp.), with BzOH in CHCl<sub>3</sub> and is converted by  $Bz_2O$  in CHCl<sub>3</sub> into benzoyl-p-bromobenzoylmethyl-pyridinium bromide, m.p. 219—220° (also  $+2H_2O$ ), transformed by aq. HBr mainly into  $p-C_6H_4Br\cdot CO_2H$ . m-Nitrophenacylpyridinium perchlorate, m.p. 170-175°, and the corresponding enol-betaine, C13H10O3N2, m.p. 145-147° (decomp.), are described. 3: 4-Dichloro-ω-bromo-2-nitroacetophenone, m.p. 139.5-140°, affords 3: 4-dichloro-2-nitrophenacylpyridinium bromide, m.p. 223° (decomp.), which yields two isomeric enol-betaines, orange-red leaflets, m.p. 160° (with transformation), and yellow needles, decomp. about 160°. ω-Acet-thienoylpyridinium bromide, m.p. 196-197°, is converted by N-NaOH into thiophen-2-carboxylic acid. The following compounds are described : phenacyl-3-nitropyridinium bromide, m.p. 210-220° (decomp.) [corresponding perchlorate, m.p. 198-199° (decomp.) after softening], and the enol-betaine, m.p. 147°; phenacyl-3-picolinium bromide, decomp. 225-230°; phenacyl-2-picolinium bromide, m.p. 214°, and dibenzoylmethyl-2-picoliniumenol-betaine, m.p. 190.5°; p-bromophenacyl-2-picolinium bromide, m.p. 178°, and the enol-betaine, m.p. (indef.) 135° (decomp.); p-bromophenacyl-3-picolinium bromide, m.p. 244-245° (decomp.) after darkening [corresponding perchlorate, m.p. 223-227° (decomp.) after softening], and the enolbetaine, m.p. 130° after blackening at 80°; acetonylquinolinium bromide, m.p. 211, and the enol-betaine, m.p. 110° (decomp.); acetonylisoquinolinium bromide, m.p. 145°, and the enol-betaine, m.p. 100-103° (slight decomp.) (perchlorate, m.p. 149-150° after softening); phenacylquinolinium bromide, m.p. 212°, and the enol-betaine, m.p. 137-139°; p-bromophenacylquinolinium bromide and the enol-betaine, m.p. 125°; p-phenylphenacylquinolinium bromide, m.p. 228-229° (decomp.), and the enol-betaine, m.p. 155° (decomp.) after darkening at 60°; phenacylisoquinolinium bromide, m.p. 204–206° (corresponding perchlorate, m.p. 194–195° after softening at 193°), the enol-betaine, m.p. 192-193°, and dibenzoylmethylisoquinoliniumenolbetaine, m.p. 251-252°; p-bromophenacylisoquinol-inium bromide, m.p. 249° after softening and decomp., and the enol-betaine, m.p. 180°; p-phenylphenacyliso-quinolinium bromide, m.p. 236°, and the enol-betaine, m.p. 203° (decomp.); desylpyridinium bromide, m.p. 157° (decomp.), which does not give reactions with chloranil or  $C_0H_2Cl(NO_2)_3$  in presence or absence of  $Na_2CO_3$ , and the enol-betaine, m.p. 138° (also +1H<sub>2</sub>O), which gradually loses C5H5N when preserved; desylquinolinium bromide, m.p. 188° after softening at 183°; desylisoquinolinium bromide, m.p. 224-225°, and the hydrated enol-betaine;  $\alpha$ -benzoyl- $\beta$ -phenylethylpyridinium bromide, m.p. 192-193°, from CHBrBz·CH<sub>2</sub>Ph and C<sub>5</sub>H<sub>5</sub>N, which gives a non-cryst. resin with K<sub>2</sub>CO<sub>3</sub> and is transformed by KOH into BzOH and  $\beta$ -phenylethylpyridinium salt; 2-phenacylpyridine hydrobromide, m.p. 156-157° [corresponding perchlorate, m.p. 207° (decomp.)], and 2-phenacylpyridine methiodide, m.p. 190-191°, whence the anhydro-base (? enol-betaine), m.p. 122-123°, which is converted by 0.33N-NaOH into BzOH; phenacyltriphenylphosphonium bromide, m.p. 271-272° after softening at 270°, formed with triphenylphosphine

oxide, m.p.  $154-155^{\circ}$ , from PPh<sub>3</sub> and CH<sub>2</sub>BrBz in CHCl<sub>3</sub>, which does not give the chloranil reaction and is stable towards 3N-NaOH at room temp.

H. W. Condensation of a-carboxylic esters of the pyridine series. K. WINTERFELD and F. W. HOL-SCHNEIDER (Arch. Pharm., 1935, 273, 305-315).-Et picolinate (I), pyrrolidone, and NaOEt in C<sub>6</sub>H<sub>6</sub> give 3-picolinoylpyrrolid-2-one, m.p.  $126-128^{\circ}$ , b.p.  $175^{\circ}/0.5-1$  mm. [HgCl<sub>2</sub> compound, m.p.  $223^{\circ}$  (decomp.)], which with hot conc. HCl yields 2-pyridyl y-aminopropyl ketone (II) [dihydrochloride, +H,O, m.p. 175° (decomp.); salt, B,2HCl,2HgCl<sub>2</sub>, +H<sub>2</sub>O, m.p. 194° (decomp.); aurichloride, m.p. 165–166° (decomp.); sulphophenylhydrazone dihydrochloride, m.p. 227° (decomp.); Bz derivative, m.p. 89–90° (HgCl. compound)]. (I) and  $(\cdot CH_2 \cdot CO)_2 NMe$  at 110–115° give similarly a-2-picolinoylsuccinmethylimide, m.p. 90-91° (picrate, m.p. 94-95°), converted by hydrolysis and esterification into Et y-picolinoylpropionate, b.p. 162-163°/11 mm. (platinichloride, decomp. 177-178°; HgCl<sub>2</sub> compound, m.p. 87-88°); the hydrochloride of the corresponding acid yields by hydrogenation (PtO2-Pt-black) in EtOH y-2-pyridylbutyrolacione, b.p. 155-157°/13 mm. (hydrochloride, m.p. 217-218°; aurichloride, m.p. 158-159°). (I) and y-butyrolactone with Na or NaOEt (at 60-70°) in C<sub>6</sub>H<sub>6</sub> afford a-picolinoylbutyrolactone, m.p. 50-51°, hydrolysed by HCl in poor yield to 2-pyridyl y-hydroxypropyl ketone, an oil (platinichloride, sinters 85-86°, decomp. 134-135°; HgCl<sub>2</sub> compound, m.p. 151-152°). Et α-picolinoylacetoacetate, CH2Br·CH2·OMe, and NaOEt give 2-pyridyl y-methoxypropyl ketone, b.p. 115-117°/ 10 mm. (hydrochloride, decomp. 143-144°), and probably a little pyridyl Me ketone (hydrochloride, decomp. 215°). Et quinoline-2-carboxylate, N-methyl- $\alpha$ -pyr-rolidone, and Na in C<sub>6</sub>H<sub>6</sub> at 110° give 2-quinolyl 3-N-methylpyrrolid-2-onyl ketone, m.p. 109—111°, hydrolysed to 2-quinolyl  $\gamma$ -methylaminopropyl ketone hydrochloride, decomp. 155—156°. 2-Pyridyl $\gamma$ -methyl-aminopropyl ketone and (II), but not the other products described above, have marked action on the uterus (isolated or in situ) of guinea-pigs at 1:100,000.R. S. C.

Derivatives of  $\beta$ -2-pyridylpentan- $\beta$ -ol. K. WINTERFELD and F. W. HOLSCHNEIDER (Arch. Pharm., 1935, 273, 315—319).—2-Acetylpyridine (modified prep.) and MgPr<sup>a</sup>Br in Et<sub>2</sub>O give  $\beta$ -2pyridyl-n-pentan- $\beta$ -ol (I), b.p. 102—103°/100 mm. [hydrobromide, m.p. 168°; Bz derivative (II), b.p. 174—175°], the hydrochloride, m.p. 180—181°, of which is hydrogenated (PtO<sub>2</sub>) in EtOH to  $\beta$ -2-piperidyl-n-pentan- $\beta$ -ol (III) (hydrochloride, m.p. 158—160°) giving with CH<sub>2</sub>O-HCO<sub>2</sub>H at 140—150° the N-Me derivative (IV), b.p. 113—114°/10 mm. (Bz derivative, b.p. 161—163°/? 10 mm.). (I) and PBr<sub>3</sub> at 100° give  $\beta$ -2-pyridyl- $\Delta^{\beta}$ -n-pentene hydrobromide, m.p. 124—125°. (II) and (III) have slight, and (IV) large (25 mg. per kg. body-wt.), pressor action on cats. (IV) also paralyses smooth stomach muscle.

R. S. C.

Pyridyl-2-acetic acid and pyridyl-2:6-diacetic acid. M. P. OPARINA (Khim. Farm. Prom., 1934, No. 4, 12-15).—The oximes of the corresponding phenacyl compounds are converted into the anilides by the Beckmann transformation; these are then hydrolysed to the acids. CH. ABS. (r)

Condensation products of pyridine bases with benzaldehyde. M. P. OPARINA and B. SMIRNOV (Khim. Farm. Prom., 1934, No. 4, 15—16).—Condensation (ZnCl<sub>2</sub>) of pyridine bases (b.p. 140—150°) with PhCHO yields a mixture containing distyrylpyridine and  $\alpha$ - and  $\beta$ -stilbazoles. Oxidation affords  $2: 4 \cdot C_5 H_3 N(CO_2 H)_2$ , decarboxylated to the 4-carboxylic acid. CH. ABS. (r)

Substituted aromatic aldehydes in Hantzsch's pyridine condensation. IV. Derivatives of 3:4-dihydroxybenzaldehyde. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1935, 816-818; cf. A., 1932, 744).-The following compounds are obtained from the appropriate aldehydes by the method previously described (A., 1931, 1072) (% yields in parentheses): Et 4-(4'-hydroxy-3'-methoxyphenyl)-(I), m.p. 164° (74.1); Et 4-(2'-nitro-4'-hydroxy-3'-methoxyphenyl)-, m.p. 118° (71.9 and 57.6, yields are inconsistent owing to difficulty of isolation of product); Et 4-(3'-hydroxy-4'-methoxyphenyl)- (II), m.p. 165° (74.1 and 72.8); Et 4-(5'-nitro-3'-hydroxy-4'-methoxyphenyl)-, m.p. 185° (75.7) (+EtOH of crystallisation, m.p. 185°); Et 4-(3': 4'-dimethoxyphenyl)-, m.p. 144° (76.1 and 76.6) [identical with methylation products  $(Me_2SO_4-NaOH)$  of (I) and (II)]; Et 4-(2'-nitro-3': 4'-dimethoxyphenyl)-, m.p. 141.5° (74.2 and 77.0); Et 4-(5'-nitro-3': 4'-dimethoxyphenyl)-, m.p. 154° (69-3 and 71.4); Et 4-(6'-nitro-3': 4'-dimethoxyphenyl)-, m.p. 229° (68.7 and 67.3); Et 4-(3': 4'-methylenedioxy-phenyl)-, m.p. 132° (71.9 and 71.3); Et 4-(6'-chloro-3': 4'-methylenedioxyphenyl)-, m.p. 139° (66.7 and 67.2); Et 4-(6'-bromo-3': 4'-methylenedioxyphenyl)-, m.p. 169° (69.9 and 69.5); Et 4-(6'-nitro-3': 4'methylenedioxyphenyl)-2:6-dimethyl-1:4-dihydropyridine-3: 5-dicarboxylate (59.6 and 61.5)  $[+AcOH \text{ of } cryst., m.p. 144^\circ; +EtOH \text{ of } cryst., m.p. 101^\circ (de$ comp.)]. Condensation with 2:6-dinitroisovanillin (III) yields only the  $NH_4$  salt of (III), m.p. 190° (decomp.), reconverted into (III) by warm dil. HCl. The influence of substituents in the aldehyde on the yield of dihydropyridine is discussed. 5-Nitroisovanillin has m.p. 121° (lit., m.p. 113°). H. G. M.

Manufacture of pyridine compounds.—See B., 1935, 585.

Compounds of 8-hydroxyquinoline with alkali metals and zirconium. P. SUE and G. WETROFF (Bull. Soc. chim., 1935, [v], 2, 1002–1007).—The prep. and analysis of the Li, Na, K(+KOH), and  $NH_4(+NH_3)$  salts of 8-hydroxyquinoline and the Zr salt,  $Zr(C_9H_6ON)_4$ , and its Br-derivative,  $Zr(C_9H_4ONBr_2)_4$ , are described. None of these salts is suitable for accurate determination of the metal it contains. H. G. M.

2-Methyl-4-quinolylhydrazines. E. KOENIGS and (FRL.) M. VON LOESOH (J. pr. Chem., 1935, [ii], 143, 59-69).—Action of  $N_2H_4$ , $H_2O$  (I) on 4-chloro-2methylquinoline (II) at 150° gives a diamine (III), new m.p. 122°, incorrectly described by Marckwald and Chain (A., 1900, i, 521) as 2-methyl-4-quinolylhydrazine (IV). (III) with HNO<sub>2</sub> yields a substance

(V), C<sub>10</sub>H<sub>8</sub>N<sub>4</sub>, m.p. 126°, resolidifying at 240°, to melt again at 300°; (V) is converted by HCl into an isomeride, m.p. 342° (hydrochloride ; Na salt, decomp. 230°). Similarly 4-chloro-6-methoxy-2-methylquinoline (VI) yields a diamine,  $C_{11}H_{13}ON_3$ , m.p. 100–103° [hydrochloride, decomp. 270°; picrate, m.p. 202° (decomp.); Cu salt], which with HNO<sub>2</sub> forms a substance, m.p. 186°, resolidifying at 240°, decomp. 305°, converted by HCl into an isomeride, m.p. 305°. 4-Chloro-6-ethoxy-2-methylquinoline (VII) gives a diamine, m.p. 116-117° [picrate, m.p. 200° (decomp.); Cu salt], which with HNO2 forms a substance,  $C_{12}H_{12}ON_4$ , m.p. 212°, resolidifying, decomp. 270°, converted by HCl into an *isomeride*, decomp. 292° (hydrochloride, decomp. 265°). The action of (I) on (II) in EtOH on the water-bath gives the true 2-methyl-4-quinolylhydrazine (IV), m.p. 200° (decomp.) [sulphate (VIII), m.p. 284—285°; hydrochloride, m.p. 306°; picrate, m.p. 204°; benzylidene derivative, m.p. 259° (all decomp.)], which with  $HNO_2$  forms 2-methyl-4-quinolylazide, m.p. 78° (+2H<sub>2</sub>O) [picrate, m.p. 181° (decomp.)]. (VIII) is reduced (Zn, H<sub>2</sub>SO<sub>4</sub>) to 4-amino-2-methylquinoline. (VI) similarly gives 6-methoxy-2-methyl-4-quinolylhydrazine, m.p. 208° [sulphate, m.p. 310°; picrate, m.p. 191° (both decomp.)], which forms 6-methoxy-2-methyl-4-quinolylazide, m.p. 106— 107° (hydrochloride, decomp. 195°), and 4-amino-6methoxy-2-methylquinoline, m.p. 211-213° [picrate, m.p. 250° (decomp.)]. (VII) gives 6-ethoxy-2-methyl-4-quinolylhydrazine, m.p. 180° [sulphate, m.p. 276° (decomp.); hydrochloride, decomp. 300°; picrate, decomp. 193°], which forms 6-ethoxy-2-methyl-4quinolylazide, m.p. 108° (picrate, decomp. 183°). E. W. W.

Synthesis of quinolinic bases from hydroxymethylene derivatives of ketones. M. ROMET (Compt. rend., 1935, 200, 1676-1678; cf. A., 1887, 940).-The hydroxymethylene derivative of COEt<sub>2</sub> affords an anilide, which is converted by ZnCl<sub>2</sub> at 180° (or at 129° in isoamyl alcohol) into 3-methyl-2ethyl- and 3-methyl-4-ethyl-quinoline, an oil. Similarly, the p-toluidide affords 3: 6-dimethyl-2-ethylquinoline, m.p. 54° (picrate, m.p. 177°). The anilide and p-toluidide of the hydroxymethylene derivative of COMe<sub>2</sub> give quinaldine and 2: 6-dimethylquinoline, respectively. The quinolines obtained indicate that the amine reacts with CO rather than CHO. COMeEt gives a mixture of two hydroxymethylene derivatives (cf. A., 1888, 671; 1916, i, 372) which give anilides, m.p. 129-130° and 96°, convertible into quinolines as above. J. L. D.

Derivatives of 8-aminoquinoline as antimalarials. IV. Compounds with long chains in position 8. O. J. MAGIDSON, O. S. MADAEVA, and M. V. RUBZOV (Arch. Pharm., 1935, 273, 320—333; cf. A., 1934, 417).—The ratio (R),  $D_{tot}/D_{cur.}$ , for 6-methoxyquinolines with NMe<sub>2</sub>:[CH<sub>2</sub>]<sub>n</sub>:NH in position 8 is greater if n is an odd than if it is an even no. up to n=9, max. occurring at n=3 and 9; higher homologues have very low R.  $\kappa$ -Bromodecyl acetate is less reactive than the  $\lambda$ -Br-ester. Periodicity is noticeable in the case of reaction of  $\omega$ -bromoalkyl acetates with NHEt<sub>2</sub> and of  $\omega$ -bromoalkyldiethylamines with 6-methoxyquinoline (I).

CH2Br·CH2·CH2·OPh and Na do not react in Et2O, and in hot PhMe give PhOH, an unsaturated ether, and a little of a substance, m.p. 61-62°. With NaI in COMe, it gives the iodide, which with Na in Et.O. affords  $OPh \cdot [CH_2]_6 \cdot OPh$ ; with 60% HBr this yields the  $\alpha$ -dibromide (II), also obtained from the glycol (modified prep.). (II) and KOAc in AcOH at 120° give ζ-bromohexyl acetate, b.p. 113-116°/12 mm., converted by hot NHEt2 into ζ-acetoxyhexyldiethylamine, b.p. 129-132°/13 mm., whence the CBramine (III), an oil (readily cyclises; hydrochloride), is obtained by 60% HBr. (I) and (III) in EtOH at 110-115° give 8-ζ-diethylamino-n-hexylamino-6methoxyquinoline, b.p. 197-202°/1 mm. [meconate, m.p. 102° (decomp.); R 13.3]. By similar reactions are obtained 8-n-diethylamino-n-heptyl-, b.p. 232-237°/2·5—3 mm., R 33·3, 8-ι-diethylamino-n-nonyl-, b.p. 248—252°/3 mm., R 40, 8-λ-, b.p. 246—247°/2 mm., R 5, and 8-k-diethylamino-n-undecyl-amino-6methoxyquinoline, b.p.  $238-240^{\circ}/1-2$  mm., R 0. Prep. of the following is modified : heptane- $\alpha\eta$ -diol (from Et<sub>2</sub> pimelate), b.p. 160-167°/24 mm., and -dibromide; nonane-ai-diol and -dibromide; Et, azelate; Et  $\lambda$ -bromoundecoate;  $\lambda$ -hydroxyundecyldiethyl-amine, b.p. 168.5—169°;  $\kappa$ -bromoundecoic acid. The following appear to be new : r,-bromoheptyl, b.p. 148-153°/23-25 mm., and i-bromononyl acetate, b.p. 144-152°/9 mm.; y-diethylaminoheptyl alcohol, b.p. 146—148°/17 mm., and bromide (hydrobromide, hygroscopic, m.p. S1— $S4^{\circ}$ );  $\alpha\eta$ -di(diethylamino)heptane, b.p. 153-154°/19 mm. (hydrobromide, m.p. 245°); i-diethylaminononyl acetate, b.p. 155-157°/9 mm., and bromide (hydrobromide); Et x-, b.p. 183-184°/11-12 mm., and *k*-diethylaminoundecoate, b.p. 184—186°/14 mm. (hydrochloride, m.p. 87—88°); λ-diethylaminoundecyl chloride, b.p. 172—175°/10 mm. (hydrochloride, m.p. 89-91°); k-diethylaminoundecyl alcohol, b.p. 167°/9 mm., and chloride (hydrochloride, m.p. 54-56°). R. S. C.

**Preparation of possible antimalarial agents.**—See this vol., 1017.

6-Methoxy-8-quinolyl ethyl ketone. I. T. STRUKOV (Khim. Farm. Prom., 1934, No. 3, 13—14).— S-Cyano-6-methoxyquinoline (Sandmeyer; from S-amino-6-methoxyquinoline) with MgEtI affords 6-methoxy-8-quinolyl Et ketone. CH. ABS. (r).

8-Amino-6-methoxyquinoline. I. T. STRUKOV (Khim. Farm. Prom., 1934, No. 5, 19-21).—A technically applicable method of reduction of 8-nitro-6methoxyquinoline is described. CH. ABS. (r).

Determination of 2-phenylquinoline-4-carboxylic acid in presence of salicylic and acetylsalicylic acids. A. CASTIGLIONI (Annali Chim. Appl., 1935, 25, 240—242).—Unlike the other two acids named, 2-phenylquinoline-4-carboxylic acid (I) is pptd. by silicotungstic acid to form

 $12WO_3$ ,SiO<sub>2</sub>,2H<sub>2</sub>O,4C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>N,2H<sub>2</sub>O, which, on calcination, gives silicotungstic anhydride; multiplication of the latter by 0.3504 gives (I). T. H. P.

Friedel and Crafts reaction in the carbazole series. S. G. P. PLANT, (MISS) K. M. ROGERS, and S. B. C. WILLIAMS (J.C.S., 1935, 741-744).—In the Friedel-Crafts reaction, carbazole (I) is substituted in the 3 and 6 positions, 3-substituted carbazoles in the 6 position, and 9-acylearbazoles in the 2 position. (I) and AcBr yield 3: 6-diacetylcarbazole (II), m.p. 232° (3:6:9- $Ac_3$  compound, m.p. 220°; 9-Me compound, m.p. 192°). p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COMe and 4-bromo-3-nitroacetophenone give (Cu) 2-nitro-4: 4'-diacetyldiphenylamine, m.p. 177°, which on reduction and addition of NaNO<sub>2</sub> forms 5:4'-diacetyl-1-phenylbenz-triazole, m.p. 224°; 2-nitro-4-acetyl-4'-ethyldiphenylamine, m.p. 85°, and 5-acetyl-1-phenyl-4'-ethylbenztri-azole, m.p. 143°, are similarly prepared, but neither triazole could be converted into the carbazole. Reduction of (II) (Clemmensen) leads to 3:6-diethylcarbazole, m.p. 119°, also obtained by oxidising (S) 3:6-diethyl-1:2:3:4-tetrahydrocarbazole, m.p. 87-88°, prepared from the *p*-ethylphenylhydrazone of 4-ethyl*cyclo*hexanone (Fischer reaction). 3-Acetylcarbazole and BzCl afford 3-benzoyl-6-acetylcarbazole, m.p. 210°, also obtained from 3-benzoylcarbazole and AcCl. 9-Benzoylcarbazole with BzCl gives 2:9-di-benzoylcarbazole, m.p. 140-142°, and with AcCl forms the 2-benzoyl-9-acetyl compound, m.p. 136-137°, both substances being hydrolysed to 2-benzoylcarbazole, m.p. 163°. F. R. S.

Manufacture of nitrogenous condensation products.—See B., 1935, 622.

Photochemical behaviour of pyridine, 2-benzylpyridine, papaverine, and some derivatives. A. MULLER and M. DORFMAN (Monatsh., 1935, 65, 411— 432; cf. this vol., 366).—The prep. of 2- (I) and of 4-benzylpyridine is improved, and their  $M_{\rm D}$  determined. When (I) is exposed to light of  $\lambda$  275 to < 238 m $\mu$ , an aldehydic substance is formed. At  $\lambda$  365— 275 m $\mu$ , the products are 2-benzoylpyridine (II) [semicarbazone, m.p. 184° (corr.)], with  $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-2-pyridylethane (?), m.p. 220—221°. In O<sub>2</sub>-free H<sub>2</sub>O vapour, C<sub>5</sub>H<sub>5</sub>N and papaverine are unaffected by light; (I), (II), and papaveraldine darken. The effects of light of each  $\lambda$  from a Hg lamp on various substances are compared. The semicarbazone, m.p. 208° (corr.), of 4-benzoylpyridine is described.

E. W. W.

Metabolism of monomethyltryptophans.—See this vol., 1015.

New derivatives of phenyldimethylaminopyrazolone. J. ERDOS and J. SURU, jun. (Magyar Társ. Ért., 1934, 10, 424—429; Chem. Zentr., 1935, i, 563).—The condensation of 4-aminoantipyrine with aldehydes to yield the following is described : salicylidene-, m.p. 198°; cinnamylidene-, m.p. 157°, and piperonylidene-, m.p. 230°, -4-aminoantipyrine.

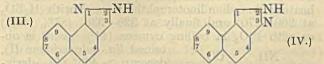
H. N. R. **Ring-formation in heterocyclic compounds.** A. SONN and (in part) W. LITTEN, H. LAURIEN, K. SCHUTZLER, and W. MEYER (Annalen, 1935, 518, 290—298).—The product obtained by interaction of PhN<sub>2</sub>Cl with CO(CH<sub>2</sub>·CO<sub>2</sub>Et)<sub>2</sub> (I) is 1-phenyl-4:6diketo-1:4:5:6-tetrahydropyridazine-3-carboxylic acid NR—N:CX (II) (A, R=Ph; X=CO<sub>2</sub>H), m.p. 244—  $\begin{vmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ &$ 

Similar condensation with CO, Et ·CHEt ·CO·CH, ·CO, Et . affords 1-phenyl-5-ethyl-4:6-diketo-1:4:5:6-tetrahydropyridazine-3-carboxylic acid, m.p. 121-122°, and a similar constitution (A,  $R = p - C_6 H_4 \cdot NO_2$ ,  $X = CO_2 H$ ) must be assigned to the anhydro-compound, m.p. 251° obtained by similar condensation of p-NO2 ·C6H4 ·N2Cl with (I) and alkaline hydrolysis (Bülow et al., A., 1901, i, 239). 4:5-Dibromo-1-phenyl-1:4:5:6-tetrahydropyridazin-6-one (IV) is converted by KOR-ROH into the corresponding 5-bromo-4-methoxy- and 5-bromo-4-ethoxy-, m.p. 135°, -derivatives, reduced to 4-ethoxy-1phenyl-1:4:5:6-tetrahydropyridazin-6-one, m.p. 124-125°, also obtained by the action of EtBr-NaOEt on (III). Prolonged heating with dil. NaOH-EtOH converts (IV) into 5-bromo-1-phenyl-1:4:5:6-tetrahydropyridazine-4: 6-dione, m.p. 270°. With the appropriate amine (IV) yields the corresponding 5-bromo-4-methyl-, m.p. 158-159°, -4-benzyl-, m.p. 203°, -4-diethyl-, m.p. 92-93°, -4-dimethyl- (V), m.p. 116°, -amino-1-phenyl-1:4:5:6-tetrahydropyridazin-6-one. The methiodide of (V) [by NMe<sub>3</sub> on (IV)] with Ag<sub>2</sub>O affords a solution from which the picrate, decomp. > 280°, of "NMe<sub>3</sub>·CH<sub>2</sub>·CH:N·NHPh is obtained. Condensation of the appropriate keto-ester with PhN2Cl affords Et benzeneazo-oxalodiethylacetoacetate, m.p.  $112-112 \cdot 5^{\circ}$ , and -diethylacetonedicarboxylate, m.p.  $76-77^{\circ}$ , the free acid, m.p. 150-151° (decomp.) (anhydride, m.p. 159-160°), of which, when kept, affords the phenylhydrazone, m.p. 78-79°, of CHEt, CO·CHO, and when heated in EtOH gives the phenylhydrazone, m.p. 68-69°, of CO<sub>2</sub>H·CEt<sub>2</sub>·CO·CHO. The formation of such 5- and 6-membered heterocyclic rings is discussed, and it is suggested that the compounds obtained by condensation of Et formylsuccinate with NHPh·NH<sub>2</sub> (Wislicenus et al., A., 1909, i, 9) and  $N_2H_4$  (von Rothenburg et al., A., 1895, i, 302) have the structure  $\stackrel{\text{NR-CO}}{\text{N=CH}} \xrightarrow{\text{CH-CH}_2 \cdot \text{CO}_2 \text{Et}} (\text{R=Ph and R=H, respec-})$ tively). J. W. B.

Pyrimidines. CXLVI. Synthesis of uracyl-5methylamine. T. B. JOHNSON and (MISS) A. LITZINGER (J. Amer. Chem. Soc., 1935, 57, 1139— 1140).—An aliphatic pyrimidine base, uracil-5-methylamine, m.p. 295—300° (decomp.) [hydrochloride, m.p. 242—243° (decomp.); sulphate, m.p. 245—246° (decomp.)], is prepared from Et 2-ethylthioluracil-5acetate by way of the urethane, which is readily hydrolysed by  $H_2SO_4$  or HCl. R. S. C.

Indazoles. 2-p-Dimethylanilino-3-carbethoxyindazole. I. TANASESCU and E. TANASESCU (Bull. Soc. chim., 1935, [v], 2, 1016—1020).—Et o-nitrophenylacetate is not oxidised by nitrous vapours (cf. A., 1909, i, 925). When heated with p-NO·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>, EtOH, and Na<sub>2</sub>CO<sub>3</sub> (or Na<sub>3</sub>PO<sub>4</sub>, but not C<sub>5</sub>H<sub>5</sub>N and C<sub>5</sub>H<sub>11</sub>N) on a water-bath it affords 2 - p-dimethylanilino-3-carbethoxyindazole 1oxide, m.p. 212° (colour reactions with HCl and alcohols described), which on reduction (Zn-EtOH-H<sub>2</sub>O-CaCl<sub>2</sub>) affords 2-p-dimethylanilino-3-carbethoxyindazole, m.p. 143° (hydrochloride, m.p. 197°), and with conc. HCl at the b.p. during 15 min. 2-p-dimethylanilino-3-chloroindazole 1-oxide, m.p. 167°, basic and readily sol. in mineral acids. H. G. M. Quinazolines. VII. Interaction of 2:4-dichloroquinazoline in alcohol with ammonia and methylamine. E. VOPICKA and N. A. LANGE (J. Amer. Chem. Soc., 1935, 57, 1068—1070; cf. A., 1933, 723).—2:4-Dichloroquinazoline and EtOH-NH<sub>3</sub> or EtOH-NH<sub>2</sub>Me at 150° give 2:4-diamino-, m.p. 259° [hydrochloride, m.p. 308°; sulphate, m.p. 330°; acetate, +H<sub>2</sub>O, m.p. 208°; nitrate, m.p. 280°; oxalate, m.p. 274°; picrate, m.p. 304° (decomp.); Ac<sub>2</sub> derivative, m.p. 230°], and 2:4-diamethylamino-quinazoline, m.p. 120° (hydrochloride, m.p. 312°; picrate, m.p. 232°), respectively. M.p. are corr. R. S. C.

Naphthindazoles. V. VESELÝ, A. MEDVEDEVA, and E. MULLER (Coll. Czech. Chem. Comm., 1935, 7, 228—238).—2:  $1-C_{10}H_6Me\cdotNO_2$  in  $(CHCl_2)_2$  with FeCl<sub>3</sub> and Cl<sub>2</sub> affords 8-*chloro-1-nitro-2-methylnaphthalene*, m.p. 114° [also obtained (Sandmeyer) from the corresponding 8-NH<sub>2</sub>-compound], and this, when dissolved in EtOH and slowly added to Fe in boiling AcOH-H<sub>2</sub>O, is reduced to the *amine*, m.p. 89° [Ac derivative (I), m.p. 214—215°]. When diazotised and poured into boiling EtOH, this amine affords some 9-*chloro-a-naphthindazole* (II), m.p. 159° (2-Ac derivative, m.p. 196°) (cf. A., 1891, 312), but no  $8: 2-C_{10}H_6CIMe$  could be isolated. (II) was also obtained by treating (I) in Ac<sub>2</sub>O with N<sub>2</sub>O<sub>3</sub>, and boiling the resulting crude N-NO-derivative in C<sub>6</sub>H<sub>6</sub> for 3 hr. (cf. A., 1908, i, 298). 4-Nitro-1-amino-2methylnaphthalene in EtOH, when diazotised and



heated, affords  $2:4 \cdot C_{10}H_6Me \cdot NO_2$  and  $5\text{-nitro-} x-naphthindazole, m.p. <math>304-305^\circ$  (2-Ac derivative, m.p.  $196-197^\circ$ ).  $6\text{-Bromo-} x-naphthindazole, m.p. <math>249-250^\circ$  (cryst. from AcOH) and  $202-204^\circ$  (pptd. from EtOH solution by  $H_2O$ ) (2-Ac derivative, m.p.  $168^\circ$ ), is similarly obtained.  $2:1 \cdot C_{10}H_6Me \cdot NHAc$  in AcOH and  $N_2O_3$  afford the N-NO-derivative, m.p.  $82^\circ$  (decomp.), converted by very cautious heating or, better, by boiling in  $C_6H_6$  or PhMe into x-naphthindazole (III), m.p.  $158^\circ$  (picrate, m.p.  $193^\circ$ ; Ac derivative, m.p.  $108-109^\circ$ ).  $1:2 \cdot C_{10}H_6Me \cdot NHAc$  is converted similarly into the N-NO-derivative, m.p.  $91^\circ$  (decomp.). This, when heated alone, or better in xylene,  $C_6H_6$ , or benzine, affords  $\beta$ -naphthindazole (IV), m.p.  $231^\circ$  (picrate, m.p.  $217-218^\circ$ ; Ac derivative, m.p.  $116 \cdot 5^\circ$ ; Ag salt). H. G. M.

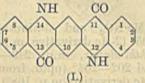
Syntheses and molecular complexes in the phenazine series. II. G. R. CLEMO and H. MCLLWAIN (J.C.S., 1935, 738—741).—There are two types of mol. compound: (i) true phenazhydrins, formed between a phenazine and a 9:10-dihydrophenazine, green to purple, forming green dihydrochlorides, (ii) phenazine-primary or -sec. aromatic base complexes, orange-red, not giving hydrochlorides. *Phenazine-N-methyldihydrophenazine dihydrochloride*, m.p. 225° (decomp.), is prepared from its components. cycloHexane-1:2-dione, o-C<sub>6</sub>H<sub>4</sub>(NHMe)<sub>2</sub>, and HCl followed by NaOH give NN'-dimethyl-2:3:9:10-tetrahydrophenazine, m.p. 78°, whilst with NaOH-AcOH, NN'-dimethyl-9:10-dihydrophenazine, m.p.

153°, is obtained [phenazine-NN'-dimethyl-9:10-dihydrophenazine dihydrochloride, m.p. 225—230° (decomp.)]. The following phenazine-base complexes have been prepared : phenazine-o-, m.p. 153°, -m-, m.p. 143°, and -p-phenylenediamine, m.p. 133°, and -diphenylamine, m.p. 57—58°. 1:2:3:4-Tetra- is reduced (Na-Hg) to 1:2:3:4:9:10:11:12-octahydrophenazine, m.p. 150°, neither compound forming a complex with phenazine. 2-Methyl-1:2:3:4tetrahydrophenazine, b.p. 147°/0·1 mm., obtained from 1-methylcyclohexane-3:4-dione, o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, and NaOAc-AcOH, and 2-methyl-5:6:7:8-tetrahydrophenazine, m.p. 78°, obtained from

 $1:3:4-C_6H_3Me(NH_2)_2$  and cyclohexane-1:2-dione, with I-AcOH give 2-methylphenazine, oxidised to phenazine-2-carboxylic acid. The nature of the complexes is discussed. F. R. S.

Neocyanine. F. M. HAMER (Chem. and Ind., 1935, 54, 640-641).—The evidence of absorption spectra indicates that the I atom is tautomerically shared between the N atoms of the carbocyanine chain rather than between the N atoms of the dicarbocyanine chain. H. W.

Rearrangement products of succinylsuccinic esters. VI. Formation of quinacridones from 2:5-diarylaminoterephthalic acids. H. LIEBER-MANN [with H. KIRCHHOFF, W. GLIKSMAN, L. LOEWY, A. GRUHN, T. HAMMERICH, N. ANITSCHKOFF, and B. SCHULZE] (Annalen, 1935, 518, 245–259).—By heating 2:5-dianilinoterephthalic acid with  $H_3BO_3$ at 260–270° and finally at 320–330° (87% yield) or with  $P_2O_5$  in boiling cymene (44% yield) is ob-

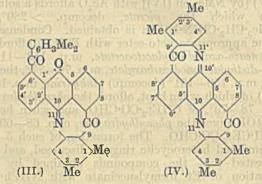


tained lin.-quinacridone (I), decomp. > 400° ( $Cl_{10}$ -derivative, m.p. 402°, by heating with SbCl<sub>5</sub>-I). Similarly from the appropriate diarylaminoterephthalic acid (II) are prepared 4:8-, m.p. 347°,

and 2 : 6-dimethyl-, m.p. 337°; 4 : 8-dimethoxy-, m.p. 318°; 1:2:5:6-dibenzo- (III) [together with a little 2-\Beta-naphthylamino-7: 8-benzacridone-3-carboxylic acid (IV) (Ba salt)] and 3:4:7:8-dibenzo-, m.p. 348° [dodecachlorodihydroxy-derivative, m.p. 410° (decomp.)], -quinacridone. Et 2: 5-di-β-naphthylaminoterephthalate and Me<sub>2</sub>SO<sub>4</sub> at 120-150° afford a little (III) and its 12: 14-Me<sub>2</sub> derivative, m.p. > 400° (decomp.), and (IV). When warmed with conc.  $H_2SO_4$  (III) gives its disulphonic acid. By heating the appropriate (II) with K<sub>2</sub>CO<sub>3</sub>, PhI, and Cu in  $C_5H_{11}$  OH at 195° are obtained 2:5-bisdiphenylamino-, m.p. 292° (decomp.) (Ag, Ba, Pb, and Cu<sup>II</sup> salts), -phenyl-o-tolylamino-, m.p. 309° (NH<sub>4</sub> salt), -phenyl-p-tolylamino-, m.p. 287° (decomp.), -phenyl- $\beta$ -, m.p. 296° (Ag and Ba salts), and - $\alpha$ -naphthylamino-, m.p. 320° (decomp.) (Ba salt), -terephthalic acid. These are converted by heating with BzCl into 12:14-diphenyl-, m.p. >  $450^{\circ}$ , 12:14-diphenyl-4:8-, m.p. 432°, and -2: 6-dimethyl-, m.p. 420°, 12: 14-diphenyl-2:6-dichloro-, 12:14-diphenyl-1:2:5:6and -3:4:7:8-dibenzo-quinacridone. J. W. B.

Morphanthridones. VI. Dehydration and cyclisation of 1:5-di-*m*-xyloylanthraquinonemono- and -di-oxime to dimethyl-*m*-xyloylo-

5:10-benzoylenemorphanthridone and tetramethyl-5:10-10':5'-dimorphanthridonylene. R. SCHOLL and J. DONAT. VII. Dehydration of 1aroylallochrysoketoneoximes to 6:7-benz-5:10phenylenemorphanthridones. R. SCHOLL and E. J. MULLER (Ber., 1935, 68, [B], 1062-1065, 1065-1068; cf. this vol., 869).-VI. 1:5-Di-m-xyloylanthracene is converted by  $HNO_3$  (d 1.48) in boiling AcOH into 9-nitro-1:5-di-m-xyloylanthracene, m.p. 251-252° after softening, transformed by boiling KOH-MeOH into 1:5-di-m-xyloylanthraquinone-9oxime (I), m.p. 219.5-220.5° (decomp.) after softening. (I) is preferably obtained by the action of NH<sub>2</sub>OH on 1: 5-di-m-xyloylanthraquinone in boiling EtOH and is separated from non-cryst. 1:5-di-mxyloylanthraquinone-9: 10-dioxime (II) by taking advantage of the solubility of the latter in aq. NaOH. (I) is transformed in boiling PhNO<sub>2</sub> containing HCl into 6'-m-xyloylo-5: 10-benzoylene-1: 3-dimethylmorphanthrid-9-one (III), m.p. 256.5-258°. Under similar



conditions (or in boiling AcOH) (II) passes more readily into 1:3:1':3'-tetramethyl- $5:10\cdot10':5'$ -dimorphanthrid-9:9'-onylene (IV), m.p. >  $350^{\circ}$ . VII. Dehydrations analogous to those observed

VII. Dehydrations analogous to those observed with 1-aroylanthraquinone-9-oximes and 1:5-diaroylanthraquinone-9:10-oximes are observed in the fluorenone series if anhyd. ZnCl<sub>2</sub> is used in place of the customary dehydrating agents, which yield only red to black amorphous resins.

1-m-Xyloylallochrysoketone is converted by  $NH_2OH$ , HCl and  $BaCO_3$  in boiling EtOH into 1-m-

xyloylallochrysoketone-9-oxime, decomp. 254—255° when rapidly heated (Na salt), converted by ZnCl<sub>2</sub> at 170—180° and then at 190° into 6 : 7-benz-5 : 10-phenylene-1 : 3-dimethylmorphanthridone (V; R=Me), m.p. 237°. alloChrysoketone-1-carboxyl chloride, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> at 60—70° afford 1-benzoylallochrysoketone, m.p. 220—222°, the oxime, decomp. about 250°, of which is

transformed by ZnCl<sub>2</sub> into 6:7-benz-5:10-phenylenemorphanthridone (V; R=H), m.p. 227-228°.

CO

(V.)

H. W.

New mode of formation of hydantoin derivatives. Z. JERZMANOWSKA-SIENKIEWICZOWA (Rocz. Chem., 1935, 15, 202—208).—Et maleate or fumarate in EtOH and  $CO(NH_2)_2$  in presence of NaOEt afford chiefly the *ureide*, decomp. at 273—274°, of hydantoin-5-acetic acid, together with the free acid (I) (*Me*  ester, m.p. 123°). Maleyl monoureide (II) affords fumaryl monoureide (III), decomp. at 262—264°, when heated with aq. HCl at 90°; the ureides yield respectively maleic and fumaric acids when hydrolysed with aq. KOH. (I) is obtained from (II) in 46%, and from (III) in 12% yield, by heating with MeOH-KOH; the reaction does not take place when EtOH is substituted for MeOH. Fumaryl diureide, decomp. at 285°, is obtained from fumaryl chloride and CO(NH<sub>2</sub>)<sub>2</sub>. R. T.

3:4-Pyridino-7:8:9-triazoles. O. BREMER (Annalen, 1935, 518, 274-289).-Reduction (Na2S2O4) of 3-nitro-4-aminopyridine (I) affords the  $3:4-(\tilde{N}\tilde{H_2})_2^{-1}$  compound (II), m.p.  $215-216^{\circ}$  (*dihydrochloride* +H<sub>2</sub>O and anhyd., not melting at 280°), converted by HNO2 into 3:4-pyridino-7:8:9-triazole +EtOH and solvent-free, m.p. 240° [K salt +0.5H2O; hydrochloride, m.p. 210° (decomp.)] (cf. this vol. 226 for nomenclature). With Br-AcOH-KOAc (I) gives its 5-Brderivative, m.p. 181°, reduced to 5-bromo-3: 4-diaminopyridine, whence 5-bromo-3: 4-pyridino-7:8:9triazole (K salt +4EtOH; hydrochloride) is obtained. (I) after reduction with SnCl<sub>2</sub>-HCl (d 1.19) and treatment with Cl2-H2O gives the 6-Cl-derivative, m.p. 157-158°, of (II), converted into 6-chloro-3: 4-pyridino-7:8:9-triazole, not melting at 280°. By condensation of 4-chloro-3-nitropyridine with the appropriate amine are obtained 3-nitro-4-methylamino-, m.p. 162-163°, -4-ethylamino-, m.p. 74° (5-Br-derivative, not pure; reduced to 3-amino-4-ethylamino-, m.p. 129–130°), -4-n-butylamino-, m.p. 47–48° (3-NH<sub>2</sub>-compound, sinters 58°, m.p. 72–73°), -4-benzylamino-, m.p. 103° (3-NH2-compound, m.p. 67-68°), -4-diethylaminoethylamino-, b.p. 166°/1 mm. (3-NH2-compound, b.p. 181:5°/1 mm.), -4-β-hydroxyethylamino-, m.p. 144° (hydrochloride, m.p. 205-206°), -4-β-aminoethylamino-, unstable in air (Ac derivative, m.p. 176°; dihydrochloride, decomp. 265°), and (from 2-chloro-5nitropyridine), 5-nitro-2-anilino-, m.p. 134° (NOderivative, m.p. 112°), -pyridine. From these, by reduction (isolated products in parentheses above) and HNO<sub>2</sub> are obtained 9-methyl-, m.p. 120° [picrate, m.p. 178.5°; hydrochloride, m.p. 223° (decomp.); methiodide, m.p. 194-195°], 9-ethyl-, sinters 40°, m.p. 48°, b.p. 121.5°/1 mm. (picrate, m.p. 177°; hydrochloride, m.p. 183°; methiodide, m.p. 166-167°), 9-n-butyl-, b.p. 128°/1 mm. (hydrochloride, sinters 143°, m.p. 148°), 9-benzyl-, m.p. 124° (hydrochloride, m.p. 220°), 9-diethylaminoethyl-, b.p. 147°/1 mm., 9- $\beta$ -hydroxyethyl-, m.p. 143—144° (converted by aq. EtOH-HCl into the 9-\beta-chloroethyl derivative, m.p. 110-111°, converted by 10% KOH-MeOH into the 9-vinyl compound, m.p. 93°), and 5-bromo-9-ethyl-, m.p. 119.5°, -3: 4-pyridino-7: 8: 9-triazole. 4-Chloro-3-nitropyridine with C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>,H<sub>2</sub>O affords  $\alpha\beta$ -di-(3-nitro-4pyridylamino)ethane, not melting at 270° (dihydrochloride), reduced (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-COMe<sub>2</sub>) to  $\alpha\beta$ -di-(3-amino-4-pyridylamino)ethane, decomp. 270°. 3-Nitro-4-pyridvlhydrazine when heated with cyclohexanone in AcOH-EtOAc affords cyclohexanone-3-nitro-4-pyridylhydrazone, m.p. 91-92°. 2-Chloro-3-bromo-5-nitropyridine (PCl<sub>5</sub> on the 2-OH-compound) has m.p. 69.5°. J. W. B.

Constitution and biological activity of flavins. R. KUHN and H. RUDY (Naturwiss., 1935, 23, 286).— Synthetic and natural lactoflavin are readily esterified with  $H_3PO_4$  by means of the glycerol extract from the small intestine of rats, whilst, under the same conditions, 6:7-dimethyl-9-*l*-araboflavin (this vol., 262, 760) is only slightly esterified, and 6:7:9-trimethylflavin remains unaffected. The extent of esterification runs parallel to the growth-promoting action of these substances. Enzymic esterification (this vol., 1035) therefore affords a new method for characterising flavins. It is expected that other factors apart from the redox potential and the ability to form an ester with  $H_3PO_4$  are of importance in the relation between the chemical constitution and growth-promoting action of flavins. H. G. M.

Synthesis of flavins. P. KARRER, H. SALOMON, K. SCHÖPP, and F. BENZ (Naturwiss., 1935, 23, 355– 356).—The lactoflavin isomeride, 6:7-dimethyl-9-d-1'lyxitylisoalloxazine, m.p. 280—282°,  $[\alpha]_{p} + 59\cdot8^{\circ} (\pm 5^{\circ})$ in 0.05*N*-NaOH ( $Ac_{4}$  derivative, m.p. 225—226°), has been synthesised. Its properties confirm the identity of lactoflavin (vitamin- $B_{2}$ ) with the ribityl-flavin (cf. A., 1934, 1233; this vol., 359, 631). F. O. H.

Porphyrins. XXXIV. Porphyrins with unsaturated side-chains. Interaction of diazomethane and ethyl diazoacetate and vinylpyrroles. H. FISCHER and C. E. STAFF (Z. physiol. Chem., 1935, 234, 97-126; cf. this vol., 362).-Sublimation of 5-carbethoxy-2: 4-dimethylpyrrole-3fumaric acid (I) (Me ester, m.p.  $177^{\circ}$ ;  $Me_2$  ester, m.p.  $126^{\circ}$ ) at 190–200° in a vac. yields an acid, m.p. 237°, isomeric with 5-carbethoxy-2:4-dimethyl-pyrrole-3-acrylic acid (II). (I) with  $Pr^{\beta}OH$  and HCl gives the  $Pr^{\beta}_{2}$  ester, m.p. 126°, of (very probably) 5-carbethoxy-2: 4-dimethylpyrrole-3-maleic acid and with Br in AcOH 5-carbethoxy-2: 4-dimethylpyrrole-3maleic anhydride (III), m.p. 208° [corresponding acid loses  $H_2O$  at 175° to give (II); Me ester, m.p. 180°;  $Me_2$  ester, m.p. 133°]. The Me<sub>2</sub> ester of (I) with Br yields the Me2 ester, m.p. 140°, of 5-carbethoxy-4methyl-2-bromomethylpyrrole-3-fumaric acid (IV), with SO<sub>2</sub>Cl<sub>2</sub> the Me<sub>2</sub> ester, m.p. 138°, of 5-carbethoxy-4-methyl-2-chloromethylpyrrole-3-fumaric acid, with 2SO<sub>2</sub>Cl, the Me<sub>2</sub> ester, m.p. 152°, of 5-carbethoxy-4methyl-2-dichloromethylpyrrole-3-fumaric acid, and with 3SO<sub>2</sub>Cl<sub>2</sub> a Cl<sub>3</sub>-compound which with H<sub>2</sub>O gives the Me. ester, m.p. 181° (Me ester, m.p. 143°), of 2-carboxy-5-carbethoxy-4-methylpyrrole-3-fumaric acid. (IV) with MeOH gives the  $Me_2$  ester, m.p. 93°, of 5-carbethoxy-4-methyl-2-methoxymethylpyrrole-3fumaric acid ( $\check{V}$ ) and with  $NH_2Ph$  the  $Me_2$  ester, m.p. 120°, of 5-carbethoxy-4-methyl-2-anilinomethyl-pyrrole-3-fumaric acid. Prolonged action (4 weeks) of  $CH_2N_2$  on the Me<sub>2</sub> ester of (V) gives the  $Me_2$  ester, m.p. 117-118° (decomp.), of 5-carbethoxy-4-methyl-2 - methoxymethyl - 3 - dicarboxypyrazolinylpyrrole. Reduction of (V) with Na amalgam gives the Me, ester, m.p. 71°, of 5-carbethoxy-4-methyl-2-methoxymethylpyrrole-3-succinic acid (VI). The Me2 ester of (IV) with  $H_2O$  at 100° for 1 hr. gives an *oil* and a cryst. substance, m.p. 132-135°. Alkaline hydrolysis of (I) gives 5-carboxy-2: 4-dimethylpyrrole-3-fumaric acid, m.p. 188° (Me3 ester, m.p. 127°). With NH2Ph at 160-170° (I) gives 5-carbethoxy-2: 4-dimethylpyrrole-3maleic anil (VII), m.p. 211°, 5-carbethoxy-2:4-di-

methylpyrrole-3-succinic acid (VIII) gives the corresponding anil, m.p. 187-188°, the Et<sub>2</sub> ester of 5-carbethoxy-2:4-dimethylpyrrole-3-methylmalonic acid gives the corresponding anil, m.p. 180°. Hydrolysis of (VII) gives 5-carboxy-2: 4-dimethylpyrrole-3maleic anil, which yields 5-carbomethoxy-2: 4-dimethylpyrrole-3-maleic anil, m.p. 204°, with  $CH_2N_2$ . (VII) with 2Br gives 5-carbethoxy-2: 4-dimethylpyrrole-3-N-phenylbromomaleic imide, m.p. 216°, and with 4Br 5-carbethoxy-4-methyl-2-bromomethylpyrrole-3-Nphenylbromomaleic imide, m.p. 221° (decomp.); this with McOH gives 5-carbethoxy-4-methyl-2-methoxymethylpyrrole-3-N-phenylbromomaleic imide, m.p. 179°, and with aq. EtOH 5-carbethoxy-4-methyl-2-ethoxymethylpyrrole-3-N-phenylbromomaleic imide, m.p. 141°. The Me<sub>2</sub> ester of (VIII) with 1.05 mols. of Br gives the  $Me_2$  ester, m.p. 123°, of 5-carbethoxy-4methyl-2-bromomethylpyrrole-3-succinic acid (IX), which with MeOH gives the Me<sub>2</sub> ester of (VI). The  $Me_2$  ester of (IX) with  $H_2O$  (1 hr.) loses  $CH_2O$  to give 5:5'-dicarbethoxy-4:4'-dimethyl-3:3'-tetramethyldisuccinyl-2: 2'-pyrromethane (X), m.p. 170°. Hydrolysis of (X) with 8NaOH gives the  $Na_6$  salt of 5:5'dicarboxy-4:4'-dimethyl-3:3'-disuccinyl-2:2'-pyrromethane, which with HCO<sub>2</sub>H and then HCl in MeOH gives the  $Me_8$  ester, m.p. 317°, of 1:4:5:8-tetramethylporphin-2:3:6:7-tetrasuccinic acid (XI) (Fe salt, m.p. 228°). The Me<sub>8</sub> ester of (XI) with dil. HCl at 210° gives coproporphyrin II. After hydrolysis and oxidation with  $CrO_3$  at  $>30^\circ$  the Mc<sub>8</sub> ester of (XI) gives carboxylated hamatic anhydride,  $C_9H_9O_7$ , m.p. 173°; by oxidation at  $<0^{\circ}$  carboxylated hæmatic acid,  $C_9H_9O_6N$ , m.p. 195° (decomp.), is obtained. The Me<sub>2</sub> ester of (VIII) with 2SO<sub>2</sub>Cl<sub>2</sub> gives an  $\alpha$ -dichloro-methyl compound, which yields the Me<sub>2</sub> ester, m.p. 113° (oxime, m.p. 128°; semicarbazone, m.p. 179°), of 2 - aldehydo - 5 - carbethoxy - 4 - methylpyrrole - 3 - suc cinic acid with MeOH and with 3.1 mols. of SO<sub>2</sub>Cl<sub>2</sub>. The Me<sub>2</sub> ester of (VIII) gives a Cl-compound which, with MeOH, yields the Me<sub>2</sub> ester, m.p. 114°, of 2carbomethoxy-5-carbethoxy-4-methylpyrrole-3-succinic acid. (I) with  $CH_2N_2$  gives the  $Me_2$  ester, m.p. 126°, of 5-carbethoxy-2: 4-dimethylpyrrole-3pyrazolinedicarboxylic acid; on the Me or Et ester of (II) the corresponding pyrazolines, m.p. 211° and 172-175°; on 5-carbethoxy-2: 4-dimethyl-3-(weyano-w-carbethoxyvinyl)pyrrole (XII) (with loss of N) the corresponding cyclopropane derivative, m.p. 116°; on 5-carbethoxy-2: 4-dimethyl-3-(ω-dicyanovinyl)pyrrole (XIII) 5-carbethoxy-2:4-dimethyl-3-(2:2'-dicyanocyclopropyl)pyrrole (XIV), m.p. 161°; on 2:4-dimethyl-3-( $\omega$ -cyano- $\omega$ -carbethoxyvinyl)-pyrrole-3-carboxylic acid a substance,  $C_{15}H_{18}O_4N_2$ , m.p. 139°; on 2:4-dimethyl-3-(ω-dicyanovinyl)pyrrole the corresponding cyclopropane derivative, m.p. 160°; and on 2-carbomethoxy-5-carbethoxy-4methyl-3-(w-dicyanovinyl)pyrrole with addition of 2CH<sub>2</sub> a substance (XV), m.p. 123°. CHN<sub>2</sub>·CO<sub>2</sub>Et with (XII) and (XIII) gives, with loss of N, the cyclopropane derivatives, m.p. 124° and 149°; with the Me ester of (II) a pyrazoline derivative, m.p. 143° (decomp.); and with mesitylene an acid,  $C_{11}H_{14}O_2$ , m.p. 140° (1CHN<sub>2</sub>·CO<sub>2</sub>Et added). 5-Carbethoxy-2:4-dimethyl-3-carbomethoxypyrazolinylpyrrole on alkaline hydrolysis and decarboxylation gives 2:4-

dimethyl-3-carboxypyrazolinylpyrrole, m.p. 165° (decomp.), which with CrO<sub>3</sub> gives pyrazoline-3: 4-di-carboxylic acid, m.p. 233° (decomp.). Me 5-carbethoxy - 2: 4 - dimethylpyrrole - 3 -  $\alpha\beta$  - dibromoacrylate [from the Me ester of (II)] with  $CHNa(CO_2Et)_2$  gives the Me ester, m.p. 159°, of 5-carbethoxy-2: 4-dimethylpyrrole  $-3 - \beta$ -bromoacrylic acid. (XIV) on alkaline hydrolysis loses HCN and gives a mono-carboxylic *acid*,  $C_9H_{11}O_3N$ , m.p. 229° (decomp.) (*Me* ester, m.p. 145–148°), and with Br in MeOH it gives 2-carbomethoxy-5-carbethoxy-4-methyl-3-(2:2'-dicyanocyclopropyl)pyrrole, m.p. 128°. Hydrolysis of (XV) gives 3-propionyl-4-methylpyrrole-2:5-dicarboxylic acid, m.p. 203° (Me2 ester, m.p. 48°). 2-Carbo-methoxy - 5 - carbethoxy - 3 - (2 - cyano - 2' - carbethoxy cyclopropyl)-4-methylpyrrole, m.p. 162°, is obtained from 5-carbethoxy-3-(2-cyano-2'-carbethoxycyclopropyl)-2: 4-dimethylpyrrole by the action of Br and MeOH. 3-Acetyl-2: 4-dimethylpyrrole-5-carboxylic acid [from 3-acetyl-5-carbethoxy-2: 4-dimethylpyrrole (oxime, m.p. 195°)] with CH<sub>2</sub>N<sub>2</sub> gives 3-acetyl-5-carbomethoxy-2:4-dimethylpyrrole, m.p. 159°. The oxime of 3-acetyl-2:4-dimethylpyrrole has m.p. 136°. W. McC.

Constitution of bile pigment. XIII. Constitution of bilirubin and its azo-dyes and the Gmelin reaction. H. FISCHER and H. W. HABERLAND (Z. physiol. Chem., 1935, 232, 236-258; cf. this vol., 632).—Catalytic hydrogenation (1 mol. of  $H_2$ ) of bilirubin (I) gives 1': 8'-dihydroxy-1: 3:5:7-tetramethyl-8- ethyl-4:5-di- $(\beta$ -carboxyethyl)-2-vinyldihydro-bilin (II), m.p. 315°. Total hydrogenation (3H<sub>2</sub>) of (II) affords mesobilirubinogen, partial (H2) yields mesobilirubin. With conc. HNO3, (II) gives methylethylmaleimide (< 50% of theory). Fusion of (II) with resorcinol yields isoneoxanthobilirubic acid. Therefore in (I) the 8'-OH and the vinyl group in the pyrrole ring IV must have formed a dihydrofuran ring. The furan ring is opened by hydrogenation before the saturation of the vinyl group. With Br in  $CHCl_3$ , (I) gives tetrabromoglaucobilin hydrobromide (III), m.p. >  $300^{\circ}$  [Me ester (IV), sinters  $160-168^{\circ}$ ; Zn salt]. Reduction of (III) with HI and subsequent oxidation with PbO<sub>2</sub> affords methylethylmaleimide. Reduction of (III) with Na-Hg and oxidation with CrO<sub>3</sub> yields a substance, m.p. 160-165°. Hydrogenation (Pd) of (IV) gives glaucobilin Me<sub>2</sub> ester. (III) is therefore diketo-1:3:6:7-tetramethyl-2:8-dibromoethyl-4:5di-(\beta-carboxyethyl)bilin hydrobromide. The stages of the Gmelin reaction of (IV) are described and the mechanism is discussed. Mesobilirubin is oxidised by benzoquinone or PbO<sub>2</sub> to the green stage which isomerises to glaucobilin (blue-green or blue), also by PbO, to a higher stage of oxidation (blue) isomeric with the violet compound.

When coupled with PhN<sub>2</sub>Cl mesobilirubin IX  $\alpha$ -Me<sub>2</sub> ester hydrochloride gives a mixture (V), m.p. 184– 185°, mesobilirubin XIII  $\alpha$ -ester hydrochloride yields 5-hydroxy-5'-azobenzene-4:3'-dimethyl-3-ethyl-4'- $\beta$ carbomethoxyethylpyrromethene hydrochloride (VI), m.p. 196–197°. Mesobilirubin III  $\alpha$ -ester hydrochloride gives 5-hydroxy-5'-azobenzene-3:3'-dimethyl-4-ethyl-4'- $\beta$ -carbomethoxyethylpyrromethene hydrochloride (VII), m.p. 213°. (V) consists of (VI) and (VII). Coprobilirubin Me<sub>4</sub> ester dihydrochloride affords 5-hydroxy5'-azobenzene-4: 3'-dimethyl-3: 4'-di-( $\beta$ -carbomethoxyethyl)pyrromethene hydrochloride (VIII), m.p. 176°. "Analytical" Me neoxanthobilirubate gives (V). Me neo- and isoneo-xanthobilirubate give, respectively, (VI) and (VII). 5-Hydroxy-4: 3'-dimethyl-3: 4'-di-( $\beta$ -carbomethoxyethyl)pyrromethene yields (VIII). The numbering of the C atoms of bilin is :

$$\frac{\vec{r} \cdot \vec{r}}{N} = CH - \frac{\vec{r} \cdot \vec{r} \cdot \vec{r}}{NH} - CH = \vec{r} \cdot \vec{r} \cdot \vec{r} \cdot \vec{r}$$
N
J. H. B.

Blood-pigment. XVII. Human hæmoglobins. XVIII. Globin and its hæmin-linking groups. XIX. Methæmoglobin and its compounds with hydrogen peroxide, cyanides, fluorides, and sulphides.—See this vol., 878.

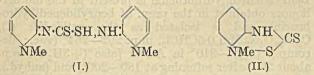
Magnetic behaviour of heavy metal compounds of the phthalocyanines.—See this vol., 924.

Synthesis of  $\Delta^2$ -oxazolines and  $\Delta^2$ -thiazolines from N-acyl- $\beta$ -aminoethyl alcohols. H. WENKER (J. Amer. Chem. Soc., 1935, 57, 1079—1080).— NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH (I) and the appropriate acid at 160—200° give the N-formyl (II), b.p. 191—193°/10 mm., -Ac, b.p. 195—196°/10 mm., -propionyl, b.p. 201—203°/10 mm., and -Bz, b.p. 230—231°/10 mm., derivatives. At 260—280° these afford 2-methyl-[picrate, m.p. 163° (lit. 159—160°)], -phenyl-, b.p. 246—248°, and -ethyl- $\Delta^2$ -oxazoline, b.p. 124—125° (picrate, m.p. 154°), in 30, 22, and 35% yield, respectively. (II), however, gives CO and (I). With P<sub>2</sub>S<sub>5</sub>  $\Delta^2$ -thiazoline and its 2-Me, -Et [picrate, m.p. 138° (lit. 135°)], and -Ph derivatives are formed.

R. S. C.

Chromate oxidation of o-toluenesulphonamide. I. G. ZILBERG (Khim. Farm. Prom., 1934, No. 4, 22-24).—The production of saccharin by this method is described;  $K_2Cr_2O_7$  is superior to  $Na_2Cr_2O_7$  for the purpose. CH. ABS. (r)

Action of carbon disulphide on methylpyridone. imide. K. S. TOPTSCHIJEV (Gazzetta, 1935, 65, 317-321).—CS<sub>2</sub> (1 mol.) reacts in EtOH with methylpyridoneimide (A., 1921, i, 450) (2 mols.) to form the salt (I), m.p. 160°, of the latter with its dithiocarbamic



acid. With  $CS_2$  in excess, the product is N-methylpyridodithiodiazolone (II), m.p. 135°, b.p. 173°/3 mm., a substance of the "Hector's base" type. E. W. W.

Alkaloids of Heliotropium lasiocarpum. III. Hydroxyheliotridane. G. MENSCHIKOV (Ber., 1935, 68, [B], 1051—1054; cf. A., 1933, 727).—Catalytic hydrogenation (Adams) of heliotrine (I) leads to the absorption of 4 H with production of hydroxyheliotridane (II),  $C_8H_{15}ON$ , b.p. 126—128°/12 mm., m.p. 60—65°,  $[\alpha]_D$  —14.5° in H<sub>2</sub>O [methiodide, m.p. 296°; picrate, m.p. 196° (decomp.) when rapidly heated], and heliotric acid. Reduction therefore occurs exclusively in the basic portion of (I) and is accompanied by reduction of the esterified OH, since similar treatment of heliotridine dibenzoate hydrochloride affords BzOH and non-cryst. hydroxyheliotridane benzoate. (II) is probably a tert.-alcohol, since it cannot be oxidised to a ketone or acid. It is transformed by conc.  $H_2SO_4$  at  $170-175^\circ$  into the base (III),  $C_8H_{13}N$ , b.p. 165-166°,  $[\alpha]_p - 160^\circ$  [picrate, m.p. 222° (decomp.)], probably identical in structure with the product of the action of NaOEt on chloroheliotridane (which is therefore greatly racemised). Catalytic reduction of (III) gives a base,  $C_8H_{15}N$ , b.p. 167-168.5°,  $[\alpha]_p - 99.5^\circ$  (picrate, decomp. 236°), which is almost certainly heliotridane in an optically purer form than that described previously. H. W.

[Simplification of Pictet's synthesis of nicotine.] E. SPATH and F. KUFFNER (Ber., 1935, 68, [B], 1125—1127; cf. this vol., 635).—An acknowledgment of the priority of Wibaut (this vol., 872). H. W.

Amidation of alkaloids with sodium and potassium amides. Structures of chloroanabasine isomerides. M. I. KABATSCHNIK and M. M. KATZNELSON (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 35—41; cf. A., 1934, 538).—The  $\alpha$ -series of compounds of Menschikov *et al.* (A., 1934, 1014) is an  $\alpha'$ -series. The authors re-state their previous conclusions. J. L. D.

Vasicine. K. S. NARANG and J. N. RAY (Current Sci., 1935, 3, 552).—The picronolate of the reduction product of the compound B (this vol., 765) is identical with that of reduced vasicine. The structure of vasicine is probably that given by Morris *et al.* (*ibid.*, 873). E. W. W.

**Ergotocine.** M. S. KHARASCH and R. R. LEGAULT (J. Amer. Chem. Soc., 1935, 57, 1140—1141; cf. this vol., 827).—Ergotocine,  $C_{21}H_{27}O_3N_3$  (? $H_{27}$  or  $H_{29}$ ), m.p. 158—160° (decomp. from 155°), obtained by extraction of a solution of ergot at  $p_{\rm H}$  6·7—7·0 with CHCl<sub>3</sub> (not Et<sub>2</sub>O,  $C_2$ HCl<sub>3</sub>, or  $C_6H_6$ ), forms onium salts (*oxalate*, *maleate*, *malonate*, *tartrate*, and *malate*) with acids and also alkali salts, contains 3 active H, is hydrolysed by alkali to (?) lysergic acid and a basic fragment, and closely resembles its maleate, ergotoxine, and ergotamine in absorption spectrum. Ergine has no oxytocic activity in doses up to 4 mg. given orally to human mothers. R. S. C.

Ergobasine, a water-soluble alkaloid from the ergot of Seigle. A. STOLL and E. BURCKHARDT (Compt. rend., 1935, 200, 1680—1682).—CHCl<sub>3</sub> extracts ergobasine,  $C_{19}H_{23}O_2N_3$  (I), decomp. at 162°,  $[\alpha]_{D}^{00} + 90^{\circ}$ , from the  $H_2O$ -sol. portion of the alkaloids of ergot. (I) fluoresces in aq. solution, and is sensitive to light and  $O_2$ . It gives the general reactions of alkaloids, and affords cryst. salts. J. L. D.

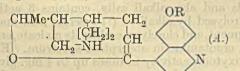
Preparation of ergometrine.—See this vol., 894.

Synthetic alkaloids from narcotine. E. V. SESHACHARYULU and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 159—168).—Condensation of cotarnine (from HNO<sub>3</sub> and narcotine) with substances containing reactive :CH<sub>2</sub> in presence of Ac<sub>2</sub>O yielded the anhydro-N-acetylcotarnine derivatives of hippuric acid, m.p. 235°, camphor, m.p. 188°, phenylacetic acid, m.p. 193°, phenylacetonitrile, m.p. 196°, Et cyanoacetate, m.p. 95°, Et malonate, m.p. 195°, Et oxaloacetate, m.p. 185°, Et acetoacetate, m.p. 192°, Et acetonedicarboxylate, m.p. 173°, Et succinosuccinate, m.p. 189°, thiohydantoin acetate, m.p. 227°, malonylcarbamide acetate, m.p. 185°, deoxybenzoin, m.p. 169°, fluorene, m.p. 201°, acetylacetone, m.p. 193°, benzoylacetone, m.p. 199°, dimethyldihydroresorcinol, m.p. 187°, phthalide, m.p. 196°, acetophenone, m.p. 183°, 2 : 4-dinitrotoluene, m.p. 155°, benzylideneacetone, m.p. 203°, mesityl oxide, m.p. 194°, cinnamylideneacetone, m.p. 190°, piperonylideneacetone, m.p. 178°, furfurylideneacetone, m.p. 197°. Reactions of these substances with alkaloid reagents are described. F. O. H.

New alkaloid from the bark of Holarrhena antidysenterica. D. H. PEACOCK and J. C. CHOW-DHURY (J.C.S., 1935, 734-735).—Lettocine,  $C_{17}H_{25}O_2N$ , m.p. 350-352° (methiodide, m.p. 235°), is isolated as the hydriodide, m.p. 256° (decomp.). The amount present is < 0.1%; it appears to be a tert.-base without OH. F. R. S.

Demethylation of quinidine. (MLLE.) R. LUD-WICZAK and J. SUSZKO (Bull. Acad. Polonaise, 1935, A, 65—78, and Rocz. Chem., 1935, 15, 209—220; cf. A., 1933, 1312; 1934, 787).—Demethylation (60%H<sub>2</sub>SO<sub>4</sub>) of both quinidine and *iso*quinidine (I) yields cupreidine (II) and an isomeric phenolic base isocupreidine (III), m.p. 242—243°,  $[\alpha]_{10}^{20}$ —7.0° in 96% EtOH [hydrochloride (+H<sub>2</sub>O), m.p. 236—237° (decomp.),  $[\alpha]_{10}^{20}$ —35.0° in H<sub>2</sub>O; picrate, m.p. 204—205° (decomp.); methiodide (IV), m.p. 299—300° (decomp.),  $[\alpha]_{10}^{20}$ —24.0° in H<sub>2</sub>O; dimethiodide, m.p. 212—213° (decomp.); Bz, m.p. 213—214° (decomp.)

 $(+2HCl, EtOH, m.p. 201-207^{\circ})$ , and p-toluenesulphonyl  $(+2HNO_3, 0.5H_2O)$  derivative, m.p. 146-147° (decomp.); amine oxide  $(+H_2O)$ , m.p. 273-274°], which regenerates (I) on methylation with Me<sub>2</sub>SO<sub>4</sub> or CH<sub>2</sub>N<sub>2</sub> and is converted into (II) by 60% H<sub>2</sub>SO<sub>4</sub>. (III) heated with 25% AcOH (100°; 20 hr.) yields isocupreicine (V), (A; R=H) [+0.5COMe<sub>2</sub>,



m.p. 133° (decomp.),  $[\alpha]_{20}^{20} + 22.5°$  in 96% EtOH]. also obtained by demethylation (15% HBr) of *iso*quinicine (A; R=Me) (cf. A., 1930, 97), formed together with *N*-methyl*iso*quinicine by methylation with CH<sub>2</sub>N<sub>2</sub> of (V). (IV) heated with NaOH (5 hr.) yields *N*-methyl*iso*quinicine (*loc. cit.*). F. R. G.

Cinchona alkaloids in pneumonia. III. apo-Cupreines (apoquinine). C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1935, 57, 1083— 1085; cf. this vol., 766).—" apoQuinine," prepared from quinine by 25% HCl at 142—143° or by boiling 60% H<sub>2</sub>SO<sub>4</sub>, is usually a mixture of  $\alpha$ - (I), m.p. 180— 190° (decomp.),  $[\alpha] -215°$  (hydrochloride,  $[\alpha] -163°$ ; dihydrochloride,  $[\alpha] -223°$ ; H sulphate,  $[\alpha]_D -224°$ ), and  $\beta$ -apocupreine, m.p. 180—190° (decomp.),  $[\alpha]$ -194° (hydrochloride,  $[\alpha] -145°$ ; dihydrochloride,  $[\alpha]$   $-206^{\circ}$ ; H sulphate, [ $\alpha$ ]  $-208^{\circ}$ ), probably geometrical isomerides containing CHMe. Occasionally only one compound is obtained. (I) has pneumococcidal effect in vitro at 1:300,000; both are very slightly toxic to mice and have high protective power. R. S. C.

apoQuinine. T. A. HENRY and W. SOLOMON (Chem. and Ind., 1935, 54, 641-642).—The  $\alpha$ -apocupreine and its salts described by Butler *et al.* (see above) are identical with the author's *apoquinine* (I) and its derivatives. The introduction of the term *apocupreine* is deprecated. Butler's  $\beta$ -*apocupreine* is a mixture of (I) and a new alkaloid of low  $[\alpha]$ .

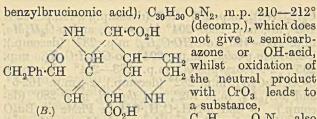
H. W. Synthesis of physostigmine (eserine). XI. Later phases of the synthetical investigations. F. E. KING and R. ROBINSON (J.C.S., 1935, 755-759).—Comparison and mixed m.p. of specimens of dl-noreserethole picrate and of dl-escrethole-b and its picrate, prepared by Hoshino and Kobayashi (cf. A., 1934, 667), show identity and the analytical figures for (I) as  $C_{15}H_{22}ON_2$  are confirmed. De-ethylation of *l*-eserethole methiodide with HI, followed by addition of picric acid, gives 1-eseroline methopicrate, m.p. 193-195° (decomp.), in small yield. Eserethole methochloride is thermally decomposed to physostigmol Et ether, whilst the methofluoride is partly unchanged and partly converted into an unknown base (picrate, m.p. 197-198°; methopicrate, m.p. 163—166°). F. R. S.

Constitution of corynanthine. C. R. SCHOLZ (Compt. rend., 1935, 200, 1624—1625).—The " $\psi$ corynanthine," obtained by treating corynanthine (I) with NaOH and re-esterifying (this vol., 365), is identical with the product from yohimbine (II) similarly treated [*i.e.*, is a Me yohimboate]. (I) and (II) are thus stereoisomeric; this is confirmed by preparing *apo*yohimbine (J.C.S., 1923, 123, 1038) from both. E. W. W.

Strychnos alkaloids. LXXXVI. isoBenzylidenedihydrobrucine and the oxidation of 11benzyl- and 11-nitroso-brucine. H. LEUCHS and H. BEYER (Ber., 1935, 68, [B], 1204-1210).—iso-Benzylidenedihydrobrucine is present in the motherliquors obtained in the prep. of benzylidenedihydrobrucine and is isolated as the methiodide (I),  $C_{30}H_{32}O_4N_2$ ,MeI,0.5CHCl<sub>3</sub>, m.p. 262-264° (vac.; decomp.),  $[\alpha]_{20}^{20}$  -310° in AcOH [also (+3H<sub>2</sub>O), m.p. about 260° after softening at 180-200°, and (anhyd.), m.p. 190-195° (vac.),  $[\alpha]_{20}^{20}$  -319.6° in AcOH,  $[\alpha]_{20}^{20}$ -565°/d in CHCl<sub>3</sub>]. In this and in the corresponding instance in the strychnine series the p position of the  $C_6H_6$  nucleus of the alkaloid cannot therefore be

PhCH CO (A.) (A.) PhCH CO (A.) involved in the condensation. The production of a new ring (cf. A) is suggested. The condensation is induced by the reagents which cause the strychnineisostrychnine isomerisation. (I) cannot be catalytically hydrogenated; it gives an Ac derivative,  $C_{32}H_{34}O_5N_2$ , MeI,  $0.5H_2O$ ,

(A.) Ac derivative,  $C_{32}H_{34}O_5N_2$ , MeI,  $0.5H_2O_7$ , m.p. 221—223° (vac.),  $[\alpha]_2^{\infty}$ —288.5° in AcOH, which also resists oxidation. Treatment of benzylbrucine with KMnO<sub>4</sub> in COMe<sub>2</sub> gives an amorphous acid (



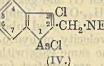
C20H22(0r24)O5N2, also obtained from the neutral by-products of the oxidation of benzylstrychninonic acid. In both cases therefore the aromatic nucleus is destroyed and the NH2-acid has the structure B. 11-Oximinobrucine when oxidised by  $\text{CrO}_3$  in  $3 \cdot 6N \cdot \text{H}_2\text{SO}_4$  at  $80 - 85^\circ$  gives the  $NH_2$ -acid,  $\text{C}_{16}\text{H}_{20}\text{O}_6\text{N}_2$ , m.p. >  $360^\circ$ ,  $[\alpha]_{12}^{20} + 54 \cdot 3^\circ$  (diperchlorate), hydrogenated to the acid,  $\text{C}_{16}\text{H}_{22}\text{O}_5\text{N}_2$ . H. W.

Use of liquid hydrogen chloride in preparation of dichloro-arsines. F. GOVAERT (Compt. rend., 1935, 200, 1603–1605).—Treatment of  $NH(C_6H_4)_2AsR$  with HCl (cf. A., 1931, 1435) is 1935, 200, 1603-1605).-Treatment of difficult when R=Bu<sup>y</sup>, since (I) decomposes at its m.p. Reaction in  $C_{10}H_{12}$ ,  $Et_2O$ , or  $SO_2$  was unsatisfactory, but in HCl at  $-85^{\circ}$  to  $-90^{\circ}$  was immediate. After evaporating off the HCl and dissolving in CCl<sub>1</sub>, 80% of NHPh<sub>2</sub>, HCl and tert.-butyldichloroarsine, b.p. 61°/16 mm., with 20% of 10-chloro-5: 10-dihydrophenarsazine, were obtained. E. W. W.

Reaction of phenylarsine with organic compounds of tin and lead. A. N. NESMEJANOV and R. C. FREIDLINA (J. Gen. Chem. Russ., 1935, 5, 53-59).-AsH<sub>2</sub>Ph reacts with HgPhCl, HgPh<sub>2</sub>, PbPh<sub>4</sub>, PbPh<sub>2</sub>Cl<sub>2</sub>, and PbPh<sub>2</sub>I<sub>2</sub> to yield (AsPh:)<sub>2</sub>, Hg or Pb, HCl, PbCl<sub>2</sub> or PbI<sub>2</sub>, and C<sub>6</sub>H<sub>6</sub>. It does not react with PbEt<sub>4</sub>, SnEt<sub>4</sub>, SnPh<sub>2</sub>Et<sub>2</sub>, and SnEt<sub>2</sub>Cl<sub>2</sub> at low temp.; at higher temp. the reaction  $3AsH_2Ph \rightarrow$  $AsPh_3+2As+H_2$  takes place, and the ppt. is a mixture of Pb or Sn with As. R. T.

Constitution of sulpharsphenamine. II. New interpretation. W. J. C. DYKE and H. KING (J.C.S., 1935, 805-813).-4-Nitro-2-aminophenol with Na formaldehyde H sulphite gives Na 5-nitro-2-hydroxy-anilino-N-methylenesulphite  $(+2.5 \text{ or } +1.5\text{H}_2\text{O})$ , whilst in HCl with CH2O and NaHSO3, followed by NaOH, it forms  $Na_3^{-5}$ -nitro-2-hydroxyanilino-NN-dimethylenesulphite (+2H<sub>2</sub>O,1.5MeOH), converted into the  $Na_2$  salt  $(+3.5H_2O)$ . Similarly prepared are Na 4-nitro-2-hydroxyanilino-N-  $(+3H_2O)$ ,  $Na_2$  4-nitro-2-hydroxyanilino-NN-  $(+2.5H_2O)$ ,  $Na_2$  2-hydroxy-5-carbomethoxyanilino-NN-di- (+2H2O), Na 3nitroanilino-N- $(+2H_2O)$ , and Na<sub>2</sub> 3-nitroanilino-NN-di-methylenesulphite (+1MeOH). Examination by the Elvove oxidative method of S analysis has shown that part of the S is oxidised to sulphate and part remains as dithionate. Sulpharsphenamine is a Na salt of 3: 3'-diamino-4: 4'-dihydroxyarsenobenzene-NNN'-trimethylenesulphurous acid. When NH<sub>2</sub>Ph, o-anisidine, o- and p-NH2·C6H4·OH, 4-amino-2-hydroxyphenylarsinic acid, and arsphenamine are treated with CH<sub>2</sub>O and NaHSO<sub>3</sub>, the solutions show a deficiency of S by the Elvove method (cf. Newbery and Phillips, A., 1928, 311). F. R. S.

New arsindole ring closure. C. MANNICH (Arch. Pharm., 1935, 273, 275-284).-When heated with AsCl<sub>3</sub> at 150-170° CPh:C·CH<sub>2</sub>·NEt<sub>2</sub> affords the hydrochloride, m.p. 118-119°, of γ-chloro-γ-phenyl-∆<sup>β</sup>-propenyldiethylamine, b.p. 155°/14 mm. (methiodide, m.p. 140-141°) {reduced to CH2Ph·[CH2]2·NEt2 (I), hydrolysed to CH<sub>2</sub>Bz·CH<sub>2</sub>·NEt<sub>2</sub> (II), and giving BzCl by ozonolysis}, and the hydrochloride (III), m.p. 199°,



of 1:3-dichloro-2-diethylaminomethylarsindole (IV) (correspond-<sup>2</sup>. CH<sub>2</sub>·NEt<sub>2</sub> ing 1-bromohydrobromide, decomp. 205°, 1-iodohydriodide, decomp. 194-195°, and 1 hydroxyhydrochloride, m.p. 135°),

converted by aq. KCN into 3-chloro-1-cyano-2-diethylaminomethylarsindole, m.p. 65-66° (hydrochloride, m.p. 135°). (III) fused with NaOH-KOH at 250° gives BzOH, AcOH, and phenolic products, and oxidation with 60% HNO3 gives o-arsinobenzoic acid, not melting at 330°, converted by HI into o-AsI2 'C6H4 CO2H. With 38% HCl at 150° (III) gives COPhMe and (II), and is reduced by HI-P to (I). Oxidation of (IV) with 30%  $H_2O_2$ -AcOH affords o-arsinophenylacetic acid, decomp. 184—185° (Me<sub>1</sub> ester, decomp. 176—177°) [reduced by HI-P to o-carboxymethylphenyldi-iodo-arsine, m.p. 155—170° (decomp.)], and (from the mother-liquor) \$-0-arsinophenylpropionic acid, decomp. 165-170°. J. W. B.

Arsenicals containing the furan nucleus. W.G. Lowe and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 1081-1083).-2-Chloromercurifuran (I) and AsCl<sub>3</sub>, best in hot  $C_6H_6$ , give furyldichloroarsine (II), lachrymatory and vesicant, unstable at room temp., rapidly resinified by heat at 10 mm. or by hot AsCl<sub>3</sub>, and giving furan with hot H.O, difurylchloroarsine (III), similar to (II) in properties, and trifurylarsine (IV), m.p. 35°, which is somewhat more stable. (II) and cold H<sub>2</sub>S-EtOH give furylarsine sulphide, m.p. 125° (decomp.), sol. in warm N-NaOH and giving furan when boiled therein. (III) gives tetrafuryldiarsine sulphide, an oil. (IV) with HgCl<sub>2</sub> in aq. EtOH regenerates (I) and with I gives 2-iodofuran. 2:5-Dichloromercurifuran and AsCl<sub>3</sub> at room temp. give a solution, which with I-CCl<sub>4</sub> gives 2: 5-di-iodofuran, but with H<sub>2</sub>O affords aliphatic compounds with 1 As. R. S. C.

Organic mercurials. M. C. HART and H. P. ANDERSEN (J. Amer. Chem. Soc., 1935, 57, 1059-1061).—The following are prepared.  $Hg^{II}$  mandelate, m.p. 183—184°; 4-acetoxy-, m.p. 187—188°, and -nitratomercuri-2-nitroanisole, m.p. 219—220°; acet-oxymercuri-m-cresol, m.p. 177°; 3:5-diacetoxymercuri-4-hydroxybenzoic acid; diacetoxymercuri-p-chlorophenol, -amyl-m-cresol, m.p. 190°, and -2-chloro-5hydroxytoluene; phenylmercuric acetate, m.p. 149°, lactate, m.p. 155-157°, and basic nitrate (Hg 63.2%), m.p. 179-183°; p-tolylmercuric nitrate, m.p. 179-180°, acetate, m.p. 138-140°, and lactate. Bacteriostatic data for these and 6 similar Hg compounds are recorded. In general simple compounds are more effective than complex ones. The most effective is o-hydroxyphenylmercuric chloride, m.p. 150-151° (1:75,000 in 5 min. to S. aureus), which is also bactericidal at 1:1000. R. S. C.

Halide-mercuri-nitrocresols.--See B., 1935, 655.

## Synthesis of dipeptides.—See this vol., 1014.

cycloPeptides arising from blood-albumin.— See this vol., 999.

Alcoholic hydrolysis of caseinogen and gelatin. A. A. CHRISTOMANOS (Biochem. Z., 1935, 277, 394– 400).—The degradation of caseinogen (I) and gelatin (II) by MeOH, EtOH, and iso-C<sub>5</sub>H<sub>11</sub>·OH at temp. between the b.p. of the alcohol and 220° in sealed tubes is investigated. The degree and velocity of hydrolysis above 180° approximate to the same vals. with all the alcohols, but at lower temp. are greatest for MeOH. Part of the total N resulting is volatile [24% with (I) and only 2·2% with (II)]. From the hydrolysis products of (I) were obtained leucine anhydride and leucine-valine anhydride, and the presence of a tyrosine-tryptophan compound was indicated, whilst from (II) glycylalanine anhydride was obtained. P. W. C.

X-Ray study of hydration and denaturation of proteins.—See this vol., 922.

Mol. wt. of proteins. (MME.) A. ROCHE (Bull. Soc. Chim. biol., 1935, 17, 704-744).—A lecture.

Identification of organic compounds by the mixed m.p. G. LOCK and G. NOTTES (Ber., 1935, 68, [B], 1200-1204).-The mixed m.-p. method for the identification of similarly constituted compounds, particularly of polyhalogenated derivatives with closely similar m.p., is valid only when distinct depression is observed, notably when the relative proportions of the components are greatly varied. It is not sufficient to use any accidental mixture; the substances in extreme ratios must also be employed. Functional derivatives of such compounds frequently have very similar m.p. and show analogous behaviour. The following compounds are incidentally described : 2: 6-dichloro-4-bromo-3-ethoxybenzaldehyde, m.p. 66.5°, from the OH-aldehyde, NaHCO<sub>3</sub>, and Et<sub>2</sub>SO<sub>4</sub>, its anil, m.p. 59°, oxime, m.p. 128.5°, phenylhydrazone, m.p. 122°, and 2: 6-dichloro-4-bromo-3-ethoxybenzoic acid, m.p. 148° (corr.); 2-chloro-4: 6-dibromo-3ethoxybenzaldehyde, m.p. 81.5°, its anil, m.p. 63.5°, oxime, m.p. 152°, phenylhydrazone, m.p. 113.5°, and 2-chloro-4: 6-dibromo-3-ethoxybenzoic acid, m.p. 167° Ĥ. W. (corr.).

Identification of linoleic and linolenic acids. T. G. GREEN and T. P. HILDITCH (Biochem. J., 1935, 29, 1552—1563).—The best method for characterising linoleic (I) and linolenic acid (II) is oxidation with alkaline KMnO<sub>4</sub> to the tetra- or hexa-hydroxystearic acid, but the yields are only 40% and 15— 18%, respectively, from (I) and (II). (I) of seed fats is very probably confined to one geometrical form. The isomeric tetrahydroxystearic acids obtained from (I) with alkaline KMnO<sub>4</sub> and with AcO<sub>2</sub>H bear no simple relationship to each other. J. N. A.

Azides. IV. p-Chlorobenzazide as a reagent for the identification of phenols. C. H. KAO, H. Y. FANG, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 109—112).—p-C<sub>6</sub>H<sub>4</sub>Cl·CO·N<sub>3</sub> and the appropriate phenol in hot PhMe give the following N-p-chlorophenylurethanes: Ph, m.p. 150— 152°, o-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>, m.p. 280—281° (decomp.), 2:4:6 $C_{6}H_{2}(NO_{2})_{3}$ , m.p. 285—286° (decomp.), o-, m.p. 162— 163°, m-, m.p. 203—204° (decomp.), and p- $C_{6}H_{4}Me$ , m.p. 188—190°, o- $CHO \cdot C_{6}H_{4}$ , m.p. 287° (decomp.), 2-aldehydo-p-tolyl, m.p. 294°, o- $CO_{2}H \cdot C_{6}H_{4}$ , m.p. 295°, 2-carboxy-p-tolyl, m.p. 283—284° (decomp.), o- $CO_{2}Et \cdot C_{6}H_{4}$ , m.p. 282° (decomp.),  $\alpha$ -, m.p. 162·5°, and  $\beta \cdot C_{10}H_{7}$ , m.p. 192°, and thymyl, m.p. 280° (decomp.). o- and p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH in PhMe or Bu<sub>2</sub>O give the carbamides (or, less probably, urethanes), m.p. 200° and 248—250° (decomp.). These derivatives may be used for identification of the phenols. B. S. C.

Pyrocatechol as reagent for identification of titanium.—See this vol., 951.

Acidimetric titration of *p*-hydroxybenzoic acid alone and in presence of acetic acid. I. M. KOLT-HOFF (J. Amer. Chem. Soc., 1935, 57, 973—974). *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (I) can be determined as a monobasic acid by titrating to  $p_{II}$  6·8 with standard NaOH, using bromothymol-blue. The results are about 0·3% high. The sum of AcOH and (I) can be determined by titrating to  $p_{II}$  6·95 with NaOH. Phenolphthalein is unsuitable as an indicator for (I).

E. S. H.

Extraction method for the determination of acids and its application to p-hydroxybenzoic acid.—See this vol., 947.

Micro-copper-pyridine reaction on organic acids. A. J. STEENHAUER (Pharm. Weekblad, 1935, 72, 667—669).—Characteristic, cryst. compounds are obtained when anisic, anthranilic, benzoic, fumaric, cinnamic, salicylic (I), and acetylsalicylic (II) acids are treated with aq.  $CuSO_4-C_5H_5N$ . The test is recommended for distinguishing (I) from (II).

S. C.

2:4-Dinitrophenylhydrazine as a quantitative reagent for carbonyl compounds. II. Benzophenone and acetone. G. W. PERKINS and M. W. EDWARDS (Amer. J. Pharm., 1935, 107, 208-211; cf. A., 1934, 425).—COPh<sub>2</sub> and COMe<sub>2</sub> are determined with an error of < 3%. Iddles and Jackson's determinations of PhCHO (cf. this vol., 101) are criticised. J. L. D.

Highly sensitive reaction of indole and pyrrole. P. SACCARDI (Annali Chim. Appl., 1935, 25, 157—159). —The reaction of Au with pyrrole in HCl solution (cf. A., 1935, 355) detects  $7.05 \times 10^{-6}$  g. of Au in 10 c.c. By H<sub>2</sub>S  $8.1 \times 10^{-4}$  g. of Au in 10 c.c. is detectable. The min. amount of pyrrole detectable is  $6.87 \times 10^{-5}$  g. in 10 c.c. Indole behaves similarly,  $1.37 \times 10^{-4}$  g. of Au or  $4.9 \times 10^{-5}$  g. of indole being detectable.

T. H. P.

Photometric determination of small amounts of pyrrole. F. FROMM (Mikrochem., 1935, 17, 141– 154).—The solution, containing 0.1—90 mg. of pyrrole (I), is made alkaline, and (I) is extracted with Et<sub>2</sub>O. The Et<sub>2</sub>O is removed by dropping the solution into glacial AcOH at 40—50°, the solution being then diluted to 100 c.c. and heated at 100° for 10 min. with HCl+0.05% isatin, forming pyrrole-blue (II), which is determined photometrically with filtered light. 90—97% of (I) present is converted into (II). (I) in turbid or tarry solutions may be separated as the HgCl<sub>2</sub> compound (III) by addition of saturated aq. HgCl<sub>2</sub>. (III) is dissolved in 5% aq. NaCN, the solution being made up to 100 c.c. and treated as before. (I) may also be determined photometrically by condensation with p-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO. J. S. A.

Bromo-acidimetric determination of 8hydroxyquinoline. A. CASTIGLIONI (Annali Chim. Appl., 1935, 25, 236—240).—The action of Br-H<sub>2</sub>O on 8-hydroxyquinoline (I) solution yields the compound  $C_9H_4NBr_2$ ·OBr, which readily loses, as HBr, the Br replacing the hydroxylic H. Thus, 1 mol. of I yields, in all, 3 HBr, and may thus be determined by titration of the resulting acidity with NaOH. T. H. P.

Colour reactions for pyramidone. N. SCHOORL (Pharm. Weekblad, 1935, 72, 669-670).-0.1N-I solution is a more sensitive and more satisfactory reagent than  $K_2S_2O_8$  in the colour test for pyramidone (cf. this vol., 877). S. C. Mercurimetric method for the determination of hydrastinine, hyoscyamine, scopolamine, eserine, and apiol. Reaction for identifying apiol. A. IONESCO-MATIU and C. POPESCO (Bull. Soc. Chim. biol., 1935, 17, 671—677).—The authors' method (A., 1934, 269) of determining substances pptd. by  $Hg^{II}$ is applied to the determination of hydrastinine, hyoscyamine, scopolamine, eserine, and apiol. Apiol may be identified by the red coloration produced on warming after addition of phosphomolybdic acid and  $H_2SO_4$ . A. L.

Reaction of Weydel and its application to the colorimetric micro-determination of caffeine. G. DENIGES (Bull. Soc. Chim. biol., 1935, 17, 657— 666).—The reaction of Weydel for the colorimetric determination of purine derivatives is modified by the substitution of aq. Br as oxidising agent and aq.  $Hg(OAc)_2$  or  $Zn(OAc)_2$  for the  $NH_3$ . A. L.

## Biochemistry.

Blood. C. C. STURGIS, R. ISAACS, S. M. GOLD-HAMER, F. H. BETHELL, and G. E. FARRAR (Arch. Int. Med., 1935, 55, 1001-1081).—A review of recent literature on diseases affecting the condition of the blood. A. L.

Permeability of the erythrocyte to glycerol. A. K. PARPART and J. C. SHULL (J. Cell. Comp. Physiol., 1935, 6, 129–135).—Data for ox erythrocytes are given. A. G. P.

Solvent-water in the normal mammalian erythrocyte. A. K. PARPART and J. C. SHULL (J. Cell. Comp. Physiol., 1935, 6, 137–150).—Approx. 50 vol.-% of the cell-H<sub>2</sub>O can act as solvent for glycerol or  $(CH_2 \cdot OH)_2$ . Urea probably dissolves in or reacts with other than aq. constituents of the cell.

A. G. P.

Variation of the protein content of the red corpuscles after intake of food. G. PETRÁNYI and A. BLAZSÓ (Z. ges. exp. Med., 1934, 94, 689-695; Chem. Zentr., 1935, i, 741-742).—The increase of protein in the red corpuscles after ingestion of food does not originate from hæmoglobin. The corpuscles apparently play a part in protein transport.

R. N. C. Absorption of light by carbon monoxidehæmochromogens. S. SCHÖNBERGER (Biochem. Z., 1935, 278, 428—436).—The max. on the curves for neutral and alkaline (Na<sub>2</sub>CO<sub>3</sub>) CO-hæmoglobin are at the same points, but the curve for the alkaline form is 4% higher than that for the neutral. The curves for CO-hæmochromogens (globin, albumin, NH<sub>3</sub>) are identical (in the visible part of the spectrum) with that of neutral CO-hæmoglobin, but the curve for CO-hæm is not. W. McC.

Determination of bilirubin in blood by the diazo-method. E. G. GODFRIED (Biochem. J., 1935, 29, 1337—1339).—The modification by McNee and Keefer (Brit. Med. J., 1925, ii, 52) of Thannhauser and Andersen's method (A., 1922, ii, 671) is satisfactory for clinical purposes. F. O. H. Method for making indefinite or invisible bloody finger-prints visible. M. WAGENAAR (Pharm. Weekblad, 1935, 72, 463-470).—The part is painted with a solution of benzidine (0.1 g.) and 3% $H_2O_2$  (3 c.c.) in EtOH (40 c.c.), when a permanent brown stain is obtained. S. C.

New hæmoglobinometer, the "Orthohæmometer." K. BÜRKER (Münch. med. Woch., 1934, 81, 1815—1816; Chem. Zentr., 1935, i, 603).—Dil. blood is treated with a little Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and compared colorimetrically with a standard. The hæmoglobin content per erythrocyte averages  $32.4 \times 10^{-12}$  g. in men and  $30.2 \times 10^{-12}$  g. in women. A. G. P.

Properties of reptilian blood. II. The gila monster (*Heloderma suspectum*, Cope). H. T. EDWARDS and D. B. DILL. III. The chuckwalla (*Sauromalus obesus*, Baird). D. B. DILL, H. T. EDWARDS, A. V. BOCK, and J. H. TALBOTT (J. Cell. Comp. Physiol., 1935, 6, 21–35, 37–42).—II. Compared with human blood that of *H. suspectum* has a low hæmoglobin (I) content and the (I) has a relatively low buffer val. The  $O_2$  dissociation curve at 20° resembles that of man at 37.5°. The effects of temp. and reaction on the combination of  $O_2$  and  $CO_2$  with blood are examined.

III. The blood of S. obesus resembles that of H. suspectum except in its response to temp. changes.

A. G. P.

Adult blood after eleven years on egg and milk diet. J. HAMEL, M. CHAVAROT, and P. AUBRY (Compt. rend. Soc. Biol., 1935, **119**, 864–866).— After feeding with egg and milk through the nose for 11 years the blood was normal. H. G. R.

Formation of cyclopeptides arising from bloodalbumin by hydrolysis in the autoclave. V. S. SADIKOV, E. V. LINDQUIST-RISAKOVA, R. G. KRIS-TALLINSKAJA, V. N. MENSCHIKOVA, L. N. RUBEL, E. G. CHALEZKAJA, and A. G. PESSINA (Biochem. Z., 1935, 278, 60-70).—Hydrolysis of this protein by different methods (e.g., with 25% HCl for 36-72 hr., with 3% H<sub>2</sub>SO<sub>4</sub> in the autoclave at 180° for 2 hr., with alkali, etc.) gives very different results. Autoclave hydrolysis with raised temp. for a shorter time enriches the yields of cyclic compounds, which must be regarded as the precursors of the  $NH_2$ -acids, and lessens the degradation, e.g. of tryptophan. The greater part of the cyclopeptides is then separated by continuous extraction with Et<sub>2</sub>O, CHCl<sub>3</sub>, and EtOAc. Tables summarise the total, amide-,  $NH_2$ -, and humin-N, and the tyrosine, tryptophan, cystine, histidine, methionine, etc. contents of the various fractions and of the acid hydrolysis products of these fractions. P. W. C.

Spectroscopic determination of gum acacia in blood. Rate of disappearance in normal dogs. S. A. PEOPLES and N. M. PHATAK (Proc. Soc. Exp. Biol. Med., 1935, **32**, 635—637).—Gum acacia (I) is determined in blood by Folin–Wu pptn., dilution of the filtrate, hydrolysis with  $H_2SO_4$ , addition of bile salts, and spectroscopic examination in comparison with a standard solution. The intensity of the absorption band  $\infty$  the (I) content. (I) is eliminated very slowly from the blood-stream in normal dogs.

R. N. C.

Diurnal variations in plasma-lipins. E. M. Boyd (J. Biol. Chem., 1935, 110, 61-70).—Free and ester cholesterol (I), phospholipins, and neutral fats in normal subjects at different times of the day showed only slight variations which could not be correlated with the intake of ordinary meals or sleep. The variation from one person to another was 2-3times > the average variation per person per day. The conditions for hydrolysis in the total (I) determination were standardised. H. D.

Blood-cholesterol and resistance to saponin in animals on liver diet. G. INGRASSIA (Riv. Patol. sper., 1934, 13, 459—468).—In dogs receiving raw liver daily, blood-cholesterol rose, but on continued liver administration returned to normal. The red blood-cells showed a greater resistance to the hamolytic action of saponin. NUTR. ABS. (m)

Determination of cholic acids in blood. B. JOSEPHSON (Biochem. J., 1935, 29, 1519-1524).--Details are given for the determination of bile acids in blood. Practically no loss of acids occurs if the proteins are pptd. with EtOH containing  $Ba(OH)_2$ . With concn. of acids > 5 mg. per 100 c.c. the error is  $\ge 6-8\%$ . J. N. A.

Determination of total fatty acids in blood. C. P. STEWART and E. B. HENDRY (Biochem. J., 1935, 29, 1677—1682).—EtOH-CHCl<sub>3</sub> and EtOHlight petroleum mixtures will extract the same amount of fatty acid from blood as do EtOH-Et<sub>2</sub>O mixtures. The yield of fatty acid is not increased by refluxing the blood with EtOH-Et<sub>2</sub>O, but some oxidation occurs giving an increase in CO<sub>2</sub>H groups. Refluxing does not increase the recovery of lipin-P. EtOH-NaOH and NaOEt are equally good as hydrolysing agents, and a single hydrolysis by the former will give the max. yield of fatty acids. The filtration method is compared with the method in which fatty acids are extracted by light petroleum. The sol. fatty acids in blood amount to < 3% of the total. P. W. C. Presence of creatinine in blood. J. A. BEHRE and S. R. BENEDICT (J. Biol. Chem., 1935, 110, 245-248).—A criticism of the conclusion by Hayman et al. (this vol., 642) that creatinine is the chief chromogenic compound in blood-plasma.

E. A. H. R.

Determination of blood-indole. P. MAZZOCCO (Compt. rend. Soc. Biol., 1935, **119**, 879-881).—The method of Garciá-Blanco and Vidal (A., 1933, 1065) has been modified utilising Et<sub>2</sub>O-extraction.

H. G. R.

Diazo-value of blood. G. BARAC (Compt. rend. Soc. Biol., 1935, 119, 545—547).—There are only traces of monophenols in the blood, the diazo-val. being due principally to glyoxalines. H. G. R.

Spectrophotometric study of the diazo-reaction of the blood. A. LAMBRECHTS and G. BARAC (Compt. rend. Soc. Biol., 1935, 119, 547—549; cf. preceding abstract).—The absorption spectrum of the diazo-reaction of blood is nearly identical with that of the glyoxalines. H. G. R.

Specific carbohydrates of blood groups. II. K. FREUDENBERG and H. EICHEL (Annalen, 1935, 518, 97-102; cf. A., 1934, 795).-A detailed description is given of the isolation of the polysaccharide mixture (I) from the urine of individuals of the blood-group A. Hydrolysis of (I) by acids leads to the isolation of glucosamine. Inactivation of (I) by alkali is caused mainly by elimination of N-Ac, since acetylation of the inactive product (II) yields an inactive acetate, sol. in CHCl<sub>3</sub>, from which O-Ac can be removed without affecting the re-introduced N-Ac; the material so obtained has about the same activity as the original substance. Keten, which in H<sub>2</sub>O acetylates solely NH2, completely restores the activity of (I). (I) is not affected by amylases or diastases, but is partly degraded with complete loss of activity by snail enzyme, whereby N-acetylglucosamine (III) is obtained. The presence of a uronic acid (IV) in small amount is established. (I) therefore contains galactose (V) and (III), but it remains uncertain whether (IV) is a component of (I) or an admixture. Considerations of the N balance indicate the presence of a further N component probably with higher % N. (V) is also obtained by the acid hydrolysis of the material obtained from the urine of individuals of blood-group O. H. W.

Blood-sugar curves after intravenous injection of hypertonic glucose. N. FIESSINGER and A. BIRON (Compt. rend. Soc. Biol., 1935, 119, 839— 841).—In normal cases the curves for arterial and capillary blood are similar, showing an elevation of 0.4-0.75 g. after 10 min. In cirrhosis, the curve rises to 0.5-1.5 g. and the duration is prolonged for  $1\frac{1}{2}$  hr. In hepatic cedema, the val. for capillary blood rises to 1 g. and that for arterial to 1.5 g.

H. G. R. Mercury-cadmium deproteinisation and microiodometric determination of blood-sugar. C. DUMAZERT and M. BIERRY (Compt. rend. Soc. Biol., 1935, 119, 737-739).—Blood is deproteinised by an acid solution of  $Hg(NO_3)_2$  and  $Cd(NO_3)_2$ . The sugar in the filtrate is oxidised with I in NaOH-Na<sub>2</sub>HPO<sub>4</sub> solution at room temp., excess of I liberated with  $H_2SO_4$ , the solution neutralised with  $Na_2B_4O_7$ , and I titrated with 0.005N- $Na_2S_2O_3$ . The method gives results concordant with those obtained by the Hagedorn-Jensen method, and permits the microdetermination of the "true" blood-sugar. R. N. C.

Determination of fructose in blood. J. PATTER-SON (Biochem. J., 1935, 29, 1398—1399).—The NHPh<sub>2</sub> method of Radt (A., 1928, 1151) for determination of fructose in aq. solution and in blood is slightly modified and used for determinations in the bloods of 2 normal and 3 pathological subjects, the results comparing closely with those obtained by the method of Scott (cf. this vol., 770). 100 ml. of blood contain about 1 mg. of fructose. P. W. C.

Blood-sugar of the fasting, gizzardectomised fowl (Gallus domesticus). W. H. BURROWS, J. C. FRITZ, and H. W. TITUS (J. Biol. Chem., 1935, 110, 39-41).—The peak in the blood-sugar curve of fowls occurring on the 4th day of fasting (A., 1934, 683) is not observed in gizzardectomised animals. H. D.

Blood-chemistry of birds after destruction of the comb or enucleation of the eyeballs. C. I. PARHON and G. WERNER (Compt. rend. Soc. Biol., 1935, 119, 630-632).—Blood-sugar rises in cockerels deprived of their combs, and in ducks deprived of their eyeballs. Blood-Ca and cholesterol fall, whilst K and the K/Ca ratio rise. R. N. C.

Fermentability of blood-sugar, especially of the bound sugar in diabetics. M. MORIMUNE (Mitt. med. Akad. Kioto, 1934, 12, 281–288).—No significant difference was found between the fermentability of both free and bound blood-sugar in diabetics as compared with normal individuals.

NUTR. ABS. (b) Spontaneous variations in blood-sugar in normal and diabetic subjects. J. O. NUNEZ (Ann. Med., 1934, 36, 234—241).—Consecutive blood-sugar determinations at intervals of 5 min. show that there are spontaneous variations in the blood-sugar levels of both normal and diabetic subjects. These may be the result of instability of the autonomic nervous system. NUTR. ABS. (b)

Glycolysis in blood. II. Glycolysis and distribution of phosphate compounds. S. MORGULIS and J. D. MUNSELL (Biochem. Z., 1935, 278, 89—100). —No quant. relationship could be detected between changes of the different blood-P fractions and the degree of glycolytic power. Under the action of arsenate, glycolysis is greatly increased in rabbit's but somewhat decreased in dog's blood (cf. A., 1932, 530, 1273), the readily hydrolysable esters increasing and the difficultly hydrolysable esters decreasing in strongly and showing a tendency to decrease in weakly glycolysing systems. P. W. C.

Determination of phosphorus in blood with the step photometer. S. A. SIWE (Biochem. Z., 1935, 278, 437—441; cf. Teorell, A., 1931, 662).—By means of a modification of the method of Fiske *et al.* (A., 1926, 443) the P content of 0.05—0.1 c.c. of bloodserum is determined with an error of  $\Rightarrow \pm 5\%$ . The results agree well with those of Briggs (A., 1922, ii, 718). W. McC. Colloidal calcium phosphate of blood and calcium partition in serum. D. M. GREENBERG, C. E. LARSON, and E. V. TUFTS (Proc. Soc. Exp. Biol. Med., 1935, 32, 647—650).—Results indicate that the colloidal salt is  $Ca_3(PO_4)_2$ , and that the equilibrium between protein-bound Ca and Ca<sup>\*\*</sup> conforms to the law of mass action. R. N. C.

Determination of calcium in blood. S. A. SIWE (Biochem. Z., 1935, 278, 442—446).—The Ca content of 0.05—0.1 c.c. of blood-serum is determined by pptg. with  $(NH_4)_2C_2O_4$ , dissolving the ppt. in HNO<sub>3</sub>, adding excess of 0.01*N*-KMnO<sub>4</sub>, and titrating with 0.01*N*-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> after addition of KI. The whole procedure is carried out in one tube, the apparatus of Linderstrøm-Lang *et al.* (A., 1931, 1445) being used. The error is  $\pm 3.6\%$ . Alternatively, the ppt. of CaC<sub>2</sub>O<sub>4</sub> is converted into CaCO<sub>3</sub> by heating at 550— 600° [the temp. given by Nordbō (A., 1932, 531) is too low], dissolved in excess of 0.01*N*-HCl, and titrated with 0.01*N*-NaOH. The error is  $\pm 3.5\%$ .

W. McC.

Comparison of wet and dry ashing methods for determination of blood-iron. A. A. FABIAN, A. SACHS, and V. E. LEVINE (Proc. Soc. Exp. Biol. Med., 1935, **32**, 662—664).—The dry method is recommended. The blood is dried, ashed at low red heat, and evaporated with HNO<sub>3</sub>. Fe is dissolved out with HCl and separated from Cu (if necessary) by pptn. with aq. NH<sub>3</sub>, Cu being determined by the McFarlane method. The Fe ppt. is dissolved in  $H_2SO_4$ ,  $K_2S_2O_8$  added, and the Fe determined colorimetrically with KCNS. R. N. C.

Mineral differences in blood composition according to sex, in *Cyprinus carpio*. E. A. PORA (Compt. rend. Soc. Biol., 1935, 119, 373-375).—Na and serum-Cl in the blood of the male are > in the female, whilst K, Ca, total protein, the alkaline reserve and the NaCl/total osmotic pressure ratio are less. R. N. C.

Citric acid content of serum in rabbits with special reference to certain diets. H. LINDHOLM (Skand. Arch. Physiol., 1934, 70, 295—302).—The serum of rabbits fed on a mixed diet of grass, roots, oats, and barley contains 10 mg. of the acid per 100 ml. (6.3 mg. after 24 hr. starvation). When the diet contains no grass or other green food the val. is 6—8 mg., and this can be raised by adding green food. NUTR. ABS. (m)

Selective accumulation of lipochrome. L. ZECHMEISTER, P. TUZSON, and E. ERNST (Nature, 1935, 135, 1039).—The blood-scrum of the horse, after feeding on green food, contains no xanthophyll, but the carotene content is increased. Xanthophylls probably do not cross the wall of the gut, and selection appears to take place in the digestive organs. L. S. T.

Globulin and albumin fractions of serum. VII. Tyrosine and cystine contents of protein fractions of fluids from sarcoma, carcinoma, and liver (in cirrhosis). B. LUSTIG and E. MANDLER (Biochem. Z., 1935, 278, 312-319; cf. A., 1931, 505; 1932, 960).—Colorimetric methods for determination (without hydrolysis and isolation) of  $NH_2$ -acids in proteins give only qual. vals. The tyrosine (I) content of the  $H_2O$ -sol. globulin fractions is > that of the globulins sol. in aq. NaCl and much > that of the globulins sol. in aq. Na<sub>2</sub>CO<sub>3</sub>. All but one of the albumin fractions have similar (I) contents. The cystine (II) content of the albumin fractions is much > that of the globulins. The H<sub>o</sub>O-sol. euglobulins from carcinoma fluid contain more (II) than do the those from the other fluids. The globulins sol. in aq. NaCl and aq. Na<sub>2</sub>CO<sub>3</sub> do not differ as regards (II) content. Albumin fractions from carcinoma and sarcoma fluids have (II) content < that of corresponding fractions from the other fluid. The euglobulins sol. in aq. Na<sub>2</sub>CO<sub>3</sub> when digested with pepsin and HCl yield a fraction, insol. in H<sub>2</sub>O and rich in P and carbohydrate, which appears to yield xanthine bases on acid hydrolysis. W. McC.

Isolation of serum-vitellin. M. LASKOWSKI (Biochem. Z., 1935, 278, 345-348; cf. this vol., 374).-Plasma from laying hens acidified with HCl ( $p_{\rm H}$  5.0— 5.5) is diluted tenfold with H<sub>2</sub>O, pptd. material is dissolved in 5% aq. NaCl, and the solution is satur-ated with NaCl. After removal of pptd. impurities the vitellin (I) is pptd. by dilution (hundredfold) with H<sub>2</sub>O. Dissolution in 5% aq. NaCl, saturation with NaCl, filtration, and dilution are repeated, and the ppt., after washing with Et<sub>2</sub>O-EtOH, is successively extracted with EtOH (24 hr.) and Et<sub>2</sub>O. (I) thus obtained is still impure (contains about 0.9% of protein-P). Plasma from cocks or non-laying hens yields no (I) when treated in this way. Possibly the (I) is identical with that of hens' eggs (cf. Calvery et al., A., 1932, 294). W. McC.

Changes in blood-serum under the influence of heat. C. ACHARD and A. BOUTARIC (Compt. rend., 1935, 200, 1697—1700).—The smallest amount of adsorbent C which will restore the surface tension of horse blood-serum, diluted 1/500 with 0.85% NaCl, to that of the diluent is about 160 mg. per 15 c.c. This quantity diminishes regularly with increasing time and rise of temp. of heating, indicating that the no. of individual protein particles decreases.

F. A. A.

Hæmolytic action of carbohydrates [?hydrocarbons]. L. P. BRIULLOVA (J. Physiol., U.S.S.R., 1934, 17, 389—391).—The presence of hydrocarbons, aliphatic or aromatic, stimulates hæmolysis by saponins. CH. ABS. (p)

[Relation between] time of coagulation and concentration of coagulant. A. FISCHER (Biochem. Z., 1935, 278, 320—325; cf. A., 1933, 522).— The rate of coagulation of blood-plasma  $\infty$  a power of the conen. of the coagulant and is calc. by means of a simple equation valid within limits much wider than those within which the equation previously given is applicable. W. McC.

Coagulating action of homologous organextracts. A. FISCHER (Biochem. Z., 1935, 278, 334-339).—As regards their power to coagulate autologous and homologous blood-plasma, extracts of organs of the hen form the series, lung>muscle> heart>kidney>spleen>brain>liver, this order being preserved at all ages of the hen from embryo onwards. As regards their relative content of heparin the extracts form the series brain>lung>spleen> liver. W. McC.

Stoicheiometric combination of heparin and coagulant. A. FISCHER and T. ASTRUP (Biochem. Z., 1935, 278, 326—333).—The proportions in which extracts of organs and blood-plasma (from hens) and heparin interact indicate that heparin and the substance which stimulates coagulation react in stoicheiometric proportions (1 mol. of each). The compound dissociates in solution. W. McC.

Coagulation of the blood as a chain reaction. A. FISCHER (Nature, 1935, 135, 1075).—An active principle of coagulation, which can be transferred indefinitely into new plasma without loss of activity, is described. It is formed during the clotting process of blood-plasma and increases and then disappears almost instantaneously at the moment of coagulation. The facts support the view that blood-coagulation is a chain reaction. L. S. T.

Combination of heparin with protein. A. FISCHER (Biochem. Z., 1935, 278, 133-160).-Heparin (I) combines with protein only on the acid side of, and in close proximity to, the isoelectric point, and is therefore always in the free condition in bloodplasma and in serum. Organ extracts which accelerate clotting of blood combine with (I), and the spontaneous changes (denaturation) in such extracts on keeping which result at first in an increase followed later by a decrease of clotting-acceleration power are accompanied by parallel changes in the extent of combination with (I). Protein combines with (I) only when it has been denatured, the liberated basic groups being utilised for the union. Addition of clotting-active lipins to protein results in denaturation and union with (I). Blood-clotting is regarded, therefore, as a special case of denaturation, and the inhibiting action with (I) depends on its great affinity for the basic groups of the active material of the organ extracts, these groups in absence of (I) reacting with the acid groups of the plasma-protein. P. W. C. protein.

Possibility of a new quantitative technique of the Wassermann reaction, based on the nullifying action of the components of alexin. O. G. BIER (Compt. rend. Soc. Biol., 1935, 119, 758—760). —The use of the alexin fractions serves to differentiate sera where the Sordelli-Miravent technique breaks down. R. N. C.

Behaviour of the fractions of alexin in the Wassermann reaction. O. G. BIER (Compt. rend. Soc. Biol., 1935, 119, 756-758).—The serum-yeast fraction has the strongest nullifying action on the Wassermann reaction. R. N. C.

Behaviour of alexin in an electric field. P. GIRARD, M. LOURAU, and E. PITRES (Compt. rend. Soc. Biol., 1935, **119**, 408—410).—Alexin in an electric field behaves like an ion the isoelectric point of which is difficult to recognise on account of its sensitivity to  $p_{\rm H}$ . Its mobility is > that of hæmolysins or agglutinins, and is apparently the same as that of globulins, to which class alexin probably belongs. R. N. C. Use of sera precipitated by N/300-hydrochloric acid in the fixation reaction for tuberculosis. R. WAHL and P. LAVAL (Compt. rend. Soc. Biol., 1935, 119, 389—390).—The sensitivity of the fixation reaction is not increased by previous pptn. of the sera with 0.003N-HCl. R. N. C.

Production of diphtheria toxin with high antigenic power. E. M. TAYLOR (Compt. rend. Soc. Biol., 1935, 119, 510-512).—The antigenic power of diphtheria toxin can be increased by peptic digestion. H. G. R.

Basal metabolism in rabbits and the Schwartzman phenomenon. G. EUSTATZIOU, I. POPESCO, and S. STAMATESCO (Compt. rend. Soc. Biol., 1935, 119, 619–621).—Basal metabolism increases similarly in rabbits injected subcutaneously with the toxic filtrate of *B. coli*, whether or not they show a positive Schwartzman phenomenon. The increase is parallel with the intensity of the local reaction, but not with the rise of temp. R. N. C.

Adsorption of purified diphtheric vaccines by aluminium hydroxide. S. SCHMIDT (Biochem. Z., 1935, 278, 257—262).—The extent to which purified, salt-free diphtheric vaccines are adsorbed by  $Al(OH)_3$ frequently varies with their N (protein) content. A high degree of adsorption increases the efficiency of the vaccine. W. McC.

Preparation of anti-vibrioseptic serum by suspension of the antigen in lanolin. M. WEIN-BERG and M. GUILLAUMIE (Compt. rend. Soc. Biol., 1935, 119, 719-721). R. N. C.

Antitoxic power of some metal-protein complexes obtained from anti-diphtheria and antitetanus sera. H. DIACONO (Compt. rend. Soc. Biol., 1935, 119, 801-804).—Diphtheria and tetanus antitoxins are pptd. unchanged by  $HgCl_2$  or  $CuSO_4$  and may be eluted from the complex with  $Na_2SO_3$ .

H. G. R.

Which component of the complement is lacking in the lymph of the peripheral vessels? S. FUNAOKA and T. SHIMAOKA (Proc. Imp. Acad. Tokyo, 1935, 11, 203—205).—The albumin, but not the globulin, fraction obtained by Liefmann's procedure from guinea-pig blood contains the complement necessary for hamolysing the corpuscles of goat blood. Lymph drawn from the popliteal sac has no hamolytic action. J. L. D.

Spectrographical study of the biochemical reactions of nerves. B. MINZ and M. PAÏC (Compt. rend. Soc. Biol., 1935, 119, 521—524).—On electrical excitation of a fragment of vagus nerve in Locke-Ringer solution, a substance having a characteristic absorption spectrum passes into the solution.

## H. G. R.

Crystal structure of the myofibrils. Metahistology of animal fibres. F. WORSCHITZ (Fortschr. Röntgenstrahlen, 1934, 50, 174—178; Chem. Zentr., 1935, i, 585).—The micelle structure of the myofibrils is not altered by drying. The X-ray diagram indicates a structure of a cryst. character, the lattice const. of which in the direction of the thread axis is 22 Å. Interference is caused by the existence of a liquid-cryst. substance of the smectic type, which 3 x originates probably from the sarcoplasm of the muscle threads or the intrafibrillary liquid. R. N. C.

Decomposition of animal substances while embedded in marine sediments. F. HECHT (Kali, 1934, 28, 209—215; Chem. Zentr., 1935, i, 652). H. J. E.

Isolated cell and tissue constituents. III. Separation of the thyroid into colloid, cells, and nuclei. M. BEHRENS (Z. physiol. Chem., 1935, 232, 263—269; cf. A., 1933, 1184).—Thyroid tissue after freezing, drying, and pulverising is separated into colloid, cells, and nuclei by taking advantage of their different densities in suitably chosen liquids. The colloid consists principally of thyroglobulin, but contains other proteins; it is sol. in cold  $H_2O$  and in AcOH on warming. Only a trace of cells is sol. in AcOH. Insulin was separated from pancreas by the same method. J. H. B.

Secretion of dyes by the kidney. R. HÖBER (J. Cell. Comp. Physiol., 1935, 6, 117–128).—The tubules of the aglomerular kidney of the toadfish are permeable to certain diffusible acid dyes. The distribution of injected dyes is examined and compared with that in the frog. A. G. P.

Seasonal variations in the contents of water, organic and mineral substances of the muscle and liver of the frog. A. GRADINESCO and C. DEGAN (Bull. Soc. Chim. biol., 1935, 47, 751-763).—In the gastrocnemius muscle and the liver of the green frog the content of org. and mineral substances increases in summer and autumn and decreases in winter and spring. These losses are compensated for by corresponding increases in the H<sub>2</sub>O content. The variations in the male are > those in the female.

A. L. Nuclein metabolism. V. Constitution of nucleic acid. K. MAKINO (Z. physiol. Chem., 1935, 232, 229-235).-Depolymerisation of yeast-nucleic acid (I) by N-NaOH at room temp., which does not decompose the mononucleotides, liberates four acidic groups. Since thymonucleic acid (II) cannot be depolymerised chemically without destruction of the mononucleotides, it was hydrolysed by nuclease. Although dephosphorylation is approx. equal to depolymerisation, no increase in acidity occurs through dephosphorylation. Four acidic groups are again liberated. Thus (I) and (II) possess four ester linkings, and as both are tetrabasic they probably possess a similar ring structure. J. H. B.

Choline, acetylcholine, and carnitine content of muscle. E. STRACK, P. WÖRDEHOFF, E. NEU-BAUR, and H. GEISSENDÖRFER (Z. physiol. Chem., 1935, 233, 189–203).—Neither choline (I) nor acetylcholine (II) was detected in the skeletal muscle of the ox and dog. (II) was also shown to be absent by the biological test. In the muscle free (I) is not produced on incubation at 37°. In the hydrolysed aq. extract of skeletal muscle, no (I) was obtained by Au pptn., although the muscle does not destroy added (I). The so-called (I) and (II) found by Kinoshita (A., 1910, ii, 631) and Bischoff *et al.* (A., 1932, 765) was probably carnitine (III). Ox-muscle contains 0.01-0.2% of (III) chloride. J. H. B. Glycogen and total carbohydrate content of the human heart. H. BLUME (Beitr. path. Anat. allg. Pathol., 1934, 93, 20–35; Chem. Zentr., 1935, i, 433).—The glycogen (I) contents of the ventricle and septum of the normal human heart are equal. (I) in the infant heart is > in the adult. The heart contains 0.46—1.46% of carbohydrate, 70\% of which is (I); a (I) content > 1.5% indicates hypertrophy. After death 90% of the (I) of the heart is converted into glucose in 9 hr., the remainder being unaltered; in infants the breakdown is slower. R. N. C.

Glycogen of the placenta. H. GUTHMANN and L. BÖHME (Arch. Gynäkol., 1934, 158, 336—344).— At the 2nd month maternal portions of human placentæ contained nearly twice as much glycogen (I) as fætal portions. By the 6th month this difference had disappeared. No evidence was obtained that (I) could pass as such from maternal to fætal tissues. If (I) transference does take place, hydrolysis and resynthesis must occur. NUTR. ABS. (b)

Quantity, distribution, and significance of placental glycogen in the different phases of pregnancy. Function of human and hæmochoroidal placentæ. B. SZENDI (Arch. Gynākol., 1934, 158, 409—425).—In rabbits the placental glycogen (I) increased rapidly from 0.3% on the 11th to 1.0% on the 17th day of gestation and thereafter fell to about 0.1% on the 30th day. In human pregnancy the placentæ contained most (I) about the 2nd month (0.5%); by the 9th month < 0.1% of (I) was present. Hence the (I) in the placenta is part of the metabolic structure of the placental cell and is not connected with the carbohydrate metabolism of the embryo. NUTR. ABS. (b)

Fatty acids of pig liver. III. General analysis. E. IRVING and J. A. B. SMITH (Biochem. J., 1935, 29, 1358–1368; cf. A., 1934, 913, 1381).— Data from bromination and from oxidation and hydrogenation of fractionally distilled Me esters are given. The main saturated acids (approx. 36%) are palmitic (14%) and stearic ( $18\cdot8\%$ ) and the unsaturated oleic (28%), C<sub>20</sub> (20%), and C<sub>22</sub> ( $7\cdot5\%$ ). The C<sub>29</sub> and C<sub>22</sub> acids have probably 2—4 double linkings. F. O. H.

Relationships of liver-lipins. F. BREUSCH and R. SCALABRINO (Z. ges. exp. Med., 1934, 94, 569— 578; Chem. Zentr., 1935, i, 737).—In man the proportion of lipochromes increases somewhat with age. Vals. were high in uræmia and hypertension, and subnormal in liver cirrhosis. The vitamin-A content decreased with age and, markedly, in uræmia and cirrhosis, but was high in diabetes. Free cholesterol varied but little. Cholesteryl esters increased in hypertension and in sclerosis. Phosphatides increased in uræmia and decreased in cirrhosis and hypertension. The total fat content was high in carcinoma and tuberculosis. With increasing total fat the I val. declined. A. G. P.

Polysaccharoproteins. V. State of glycogen in muscle. E. M. MYSTKOWSKI (Biochem. Z., 1935, 278, 240—245; cf. this vol., 882).—In muscle (rabbit, dog) there is equilibrium between the various forms (free, dissolved, protein-bound) of glycogen. Part of it is bound to myosin, but probably none to myogen. The globulin-X also binds a small amount, and the stroma always contains some. The results of Willstätter *et al.* (A., 1934, 913) are confirmed.

W. McC.

Ammonia content and ammonia formation in muscle. XXII. I. Determination of adenosinetriphosphoric acid. II. Second ammoniaforming substance of muscle. J. K. PARNAS and C. LUTWAK-MANN (Biochem. Z., 1935, 278, 11—22).— A method for determination of adenosinetriphosphoric acid (I) is described with the help of which it is shown that muscle contains no adenylic acid. The sum of NH<sub>3</sub>-N and of the (I)-NH<sub>2</sub>-N of muscle increases during NH<sub>3</sub> formation by 2 mg. of N per 100 g., and it appears, therefore, that muscle contains in addition to (I) some other NH<sub>3</sub>-forming substance. P. W. C.

Constitution of adenosinetriphosphoric acid. K. MAKINO (Biochem. Z., 1935, 278, 161–163).—The readily hydrolysable  $H_3PO_4$  groups are not attached to OH at C2 or C3 of ribose or to  $NH_2$  of adenine. P. W. C.

Synthesis of asterubin. D. ACKERMANN (Z. physiol. Chem., 1935, 234, 208—211; cf. this vol., 771).—Aq. taurine (I) heated at 120° for 5 hr. with dimethylcyanamide gives asterubin in poor yield. The biological synthesis probably takes the form of a reaction between (I) and guanidine. W. McC.

Total nitrogen of the liver of frogs in summer and winter and during fasting and administration of nitrogen-rich diet. C. GAUTIER, J. RATELADE, and R. CASATI (Bull. Soc. Chim. biol., 1935, 17, 745—750).—The total N of the liver of frogs decreases considerably in summer and winter when the animals are fed on frog-muscle. A. L.

Structure of tooth-tartar (Calculus dentalis supragingivalis). H. PHILIPP (Z. physiol. Chem., 1933, 233, 209—214).—X-Ray diagrams of toothtartar indicate that the phosphate belongs to the apatite group and is, from its behaviour at 1000° [combination with adsorbed phosphate, yielding  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>], a hydroxyapatite. Owing to adsorbed phosphate it analyses approx. as Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, but contains 0.28% of CO<sub>2</sub>. J. H. B.

Molybdenum content of sound and carious teeth. H. TER MEULEN (Chem. Weekblad, 1935, 32, 350).—Sound and carious human teeth contain 0.55 and 0.03—0.06 mg. Mo per kg., respectively. Ox and calves' teeth contain 0.21—0.34 mg. and the bones 0.04 mg. Mo per kg. S. C.

Chemistry of bone-salts. J. MAREK, O. WELL-MANN, and L. URBANYI (Z. physiol. Chem., 1935, 234, 165—175; cf. A., 1934, 1133; this vol., 234; Gabriel, A., 1894, ii, 21).—The bones of calves and cows, on boiling with  $H_2O$ , aq. KOH, aq.  $K_2CO_3$ , glycerol (I), (I)+KOH, or aq. Na<sub>2</sub>HPO<sub>4</sub>, are converted into material similar to Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Most of the combined CO<sub>2</sub> is present as CaCO<sub>3</sub>. These and other facts indicate that the mineral part of the bones consists chiefly of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and CaCO<sub>3</sub> with small amounts of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Ca alkali phosphate. Klement's conclusions are erroneous. W. McC. Role of zinc in reproduction. Experiments with castrated silk-worms (Bombyx mori, L.). A. AKAO (Keijo J. Med., 1935, 6, 49–60).—The [Zn] in the ovaries and testes is similar, and the total quantity in the former is therefore greater (24 times). The Zn content of the blood of normal and castrated males and normal females is similar, but there is a sudden rise with ovariectomised females shortly before emergence from the cocoon. The [Zn] in the bloodcells is 4 times that in the plasma. K is not subject to a similar variation in the ovariectomised female. P. G. M.

Composition of the fishes Bothus maeoticus, Pall, and Gobius melanostomus, Pall. K. WOY-NOFF (Z. Unters. Lebensm., 1935, 69, 174–176).— The % of H<sub>2</sub>O, protein, fat, and ash are given.

E. C. S.

Lipochromes of sea anemones. I. Carotenoid pigments of Actinia equina, Anemonia sulcata, Actinoloba dianthus, and Tealia felina. I.M. HEILBRON, H. JACKSON, and R. N. JONES (Biochem. J., 1935, 29, 1384-1387) .- Hydrolysis of actinioerythrin (I) from A. equina (A., 1934, 676) yields a violet pigment, violerythrin, m.p. 191-192°, absorption spectrum max. at 625, 576, and 540 mµ in CS<sub>2</sub>. The pigment of A. sulcata is mainly sulcatoxanthin,  $C_{40}H_{52}O_8$  (?), ill-defined m.p. 125–130°, absorption max. at 516, 482, and 450 m $\mu$  in CS<sub>2</sub>; the tentacles contain chlorophyll-a (Elmhirst and Sharpe, Biochem. J., 1920, 14, 48). A. dianthus yields a red acidic pigment, m.p. 195-197°, whilst T. felina contains two lipochrome esters, one possibly identical with (I) and the other (max. at 500 m $\mu$  in CS<sub>2</sub>) giving an acidic pigment, m.p. 205-208°. F. O. H.

Coalescence of fat particles. W. FRITZ (Milch. Forsch., 1934, 16, 476–484; Chem. Zentr., 1935, i, 813).—Chain formation of fat globules in milk exposed to an electric field is followed by coalescence if the temp. is raised to  $< 90^{\circ}$ . The relationship between this phenomenon and the ionic layer surrounding the globules is discussed. A. G. P.

Occurrence of an octadecadienoic acid in cow butter-fats. T. G. GREEN and T. P. HILDITCH (Biochem. J., 1935, 29, 1564—1575).—The mixture of unsaturated  $C_{18}$  acids from cow butter-fat consists of oleic acid (75%), tri- or tetra-ethenoid  $C_{18}$  acids (1.5%), and octadecadienoic acid (I) (23.5%). Oxidation of the octadecadienoic acids from butter-fat and ground-nut oil shows that they are structurally similar, but that (I) is a different geometrical isomeride of the  $\Delta^{03}$ -acid of seed-fats. It is concluded that the kind of (I) in butter-fat depends on the diet of the cow, and that linoleic acid when present in the glycerides of land animals is a product of assimilation and not of synthesis. J. N. A.

Cause of low stability of vitamin-C in milk. J. E. JACOBSEN (Z. Unters. Lebensm., 1935, 69, 306-313).—Vitamin-C is determined in a serum prep. from milk by titration at  $p_{\rm H} 2.5$  with dichlorophenolindophenol. The extremely small amount of -C in milk is readily destroyed by mixing or by pouring from one vessel to another. -C is more resistant in fresh than in stored milk. Change from winter feeding to pasture caused no increase in % of -C. It is calc. that the adult must consume 3 litres of the best milk *per diem* to satisfy completely his -C requirement. E. C. S.

Cryoscopic measurements of Indian milk. P. S. MACMAHON and L. N. SRIVASTAVA (Analyst, 1935, 60, 307–309).—The mean f.-p. depressions of cow's and buffalo's milk were 0.551° and 0.562°, respectively. E. C. S.

Magnesium content of the cerebrospinal fluid : relation to blood-magnesium. C. B. UDAONDO, M. SCHTEINGART, and R. GAIBROIS (Rev. Soc. Argentin. Biol., 1933, 9, 321–324).—The Mg contents of spinal fluid and of serum were practically the same and were unchanged in chronic affections of the central nervous system. CH. ABS. (p)

Van den Bergh reaction of bilirubin in xanthochromic cerebrospinal fluid. S. L. VAUGHAN and R. S. HUBBARD (Proc. Soc. Exp. Biol. Med., 1935, 32, 618-620).—The reaction occurs promptly when the protein (I) concn. is normal, or the bilirubin (II) concn. is high. It is increasingly delayed as (II) falls and (I) rises. R. N. C.

Adenylic acid in the central nervous system. C. RIEBELING (Klin. Woch., 1934, 13, 1422—1424; Chem. Zentr., 1935, i, 744).—The mean NH<sub>3</sub> content of the cerebrospinal fluid is 0.07 mg. per 100 c.c. It increases considerably in epilepsy, the extra NH<sub>3</sub> probably originating in the brain. Brain-NH<sub>3</sub> increases rapidly after death through enzymic deamination of a parent substance, probably adenylic acid. NH<sub>3</sub> is high in the brains of patients who have died in convulsions. R. N. C.

Acid secretion by the stomach. IV. Effect of alkalosis on the secretion of acid in the dog. Effect of the ionic environment in the blood. G. DELRUE and A. LACQUET (Arch. internat. Physiol., 1934, 39, 295–310).—The production of alkalosis in a dog by prolonged ingestion of NaHCO<sub>3</sub> altered neither the  $p_{\rm H}$  nor the total acid content of the gastric juice secreted. NUTR. ABS. (b)

Influence of the acid-base equilibrium on gastric secretion. N. F. MACLAGAN (J. Physiol., 1934, 83, 16–17P).—There was no correlation between the acidity of the gastric juice and the acid-base ratio of the blood. The induction of  $NH_4Cl$  acidosis had no influence on the acidity of gastric secretion in response to histamine or EtOH test meals.

NUTR. ABS. (b)

Spectrographic study of the gastric content in fasting men. I. L. KARCZAG and M. HANAK. II. L. KARCZAG (Biochem. Z., 1935, 278, 105—107, 108—111).—I. Normal gastric and duodenal juice and their ultrafiltrates possess a selective absorption in the ultra-violet, which is considerably modified by alkali and acid and is not accounted for by the content of protein, polypeptides, aromatic NH<sub>2</sub>acids, uric acid, etc.

II. The above properties of gastric juice closely resemble those of the vitamin-*B* complex.

P. W. C.

Gastro-intestinal  $p_{\rm H}$  in rats. I. M. EASTMAN and E. G. MILLER, jun. (J. Biol. Chem., 1935, 110, 255-262).—Normal rats generally show an acid reaction in the gastro-intestinal tract, with the  $p_{\rm H}$  rising from the stomach to the ileocæcal valve, falling in the cæcum, and again rising in the colon. Young rats have a higher alimentary  $p_{\rm H}$  than adult rats. On a bread diet the contents of the colon tend to be more acid than in the cæcum. The McCollum rachitogenic diet causes a slight but consistent rise in the intestinal  $p_{\rm H}$  throughout, otherwise wide variations in diet have no significant effect. Local conditions of absorption, secretion, and bacterial action, rather than the  $p_{\rm H}$  at higher levels, determine the  $p_{\rm H}$  at a given level. E. A. H. R.

Gastro-intestinal studies. IV. The relation of  $p_{\rm H}$  to the pepsin and rennin content of the gastric juice. O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (Amer. J. Digest. Dis. Nutrit., 1934, 1, 120—123).—The presence of pepsin and rennin in human gastric secretion after histamine stimulation is dependent on  $p_{\rm H}$ . Pepsin and rennin were present when the  $p_{\rm H}$  was > 7, but neither could be detected when the  $p_{\rm H}$  was > 7. The concn. of the enzymes, however, did not depend on the amount of acid secreted. When the acidity is determined by  $p_{\rm H}$ methods or titration, stomach contents which show a  $p_{\rm H}$  of 7 are considered to have an anacidity, a condition in which there is an absence of free acid, pepsin, and rennin. NUTR. ABS. (b)

 $p_{\rm R}$  of the duodenal contents in absence of bile. G. LOEWY (Compt. rend. Soc. Biol., 1935, **119**, 382— 384).—Deprivation of bile causes a rise of duodenal  $p_{\rm R}$ , the increase at the pyloric end being > at the jejunal end. R. N. C.

 $p_{\rm H}$  of the duodenal contents in the absence of pancreatic juice. G. LOEWY (Compt. rend. Soc. Biol., 1935, **119**, 490—491).—In the absence of pancreatic juice the stomach, duodenum, and jejunum of the dog have the same  $p_{\rm H}$ . No inflammation of the mucous membrane of the duodenum or jejunum is observed. H. G. R.

Duodenal secretion and sugar metabolism. J. LA BARRE and P. HOUSSA (Compt. rend. Soc. Biol., 1935, 119, 538-540).—Sugar tolerance is decreased if secretion is removed by prolonged washing of the intestine with dil. HCl. H. G. R.

Elimination of dyes in gastric and pancreatic secretions. Mechanism of secretion of acid and base. R. C. INGRAHAM and M. B. VISSCHER (J. Gen. Physiol., 1935, 18, 695—716).—Following intravenous injection into dogs, dyes appearing in the gastric and pancreatic juice (invoked by histamine and secretin, respectively) ionise with the chromogen electro-positively and -negatively, respectively. An explanation of the phenomena based on polar adsorption at the membrane pores of the glands (*i.e.*, electrostatic filtration) agrees with the conception of the mechanism of the natural secretions. F. O. H.

Keratin digestion in the larvæ of the clothes moth. K. LINDERSTRØM-LANG and F. DUSPIVA (Nature, 1935, 135, 1039—1040).—The secretion of the middle intestine of *Tineola biselliella* contains a powerful proteinase (I) ( $p_{\rm H}$  optimum at 9.3) which is little sensitive to SH-compounds. The secretion contains a reducing agent of unknown nature, which appears capable of reducing the S·S linkings in the hair. The reduction of the hair-keratin then opens the peptide chains to attack by (I). Digestion of sheep-wool by (I) using Na thioglycollate as reducing agent at  $p_{\rm H}$  10 resulted in rapid degradation of the wool with the formation of equiv. amounts of NH<sub>2</sub> and CO<sub>2</sub>H. Pancreatic trypsin-kinase had no effect owing to inhibition by the SH-compounds.

L. S. T.

Formation of gall-stones. A. DE KUTHY (Bull. Soc. Chim. biol., 1935, 17, 774—779).—Since in the intact bile vesicle the ratio of the amount of bile salts (I) to that of cholesterol (II) remains const. during a stoppage and the solubility of (II) increases as the square of the concn. of (I), a stoppage does not lead to the pptn. of (II). Infections and metabolic disturbances, however, which cause a diminution of the concn. of (I) increase the tendency for (II) pptn. A. L.

Constituents of human seminal plasma. M. W. GOLDBLATT (Biochem. J., 1935, 29, 1346-1357).-The concns. of constituents of the plasma (from centrifuging normal semen) have the following ratios to those of blood-plasma: Cl', cholesterol, 0.3-0.5;  $HCO_3'$ , 0.7-1.0; Ca, glucose, urea, 2.0-3.0; lactic acid, 5.0-6.0; acid-sol. P (inorg. 50, spermine- 30, and undetermined 20%), 30. Proteins present include mucin, nucleoprotein, albumin, globulin, and proteoses (primary and occasionally secondary). Protamines, histones, and SH groups are absent. Glycolysis (demonstrable only if active sperm cells are present) is associated with a large increase in lactic acid, which, however, is insufficient to account for the loss in reducing power. Diastase and thrombokinase, but not protease, are present. F. O. H.

Action of monohalogenoacetic acids on the glycolysis and mobility of sperms. E. E. IVANOV (Biochem. Z., 1935, 278, 101—104).—The mobility of mammalian sperms can be retained in presence of either HCN or of the monohalogenoacetic acids even when the concn. of these reagents is sufficient to inhibit respiration or glycolysis, respectively.

**P.W.C.** 

Urine analysis. N. S. KING and O. UVAROV (Vet. Rec., 1935, 15, 553-555).-Results are given for urine analysis in typical cases of illness in dogs. R. N. C.

Application of the iodide-thiocyanate process in the determination of urinary sugar. E. TSCHIRCH and D. KRÜGER (Pharm. Ztg., 1935, 80, 695—696).—Urinary sugar is determined rapidly and accurately by boiling with a known quantity of Fehling's solution, acidifying, removing excess of Cu<sup>"</sup> with KI and KCNS, and titrating the liberated I with 0.1N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The urine generally requires dilution. R. N. C.

Excretion and determination of thiosulphate in urine. W. ZÖRKENDÖRFER (Biochem. Z., 1935, 278, 191—194; cf. Wollak, A., 1929, 1030).—0.1N-I is slowly added to urine (made just acid, if necessary, with AcOH) until interaction with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is slow, and large excess of I is added. After < 15 min. aq. Pb(OAc)<sub>2</sub> is added, the mixture is filtered, and K<sub>2</sub>SO<sub>4</sub> added until pptn. ceases. After several hr. the mixture is filtered and KI, aq. starch, and a few drops of dil.  $H_2SO_4$  are successively added to the filtrate (vol. 200 c.c.). If a blue colour develops it is destroyed with just sufficient 0.01% aq. NaHSO<sub>3</sub>. One drop of phenolphthalein solution, 5% aq. NH<sub>3</sub> (to rosepink colour), and 5 c.c. of 10% aq. KCN are now successively added. After 15 min. 25 c.c. of dil.  $H_2SO_4$  (1:3) are added and the liquid is titrated with 0.01N-I, more starch being added if necessary. The Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> thus determined is half of that originally present. For determination of Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> the procedure prior to addition of NH<sub>3</sub> and KCN is omitted. In rabbits and man the amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> excreted increases with that administered (intravenous>subcutaneous>oral). Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> not so excreted is quantitatively removed in the urine as Na<sub>2</sub>SO<sub>4</sub>. Injection of S causes no increase in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> excretion.

W. McC.

Volatile amines of human urine. H. LÖFFLER (Z. physiol. Chem., 1935, 232, 259—262).—The method of isolation and detection of the amines is described.  $NH_3$  and  $NHMe_2$  are the chief volatile bases of normal human urine;  $NMe_3$  and  $NH_2Me$  occur in smaller amount. J. H. B.

Thyrotropic substances in human urine. B. GIEDOSZ (Klin. Woch., 1934, 13, 1507; Chem. Zentr., 1935, i, 741).—Intravenous injection in rabbits of urine from healthy or sick individuals produces in some cases a thyrotropic effect, and in other cases an increase of colloids, due to folliculin-like substances. R. N. C.

Effect of exercise on excretion of uric acid. Effect of benzoic acid on uric acid elimination in liver diseases. A. J. QUICK (J. Biol. Chem., 1935, 110, 107—112; cf. A., 1932, 1277).—In man excretion of uric acid (I) is unaffected by mild, but is diminished by strenuous, exercise, the excretion of creatinine remaining unaffected and the lactic acid (II) of the blood increasing at the same time. Since administration of (II) diminishes excretion of (I), (I) retention may be due to over-production of (II). In liver diseases administration of BzOH causes prolonged (I) retention, but the degree of retention does not run parallel with the accompanying diminution in the rate of hippuric acid production. W. McC.

Dehydroandrosterone [in urine].—See this vol., 981.

Differentiation of chloride and bromide by the kidney. M. A. B. TOXOPEUS (Arch. exp. Path. Pharm., 1935, 178, 416-419).—Determinations of Br' and Cl' in urine, blood, plasma, and serum after oral administration of aq. NaBr to rabbits and dogs fail to support the contention of Frey (A., 1932, 89) and of Möller (*ibid.*, 412, 639) that the kidney does not distinguish between Cl' and Br' (cf. A., 1930, 639). F. O. H.

Protein-free urines giving a biuret-like reaction. E. G. GODFRIED (Biochem. J., 1935, 29, 1340—1345).—Fresh urine of healthy or diseased persons gives a rose or purplish-red colour with 1% aq.  $CuSO_4$  and 5% aq.  $Na_2CO_3$ , the reaction not being identical with the biuret test. The substance responsible is not a peptone or urobilin, but either a pigment or associated substance of the urochrome group. F. O. H.

Xanthurenic acid. II. L. MUSAJO. III. Origin of xanthurenic acid. L. MUSAJO and F. M. CHIANCONE (Atti R. Accad. Lincei, 1935, [vi], 21, 461-467, 468-470).—II. The urine of animals fed on fibrin contains, in the albino rat and the rabbit, xanthurenic acid (I), kynurenine (II), and kynurenic acid (III); in the dog, (III) and (II), without (I). The isolation of (II) is described.

III. Albino rats fed on a diet containing tryptophan (IV) or (II) excrete (I); those fed on gelatin do not, and those fed on (III) excrete only minute amounts of (I). It is concluded that (I) is produced in the animal from (IV) by way of (II), which gives either (I) or (III); (I) may be a hydroxykynurenic acid.

E. W. W. Crystal structure data and calculus (urate) formation. F. WORSCHITZ and J. VON HERMAN (Fortschr. Röntgenstrahlen, 1934, 50, 305—307; Chem. Zentr., 1935, i, 585).—The structure of spherical calculi is that of a polycryst. aggregate, generally with orientation and inner strain along the radii. R. N. C.

Porphyrin metabolism. Spectroscopic determination of porphyrins. K. LAGEDER (Arch. Verdauungs-Krankh., 1934, 56, 237-256).—A spectroscopic method of porphyrin (I) determination is described. The normal rate of urinary excretion of (I) is 0.01-0.08 mg. per 24 hr. It is frequently very low in subjects on a meat-free diet. It is increased in cirrhosis of the liver, icterus, pulmonary tuberculosis with fever, sometimes in pernicious anaemia, but seldom or not at all in cancer of the stomach, hæmolytic jaundice, and Addison's disease. There is a correlation between abnormal skin pigmentation (e.g., in psychopathic states) and disturbance of (I) metabolism. NUTR. ABS. (m)

Experimental acidosis. V. Acidosis and liver function. S. TATSUZAWA (Sei-i-kwai Med. J., 1933, 52, No. 10, 91–103).—Liver function in rabbits is disturbed in experimental acidosis.

Сн. Авз. (р)

Relation between the respiration of the red corpuscles, glutathione, and the reticulocytes in secondary anæmias in the rabbit. G. LITARCZEK, S. BAICOIANO, and M. BALS (Compt. rend. Soc. Biol., 1935, 119, 764—768).—Corpuscular respiration  $\infty$  the reticulocyte content of the blood, but is not absolutely dependent on the blood-glutathione. R. N. C.

Corpuscular respiration in secondary anæmias in the rabbit. G. LITARCZEK, S. BAICOIANO, and M. BALS (Compt. rend. Soc. Biol., 1935, 119, 761— 763).—The increase of respiration of the blood of anæmic rabbits is a function of the red corpuscles alone. R. N. C.

Treatment of hæmophilia : action of Congored. C. P. WALDORP and A. G. ALVAREZ (Semana méd., 1935, I, 6—11).—Among many substances examined, Congo-red, injected intraveneously or intramuscularly, gave best results. CH. ABS. (p)

Mouse leucæmia. X. Metabolic differences between transmission lines of mouse lymphatic **leucæmia.** J. VICTOR and M. R. WINTERSTEINER (Amer. J. Cancer, 1934, 22, 561—571).—Metabolic differences, as shown by  $O_2$  consumption, aërobic and anaërobic glycolysis of lymph nodes, are exhibited between lines of transmissible leucæmia from the same organ and between those derived from different organs in the same case. CH. ABS. (p)

Blood-potassium after extirpation of the adrenal glands. C. I. URECHIA, G. BENETATO, and (MME.) RETEZEANU (Compt. rend. Soc. Biol., 1935, 119, 439-440).—Extirpation of both adrenals in the cat produces a marked rise of blood-K. Extirpation of one adrenal in the cat or dog produces a slight rise followed by a fall. R. N. C.

Calcification process of the aorta studied radiographically. F. WORSCHITZ and J. VON HERMAN (Fortschr. Rontgenstrahlen, 1934, 50, 307—309; Chem. Zentr., 1935, i, 585).—The X-ray picture of the sclerotic aorta is marked by additive Ca rings, whilst the interference of the fibres declines. The deposition of the sclerotising substance takes place intracellularly or intramicellarily according to the crystal structure, the deposited crystals not exceeding 10<sup>-6</sup> cm. in size. The calcified centre appears as a homogeneous substance, showing no stratification of the crystals. R. N. C.

Carbohydrate tolerance in cancer patients and the effect thereon of X-radiation. F. H. L. TAYLOR and H. JACKSON, jun. (Amer. J. Cancer, 1934, 22, 536—547).—Lowered carbohydrate (I) tolerance in cancer results from malnutrition and cachexia. Irradiation has no effect on (I) metabolism. CH. ABS. (p)

Therapy of spontaneous mouse tumours: failure of additional inorganic compounds. M. C. MARSH (Amer. J. Cancer, 1934, 22, 572—577).— Injection of saturated aq. NaCl into epithelial tumours destroyed these. Other inorg. salts, oxides, hydroxides, I, and CHCl<sub>3</sub> had no effect.

CH. ABS. (p)

Effect of radiation, lactate, and iodoacetic acid on turnours. W. R. FRANKS, M. M. SHAW, and W. H. DICKSON (Amer. J. Cancer, 1934, 22, 601— 605).—Growth of turnours was not inhibited by injections of Na lactate and the efficiency of subsequent X-irradiation was unchanged.  $CH_2I \cdot CO_2H$  slightly inhibited growth of turnours, and its effect was increased by previous irradiation. CH. ABS. (p)

Co-enzyme of glycolysis from tumours. III. H. KRAUT and R. W. NEFFLEN (Z. physiol. Chem., 1935, 232, 270—279; cf. A., 1933, 1202).—Co-enzyme T (I) from ox-brain is purified by adsorption on kaolin and elution with 0.0001*N*-NaOH. The presence of AcCO<sub>2</sub>H cannot be detected. Further purification is attained by pptn. with 25% aq. HCl, (I) being an acid. It may also be pptd. as the Ba salt, which is then decomposed by H<sub>2</sub>SO<sub>4</sub>. Purified (I) shows no loss of activity after 5 min. at 100°.

J. H. B.

Enzymic efficiency in malignancy. I. Influence of growing Walker carcino-sarcoma on concentration of blood and tissue enzymes of the albino rat. B. SURE, M. C. KIK, and K. S. BUCHA- NAN (Biochem. J., 1935, 29, 1508—1514).—Subcutaneous inoculation of Walker carcino-sarcoma No. 256 in the rat caused marked decreases in the serumamylase, -esterase, and -trypsin, and small decreases in hepatic esterase, pancreatic amylase, and serumphosphatase. H. D.

Chemical composition of normal and cataract crystalline lenses. M. PAGET, G. PAR-TURIER, and G. LEVIN (Compt. rend. Soc. Biol., 1935, 119, 581-583).—In the cryst. lens in senile cataract, cholesterol, Ca, and total S are increased, whilst Na and K are relatively decreased. R. N. C.

Carbohydrate metabolism in circulatory insufficiency. V. C. VASILENKO and M. L. JEVTU-CHOVA (J. Cycle méd., 1933, 3, 319–330).—Of 52 cases of cardiac disease, 30% showed some variation of the blood-sugar (I) from normal (16% hypo- and 14% hyper-glycæmia), under-nourished patients always having a low (I). The curve of alimentary hyperglycæmia in circulatory insufficiency showed a much slower rise, but eventually attained a higher level than in a normal subject. The (I) bore no stable relation to the sugar content of ascitic fluid or fluid from ædematous areas. NUTR. ABS. (b)

Effect of ingestion of minute quantities of cobalt by sheep affected with "Coast disease." E. W. LINES (J. Counc. Sci. Ind. Res. Australia, 1935, 8, 117—119).—Diseased sheep improved rapidly after feeding 1 mg. of Co as  $Co(NO_3)_2$  daily. Ironstone gravel produced no beneficial effect. A. G. P.

Metabolism of sulphur. XXII. Cystine content of hair and nails of cystinurics. H. B. LEWIS and L. FRAYSER (J. Biol. Chem., 1935, 105, 23—27).— The cystine content of the hair and nails of cystinurics was not different from normal. H. D.

Experimental "superabundance" diabetes in a normal dog. M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1935, 119, 664—666).—The R.Q. rises steadily to a val. slightly > 1 in a normal dog receiving glucose (I) intravenously for 6 hr. at 1—9 g. per kg. per hr.; it remains at this steady max., independent of the rate of injection and the intensity of glycolysis, until the end of the injection, when it falls again to normal. The amount of (I) oxidised increases with rate of injection, the curve being a hyperbola until oxidised (I) reaches a max. when the rate is 6 g. per kg. per hr. The oxidation quotient of (I) increases with rate of injection, reaching 3.6 at 5 g. per kg. per hr. R. N. C.

Relation between the metabolism of carbohydrates, uric acid, and oxalic acid in diabetes. M. MAIO (Riv. Patol. sper., 1934, 13, 469–485).— The blood- $H_2C_2O_4$  (I) in diabetes was raised, but there was no relationship between the blood and urine vals. or between (I) and uric acid vals. There was, however, parallelism between blood- and urine-(I) and the glycamic level, but not abs. proportionality. With dietary control, (I) fell somewhat, and with simultaneous insulin administration the fall was more pronounced, particularly for blood-(I).

NUTR. ABS. (b)

Hypoglycæmia provoked in diabetics. A. BAU-DOUIN, J. LEWIN, and E. AZÉRAD (Compt. rend. Soc. Biol., 1935, 119, 686—688).—The blood-sugar curves of diabetics after injection of insulin fall into two groups, depending on whether or not the blood-sugar recovers after reaching its min. R. N. C.

Elimination of chlorine in skin diseases. J. R. PRAKKEN (Nederl. Tijdschr. Geneesk., 1934, 78, 3851).—Urinary elimination of Cl was moderately diminished in eczema and dermatitis exfoliativa, and very greatly in a case of pemphigus, the Cl and albumin contents of the blood-plasma being also lowered. NUTR. ABS. (m)

Guanidine, glucose, and calcium content of the blood in eclampsia. V. I. KRIEGER (Med. J. Austral., 1934, ii, 746—749).—Vals. for guanidine (I) are not markedly > in normal pregnant women (eclamptics: 0.21-0.54; mean, 0.39; normal: 0.27-0.39; mean, 0.34 mg. per 100 ml.). Hypoglycæmia is present in some cases, but, contrary to Minot and Cutler, there is no correlation of glucose and Ca with (I). NUTR. ABS. (m)

Role of the marrow in the production of hyperglycæmia following experimental "cerebral" embolism. H. HERMANN, F. JOURDAN, and P. CORNUT (Compt. rend. Soc. Biol., 1935, 119, 601— 603).—The spinal marrow plays a part in the production of the hyperglycæmia provoked by experimental encephalomedullary embolism, this function being important in animals that have not been decapsulated, on account of the release of adrenaline by anæmic excitation of the spinal adrenaline-secreting centres. R. N. C.

Liberation of histamine-like substances in experimental cerebral embolism. J. TINEL, G. UNGAR, and A. GROSSIORD (Compt. rend. Soc. Biol., 1935, 119, 702—703).—Injection of lycopodium powder in the primitive carotid of the dog produces increased gastric secretion both in the injected animal and in another animal with which its circulation is crossed; the effect is thus due to histamine-like substances. R. N. C.

Carbohydrate metabolism in Graves' disease and goitre: effect of operative treatment. T. CHIBA (Tõhoku J. Exp. Med., 1934, 23, 474—493).— The fasting blood-sugar was within normal physiological limits in 14 cases of Graves' disease and goitre. Carbohydrate tolerance, as measured by glucose "double loading," was impaired in proportion to the degree of toxicosis in Graves' disease, but was normal in simple goitre without thyrotoxicosis. Following thyroidectomy in Graves' disease, normal carbohydrate metabolism was either entirely or partly restored. NUTR. ABS. (b)

Iodine metabolism and the thyroxine content of nodular goitres. I. ABELIN and N. E. FINKEL-STEIN (Schweiz. med. Woch., 1934, 64, 985—987).— Inorg. I in simple goitre was 19% of the total compared with the normal mean. 56% of all the glands were deficient in thyroxine-I (about 10% instead of the normal mean of 25%). Total I per g. was subnormal in all goitrous glands. I present in di-iodotyrosine (I) and I organically bound other than in thyroxine and (I) were also determined.

NUTR. ABS. (m)

Iodine and thyroid hyperplasia. I. Iodine content of human skimmed milk from goitrous and non-goitrous regions. R. G. TURNER (Amer. J. Dis. Children, 1934, 48, 1209—1227).—The I content of milk from mothers in goitrous regions was >that from non-goitrous regions. The Ca and inorg. P of milk from the former were > those from the latter during the first 3—4 months of lactation, but subsequently became lower. CH. ABS. (p)

Fat tolerance in hyperthyroidism. O. E. HEPLER (Arch. Int. Med., 1935, 55, 979–996).— Administration of thyroid to dogs, after causing a slight decrease, resulted in a considerable increase in blood-fat (I), blood-cholesterol (II) remaining normal. During a rest period immediately following, (I) and (II) increased greatly, then during a second period of thyroid administration both decreased somewhat, although they were still > normal. During hyperthyroidism the metabolism of the body may be at a higher level, thus requiring the maintenance of the (I) and blood-sugar also at a higher level. A. L.

Iodine metabolism in hyperthyrosis. L. SCHEF-FER (Klin. Woch., 1934, 13, 1570—1572; Chem. Zentr., 1935, i, 588).—I excretion is in equilibrium with I intake in hyperthyrosis; a considerable proportion of the I is excreted in the faces, which normally contain only very small quantities. In Basedow's disease, where the excretion is > the intake, the principal excretory organ is the kidney. Hence urinary and fæcal I determinations provide a means of distinguishing between hyperthyrosis and thyrotoxicosis. R. N. C.

Lipoidosis. S. J. THANNHAUSER (Klin. Woch., 1934, 13, 161—167; Chem. Zentr., 1935, i, 589— 590).—A review. R. N. C.

Reaction of lipins in blood-leucocytes to fever and infection. E. M. BOYD (Surg. Gynecol. and Obstet., 1935, 60, 205-213).—The lipin content of leucocytes from persons recovering from fever was high; that from those who did not recover was low. CH. ABS. (p)

Influence of infection on tissue respiration. W. FREI and O. FROEBEL (Biochem. Z., 1935, 278, 1-10).—The  $O_2$  utilisation of liver and kidney slices from guinea-pigs infected with fowl cholera, paratyphosus Gärtner, Rauschbrand's bacillus, etc. is > with slices of normal animals, but no relationship could be detected between respiration, clinical results, and body-temp. The respiration of slices from animals poisoned with the culture filtrates of these organisms and also of normal liver and kidney slices on addition of culture filtrates was increased. No essential difference was detected with aërobic and anaërobic organisms. P. W. C.

Treatment of cutaneous Streptococcus infections with intravenous cuprammonium sulphate. E. OTHAZ (Rev. assoc. med. Argentin., 1934, 48, No. 336).—Injection with NaOBz or caffeine gave satisfactory results, but secondary effects were observed. CH. ABS. (p)

Hyperglycæmia and hypoglycæmia provoked in myxædema. A. BAUDOUIN, E. AZÉRAD, and J. LEWIN (Compt. rend. Soc. Biol., 1935, **119**, 688690).—Blood-sugar in two cases of myxœdema recovered after ingestion of glucose, but not after insulin (I). The so-called "hypoglycæmia troubles" appeared when hypoglycæmia due to (I) was relatively small, but not at higher vals., and hence are independent of the blood-sugar. R. N. C.

Blood-sugar in internal disease. F. W. LAPP and H. DIBOLD (Deut. Arch. klin. Med., 1934, 177, 40-47).-Variations in the fasting blood-sugar (I) were observed according to the time of day. In gastric, intestinal, and hepatic disease the fasting (I) averaged 70-110 mg. per 100 ml.; vals. were low in gastric and intestinal conditions and high in obesity. Under normal conditions fasting (I) shows a fall at noon: in duodenal ulceration, hyperchlorhydric gastritis, and intestinal conditions the noon and evening vals, were raised; in hypochlorhydric gastritis, achylia, and obesity these findings were reversed. The tolerance to glucose in the above conditions did not agree with the daily "profile" of the (I), being increased in the former and somewhat diminished in the latter group. Seasonal variations were detected in the fasting (I), the val. being max. during February to April and min. during the winter months. NUTR. ABS. (b)

Decrease in sodium chloride content of blood after vomiting. A. TORDAY (Orvosi Hetilap, 1934, 78, 959-961).—Ill effects of vomiting are caused not only by loss of fluid, but also by loss of Cl'.

Сн. Авз. (p)

Iron metabolism in infancy. Relation to nutritional anæmia. H. W. JOSEPHS (Bull. Johns Hopkins Hosp., 1934, 55, 259—272).—Infants up to 2 months old have a small negative Fe balance which subsequently changes to positive at approx. 6 mg. per month. Infection causes a negative Fe balance. An exclusive milk diet cannot cause severe anæmia in the absence of other factors disturbing Fe metabolism. CH. ABS. (p)

Thyroxine in infancy. J. C. PELLARANO and S. SCHERE (Semana méd., 1935, I, 133-143).—Thyroxine gave better results than thyroid extracts.

Сн. Авз. (р)

Elimination of the gonadotropic hormone of the anterior pituitary and of folliculin in mania, depression, and schizophrenia at puberty. W. OESTERREICHER (Wien. klin. Woch., 1934, 47, 1385—1388; Chem. Zentr., 1935, i, 586).—Folliculin elimination is considerably reduced in women with mania or depression, but in schizophrenia it is found only in hebephrenics. R. N. C.

Hyperglycæmia provoked in nephritics. F. RATHERY, P. DE TRAVERSE, and V. FARLEY (Compt. rend. Soc. Biol., 1935, 119, 386—389).—Hyperglycæmia after ingestion of glucose in nephritics is > in normal subjects, and more prolonged. There is no correlation between hyperglycæmia and glycosuria or increased blood-urea. R. N. C.

Ability of nephritic patients to deaminise and form urea from ingested glycine. E. KIRK (J. Clin. Invest., 1935, 14, 136–141).—Following ingestion of glycine, the increase in plasma-NH<sub>2</sub>-N was greater in uræmic than in normal cases. The return to predigestive levels also occurred more slowly. The delayed conversion into urea in uræmic cases is due to the retardation of the deaminising function rather than of the urea-forming reaction. CH. ABS. (p)

Causes of the brevity of the hyperglycæmic effect produced by section of the four depressors in the dog. J. MALMÉJAC, E. DESANTI, and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 119, 731-733).—The brief hyperglycæmia following section of the depressors is due to increased secretion of adrenaline, which is rapidly corr. by increased insulin secretion. R. N. C.

Clinical significance of a very low concentration of urea in blood. A. E. OSTERBERG and N. M. KEITH (J. Lab. Clin. Med., 1934, 20, 141-144).—Low blood-urea vals. are associated with wasting diseases and with bilateral renal disease. In the latter, there may be increased excretion of urea by kidneys or a decreased production through disturbed N metabolism. CH. ABS. (p)

Salyrgan and ammonium chloride in cardiac cedema. I. HARRIS, E. L. RUBIN, and J. S. LAW-RANCE (Acta med. Scand., 1934, 83, 23—40; Chem. Zentr., 1935, i, 745—746).—Salyrgan diuresis is associated with hydramia which is probably related to the decreased cation concn. of the serum.  $\rm NH_4Cl$ -diuresis is associated with a concn. of blood. Serum-cations are reduced by  $\rm NH_4Cl$  with restricted, and remain normal with excessive, amounts of fluid.

A. G. P.

Calcium and phosphorus metabolism in osteomalacia. III. Effects of varying levels and ratios of intake of calcium to phosphorus on their serum levels, paths of excretion, and balances. S. H. LIU, R. R. HANNON, S. K. CHOU, K. C. CHEN, H. I. CHU, and S. H. WANG (Chinese J. Physiol., 1935, 9, 101—117).—In healing osteomalacia, serumand fæcal Ca  $\propto$  Ca intake. When Ca : P is high serum- and urine-P are low and fæcal P and urine-Ca increase. On lowering the ratio, urine-Ca tends to disappear and -P to increase. P retention depends on Ca and P intake, but excess Ca can be retained without an equiv. amount of P for bone formation.

H. G. R.

Guanidine and parathyroid glands. J. A. SAUNDERS (Biochem. J., 1935, 29, 1597—1598).— Guanidine (I) is not isolated from the blood of parathyroidectomised cats and dogs in tetany, nor is (I), injected into the operated animals, excreted any less rapidly than normally. H. D.

Action of the diet-factor J on the development of pneumonia in guinea-pigs. H. VON EULER, H. SODER, and M. MALMBERG (Z. Hyg. Infektionskr., 1935, 116, 672—682).—Guinea-pigs inoculated with pneumococci while on a complete basal diet containing vitamin-A, -B, and -D develop fatal bronchopneumonia. This is not avoided by administration of ascorbic acid, but is prevented by daily doses of lemon, blackberry, or elderberry juice, which contain factor J. R. N. C.

Chemo- and sero-therapy of pneumococcal pneumonia in the mouse. F. NEUFELD and W. A. Collier (Z. Hyg. Infektionskr., 1935, 117, 129– 136).—At early stages the effect of Au and immuneserum combined is > that of either alone. At later stages the combination is less effective, whilst the separate effects of Au and serum are increased.

R. N. C.

Changes in the distribution of fats in the cells of the corpus luteum of pseudo-gestation in rabbits. A. PERAUS (Compt. rend. Soc. Biol., 1935, 119, 771-772).—The distribution of fats in the corpus luteum in pseudo-pregnancy is the same as in pregnancy, but the activity of the corpus luteum is of short duration. R. N. C.

Histidine secretion in pregnancy. B. BODÓ (Orvosi Hetilap, 1934, 78, 761-763).—A positive Kapeller-Adler reaction was obtained in pregnancy urines. Histidinuria is probably related to altered protein metabolism following disturbed liver functions in pregnancy. CH. ABS. (p)

**Renal rickets.** H.A.SALVESEN (Acta med. Scand., 1934, 83, 485—500).—In a case of renal rickets (I) (boy aged 15 years) the urine had low sp. gr. Bloodurea (II) increased from 170 to 368 mg., serum-Ca (III) was  $4\cdot8$ —7 mg., and inorg. P 7 mg. per 100 ml., whilst plasma-CO<sub>2</sub> was  $31\cdot8$  vols.-% and  $p_{\rm H}$  7.28. There was a reduction of 24 millimols. in total bases of the blood. Ca lactate and cod-liver oil by mouth produced a decrease in (II), an increase in (III), and temporary clinical improvement. (I) is due to Ca deficiency effected through phosphate retention. Parathyroid over-activity may be a factor.

NUTR. ABS. (m)

Rickets and spasmophilia. I, II, III. S. SIWE (Acta paediat., 1934, 17, 1—71, 157—183, 184— 214).—There is frequently no alteration in the composition of cerebrospinal fluid in tetany. Manifest tetany may be present even with normal vals. for serum-Ca. It may occur in breast-fed infants when the breast-milk is low in Ca. The occurrence of rickets with low serum-Ca may be due to associated tetany. NUTR. ABS. (m)

Thyroid in the pathogenesis of human rickets and tetany. Blood-iodine. A. NITSCHKE and H. DOERING (Acta paediat., 1933, 16, 473-479).— The blood of normal infants contained, on an average,  $9\cdot3 \times 10^{-6}$  g. of I per 100 ml., but with rickets or tetany  $2\cdot9$  and  $2\cdot8 \times 10^{-6}$  g., respectively. The blood-I of such children after treatment with vitamin-D (I) rose from  $2\cdot4$  to  $8\cdot8 \times 10^{-6}$  g. Excess of (I) in rabbits caused a rise in blood-I well above normal. In rickets and tetany there was also a fall in basal metabolic rate. (I) may have an indirect, stimulating action on the thyroid. NUTR. ABS. (b)

Production of calcæmia after intravenous injection of calcium gluconate in dogs with acute and chronic tetany. F. MATHIEU (Compt. rend. Soc. Biol., 1935, 119, 549—551).—After injection of Ca gluconate, calcæmia persists longer in latent than in acute tetany. H. G. R.

Phosphorus retention and alkalosis in infantile tetany. N. MORRIS (Acta paediat., 1933, 16, 580— 587).—Tetany, complicating rickets in children, may occur without excessive retention of P over Ca, and excessive P retention may occur without signs of tetany. Alkalosis is not necessarily a concomitant of tetany or acidosis of active rickets. Acidosis induced by administration of  $NH_4Cl$  cures tetany probably by making available the body-store of Ca. No support is given to the view that tetany and rickets are due to disturbance in the acid-base balance of the body. NUTR. ABS. (m)

Ammoniogenesis. Blood-ammonia in tetany from hyperventilation. G. POPOVICIU, G. BENE-TATO, and C. OPRISIU (Compt. rend. Soc. Biol., 1935, 119, 443—444).—Blood-NH<sub>3</sub> increases in simple and adrenaline hyperventilation, but falls in that due to ergotamine. Acid-base equilibrium is shifted towards alkalosis, and blood-P falls. R. N. C.

Non-protein-nitrogen content of serum and elimination of glycine during experimental tuberculosis. F. PEZZANGORA (Compt. rend. Soc. Biol., 1935, 119, 513—515).—After infection, the nonprotein-N increases rapidly and gradually returns to normal; after injection of glycine, it falls rapidly and slowly returns to normal. H. G. R.

Effect of the tuberculin reaction on metabolism of residual nitrogen, and curve of elimination of glycine in normal, tuberculous, or *BCG*-inoculated rabbits. F. PEZZANGORA (Compt. rend. Soc. Biol., 1935, **119**, 727-730).—Residual N metabolism is unchanged by tuberculin in normal, slightly raised in *BCG*-inoculated, and considerably in tuberculous, rabbits. R. N. C.

Blood-cholesterol in typhoid fever. H. SZPID-BAUM (Compt. rend. Soc. Biol., 1935, 119, 667—668). —The blood-cholesterol curve proceeds in the inverse sense to the temp. curve in typhoid fever.

R. N. C.

Effect of the gonadotropic hormone on bloodcholesterol and evolution of typhoid fever. H. SZFIDBAUM (Compt. rend. Soc. Biol., 1935, 119, 668-672).—Injection of the gonadotropic hormone of pregnancy urine in cases of typhoid fever produced increases in blood-cholesterol and falls of temp.

R. N. C.

Resistance of capillaries. II. Fall of capillary resistance in patients on gastro-intestinal diets, particularly ulcer diet, and its behaviour with vitamin-C. III. Improbability of avitaminosis-C as the ætiological factor in gastric ulcer. P. SCHULTZER (Acta med. Scand., 1934, 83, 544—554, 555—564; Chem. Zentr., 1935, i, 431; cf. A., 1934, 1389).—II. Capillary resistance falls in patients with gastric ulcer on a diet deficient in vitamin-C, and is restored to normal by -C.

III. The distribution of decreased capillary resistance in patients is apparently independent of the type of disease, which makes it improbable that -C deficiency is the ætiological factor in gastric ulcer. R. N. C.

 $p_{\rm H}$  of gastric juice in gastroduodenal ulceration. G. SELVAGGI (Policlin., 1934, 41, 674-684). —Before injection of histamine (1 mg.) the average  $p_{\rm H}$  of the juice was about 1.75 in healthy persons and in persons with ulcers. After injection the vals. were about 2.6 and 1.12-2.67, respectively.

NUTR. ABS. (m)

Chemical and electrical properties of connective tissue. R. KELLER (Biochem. Z., 1935, 278, 447-453; cf. A., 1934, 1246).—The tissue is electronegative. W. McC.

Distribution of electrolytes in a solution of albumin. L. AMBARD and C. DEVILLER (Compt. rend. Soc. Biol., 1935, 119, 575–576).—Distribution of Cl' is not uniform, the concn. being max. in the intermicellary zone, and, in the micelles, inversely  $\infty$  their size. R. N. C.

Hofmeister's series and the grouping of ions. R. KELLER (Biochem. Z., 1935, 278, 454–459).—The diffusion of ions into and out of different parts of the animal organism and their ionic contents accord with the predominantly (biologically) electro-positive or -negative nature of the parts and suggest a classification of the ions similar to or identical with that of Hofmeister. Account must be taken of non-ionised electrolytes, however, and physiological concus. only considered. W. McC.

Relation of water and electrolytes to metabolism. H. A. DAVIS (Science, 1935, 81, 493— 494).—The  $O_2$  consumption of dogs is markedly increased by intravenous injection of isotonic solutions of 0.9% NaCl and 5% glucose solutions, the effect produced by glucose being the greater. The H<sub>2</sub>O lost  $\propto$  the increase in  $O_2$  consumption and metabolic rate. H<sub>2</sub>O given by mouth increased the consumption only slightly and is retained longer than that given by vein. Repeated blood-letting lowered the metabolic rate and isotonic solutions were then retained for longer periods. The  $O_2$  consumption of the body-tissues appears to be one of the fundamental factors concerned in H<sub>2</sub>O regulation. L. S. T.

Effect of salt and sugar solutions on water exchange through the skin of frogs. B. B. RUBENSTEIN (J. Cell. Comp. Physiol., 1935, 6, 85–99). —Passage of  $H_2O$  through frog-skin may occur in both directions and is probably under nervous control. Mucus or slime covering the skin exerts an anti-osmotic effect which is abnormally high in relation to its osmotic activity. This effect corresponds with a "protective" action depending on some form of structural fixation of the protein on the cell surface. A. G. P.

Theory of permeability of thin films. J. F. DANIELLI and H. DAVSON (J. Cell. Comp. Physiol., 1935, 5, 495—508).—The permeability of living cells is explicable if the plasma membrane be assumed to consist of lipoid matter. Such a membrane is capable of distinguishing mols. of different sizes and solubility characteristics and ions of different charge. Salt antagonism is also explained. A. G. P.

Permeability of living cells to heavy water. B. LUCKÉ and E. N. HARVEY (J. Cell. Comp. Physiol., 1935, 5, 473–482).—The rate of penetration of  $D_2O$ was the same as that of  $H_2O$ . High concess of  $D_2O$ inhibited the development of fertilised cells.

A. G. P. Effect of temperature on osmotic equilibrium of living cells (unfertilised eggs of Arbacia punctulata). B. LUCKÉ (J. Cell. Comp. Physiol., 1935, 5, 465-471).—In the range  $5\cdot4-29\cdot3^{\circ}$  temp. had no effect on the osmotic equilibria. A. G. P.

Osmotic regulation in Gunda ulvæ. L. C. BEADLE (J. Exp. Biol., 1934, 11, 382–396).—G. ulvæ can live in any concn. of sea-H<sub>2</sub>O down to 5%. Internal osmotic relationships are examined.

Tension at the surface of mackerel-egg oil: nature of the cell surface. J. F. DANIELLI and E. N. HARVEY (J. Cell. Comp. Physiol., 1935, 5, 483—494).—The low interfacial tension between the aq. and the oily matter of the egg is attributable to the absorption of a globulin-like protein at the oil surface. The denaturation of egg-proteins at the oil-H<sub>2</sub>O interface is examined and the nature of the cell surface is discussed. A. G. P.

Influence of variations of the cryoscopic depression of the external medium on that of the blood and urine of anodonts. M. FLORKIN (Bull. Acad. roy. Belg., 1935, [v], 21, 432–435).—Specimens of Anodonta cygnea were kept in fresh H<sub>2</sub>O to which varying amounts of sea-H<sub>2</sub>O were added. The blood and urine were always isotonic and became isotonic with all external media having a cryoscopic depression >0.1. W. R. A.

Relative values of cations in antagonising the action of hydroxyl ions on the premembrane system of the eggs of five echinoids. A. R. MOORE (J. Cell. Comp. Physiol., 1935, 5, 433-440).—The crit. concns. of cations adequate to preserve the membrane-forming capacity of eggs were determined in solutions of urea isosmotic with sea-H<sub>2</sub>O at  $p_{\rm H}$  S·O. Vals. for alkali metals were similar for an individual species, but differed with the species. The effective-ness (1/crit. concn.) of Mg, Sr, Ca, and Ba, as chlorides, increased in the order named, and was much > that of the alkali metals, whilst that of cobaltammine salts increased with valency, bivalent compounds being more effective than alkaline earths. A. G. P.

Binuclear cells in tissue cultures. J. ZWEIBAUM and M. SZEJNMAN (Bull. Acad. Polonaise, 1935, B, 37–48).—The formation of binuclear cells in cultures of fowl embryo *in vitro* is favoured by low  $p_{\rm H}$ , excess of CO<sub>2</sub>, O<sub>2</sub> insufficiency, evaporation, hypertonia or hypotonia of the medium, and a temp. of 34–36°. Prolonged cultivation in the same medium favours binuclear cell production by formation of acid metabolic products. R. N. C.

Inducing agent in embryonic development. F. G. FISCHER, E. WEHMEIER, H. LEHMANN, L. JUHLING, and K. HULTZSCH (Ber., 1935, 68, [B], 1196—1199).—Evidence is adduced in favour of the view that the inducing agent of unorganised materials may be an acid. Whether this is also the case with living agents is not established. H. W.

Linking of chemical changes in muscle. D. M. NEEDHAM and W. E. VAN HEYNINGEN (Nature, 1935, 135, 585-586).—Working with dialysed muscle extracts, it is shown that adenylic acid and creatine are essential intermediaries in the reaction by which muscle obtains its energy from the transformation of glycogen into lactic acid. W. P. R.

CH. ABS. (p)

**Permeability of the intestine** *in vitro*. H. G. K. WESTENBRINK (Arch. néerl. Physiol., 1935, 20, 116—122).—The permeability to glucose of rat intestine immersed in Ringer's solution saturated with air at 37° increases with the time of immersion. The adaptation of glucose resorption through the intestinal walls in presence of carbohydrate in the food, observed *in vivo*, cannot be demonstrated *in vitro*, nor can the partial conversion of fructose into glucose during its passage through the walls. R. N. C.

Basal metabolism and prolonged exogenous hyperthermia. S. GELINEO (Compt. rend. Soc. Biol., 1935, 119, 645—647).—The basal metabolism of rats placed in high external temp. for long periods increases at the outset, but soon falls to normal, showing no further change throughout the period.

Ř. N. C.

Metabolism in undernutrition. J. M. STRANG, H. B. MCCLUGAGE, and M. A. BROWNLEE (Arch. Int. Med., 1935, 55, 958—978).—During the treatment of human undernutrition by administration of diets of high calorific val. only very slight changes in the basal metabolism were observed. The levels of N metabolism were within normal limits, and the digestive and absorptive capacities of the patients were adequate. A. L.

Effect of prolonged feeding with tomatoes. A. SCHEUNERT and M. SCHIEBLICH (Z. Unters. Lebensm., 1935, 69, 127—131; cf. Z. Krebsforsch., 1931, 34, 348, 362; 1932, 36, 128).—No harmful consequences resulted from feeding rats for 1 year on a diet containing 42% of raw or cooked tomatoes. E. C. S.

Nutrition of Flabellula mira, Schaeffer. N. E. RICE (J. Elisha Mitchell Sci. Soc., 1934, 50, 39–40).— F. mira reproduces in media containing 20–150% of the total salts in normal sea-H<sub>2</sub>O, rarely in 20% sea-H<sub>2</sub>O, and not in distilled H<sub>2</sub>O, or in solutions isotonic with sea-H<sub>2</sub>O containing single salts or combinations of salts lacking in NaCl. Reproduction is normal in solutions containing MgCl<sub>2</sub> and CaCl<sub>2</sub> in proportions occurring in sea-H<sub>2</sub>O and less frequent in those containing NaCl and either MgCl<sub>2</sub> or CaCl<sub>2</sub>. The rate of reproduction is correlated with osmotic concn., and to the ratio of uni- to bi-valent cations. In the range examined  $p_{\rm H}$  had no influence.

CH. ABS. (p)Metabolism of the lung-fish. I. Fasting metabolism in active fish. H. W. SMITH [with N. FARANACCI and A. BREITWEISER] (J. Cell. Comp. Physiol., 1935, 6, 43—67).—From the beginning of fasting the O<sub>2</sub> consumption falls in a regular (approx. logarithmic) manner for at least 300 days, reaching a val. of 10—20% of that in the fully-fed condition. The decline in O<sub>2</sub> consumption is related to a change in the nutritional state rather than to the wt. of the fish. The latter decreases more slowly as fat and protein are consumed. A. G. P.

Changes in the body constituents during metamorphosis of *Bombyx mori*, L. Y. YONEZAWA and K. YAMAFUJI (Bul. Sci. Fak. Terkult. Kjusu, 1935, 6, 126–138).—A detailed account is given of the variation during the life-cycle of the insect of its carbohydrate, fat, total and protein-N, total and org. phosphate, ash, and Fe contents. During the spinning of the cocoon most of the protein is excreted and fat and glycogen are stored for utilisation in the pupal stage. Variations in the nature of the fat and protein in the various stages of development are also described. E. A. H. R.

Respiration of fragments obtained by centrifuging the egg of the sea urchin, Arbacia punctulata. R. SHAPIRO (J. Cell. Comp. Physiol., 1935, 6, 101—116).—The unfertilised but nucleated half of the cell consumes  $O_2$  at a rate similar to that of the whole, whereas the pigmented half containing most of the yolk and echinochrome but no nucleus shows much higher vals. On fertilisation the  $O_2$  consumption of the nucleated half increases, but that of the pigmented half is unchanged. A. G. P.

Relative effects of increased carbon dioxide tensions and decreased oxygen tensions on the heart frequency of young trout. C. HAYWOOD, T. O. STEVENS, H. M. TEWINKEL, and M. SCHOTT (J. Cell. Comp. Physiol., 1935, 5, 509—518).—Increased  $CO_2$  tension causes a rapid decline in heart frequency of trout. A lowered  $O_2$  tension produces a similar effect after a preliminary lag period. Rates of recovery from these effects are examined. A. G. P.

Mechanism of [tissue] respiration. A. SZENT-GYÖRGYI (Nature, 1935, 135, 1040).—A reply to criticism (cf. this vol., 777). L. S. T.

Mechanism of the Pasteur effect. K. DIXON and E. HOLMES (Nature, 1935, 135, 995-996).-KCl produces increased O2 uptake in brain-tissue with substrates other than glucose (I), e.g., fructose and lactate, which cannot form lactic acid (II) in N<sub>2</sub>. The rate of disappearance of lactate is increased by K. KCl also causes aerobic glycolysis of mannose which can form (II) anaërobically. The co-existence of aerobic glycolysis and increased respiration with (I), and the slight action of  $O_2$  on the glycolysis of normal cells, is probably due to a change in the permeability of the cell-membrane which limits the rate at which (I) can reach the cell-enzymes. Inhibition of the Pasteur effect consists of a removal of this limitation, and the increase in permeability results in increased rates of respiration and (II) formation.  $O_2$  and Ca decrease this permeability. Rb and Cs have a similar effect to K in causing aerobic glycolysis. L. S. T.

Metabolism of normal and tumour tissues. XIII. Neutral salt effects. F. DICKENS and G. D. GREVILLE (Biochem. J., 1935, 29, 1468—1483).— Alkali chlorides when added in 0·1M concn. to Ringer's solution increase the respiration of rat brain-tissue, the order of activity being Li, Na <Rb, Cs, K. KCl increases the glucose oxidation, but decreases the anaërobic glycolysis. The effects on the brain metabolism of leaving out, in turn, various cations of the solution are described. Neutral salt effects on brain metabolism are ascribed to changes in the colloidal state of the protoplasm, and the similarity between control of brain metabolism by changes in the medium, and the control of muscle contraction is pointed out. J. N. A.

Effect of high-protein diet on arterial pressure in cases of hypertony. I. HARRIS, C. N. ALFRED, and A. G. H. ENGLISH (Lancet, 1935, i, 1327-1328).—When a high-protein diet does not raise the blood-pressure there is an increase of non-protein-N, and when it raises the blood-pressure conspicuously non-protein-N does not increase but may even fall. When the blood-pressure falls, non-protein-N increases. L. S. T.

Amino-acid composition of important foodproteins. I. Theoretical. A. E. SCHARPENAK. II. Method of determining the amino-acid composition of proteins. III. Amino-acid composition of meat-proteins (beef). O. N. BALA-SCHOVA, V. V. LVOVA, E. M. SOLOVEEVA, and A. E. SCHARPENAK (J. Physiol. U.S.S.R., 1934, 17, 264-267, 268-276, 277-286; cf. this vol., 652).-II. Hydrolysed proteins were extracted with BuOH prior to fractionation.

III. Analytical data are given. Cystine vals. are low (1.2%). CH. ABS. (p)

Biological value of proteins and the digestibility of food constituents of mixed vegetarian diets containing processed wheat brans. S. WAN (Chinese J. Physiol., 1935, 9, 125—140).—15% of bran does not affect the biological val. or digestibility of the other constituents, the biological val. being increased slightly if processed bran is used. On reducing the protein to 10% both biological val. of the protein and digestibility of the fat and carbohydrate are increased, but digestibility of the ash and fibre is decreased. All bran diets gave fairly good growth, reproduction, and lactation.

H. G. R.

Metabolism of amino-acids. III. Deamination of amino-acids. H. A. KREBS (Biochem. J., 1935, 29, 1620—1644).—The enzymic system cata-lysing the deamination of the natural ("*l*-") NH<sub>2</sub>acids is different from that catalysing the deamin-ation of the non-natural "d"-acids, in that the former system is destroyed by drying, cannot be extracted, and is inhibited by octyl alcohol and 0.01M-KCN, whilst the latter is not destroyed by drying, is readily extracted from fresh or dried tissue by aq. solutions, and is not affected by octyl alcohol or KCN. The activity of the "d"- and "l"-NH2-acid deaminases under varying conditions, and their occurrence in various tissues and animals, is investigated. The "l"-NH<sub>2</sub>-acid deaminase is active in ground tissue when suspended in a small vol. of fluid, but activity disappears on dilution, approx.  $\infty$  the extent of dilution. The cell respiration shows a similar sensitivity to dilution. The effect of dilution is explained on the assumption that a ternary collision plays a role in the reaction. The deamination of land d-NH<sub>2</sub>-acids in kidney slices is inhibited by substances which can be oxidised by kidney. If two different substances, each of which causes an increase in O<sub>2</sub> consumption, are added together to kidney or yeast, no summation of the effects on the  $O_2$  uptake ensues, the substrates competing for the  $O_2$  and displacing each other. The process of activation of  $O_2$  is identical for all substrates which show no summation. P. W. C.

Synthesis of dipeptides with an amino-group in a serine residue. E. ABDERHALDEN and A.

BAHN (Z. physiol. Chem., 1935, 234, 181-195; cf. A., 1933, 1063).-Advantage is taken of the fact that N-Bz derivatives of NH2-acids and peptides vary greatly in their resistance to acid hydrolysis (e.g., with 10% H<sub>2</sub>SO<sub>4</sub> for 3 hr. at 70-80°) in the separation of the constituents of mixtures (e.g., of aspartic and glutamic acids) and in the synthesis of peptides containing a serine residue, this residue having the free  $NH_2$  group. The peptides are identified by treatment with  $PhSO_2Cl$  and hydrolysis of the product to benzenesulphonylserine and the NH2-acid with which it was combined. dl-Leucyl-dl-serine treated with MeOH at 0° and then (3 days) with MeOH saturated with NH<sub>3</sub> gives the anhydride, m.p. 224°, which with 10% H<sub>2</sub>SO<sub>4</sub> (4 days) yields dl-seryl-dl-leucine, m.p. 216° (benzenesulphonyl derivative). Simi-larly glycyl-dl-seryl anhydride, m.p. 218—220°, gives dl-serylglycine (benzenesulphonyl derivative). 1 mol. of serine reacts with dicarbobenzyloxytyrosyl chloride (I) to give di(dicarbobenzyloxytyrosyl)serine (II), m.p. 158—159°,  $[\alpha]_{D}^{\infty}$  +22.5° in 20% HCl [no (II) is produced if 2 mols. of serine are used], and dicarbobenzyloxytyrosylserine (III). (III) on reduction (H<sub>2</sub>-Pd) gives 1-tyrosyl-dl-serine, which yields the anhydride (IV), m.p. 253-255°, as before. dl-Seryl-l-tyrosine (dibenzenesulphonyl derivative) is obtained from (IV) by acid hydrolysis (alkaline hydrolysis gives tyrosylserine). (II) is rapidly hydrolysed by erepsin and less rapidly by trypsin. (III) on treatment with erepsin gives 1-tyrosyl-d-serine,  $[\alpha]_{D}^{20}$  +18° in 20% HCl, but is not attacked by trypsin. The anhydride from l-tyrosyl-l-serine on acid hydrolysis gives l-seryl-1-tyrosine, m.p. 293—298°,  $[\alpha]_2^{20} + 27.5°$  in 20% HCl. 2 mols. of (I) with 1 mol. of tyrosine give di(dicarbo-benzyloxytyrosyl)tyrosine, reduced (H<sub>2</sub>-Pd) to dityrosyltyrosine (hydrochloride), which readily decomposes into tyrosine and tyrosyltyrosine. W. McC.

Blood-arginine and growth. M. REISS, L. SCHWARZ, and F. FLEISCHMANN (Z. physiol. Chem., 1935, 234, 201—207).—100 c.c. of normal rabbit blood contain 5—7 mg. of free arginine (I). This amount is reduced to about half in pregnant rabbits (normal vals. restored *post partum*). Rabbits with carcinoma and rats with sarcoma have diminished amounts of (I) in their blood. In virgin rabbits (but not in those from which the ovaries have been removed) administration of the hormone of the anterior lobe of the pituitary causes decrease in blood-(I), but the normal vals. are then attained if the ovaries are removed. Intravenous injection of arginase activators (cysteine, glutathione, FeCl<sub>2</sub>) causes decrease in blood-(I). W. McC.

Adrenaline synthesis in vitro under physiological conditions. W. SCHULER and A. WIEDE-MANN (Z. physiol. Chem., 1935, 233, 235—256).— Slices of the surviving adrenal of the guinea-pig can synthesise adrenaline (I) [or a substance reacting as (I)] from tyramine, but not from dihydroxyphenylalanine or phenylhydroxyethylamine. The (I) was determined by the Folin reaction using the stepphotometer and in some cases was identified by the biological method (effect on blood-pressure). The adrenal medulla is active, but not the cortex. Tyramine is probably synthesised in another organ, possibly the kidney. The synthesis is but little affected by the concn. of the substrate or the amount of tissue employed, but depends almost entirely on the synthetic power of the sample of tissue, which varies widely with different samples and is a vital function of the cell. J. H. B.

Metabolism of monomethyltryptophans. W. G. GORDON and R. W. JACKSON (J. Biol. Chem., 1935, 110, 151—164; cf. A., 1929, 1485; Matsuoka et al., A., 1931, 513).—3-Indolyl-5-(1-methylhydantoyl)methane, m.p. 213—214° (obtained from the product of interaction of 3-indolealdehyde and 1-methylhydantoin by reduction with Na-Hg), when boiled with aq. Ba(OH)<sub>2</sub> gives  $\alpha$ -methylamino- $\beta$ -3-indolylpropionic acid (I), m.p. 297° (decomp.) [picrate; m.p. 186° (decomp.)]. Although 5- and 2-methyltryptophan cannot replace tryptophan (II) in the diet of rats, (I) stimulates their growth, although not so efficiently as does (II), when they are subsisting on a diet deficient in (II). W. McC.

Organs which regulate indolæmia and indoxylæmia after injection of indole. B. A. Hous-SAY, V. DEULOFEU, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1935, 119, 875—876).—Indole (I) is transformed into indoxyl (II) in the liver. Only one third of the (I) introduced into the circulation can be recovered as (II). H. G. R.

Indoxylogenic substances in the organism. B. A. HOUSSAY, V. DEULOFEU, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1935, 119, 877-879).— Substances which increase indoxylæmia when introduced into the blood are tabulated. H. G. R.

Fate of nicotine in fresh liver. A. WENUSCH (Biochem. Z., 1935, 278, 349-350).—In 24 hr. at 37° fresh minced pig-liver has no effect on nicotine, which is recovered unchanged. W. McC.

Diffusion equilibria for the isolated frog's kidney. II. Urea. E. J. CONWAY and F. KANE (Biochem. J., 1935, 29, 1446—1458).—Active isolated frogs' kidneys can concentrate urea from an external urea-Locke solution, whereas inactive kidneys (urea-cyanide-Locke) do not possess this power. Determination of urea in the frog's kidney by the xanthhydrol and the urease methods gave identical results. P. W. C.

Nitrogen catabolism in invertebrates. IV. Synthesis of uric acid in *Helix pomatia*. E. BALDWIN (Biochem. J., 1935, **29**, 1538—1546).— Surviving slices of the hepatopancreas of *H. pomatia* convert a mixture of urea and tartronic acid into uric acid. It is suggested that urea is synthesised in *H. pomatia* by means of the ornithine cycle, and then converted into uric acid probably by way of dialuric acid. J. N. A.

Endogenous nitrogen metabolism of hypophysectomised rats. B. BRATER and R. MOREA (Compt. rend. Soc. Biol., 1935, 119, 881-882).-On a protein diet, urinary N does not vary, but the creatinine is < normal. On a protein-free diet, endogeneous protein catabolism is < normal.

H. G. R.

Cholesteryl esters as a mechanism of fat metabolism. H. PETERSILIE (J. Lab. Clin. Med., 1934, 20, 144—149).—Abnormal variations in the %of cholesteryl esters in blood, in cases of liver and kidney diseases, depend on conditions of diet and therapy, and are closely related to carbohydrate metabolism. CH. ABS. (p)

Fate of vegetable sterols in the animal organism. II. H. DAM and U. STARUP (Biochem. Z., 1935, 278, 342—344; cf. this vol., 113).—In the dog, intraveneously injected vegetable sterol is excreted in the fæces. In the rat, the amount excreted is 82% of that injected. New-born rats of a mother receiving injections of the sterol excrete no sterol in the fæces. W. McC.

Fat metabolism. B. FLASCHENTRAGER and K. BERNHARD (Naturwiss., 1935, 23, 356).—Ingestion of Me decoate by dogs fed on a diet including coconut oil and butter is followed by the occurrence of sebacic (I) and suberic acids in the urine. Et, but not Me, dodecoate behaves similarly, but to a smaller extent, whilst Na decoate and cooking-fat yield (I). The bearing of the data on  $\omega$ -oxidation is discussed (cf. A., 1934, 1027). F. O. H.

Fat absorption. Its value as an index of function of the liver. M. SULLIVAN and J. A. B. FERSHTAND (Arch. Int. Med., 1935, 55, 834-841).— Using the Rückert method, the average total serumlipin of man in the fasting state was 0.576 c.c. per 100 c.c., which was not affected by body-wt. or fasting. The absorption curves, after ingestion of cotton-seed oil, were characteristic for diseases of the liver and for diabetes. H. G. R.

Is it possible, in a balanced ration, to substitute for glycerides the corresponding fatty acids? B. LECOQ (Compt. rend., 1935, 200, 1979— 1980).—Oils (castor, olive, etc.) cannot be replaced by mixtures of glycerol and the fatty acids in a pigeon ration, without nutritional disturbance, even when yeast is supplied to provide vitamin-B. A. G. P.

Comparative value of fat and carbohydrate in the utilisation of protein. E. F. TERROINE (Bull. Soc. Chim. biol., 1935, 17, 690-692).—A criticism of the results of Maignon (this vol., 388). A. L.

Comparative value of fat and carbohydrate in the utilisation of protein. F. MAIGNON (Bull. Soc. Chim. biol., 1935, 17, 693—695).—A reply (cf. preceding abstract). A. L.

Influence of lipin on the carbohydrate metabolism. I. Changes in the content of glucose and lactic acid in blood and of the latter in urine of rabbits caused by the injection of cholesterol and lecithin. N. HOSAKA (Japan. J. Exp. Med., 1934, 12, 455-495).-Starvation of rabbits caused a decrease in the blood- and urinary lactic acid (I) and in the blood-sugar (II). Injection of cholesterol (III) during starvation caused the blood-(I) first to rise and then gradually to fall, and the urinary (I) and (II) to decrease. Injection of lecithin (IV) produced a fall in blood-(I), and an increase in the urinary (I) and (II). Injection of these lipins into rabbits which were being fed produced no changes. The results produced by injection of (III) and (IV) irradiated with X-rays or a quartz lamp were also investigated. NUTR. ABS. (b)

Mutual displacement of glycogen and fat in liver cells. S. NAGAO (Tôhoku J. Exp. Med., 1934, 24, 555-564).-In rabbits on a normal diet, intravenous injection of fat caused a complete disappearance of liver- and muscle-glycogen. The fat content of the liver and, to a smaller extent, of the muscles was raised. Increased deposition of liver-glycogen following intravenous injection of glucose was accompanied by a decrease in liver-fat. With simultaneous administration of fat and glucose there was no significant change. NUTR. ABS. (b)

Law of mass action and specific dynamic action of carbohydrates. M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1935, 119, 436-438).-The sp. dynamic heat increase in the dog on continuous injection of glucose  $\infty$  the rate of injection when this is small; it increases less rapidly than the rate, reaching a steady max. at 6 g. per kg. per hr. The ratio of the heat evolved by all the glucose assimilated to sp. dynamic heat increase is const. for the whole range of rates of assimilation. The sp. dynamic action of glucose is almost entirely of oxidative action of glucose is annose origin when the rate of injection is > 1 g. per kg. R. N. C.

Mechanism of alimentary hyperglycæmia. I. Blood-sugar after oral and intraduodenal glucose administration. II. Rate of absorption of glucose in the small intestine. III. Sugar content of blocd in various vessels after intraduodenal glucose administration. F. MEYTHALER and H. SEEFISCH (Arch. exp. Path. Pharm., 1935, 178, 461-466, 467-469, 470-479).-I. Oral or intraduodenal administration of glucose to men and dogs is followed successively by an alimentary pre-hyperglycæmia (1—5 min. duration), pre-hypoglycæmia (1-5 min.), and hyperglycæmia (approx. 1 hr.) and finally a post-hyperglycæmic hypoglycæmia (approx.

I hr.). II. Glucose intraduodenally administered to nar-if and dome is rapidly absorbed. The portal vein blood-sugar (I) curve indicates that the absorption is related to the rhythmic function of the intestinal mucous membrane. The initiation of absorption is independent of the concn. of glucose, whilst its rapidity and extent are not related to the fasting val. of the (I).

III. Intraduodenal administration of glucose to dogs produces an immediate (within 1 min.) increase of the portal (I), the rate of absorption being independent of the nutrition of the animal. The portal (I) is > that of the hepatic vein, whilst the difference between the latter and that of the inferior vena cava represents the peripherally retained sugar. The variations in (I) immediately following absorption are described and the mechanism involved is discussed. F. O. H.

Metabolism of galactose. I. Phosphorylation during galactose fermentation and its relation to the interconversion of the hexoses. G. A. GRANT (Biochem. J., 1935, 29, 1661-1676).-The sp. mechanism developed in certain yeasts during the process of adaptation on galactose (I) and required for fermentation of (I) is largely destroyed when the adapted yeast is treated with PhMe or dried or used for the prep. of cell-free juice. During the fermentation of (I) by adapted yeast, chiefly 1: 6-diphosphofructofuranose together with diglucose phosphate, trehalose monophosphate, and possibly smaller amounts of Robison's ester accumulate in solution, but no evidence was obtained of the production of a (I) phosphate and moreover synthetic (I) 6-phosphate was not readily fermented by this yeast. The polysaccharides synthesised by the adapted yeast when grown on (I) consist mainly of glucose and to a smaller extent of fructose and mannose. The mechanism of the transformation of (I) into the other hexoses is discussed. P. W. C.

Gastric and duodenal function in relation to sugar tolerance tests. M. PELLEGRINI (Atti R. Accad. Fisiocr. Siena, 1934, 11, 478).-Changes in motor and secretory activity of the stomach are reflected in changes in the level of blood-sugar (I) after ingestion of sugar. Hypersecretion and hypermotility frequently give a curve showing an early max. concn. of (I), whilst hypo- and a-chlorhydria give a retarded rise in (I). The shape of the (I)curve is very variable in cases of gastric and duodenal ulcer. NUTR. ABS. (b)

Post-mortem glycogenolysis in rabbit liver. H. R. NOLTIE (Quart. J. Exp. Physiol., 1934, 24, 261—270).—The rate of glycogenolysis in rabbit liver incubated at 38° is not determined by the initial glycogen %. Although "free sugar" increases markedly, lactic acid rises but little, and the two together are always insufficient to account for the glycogen loss. The results are similar whether the glycogenolysis occurs in air or in  $N_2$ . NUTR. Abs. (b)

Effect of prolonged muscular work on the metabolism of carbohydrates introduced at constant velocity into the circulation. M. WIERZU-CHOWSKI, T. CHMIELEWSKI, A. GOSTYNSKA, and H. FISZEL (Compt. rend. Soc. Biol., 1935, 119, 433-435).—The rate of assimilation of glucose in the dog is increased by muscular work; maltose assimilation also increases proportionally with the rate of hydrolysis by blood-maltase. Assimilation of sucrose is slightly diminished, whilst that of fructose is unaffected.

R. N. C.

Comparative determination of the rate of oxidation of alcohol in the organism by bloodalcohol curves and direct measurement. E. LE BRETON (Compt. rend. Soc. Biol., 1935, 119, 568-571).—In the case of EtOH ingested or introduced intraperitoneally in rabbits, determination of the rate of oxidation by blood-EtOH curves is not trustworthy. Widmark's results for man are only R. N. C. approx.

Effect of the concentration of alcohol attained at the surface of the tissues on its rate of oxidation in vivo. E. LE BRETON (Compt. rend. Soc. Biol., 1935, 119, 572-575).-In rats and mice the rate of oxidation of EtOH is independent of the blood-EtOH (I); in the guinea-pig, cock, and rabbit, R. N. C. it decreases with (I).

Transformation of natural *l*-phosphoglyceric acid by animal tissue. II. Conversion into

phosphopyruvic acid. H. K. BARRENSCHEEN, G. LORBER, and W. MEERAUS (Biochem. Z., 1935, 278, 386—395; cf. this vol., 521).—Since Hg<sup>II</sup> salts convert phosphopyruvic acid (I) into  $AcCO_2H$  (II), (I) and (II) can be determined in presence of each other as dinitrophenylhydrazone. In fresh muscle extract and pulp and kidney pulp (rabbit) and in human erythrocytes the conversion of phosphoglyceric acid (III) into (I) rapidly (< 30 min.) reaches its max., but the conversion of (I) into (II) proceeds much more slowly. When HgCl<sub>2</sub>+HCl are used to deproteinise, more H<sub>3</sub>PO<sub>4</sub> isfound than when CCl<sub>3</sub>·CO<sub>2</sub>H is used, the excess corresponding with the amount of (II) produced from (I). Only part of the easily hydrolysed phosphate produced during transformation of (III) is accounted for by production of (I).

W. McC.

Production of phosphoric esters in the intestinal mucous membrane during resorption of sugars, glycerol, [and fat]. L. LASZT and H. SULLMANN (Biochem. Z., 1935, 278, 401-417; cf. this vol., 521).—The amount of acid-sol. org. phosphate in the rat intestine is greatly (about 100%) increased by administration of glucose, fructose, galactose, glycerol, and olive oil and increased to a smaller extent by that of sorbose. No increase follows administration of xylose, arabinose, or mannose. Most of the org. phosphate produced is easily hydrolysed. Hence the resorption of carbohydrates (and glycerol) and fats in the intestine is associated with phosphorylation. W. McC.

Interference of hepatic fructolysis and adrenaline glycogenolysis in a normal dog at three states of assimilation. M. WIERZUCHOWSKI and F. SEKURACKI (Compt. rend. Soc. Biol., 1935, 119, 661— 664).—Blood-lactic acid (I) in the normal dog on continuous injection of fructose reaches different levels according to the diet previously administered to the animal; (I) after protein < after carbohydrate (II) < after starvation. All three levels are raised proportionately by adrenaline (III). Urinary lactic acid also reaches similarly dependent levels, but the max. effect with (III) is obtained after the (II) diet. Glycogenolysis also plays a part in lactic acid increase. R. N. C.

Significance of lactic acid in heart metabolism. A. RtHL (Klin. Woch., 1934, 13, 1529–1534; Chem. Zentr., 1935, i, 592–593).—The intact heart in a heart-lung prep. takes up lactic acid (I) from the coronary blood in normal conditions and partial  $O_2$ deficiency, but liberates it in complete anoxæmia due to HCN. (I) is also consumed in CH<sub>2</sub>I·CO<sub>2</sub>H poisoning. Glucose is taken up only in the hyperglycæmic state. Only 30% of the O<sub>2</sub> consumed is accounted for by oxidation of (I) and carbohydrates. In an insufficient heart an increase of (I) uptake corresponds with a decreased O<sub>2</sub> consumption. R. N. C.

Effect of diet on ketogenesis. H. TRIMBACH (Arch. internat. Physiol., 1934, 39, 434–461).—An exclusive fat diet produces a greater ketonuria than does a strict carbohydrate diet in the rat and pig, but not in the dog. Proteins are not ketogenic. A diet of fat and carbohydrate reduces the ketonuria caused by an exclusive fat diet. NUTR. ABS. (m) Effect of the hydrogen carbonate ion on muscle metabolism. E. M. BERKOVICH (J. Physiol. U.S.S.R., 1934, 17, 383–388).—The lactic acid content of muscle is increased by  $CO_2$  and  $HCO_3'$ , but not by  $CO_3''$ . CH. ABS. (p)

Distribution of potassium in cells and the changes taking place during stimulation. V. BUREAU (Arch. internat. Physiol., 1934, 39, 311-328).-The reagent used by Macallum to demonstrate the presence of K in tissues is hypertonic and toxic, so that the cells are stimulated and the distribution of K is changed before pptn. of the K can occur. The reagent was therefore modified to make it isotonic and to ensure rapid fixation of the tissues. Under such conditions, when the cell was at rest, the intracellular K was most abundant close to the cellmembrane and the nuclear membrane. K was also distributed uniformly, but in smaller concn., throughout the cytoplasm and nucleoplasm. In striped muscle, K was condensed on the cell-membrane and inside the anisotropic discs. There was no K in the isotropic discs. Stimulation of cells led to passage of K to the outside of the cell. NUTR. ABS. (b)

Sodium and calcium requirements of the animal organism (*Drosophila*). D. L. RUBIN-STEIN, V. LVOVA, and H. BURLAKOVA (Biochem. Z., 1935, 278, 418—427; cf. A., 1934, 1035).—*D. melano*gaster lives and reproduces normally when almost completely deprived of Na and Ca (95% and 99% removed) by propagation on a medium (purified yeast, salts, and glucose on SiO<sub>2</sub> gel) free from Na and Ca. W. McC.

Metabolism of copper. E. J. COULSON, R. E. REMINGTON, and K. M. LYNCH (U.S. Dept. Commerce, Bur. Fisheries Invest. Rept., 1934, 23, 1—12). —Prolonged feeding of Cu (525 mg. per kg. of diet) in the form of "green" oysters or CuSO<sub>4</sub> had no toxic effect on rats. Oysters fed in conjunction with a high-Cu diet inhibited storage of Cu in the liver.

Сн. Авз. (р)

Preparation of possible antimalarial agents. R. F. A. ALTMAN (Chem. Weekblad, 1935, 32, 345).— Derivatives of 6-methoxyquinoline with

 $NH \cdot [CH_2]_u \cdot NEt_2$  in position 8 show antigametocidal properties similar to those of "plasmoquin." Derivatives of quinine containing substituents in the sec.-OH and  $\cdot CH:CH \cdot$  groups have no therapeutic activity. S. C.

Derivatives of 8-aminoquinoline as antimalarials.—See this vol., 989.

Identity of the reducing substance in the urine of normal persons after the ingestion of amidopyrine. M. ENKLEWITZ (J. Pharm. Exp. Ther., 1935, 54, 100-104).—A reducing substance appearing in urine after the ingestion of amidopyrine (I) has been identified as the glycuronate of (I). M. T.

Rôle of amidopyrine in the ætiology of granulocytopenia with special reference to its chemical structure. L. F. HERZ (J. Lab. Clin. Med., 1934, 20, 33-40).—Amidopyrine is a very frequent cause of granulocytopenia. Its toxicity is due to the imido-group and its action resembles that of NHPh·NH<sub>2</sub>. CH. ABS. (p) Reaction of the blood-vessels. I. Electrical stimulation. II. Influence of various medicaments on electrical excitation. III. Influence of various nerve or muscle poisons on electrical excitation. IV. Influence of paralysing drugs on electrical excitation. V. Influence of stimulative drugs on electrical excitation. Y. Kosuge (Acta Schol. Med. Kioto, 1934, 17, 22-26, 27-29, 123-131, 132-136, 137-145).-I. The technique is described.

II. Codeine phosphate decreased electrical response. Theocin Na acetate in small concns. (to 0.01%) increased and in higher concns. decreased electrical stimulation.

III. Atropine, eserine, cocaine, and nicotine decreased and  $Ba(ClO_3)_2$  increased response. Pilocarpine and adrenaline in low concess. had a positive and in large proportions a negative effect.

IV. Morphine, Na phenobarbital, urethane, dial, and chloral hydrate caused a decrease in response.

V. Increased response followed treatment with caffeine, NaOBz, diuretin, gadamin, digifolin, strophanthin, pituitrin, or EtOH. Strychnine had the opposite effect. CH. ABS. (p)

Action of pilocarpine group on alkali reserve and blood-sugar. A. M. PREOBRASHENSKI (J. Physiol. U.S.S.R. 1934, 17, 886—895).—Intravenous injection of pilocarpine alkaloids into dogs increases blood-sugar and lowers the alkali reserve. Eserine, pilocarpine, and arecoline were the most active in this respect. A. G. P.

Vasodilating action of quinine; cardiovascular effects of quinine phenylethylbarbiturate. H. BUSQUET and C. VISCHNIAC (Compt. rend. Soc. Biol., 1935, 119, 503—506).—The contractions of the heart are increased and blood-pressure is lowered. H. G. R.

Absorption of drugs through oral mucosa. R. P. WALTON and C. F. LACEY (J. Pharm. Exp. Ther., 1935, 54, 61–76).—The ratios of sublingual dosages to similarly effective subcutaneous dosages as determined on dogs are as follows: Na pentobarbital (I) 1:1; apomorphine (II) 2:1; strychnine 4:1; atropine (III) 8:1; morphine (IV) 10:1; dilaudid (V) 15:1; codeine, > 15:1. No distinct effect was produced by sublingual application of adrenaline (VI) and insulin, even in large doses. With alcoholic solutions there was an increase of absorption of (III). With men, results comparable with those produced in dogs were obtained for (I)— (VI). M. T.

Metabolic action of strophanthin on the warmblooded heart. B. WEICKER (Arch. exp. Path. Pharm., 1935, 178, 524—533).—With the perfused cat's heart, therapeutic doses of strophanthin do not affect the total acid-sol.  $PO_4$  content, whilst toxic doses decrease phosphagen (I), adenylpyrophosphoric acid (II), and free adenylic acid (III). Stimulation of work output by the impaired heart may produce aerobic resynthesis of (I) followed by that of (II) and (III). Transient anaërobic increase in work output increases (I) practically to normal vals.; resynthesis of (II) or (III) does not occur. The mechanism of the cardiac action of *Digitalis* preps. is discussed. F. O. H.

Distribution of therapeutic substances in various parts of the central nervous system and their micro-determination in tissues. I. Scopolamine and atropine. F. VEIT and M. VOGT. II. Quinine and mezcaline. M. VOGT. III. apoMorphine and bulbocapnine. IV. Strychnine. F. VEIT. V. Barbituric acid derivatives. VI. Chloral hydrate. M. VOGT (Arch. exp. Path. Pharm., 1935, 178, 534-559, 560-576, 577-592, 593-602, 603-627, 628-638) .-- I. The determination of scopolamine (I) and atropine (II) ( $< 10^{-4}$  and  $10^{-1}$  mg., respectively) in brain-tissue (2 g.) is described. Administration to dogs and cats is followed by a transient period during which the greatest concn. occurs in the cell-rich parts of the nervous tissue; the distribution then becomes more equalised. Finally (I) and (II) disappear from the nervous tissue and appear in liver, kidney, and blood.

II. A micro-extraction method for quinine and mezcaline ( $\beta$ -3:4:5-trimethoxyphenylethylamine) in tissue is described. Following injection into animals their distribution in nervous and other tissues is similar to that of (I) and (II).

III. apoMorphine and bulbocapnine (method of determination in tissues given) behave similarly to (I) and (II). The liver content attains vals. > those of the brain.

IV. The distribution of strychnine (method of determination in tissues given) in animals in which the tolerated dose is increased by  $Et_2O$  narcosis is similar to that of (I) and (II), marked preferential localisation occurring in certain parts of the nervous system. The content in liver and kidney is > that of brain and, to a greater extent, that of blood. Only traces occur in the cerebrospinal fluid.

V. The equalisation of distribution of dial and phanodorm in nervous tissue occurs more rapidly than that of veronal, the irregular distribution phase of which is detected with difficulty. The narcotic effect of each  $\infty$  the content in the brain. The content of liver or kidney is  $\leq$  that of the brain, whilst small amounts occur in the cerebrospinal fluid.

VI. The micro-determination of chloral hydrate by reduction to Cl' (Zn-AcOH) followed by Volhard titration is applied to nervous tissue. Following administration to cats or dogs, the content in nervous tissue rapidly attains a max. and then diminishes, during which period the distribution in various parts is irregular. Only traces appear in the cerebrospinal fluid. F. O. H.

Respiratory effects of morphine, codeine, and related substances. IV. Effect of  $\alpha$ -monoacetylmorphine, monoacetyldihydromorphine, diacetylmorphine (heroin), and diacetyldihydromorphine on the rabbit. C. I. WRIGHT and F. A. BARBOUR (J. Pharm. Exp. Ther., 1935, 54, 25-33).-- $\alpha$ -Mono- and di-acetylmorphine have very nearly the same effect on the respiration of the rabbit. A dose of 0-03 mg. per kg. definitely decreases the respiratory rate, minute vol., and the response to CO<sub>2</sub> stimulation. The hydrogenated derivatives of acetylmorphines are much less effective as respiratory depressants. > 0.1 mg. of mono- or di-acetyldihydromorphine is required to decrease the minute vol. and to change significantly the response to CO<sub>2</sub> stimulation. Also the rate of O<sub>2</sub> consumption, the heart rate, and rectal temp. are more strongly affected by the above acetylmorphine compounds than by their hydrogenated derivatives. M. T.

Motor effects of morphine and some derivatives on Thierry fistulæ. R. P. WALTON and C. F. LACEY (J. Pharm. Exp. Ther., 1935, 54, 53—60).— The min. dilaudid (I) dose producing a definite spastic effect is about 1/30 the min. dose of morphine (II) and 1/300 that of codeine (III). The abs. doses producing a 20-min. spastic period are respectively 0.01, 0.3, and 3.0 mg. per kg. body-wt. There is no indication of a connexion between the initial stimulating effect and the constipating effect of (I). It does not produce prolonged periods of spasticity to the same degree as (II) and (III). M. T.

Cardiostimulant effect of Japan camphor: *d-trans-7-aldehydoapocamphor as the true active substance.*—See this vol., 865.

Diuresis following the administration of salyrgan; its effect on the specific gravity, the total nitrogen, and the colloid osmotic pressure of the plasma of normal and ædematous dogs. A. H. BRYAN, W. A. EVANS, jun., M. N. FULTON, and E. A. STEAD, jun. (Arch. Int. Med., 1935, 55, 735-744).—In normal dogs the effect of salyrgan was slight, but in ædematous dogs a prolonged diuresis was observed together with a rise in sp. gr., total N, and colloid osmotic pressure of the plasma, indicating a direct effect on the kidney. H. G. R.

Pharmacology of convolvine. J. K. NoLLE (Khim. Farm. Prom., 1934, No. 5, 39–46).—Convolvine (from Convolvulus pseudocantabrica),  $C_{15}H_{21}NO_2$ , m.p. 114—115°, is a strongly basic, optically inactive cryst. substance, the hydrochloride of which is anæsthetic. CH. ABS. (p)

Effect of some barbituric acid derivatives on the intestine of the cat. N. B. DREYER and C. O. HEBB (Proc. Nova Scotian Inst. Sci., 1933-1934, 18, 282-285).—Many barbiturates, even in massive doses, increase the tonus of cat intestine if respiration and the circulation are unimpaired. Section of the vagi or splanchnics has no effect. J. L. D.

Distribution of barbiturates in brain. T. KOPPANYI and J. M. DILLE (J. Pharm. Exp. Ther., 1935, 54, 84—86).—There is no sp. distribution of Nabarbital nor any accumulation in the sleep centres after the administration of small hypnotic doses. The distribution in the different parts of the central nervous system is approx. the same after large and st all doses, with the exception of cerebellum and medulla, the amount in these being somewhat < in the rest of the brain. M. T.

Antagonism between thyroxine and narcotics with regard to their structure. I. ZARDAY and P. WEINER (Orvosi Hetilap, 1934, 78, 682-684).— Antagonism is demonstrated between narcotics of the barbituric group and thyroxine. CH. ABS. (p)

3 Y

Effect of specific substances of the body on blood-pressure in man. IV. Action of liver preparations (Campolon, Degewop, Hepatrat, and Hepatopson) administered intravenously. H. A. HEINSEN and H. J. WOLF (Klin. Woch., 1934, 13, 523-526; Chem. Zentr., 1935, i, 589).—Liver preps. provoke falls of blood-pressure, suggesting the presence of histamine-like substances or of Lange's "fourth substance." R. N. C.

Plants with cardiac action. R. JARETZKY (Arch. Pharm., 1935, 273, 334-348).—A lecture. Adonis vernalis, L., but not 4 other varieties or 2 related plants, contains (most in the stems) substances with cardiac action and yields eranthin-A, insol. in CHCl<sub>3</sub>, and -B, CHCl<sub>3</sub>-sol., which give some strophanthin colour reactions. Gratiola officinalis, L., yields gratiotoxin, which has great cardiac action. Purified gratiolin has m.p. 268—269° (decomp. from 255°) (cf. lit.). Baviea volubilis, Harv., bulbs, but not related plants, contain extremely active glucosides. R. S. C.

Assay of Allium preparations. U. HINTZEL-MANN (Arch. exp. Path. Pharm., 1935, 178, 480– 485).—The survival period of mice poisoned by 0.2—0.3 c.c. daily of vigantol is prolonged two- to three-fold by simultaneous administration of preps. from A. ursinum. The application of this phenomenon to the assay of Allium preps. is discussed. F. O. H.

Pharmacodynamic action and chemistry of secretin. G. ÅGREN (Skand. Arch. Physiol., 1934, 70, 10-87).—A method for preparing pure secretin in quantity is described. It can be prepared only from the mucosa of the small intestine. Injected intraveneously, a concn. of  $1:40 \times 10^6$  in the blood of a urethanised cat is sufficient to cause pancreatic secretion. Administered subcutaneously, intramuscularly, or intraperitoneally it is rapidly destroyed and consequently without action on the pancreas. It is a true cholagogue, increases the flow of succus entericus, but does not affect gastric secretion or urine formation by the kidney. There is no action on blood-sugar level, on blood-pressure, or on the musculature of the gall-bladder or gut. The chemistry of the substance is discussed.

NUTR. ABS. (m)

Influence of vitamin- $B_2$  on hæmatopoiesis in experimental anæmia in the albino rat. M. I. SMITH and E. F. STOHLMAN (U.S. Publ. Health Repts., 1934, No. 49, 1569—1575).—Recovery of rats from NHPh·NH<sub>2</sub>-induced anæmia is not materially affected by the absence of vitamin- $B_2$  from the diet.

Сн. Авз. (р)

Biological action of 7-methyl-9-[d-1'-ribityl]isoalloxazine. P. KARRER, H. VON EULER, M. MALMBERG, and K. SCHÖPP (Svensk Kem. Tidskr., 1935, 47, 153-154).—The compound exhibits vitamin- $B_2$  activity so that the Me in position 6 is not essential, but the min. dose for normal growth is probably about double that for the Me<sub>2</sub> derivative.

W. O. K.

Phenanthrene derivatives. IV. Veratrinelike action on skeletal muscle. R. G. SMITH (J. Pharm. Exp. Ther., 1935, 54, 87-99).—The BRITISH OHEMICAL ABSTRACTS .---- A.

veratrine-like effect could be obtained in cats, rabbits, and mice only with the Na phenanthrene-9-carboxylate (I). Other phenanthrene derivatives examined, *e.g.*, salts of the 2- (II) and 3-carboxylic acids (III), yielded no comparable results. On direct and indirect stimulation with the sciatic nerve being cut and on direct stimulation in the curarised animals, there was a distinct muscular effect by (I) and to a smaller degree by four other 9-substitution products of phenanthrene, but not by (II) and (III). In frogs, this effect was replaced by a morphine-like picture when (I) was used. M. T.

Effect of trimethylenetetrazole on the heart. A. DE CHATEL (Orvosi Hetilap, 1934, 78, 813—814).— Relatively large doses restore normal rhythm in a heart poisoned by  $CHCl_3$ . CH. ABS. (p)

Pharmacological action of phenaceturic acid. II. Y. Tozawa (Folia Pharmacol. Japon., 1934, 19, No. 1, 90-101).—Diuretic effects are described.

CH. ABS. (p) Effect of some isomeric sodium aminonaphthalenetrisulphonates on the structure of diphtheria toxin and antitoxin. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 119, 402-405).-Na naphthalencsulphonates permit the pptn. of globulins by citric acid at  $p_{ii}$  5, this effect being independent of the no. and positions of the SO<sub>3</sub>H, and of the presence or absence of an NH<sub>2</sub>. Albumins are partly pptd. Complete pptn. of the active principles of diphtheria toxin (I) and antitoxin is permitted only by  $\beta$ -naphthylaminetrisulphonates (II). Pptn. with  $\alpha$ -naphthyl-aminetrisulphonates is slow and incomplete, but is complete with Na 8-hydroxy-a-naphthylamine-3:6disulphonate, which also ppts. peptones in acid solution. (II) do not affect the toxic and antigenic R. N. C. powers of (I).

Effect of histamine, adrenaline, and destruction of the spinal cord on the osmotic pressure of the blood in the skate. A. F. CHAISSON and M. H. F. FRIEDMAN (Proc. Nova Scotian Inst. Sci., 1933—1934, 18, 240—244).—Adrenaline subcutaneously has no effect on the blood-Cl' (I), blood concn., or the vol. of gastric secretion. Histamine lowers the first two (and later increases Cl'), but has no effect on the secretion. Destruction of the cord invokes a large and highly acid gastric secretion and lowers blood concn., probably a result of loss of urea. J. L. D.

Mobilisation of calcium by salts of pyrocatecholdisulphonic acid. O. RIESSER and L. KARBE (Arch. exp. Path. Pharm., 1935, 178, 455— 460).—Oral or intramuscular administration of the Na salt increases the total and, to a greater extent, the ultrafilterable Ca of the blood. With daily administration, the effect rapidly diminishes, being approx. zero on the third day. This diminution, but less marked, also occurs with the Ca salt. The Ca content of brain and heart also slightly increases. The source of the mobilised Ca is unknown.

F. O. H.

Oral toxicity of o-n-alkylphenols to white rats. H. W. BROWN and P. D. RAMSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 592-594).—The toxicity decreases as the alkyl chain increases in length. The o-n-alkylphenols are less toxic than the corresponding 4-n-alkylresorcinols, but equally toxic with the corresponding 6-alkyl-m-cresols. R. N. C.

Dinitrophenol. Blood, urine, and tissues of dogs on continued medication and after acute fatal poisoning. M. L. TAINTER, W. C. CUTTING, D. A. WOOD, and F. PROESCHER (Arch. Path., 1934, 18, 881—890).—Administration to healthy dogs of 5—10 mg. of 2 : 4-dinitrophenol per kg. of body-wt. daily for 27 weeks caused no change in wt., O<sub>2</sub> capacity of the blood, fragility of red cells, blood picture, or serum-bile pigment. Slight transient albuminuria occurred, but no increase in blood-urea. The animals remained healthy. NUTR. ABS. (b)

Pharmacology of *l*-ascorbic acid. J. V. SUP-NIEWSKI and J. HANO (Arch. exp. Path. Pharm., 1935, **178**, 508—523).—Parenterally administered *l*-ascorbic acid (Na salt) rapidly disappears from the blood and appears in the urine, the vol. of which increases. In mammals a pressor action follows cardiac stimulation, whilst the respiration is first stimulated and then depressed. The sensitivity of mice to McCN poisoning is diminished. F. O. H.

Toxicity and hypoglycæmic effect of guanidine compounds. G. S. SAMUELSEN (J. Pharm. Exp. Ther., 1935, 54, 17—24).—Benzthiazolylguanidine (I) produces, in fairly large doses, a rise in the bloodsugar level in rabbits. Benzselenazolylguanidine (II) and  $\alpha$ -m-tolyl-,  $\alpha\alpha$ -diphenyl-,  $\alpha$ -3 : 6-dimethylphenyl-, and  $\alpha$ -o-tolyl-diguanide show, if any, only a slight effect on blood-sugar level, raising it in some cases, when lethal doses are used. In all cases except (I), there is a rise in blood-N. All preps., with the exception of (II), are more or less toxic, the order of toxicity increasing with the no. of Ph and Me groups. M. T.

Gastric motility in experimental hyperaminoacidanæmia. J. LA BARRE and P. DESTRÉE (Compt. rend. Soc. Biol., 1935, 119, 536-538).--Intravenous injection of glycine causes a hypermotility of the stomach. H. G. R.

Action of monoiodoacetic acid on carbohydrate metabolism in rabbits. Y. NISHIDA (Mitt. med. Akad. Kioto, 1934, 12, 1379—1380).—For 5 hr. after subcutaneous injection of the min. lethal dose of  $CH_2I \cdot CO_2H$  in rabbits there was a progressive increase in blood-sugar and -lactic acid and a decrease in the alkali reserve. In comparable muscles, frozen *in situ* with liquid  $CO_2$  and removed at intervals, glycogen decreased slightly and lactic acid increased steadily. If both splanchnic nerves were cut all these changes were less marked. NUTR. ABS. (b)

Chemical constitution and antitoxic activity (in vitro) of some organic molecules. L. VELLUZ (Bull. Soc. Chim. biol., 1935, 17, 838—847).—The antitoxic action of certain org. compounds for tetanus and diphtheria toxin is associated with the presence of the  $CO_2H$ . Substituted benzoic acids are active for tetanus and naphthenic and benzofuran derivatives are sp. for diphtheria. Phenolic and halogen groups, inactive alone, increase the antitoxic action when associated with  $CO_2H$ ; the free NH<sub>2</sub>, however, has an inhibiting action. The position of the substituents in active isomeric compounds has a marked effect on antitoxic action. A. L.

Poisoning by potassium borotartrate. P. O. SAGRERAS and L. TREPAT (Rev. Assoc. med. Argentin., 1932, 46, No. 318, 1670—1675). CH. ABS. (p)

Action of hypertonic solutions on the crystal structure of animal fibres. F. WORSCHITZ and J. VON HERMAN (Fortschr. Röntgenstrahlen, 1934, 50, 178–180; Chem. Zentr., 1935, i, 585).—The micello structure of muscle fibres is destroyed irreversibly by hypertonic solutions of NaCl, homatropine, pilocarpine, urea, or AcOH, the extent of the change increasing with the concn. R. N. C.

Influence of a calcium diet on disturbances of the liver function. I. Calcium diet and bilirubin metabolism. II. Calcium diet and the metabolism of urobilin substances. Y. ASODA (Japan. J. Gastroenterol., 1934, 6, 51-55, 56-60)... I. After liver injury with CCl<sub>4</sub> the appearance of bilirubin (I) in the blood was less frequent, and injected (I) disappeared more rapidly in rabbits receiving Ca lactate.

II. The urobulin substances of blood, urine, and bile were unaffected by Ca feeding, but  $CCl_4$  injury to the liver was somewhat less severe. CH. Abs. (p)

Influence of thyroid and pituitary glands on chloride distribution. M. A. B. Toxorfus (Arch. exp. Path. Pharm., 1935, 178, 412-415).—Following intravenous injection of aq. NaCl into dogs, the NaCl content of the skin, but not that of the muscle, increases. With simultaneous subcutaneous injection of thyroxine or posterior pituitary extract there is a relative displacement of NaCl from skin to muscle. F. O. H.

Penetration of the rapeutic substances from the organism of the mother into the embryo. M. N. LEBEDEVA (Khim. Farm. Prom., 1934, No. 4, 44-45).—Arsphenamine, Sb, Bi, As, and germanin, following injection into pregnant animals, were found in  $\Rightarrow$  traces in the embryo. CH. ABS. (p)

Inclusions in renal epithelial cells following the use of certain bismuth preparations. A. M. PAPPENHEIMER and E. H. MAECHLING (Amer. J. Path., 1934, 10, 577-588).—Globules occurring in nuclei and cytoplasm of the cells following intramuscular injection of various Bi preps. gave equivocal tests for Bi, were insol. in lipin solvents or in strong acids or alkalis, resisted tryptic digestion, gave no reaction for Ca or Fe, but stained as myelin.

Сн. Авз. (р)

Pathological changes encountered in wild ducks. J. P. TORREY, F. THORPE, jun., and R. GRAHAM (Cornell Vegetarian, 1934, 24, 289—298).— Inclusion of Pb shot in the diet caused Pb poisoning in ducks. CH. ABS. (p)

Lead compounds R232 and R237b used in experimental therapy of tumours and leucosis. C. KREBS and J. CLEMMESEN (Z. Krebsforsch., 1934, 41, 260-266; Chem. Zentr., 1935, i, 437).—The compounds R232 and R237b (K and Na plumbodithiopyridinecarboxylates), dissolved in  $H_2O$  and stabilised at  $p_{\rm H}$  7.4 with glycine, show relatively low toxicities to their high Pb contents, but are apparently without therapeutic effect on mouse carcinoma.

R. N. C. **Poisoning by thallium acetate.** A. Buzzo and C. F. GANDOLFO (Rev. Assoc. med. Argentin., 1932, 46, No. 313, 97—99).—Toxic effects of TIOAc, used as a depilatory, were cured by hypertonic glucose, serum, insulin, and Na "hyposulphite." CH. ABS. (p)

Growth of human fibroblasts in media containing silver. J. P. M. VOGELAAR and E. EHR-LICHMAN (Amer. J. Cancer, 1934, 22, 555-560).— Fibroblasts from the thyroid grew normally in media containing 0.0028 mg. of Ag per c.c., but not in those having 0.04 mg. Activation of the proteolytic enzymes with certain [Ag] is indicated.

CH. ABS. (p)Influence of metals on adrenaline hyperglycæmia in rabbits. H. SCHNETZ (Arch. exp. Path. Pharm., 1935, 178, 420—438).—Injection of simple or complex salts of Cu, Zn, Cd, Mn, Ni, Co, Fe<sup>II</sup>, and Fe<sup>III</sup> has no effect on the fasting blood-sugar of rabbits. The hyperglycæmia due to injection of 0·1 mg. of adrenaline per kg. of body-wt. is, however, considerably reduced by previous daily subcutaneous injection of the salts of the analogous metals Cu, Zn, and Cd, but not with those of Mn, Ni, Co, Fe<sup>II</sup>, or Fe<sup>III</sup>. Daily injection of 0·5—2·0 mg., but not of 0·2—0·1 mg., of Cu or Zn per kg. will produce the effect (cf. this vol., 410). F. O. H.

Influence of metallic couples on the growth in vitro of fibroblasts and osteoblasts. G. MENEGAUX and D. ODIETTE (Compt. rend. Soc. Biol., 1935, 119, 485-486).—The toxicity of a metal is not affected by the presence of another metal as a couple. H. G. R.

Action of metallic chlorides on tissue cultures. II. Hepatic, renal, and nerve tissue. J. VERNE and C. SANNIÉ (Bull. Soc. Chim. biol., 1935, 17, 678—689).—The toxicity of the alkali and alkalineearth metals is small; that of the heavy metals is considerable and varies according to the nature of the metal. The fibroblasts of the liver, kidney, and nerve tissue, although more resistant than the functional cells, are more sensitive than those of the chicken-embryo heart. A. L.

Effect of physico-chemical changes in environment on embryo formation in the frog. J. W. CULBERTSON and H. V. WILSON (J. Elisha Mitchell Sci. Soc., 1934, 50, 50–51).—Exposure to low temp. or to dil. solutions of NaCl or LiCl disturbs the physiological organisation of the embryos of artificially inseminated frog eggs. CH. ABS. (p)

Preventive rôle of methæmoglobin-forming substances (sodium nitrite) in intoxication by fluorides. V. KARASSIK, V. ROCHKOV, and O. VINOGRADOVA (Compt. rend. Soc. Biol., 1935, 119, 807—809).—The mortality of white mice injected with NaF is decreased from 80 to 24% by previous injection of NaNO<sub>2</sub>. H. G. R.

Effects of fluorine on respiration, bloodpressure, coagulation, and blood-calcium and -phosphorus in the dog. D. A. GREENWOOD, E. A. HEWITT, and V. E. NELSON (J. Amer. Vet. Med. Assoc., 1935, 39, 28—42).—Intravenous injection of NaF increased respiration and lowered bloodpressure. Oral administration (0.45-4.52 mg. of Fas NaF per kg. body-wt.) did not affect the total Ca, acid-sol. inorg. P, hæmoglobin, or coagulation time of blood. Bones were unchanged, but teeth became mottled. CH. ABS. (p)

Fluorine poisoning. A. SLAVIERO (Arch. Ist. Biochim. Ital., 1934, 6, 285–310; Chem. Zentr., 1935, i, 746).—Physiological effects on dogs are recorded. A. G. P.

Fluorine toxicosis. M. C. SMITH (Amer. J. Publ. Health, 1935, 25, 696—702).—Drinking-H<sub>2</sub>O containing < 1 p.p.m. of F will cause the permanent teeth of children to have faulty enamel, but if [F] is > 12 p.p.m. the first set also will be affected. The action is not directly in the mouth, but through the blood-stream on the organ producing the enamel. Later, this organ disappears, and the enamel of adults is unaffected, although the dentine which receives nutrient from the blood may be affected and result in a general weakening which does not show externally. The decalcification is not prevented by an increased Ca content of the diet or by a liberal intake of vitamin-D, e.g., from cod-liver oil. Since the level of human tolerance to F is so low, the growing use of insecticides containing it is to be deprecated.

C. J.

Pathologico-anatomical conditions in arsine poisoning. H. HILTERHAUS (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 70—79).—Conditions in two cases of  $AsH_3$  poisoning are described, including hæmolytic action and methæmoglobin content.

R. N. C.

Determination of minimal concentrations of arsenic in expired air. A. PLESCHTIZER and A. A. PREOBRAJENSKY (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 80—86).—The expired air of cases of As poisoning contains traces of As, which can be detected by Feigl's reaction, or by absorption with Br and NH<sub>3</sub> and cultivation in the solution of *P. brevicaule*, which forms AsHEt<sub>2</sub>. R. N. C.

Toxic effects of sulphur on guinea-pigs and rabbits. G. B. LAWSON, K. T. REDFIELD, and O. D. BOYCE (J. Lab. Clin. Med., 1934, 20, 169-171).—Effects of ingestion and injection of S are examined. CH. ABS. (p)

Action of sulphur-containing gases on the cocoons of Bombyx mori, L. I. HIRAIWA, K. YAMAFUJI, and Y. YONEZAWA (Bull. Sci. Fak. Terkult. Kjushu, 1935, 6, 119—125).—2 parts of SO<sub>2</sub> in 10,000 and 2 parts of  $H_2S$  in 100,000 interfere with the formation of the cocoon and affect the quality of the silk. E. A. H. R.

Toxic gases. Adjuvant groups in organic halogen compounds. M. HANNE (Chim. et Ind., 1935, 33, 1317—1320).—The effect of modifying groups in the mol. on the toxic, vesicant, lachrymatory, and sternutatory properties of known org. Clcompounds is discussed. F. N. W.

Influence of carbon dioxide and ammonia on cocoon formation of *Bombyx mori*, L. K. YAMAFUJI, Y. YONEZAWA, and I. HIRAIWA (Bull. Sci. Fak. Terkult. Kjushu, 1935, 6, 111—118).— $CO_2$ , expired by the larvæ, and NH<sub>3</sub> (in very low concns.) have a damaging effect on the formation of the coccoon. E. A. H. R.

Toxicity for sheep of aqueous solutions of hydrocyanic acid and the effectiveness of the nitrite-thiosulphate combination as a remedy. J. F. COUCH, A. B. CLAWSON, and H. BUNYEA (J. Washington Acad. Sci., 1935, 25, 272—276).—The min. lethal dose of HCN administered to sheep in a drench is  $2\cdot3$  mg. per kg. Intraperitoneal administration of 15 c.c. of a solution containing 1 g. of NaNO<sub>2</sub> and 2 g. of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> produced recovery in about 50% of cases with doses up to 4 times the min. lethal dose. W. O. K.

Pathogenesis of silicotic tissue changes. I. Experimental production of silicotic welts by quartz and colloidal silicic acid. H. SIEGMUND. II. Behaviour of quartz dust in silicotic tissue. III. Nature of asbestosis particles. G. F. KOPPENHÖFER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 1–17, 18–37, 38–62).—I. Quartz particles injected into the blood-stream in rabbits are removed by the reticulo-endothelial cells, but are deposited in different tissues according to their size, where they produce characteristic changes. Colloidal  $H_2SiO_3$  injected intravenously produces fibrosis in the liver.

II. The morphological changes produced in silicotic tissues by quartz particles are described.

III. The gelatinous shell of asbestosis particles in tissue sections is of inorg. origin, and contains Fe, Mg, and SiO<sub>2</sub>. R. N. C.

Atmospheric ozone and heliotherapy. R. LATARJET (Compt. rend. Soc. Biol., 1935, 119, 610–612).—The therapeutic effect of solar radiation is diminished considerably by  $O_3$  in the atm.; it falls more rapidly than  $O_3$  increases. The  $O_3$  content is influenced by the height of the sun at noon.

R. N. C.

Physico-chemical effects of irradiation of crystalline ovalbumin solutions with  $\alpha$ -particles. L. E. ARNOW (J. Biol. Chem., 1935, 110, 43—59).— Irradiation of ovalbumin (I) solutions by  $\alpha$ -particles produced coagulation at the isoelectric point only; quantities of gas (chiefly H<sub>2</sub>) were evolved; there was no change in the N content of the solution. The  $\eta$ , ultra-violet absorption, and coagulation temp. of the solution were raised at  $p_{\rm H} < 4.8$  and lowered at  $p_{\rm H} > 4.8$  by the irradiation. From the curves of gas evolution against Rn disintegration it is deduced that H<sub>2</sub> and O<sub>2</sub> are utilised by (I), the former process involving at least two reactions.

Effect of light on the sensitivity of wheat seedlings to X-rays. L. C. CHESLEY (J. Cell. Comp. Physiol., 1935, 6, 69—84).—Seedlings sprouted in light were less sensitive to X-rays than were those sprouted in darkness, when compared on a fresh wt. or respiration basis. Linear growth was not protected by light. The influence of light decreased as irradiation was increased, and also tended to become less with time. Results are discussed in relation to the theory of the destruction of auxin by X-rays.

A. G. P.

Effects of radiations on biological systems. II. Immediate and subsequent effects of X-irradiation on respiration of Drosophila larvæ. R. HUSSEY and W. R. THOMPSON (J. Gen. Physiol., 1935, 18, 669—674; cf. A., 1932, 1150).— X-Irradiation of the larvæ produces an immediate decrease in the CO<sub>2</sub> respiration [which  $\propto$  the time of irradiation] and a latent effect persisting for several days. F. O. H.

Radium emanation and elimination of phosphorus by frog's muscle. O. V. HYKEŠ and J. REŘÁBEK (Biochem. Z., 1935, 278, 123—132).— Rn increases  $PO_4$  elimination to a greater extent than does rise of temp. of both resting muscle and of muscle undergoing nervous stimulation. Under the prolonged action of Rn, the  $PO_4$  elimination is not linear, but is greatest for the first few min. Rn affects first the permeability, and may also affect the chemical processes occurring in muscle. P. W. C.

Photons in chemistry and biology. F. DANIELS (Science, 1935, 81, 523-528).—A lecture. L. S. T.

Action of electrolytes on electrical stimulation of skeletal muscle. I. CHAO (J. Cell. Comp. Physiol., 1935, 6, 1–19).—The immediate sensitising effect of Na salts was in the order  $Cl' < Br' < NO_3' <$ I' < SCN'. The action of NaSCN is characterised by a period of secondary depression which is probably related to the presence of CaCl<sub>2</sub>. KCl produces at first an increase followed by a decrease in response, the relative intensity of these effects increasing with concn. CaCl<sub>2</sub> at all concns. decreased contraction. Antagonism between the actions of Ca and K salts occurs within certain narrow ranges of concn.

A. G. P.

Theory of diffusion in cell models. II. Solution of the steady state for three diffusing substances. L. G. LONGSWORTH (J. Gen. Physiol., 1935, 18, 627-642).—Theoretical considerations of diffusion in cell models (A., 1934, 107) have been extended to the simultaneous penetration of  $H_2O$ and two salts. Vals. thus calc. for the steady state agree with experimental data. F. O. H.

Elementary actions of mineral waters. P. TESTONI (Annali Chim. Appl., 1935, 25, 111—116).— Classification of a mineral water according to its elementary composition is insufficient to indicate its biological effects. T. H. P.

Dinner demonstration of threshold differences in taste and smell. A. F. BLAKESLEE (Science, 1935, 81, 504-507).—Results of a largescale experiment are described. L. S. T.

Mechanism of enzyme actions. K. G. FALK (Science, 1935, 81, 471-475).-A discussion.

L. S. T. Catalytic causation of physiological phenomena. A. MITTASCH (Naturwiss., 1935, 23, 361— 369).—A review of the characteristics of catalytic action and the types of bio-catalysts. The connexion between bio-catalysis and stimulation and instinctive reaction is considered. A. J. M.

Synthesis of synthetic enzymes. W. LANGEN-BECK (Bull. Soc. Chim. biol., 1935, 17, 627-636).-A résumé. A. L. Tissue-enzymes. F. MAIGNON (4me. Congr. Chim. biol., Paris, Nov., 1934).—Extracts of fresh organs of healthy animals (Lebedev's method) contain substances which restore functional activity in cases of insufficiency of liver, kidney, ovary, thyroid, etc. The extracts show marked specificity and have no effect on the healthy organism. In old dogs with hepatic or renal insufficiency, a single dose of 1 mg. maintains normal conditions (bloodurea etc.) for a week or more, and a second dose has a similar effect. NUTR. ABS. (b)

Ascorbic acid oxidase. H. TAUBER, I. S. KLEINER, and D. MISHKIND (J. Biol. Chem., 1935, 110, 211-218).—The isolation of an enzyme, from the pericarp of the Hubbard squash, which oxidises ascorbic acid (I) instantaneously and completely is described. Its kinetics are those of a single enzyme, and in this it differs considerably from Szent-Gyorgyi's hexoxidase (cf. A., 1931, 533). (I) is probably oxidised by the introduction of two OH at the double linking. The oxidation product of (I) can be reduced again by H<sub>2</sub>S. No oxidation takes place in an atm. of N<sub>2</sub>. The enzyme shows activity only between  $p_{\rm H}$  4 and 7 (max. activity about  $p_{\rm H}$  5.6). It is more easily destroyed by excess of H than of OH'; it is stable to  $O_2$ , CO, and to small concns. of KCN (0.005%). It is irreversibly inactivated by 0.01%KCN and by H2S. Trypsin slowly inactivates it, so that it must either be a protein or have protein as an indispensable part. E. A. H. R.

Enzymic dehydrogenation of citric acid. T. WAGNER-JAUREGG and H. RAUEN (Z. physiol. Chem., 1935, 233, 215—222).—The rate of methyleneblue reduction by citric acid (I) in presence of phosphate extracts of various seeds and of frog muscle is accelerated by addition of co-enzyme (from horse erythrocytes) and yellow enzyme (from yeast). This holds with bean extracts for the substrates *l*-malic acid, EtOH, and hexosemonophosphoric acid. The degradation of (I) occurs in stages with the co-operation of two different co-enzymes, yellow enzyme only assisting at a later stage. Acetonedicarboxylic acid is not a stage, and is probably not the end-product of the dehydrogenation. J. H. B.

Synergistic action of milk- and muscleoxidases. D. I. MACHT and H. F. BRYAN (J. Biol. Chem., 1935, 110, 101-105).--Methylene-blue is decolorised by juice or suspensions of muscle (rat, ox, chicken, rabbit, frog, gold-fish, pike) much more rapidly than by milk, but the times required for decolorisation are greatly reduced when small amounts ( $\leq 1$  part in 60) of milk are added to the juice (or suspension) or small amounts of juice (or suspension) to the milk. W. McC.

Correlation of oxidation and phosphorylation in hæmolysed blood in presence of methyleneblue and pyocyanine. J. RUNNSTRÖM and L. MICHAELIS (J. Gen. Physiol., 1935, 18, 717—727).— Aerobic oxidation of glucose (I) or anaërobic glycolysis does not occur in hæmolysed blood (horse)–(I) systems. With blood-hexose phosphate in presence of methylene-blue (II), aërobic oxidation occurs, and is increased by cozymase (when phosphorylation occurs). Replacement of (II) by pyocyanine does not change the rate of oxidation, but phosphorylation occurs in absence of cozymase. Oxidation always occurs during phosphorylation, but not vice versa.  $GH_2I \cdot CO_2H$  always inhibits phosphorylation, but only under certain conditions decreases oxidation; neither process is affected by CN'. F. O. H.

Yellow oxidation enzyme. H. THEORELL (Biochem. Z., 1935, 278, 263-290).-By treatment in the modified cataphoresis apparatus (see below) followed by pptn. with aq.  $(NH_4)_2SO_4$  (67% at  $p_{\rm H}$  5·2) the enzyme,  $[\alpha] -30^{\circ}$  in H<sub>2</sub>O, mol. wt. 70,000– 75,000, isoelectric point at  $p_{\rm H}$  5·25 $\pm$ 0·03, is obtained pure and cryst. in about 60% yield. It exhibits absorption max. at 265, 380, and 465 mµ and min. at 240, 320, and 415 mµ. The polysaccharide associated with (but not bound to) the enzyme acts as protective colloid. Enzyme reconstituted from the components after hydrolysis is as active as non-hydrolysed enzyme. Heating (to 75°) causes irreversible hydrolysis. The protein component, which is very labile and easily denatured, combines with hæmins to give hæmochromogens. The yellow component (flavinphosphoric ester) is readily sol. in  $H_2O$ , but insol. in MeOH, COMe<sub>2</sub>, or CHCl<sub>3</sub>. When dry this component is stable in the dark. In aq. solution the Ca salt is more stable. Since the yellow component is only very slowly inactivated by blood-serum, it probably has a more powerful vitamin action than has lacto-W. McC. flavin.

Cataphoresis apparatus for preparative purposes. H. THEORELL (Biochem. Z., 1935, 278, 291—297; cf. this vol., 188).—Materials (e.g., yellow respiratory enzyme) which cannot otherwise be isolated can be purified in quantity in a modified form of the apparatus previously described. Conducting liquids (buffer solutions) and semi- or non-permeable membranes appropriate to the substances to be purified are required. W. McC.

Catalase in body-fluid of the silkworm. S. MATSUMURA (Bull. Sericult. Japan, 1935, 7, 5).— The body-fluid catalase activity in the male silkworm is > in the female. It is strong soon after the 4th moult, but becomes weaker at maturity. It varies with race and strain, but is not related to blood colour. E. A. H. R.

Mechanism of increase in amylase activity during autolysis of barley powder. R. H. R. RAU (Proc. Indian Acad. Sci., 1935, 1, B, 686—692).— Amylase activity in barley powder increases during autolysis as a result of liberation of  $\beta$ -amylase. No amylokinase is formed. A. G. P.

Protective action in ultra-violet irradiation of amylase solutions. W. R. THOMPSON and R. THOMPSON (J. Gen. Physiol., 1935, 18, 675-680).— The protective action of dog's sera against the destruction of aq. pancreatic amylase preps. by ultraviolet irradiation is due to competitive absorption by the sera for inactivating radiations. F. O. H.

Rennin and the diastatic power of ungerminated grains. T. CHRZASZCZ and J. JANICKI (Biochem. Z., 1935, 278, 112-122).—Rennin is able to increase the amylolytic power of various grains, the effect being greatest in respect to the saccharifying power and only slight in respect to the dextrinifying and liquefying powers. With most grains the effect is as great as that with papain, whilst with oats and buckwheat it is even greater. The effect is not due to the traces of pepsin in rennin. Addition of CaCl<sub>2</sub> inhibits this increase of the active amount of amylase by rennin. P. W. C.

Inactivation of heparin in blood. A. SCHMITZ and L. KÜHL (Z. physiol. Chem., 1935, 234, 212—215). —The inactivation is almost complete in 3 hr. at 56° in blood-serum, and only a small part of the inactivating power remains after 18 hr. at room temp. in plasma (hen) or albumin or globulin solutions.

W. McC. Determination of the unit of heparin. A. SCHMITZ (Z. physiol. Chem., 1935, 234, 216—217; cf. A., 1932, 1054).—The procedure of Scott *et al.* (A., 1933, 1317) is untrustworthy. The coucn. of heparin  $\infty$  the log of the coagulation time. Determinations must be made at 38° in 2—20 min. A "heparin unit" is 30 times that amount which increases the log of the coagulation time of hen plasma, under given conditions, by 0·1. W. McC.

**Preparation of thrombin.** A. C. ROBERTS (Proc. Soc. Exp. Biol. Med., 1935, 32, 606–608).— Fibrin from calves' blood, after being freed from hæmoglobin, is extracted for 24 hr. with Et<sub>2</sub>O, and then with cold 8% NaCl. The NaCl extract is filtered, and excess of NaCl removed by dialysis against  $H_2O$ ; this is followed by further dialysis against a PO<sub>4</sub><sup>'''</sup> buffer at  $p_{\rm ff}$  7.38, and against  $H_2O$ . The solution is filtered, and thrombin obtained by evaporation at room temp. R. N. C.

Coagulation and inactivation of emulsin by heat. Influences of crystalloidal and of colloidal solutes. D. L. Fox and L. L. SORKNESS (Biochem. J., 1935, 29, 1532—1537).—Emulsin (I) in dil. aq. solution is inactivated by incubation for 0.5 hr. at a temp.  $> 75^{\circ}$ , but is not pptd. Fluorescein, Congo-red, and neutral-red lower the inactivation temp., as does a  $p_{\rm H}$  val. of 1.97 or > 7.65. Glucose raises it several degrees, whilst 0.5% lactose solution has no effect. Dil. acids and phosphates cause pptn. of (I). In the absence of H<sub>2</sub>O, (I) can be heated to 150° without loss of activity. There is no direct relationship between heat-inactivation and heatcoagulation of (I). J. N. A.

Baicalinase, an enzyme causing fission of flavoneglucuronide. II. T. MIWA (Acta Phytochim., 1935, 8, 231–243).—Scutellarein (Ac<sub>4</sub> derivative, m.p. 237°) is identified among the products of the hydrolysis of scutellarin (I) by baicalinase (II). Fission of (I) and of baicalin by (II) is a reaction of the first order after 25% hydrolysis, proceeding most rapidly at  $p_{\rm H}$  5.7 and 50–60°. H. W.

[Properties of] highly purified cozymase. H. VON EULER, H. ALBERS, and F. SCHLENK (Z. physiol. Chem., 1935, 234, I—II).—Cryst. cozymase (possibly  $C_{12}H_{19}O_4N_4P$ ) regenerated (in 80% yield) from the Cu<sup>1</sup> salt is much more active than the starting material and is almost free from S. No increase in activity is achieved by repeated conversion into the salt and regeneration. The degree of activity attained is independent of that of starting material which has activity  $\not\ll$  a certain val. The purification is without effect on the co-enzyme activity towards EtOH dehydrase, but destroys the activator effect in the hexose phosphate dehydrogenation system if purified dehydrase solutions are used. W. McC.

Enzymes of Bombyx mori, L. X, XI. Gastric lipase. K. YAMAFUJI and Y. YONEZAWA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 14—16, 30—33).— X. The gastric lipase (I) of silkworms has its  $p_{\pi}$  and temp. optima at 9.8 and 40°, respectively. Heating at 70° for 1 hr. nearly destroys (I). Quinine and atoxyl have only a slight toxic effect. Its activity increases on starvation for 1 day, but decreases if starvation is prolonged. The (I) content of the male is > that of the female, and increases during growth up to the 5th day, while the body-fat is built up, after which it decreases. There is no significant difference in the (I) content of different species of silkworm.

XI. A prep. of lipase from the gastric juice of silkworms is described and an account of its kinetics given. The pancreatic lipase of vertrebrates and (I) have similar activators and inhibitors. E. A. H. R.

Castor-bean lipase. VIII. E. TAKAMIYA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 46–48).—Castor beans contain a lipase-activating substance the power of which is destroyed by autoxidation. E. A. H. R.

Determination of lipase in pancreas. L. VOGEL and P. LAEVERENZ (Z. physiol. Chem., 1935, 234, 176—180).—When the method of Willstätter *et al.* (A., 1923, i, 403) is applied to impure preps., the vols. of aq. CaCl<sub>2</sub> and albumin should be increased to 1.6 c.c., and 1.6 c.c. of 2% Na oleate solution should be added. W. McC.

Lipase activity of mammalian organs in the healthy and carcinomatous organism. S. EDLBACHER and M. NEBER (Z. physiol. Chem., 1935, 233, 265—275).—The lipase activity of brain extract is only about 0.02 of that of liver. Fission by lipase in the organs examined is the same in  $O_2$ , air, and  $N_2$ . The characteristic inhibition by atoxyl and quinine of human lipase is not shown by lipase from rat's liver and brain. Tumours and necrotic tissue show activity of the same order as brain. The lipase activity of organs of carcinomatous animals is much < that of normal animals. J. H. B.

Extraction and preservation of  $\alpha$ -lipase of blood-serum. Z. GRUZEWSKA and E. BERAUT (Compt. rend. Soc. Biol., 1935, 119, 699—700).—Dried serum is freed from fat with EtOH and Et<sub>2</sub>O, and  $\alpha$ -lipase extracted with pure or 87% glycerol. The extracts retain their hydrolysing power for long periods in the cold, and the active principles of the serum are unaltered. R. N. C.

Rachitogenic action of cereals. Calcium and phosphorus liberated by digestion of cereals *in* vitro, with or without sodium chloride. G. POPOVICIU, G. BENETATO, and R. OFREAN (Compt. rend. Soc. Biol., 1935, **119**, 445—447).—Digestion of cereal flours *in vitro* by pancreatic enzymes and enterokinase at  $p_{\Pi} \otimes 4$  liberates small quantities of Ca and P. Addition of NaCl increases Ca liberation. R. N. C. Occurrence of trypsin in the stomach. M. HIRVONEN (Skand. Arch. Physiol., 1934, 71, 16—17). —In most cases the contents of the fasting human stomach contained trypsin (I). After a test meal, (I) was also present; the more acid the gastric contents, the greater was the amount of (I). NUTR. ABS. (b)

Enzymic histochemistry. IX. Pepsin in gastric mucosa of pigs. X. Acid localisation in gastric mucosa of pigs. XI. Peptidase in gastric mucosa of pigs. K. LINDERSTRØM-LANG and H. HOLTER. XII. Esterase in gastric and duodenal mucosa of pigs. D. GLICK. XIII. Enzyme distribution in the stomach of pigs as a function of histological structure. K. LINDER-STROM-LANG, H. HOLTER, and A. S. OHLSEN (Compt. rend. Trav. Lab. Carlsberg, 1935, 20, No. 11, 1-32, 33-41, 42-56, 57-65, 66-125).-Pepsin (I) is found mainly in the chief cells of the fundus, but is also found in the fundus, in the neck chief cells, and in the pylorus, cardia, and duodenum. (I) in the neck chief cells is not so easily extracted by glycerol as that in the fundus chief cells. In different layers of the fundus mucosa glycerol extracts very varying amounts of (I), and this may be in accord with the concept of a desmo- and a lyo-pepsin. HCl is found exclusively in the fundus, and, probably, in its parietal cells. Peptidase is found in the fundus and cardia only in the chief cells, in the pylorus also in the neck chief cells, and in the duodenum in the cylinder cells and Brunner cells. There is no typical localisation of esterase activity in definite regions or layers of the gastric mucosa. E. A. H. R.

Effect of mucin and mucinoids on peptic digestion. H. C. BRADLEY and M. HODGES (J. Lab. Clin. Med., 1934, 20, 165—169).—The digestion of caseinogen, native and coagulated fibrin, etc. is retarded by the presence of gastric mucin for 3—4 days, but subsequently normal amounts are digested. Chondroitin sulphate and vegetable mucinoids produce similar effects. CH. ABS. (p)

Adsorption of crystalline pepsin by denatured ovalbumin and silk-fibroin. P. S. YANG (Chinese J. Physiol., 1935, 9, 189—196).—Loss of activity of pepsin solution by adsorption on ovalbumin or silkfibroin involves an equiv. loss of pepsin-protein.

H. G. R.

Proteases of Ficus carica. G. DE VITO (Annali Chim. Appl., 1935, 25. 151—156).—As with papain and bromelin, the proteolytic action of these enzymes is greatly enhanced by HCN. T. H. P.

Thiol nature of papain. T. BERSIN (Biochem. Z., 1935, 278, 340-341).—The activation of papain by  $K_3Fe(CN)_6$  in presence of veronal is due to reduction of the  $K_3Fe(CN)_6$ . Since the author's results have been confirmed by Hellermann *et al.* (A., 1934, 1402), Purr (this vol., 252), and Mirsky *et al.* (*ibid.*, 506), the criticisms of Maschmann *et al.* (*ibid.*, 897) are rejected. W. McC.

Nature of urease; fractional ultrafiltration. P. GRABAR and A. RIEGERT (Compt. rend., 1935, 200, 1795—1797).—The behaviour of cryst. urease (I) towards ultrafiltration resembles that of globulin; other (I) preps. were less homogeneous. Such smaller particles as are produced by partial tryptic digestion of cryst. (I) have no (I) activity. F. A. A.

Arginase activation. L. WEIL (J. Biol. Chem., 1935, 110, 201-209).—The cysteine-Fe" complex, unlike cysteine or Fe" alone, activates arginase (I) independently of the origin or purity of the enzyme prep. After depletion of Fe" by feeding with 2:2'dipyridyl, addition of Fe" to liver-(I) preps. produces a strong activation. The liver-(I) of carcinomatous animals shows similar activation, but the amount is < in normal animals. E. A. H. R.

Glyoxalase. V. Enzymic nature of kidney antiglyoxalase. E. F. SCHROEDER, M. P. MUNRO, and L. WEIL (J. Biol. Chem., 1935, **110**, 181–200).— The action of kidney antiglyoxalase (I) is explained as an enzymic hydrolysis of glutathione (II) (the glyoxalase co-enzyme), probably into glycine and glutamylcysteine,  $p_{\rm H}$  optimum 7. Pancreatic (I) is probably identical with pancreatic carboxypolypeptidase, as this hydrolyses reduced (II) slowly and oxidised (II) more rapidly. High concess. of *d*- and *l*-histidine have no effect on glyoxalase activity, so that the claim that the (I) action of a pancreas prep. is due to histidine is disproved. E. A. H. R.

Production and properties of dry glyoxalase. P. G. EFENDI, J. O. GIRŠAVIČIUS, and A. P. RIZHOVA (Biochem. Z., 1935, 278, 246—251).—Liver (fresh or dried with COMe<sub>2</sub> and Et<sub>2</sub>O) is extracted with H<sub>2</sub>O, and 0·1N·NaOAc ( $p_{\rm H}$  4) is added; purified material is obtained from the filtrate, after neutralisation with aq. NaHCO<sub>3</sub>, by repeated pptn. with COMe<sub>2</sub>, drying, and re-extraction with H<sub>2</sub>O or physiological aq. NaCl. Most or all of the glutathione is removed. The enzyme exhibits no special sensitivity towards EtOH. Dried preps. lose a great part of their activity within 1 month. W. McC.

Antiglyoxalase action of histidine. J. O. GIRŠAVIČIUS and A. P. RIZHOVA (Biochem. Z., 1935, 278, 252—256; cf. this vol., 122, 476).—When the change of  $p_{\rm H}$  caused by histidine (I) is prevented, the amounts of (I) required to inhibit the action of glyoxalase are > those required when there is no prevention. Inhibition is gradual when fresh liver extracts are used, but when dried preps. are used inhibition is independent of time. No competition for AcCHO occurs between (I) and glutathione.

W. McC.

Enzymic hydrolysis of dihydroxyacetonephosphoric acid. H. COLLATZ (Biochem. Z., 1935, 278, 364-371).—The views of Schäffner *et al.* (this vol., 661) notwithstanding, K dihydroxyacetonephosphate and (better) its NaHSO<sub>3</sub> compound are completely hydrolysed in a few days by taka-phosphatase to  $CO(CH_2 \cdot OH)_2$  and  $H_3PO_4$ . W. McC.

Phosphatases. III. Mechanism of the inactivating action of sodium oxalate and phosphates on "alkaline" phosphatases of animal tissue. S. BELFANTI, A. CONTARDI, and A. ERCOLI (Biochem. J., 1935, 29, 1491—1507; cf. this vol., 660).—The hydrolysis of  $\beta$ -glycerophosphate (I) in the presence of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> by liver extracts at alkaline  $p_{\rm H}$  is slow at first, then increases rapidly, and finally attains approx. the same rate as without Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Bone extracts do not show the phenomenon. By varying the concns. of enzyme and (I) it is shown that the inhibitory action of  $Na_2C_2O_4$  ceases when a certain concn. of inorg. P is freed. Added inorg. P prevents the inhibition of both liver and bone extracts;  $Na_2C_2O_4$  tends permanently to deactivate the latter. Pig's kidney extract behaves similarly to that of rabbit's liver. H. D.

Phosphatase in fractures. E. H. BOTTERELL and E. J. KING (Lancet, 1935, i, 1267—1270).— The phosphatase (I) content of callus and bone near healing fractures, produced experimentally in rabbits, is > that of normal bone. This increase appears to accompany the formation of hypertrophic cartilage cells, osteoblastic activity, and the formation of bone matrix. There is little indication of concomitant changes in the serum-(I) of man or rabbits during the repair of fractures. Introduction of (I) into the site of experimental fractures produces no change in the rate or apparent quality of the calcification of the bone matrix. L. S. T.

Degradation of  $\alpha$ - and  $\beta$ -glycerophosphate by fresh yeast and by dissolved yeast-enzymes. W. SCHUCHARDT (Biochem. Z., 1935, 278, 164—172).— Yeast-phosphatase can degrade at  $p_{\rm H}$  4 and 6 both  $\alpha$ - and  $\beta$ -glycerophosphates, but the  $\beta$ -isomeride is more readily attacked than the  $\alpha$ . With aq. suspensions of dried yeast at  $p_{\rm H}$  4 the  $\beta$ -form and at  $p_{\rm H}$  6 the  $\alpha$ -form is the more readily attacked. With yeast maceration juice and with glycerol extracts of yeast before and after dialysis, the  $\alpha$ -variety is more readily decomposed. P. W. C.

Fermentation enzymes. III. First phases of phosphorylation in alcoholic fermentation. A. SCHAFFNER, H. BERL, and E. BAUER (Z. physiol. Chem., 1935, 234, 146-150; cf. this vol., 784).-Added hexosediphosphoric acid (I) has no catalytic effect in a purified enzyme system [the reaction ceasing when all (I) has been consumed], and (I) cannot be replaced by hexosemonophosphoric acid (II). The Neuberg and Robison esters yield dihydroxyacetonephosphoric acid when attacked by zymohexase only after addition of yeast maceration juice which contains an enzyme (or component of an enzyme) capable of converting (II) into (I). The primary product of phosphorylation is a hexose mono-ester identical with or easily convertible into the Robison ester. W. McC.

Yellow pigment containing sulphur from yeast. R. KUHN, T. WAGNER-JAUREGG, F. W. VAN KLA-VEREN, and H. VETTER (Z. physiol. Chem., 1935, 234, 196—200).—Yeast, milk, sugar-beet, and similar materials contain at least 3 structurally different blue-fluorescent substances, the fluorescence of which is removed by reduction (e.g., with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) and restored by shaking with air. One of these is thiochrome (I) (20 mg. from 1200 kg. of yeast),  $C_{12}H_{14}ON_4S$ , m.p. 222° (decomp.), a H<sub>2</sub>O-sol. base containing NMe; absorption max. 358 and 375 mµ (hydrochloride, max. 348 mµ). The fluorescence of (I) in alkaline solution is irreversibly destroyed by sunlight. In yeast (I) is probably present entirely as a colourless, nonfluorescent chromogen possibly identical with vitamin- $B_1$  (II) (cf. Peters, this vol., 415). Me is quantitatively eliminated from (I) and (II) picrolonate during determination of NMe by the method of Slotta *et al.* (A., 1932, 291). W. McC.

**Reproduction in yeast cultures.** A. KLEM (Hvalrad. Skrift., 1933, No. 7, 55—91; Chem. Zentr., 1935, i, 734—735).—The rate of  $CO_2$  production per single cell is examined. Relationships between the EtOH concn. and that of sugar in the culture liquid are determined. A. G. P.

**Respiration of yeast.** J. GIAJA and L. MARKO-VIC (Compt. rend. Soc. Biol., 1935, 119, 639—641).— Variation of the concn. of yeast suspension in a medium containing EtOH or glucose, through vals. >7%, scarcely affects the  $O_2$  consumption, which, however, is increased by dilution to < this val. In a mineral medium the variations of  $O_2$  consumption are less marked; NaF suppresses it in a glucose or EtOH medium, but not in a mineral medium. Hence there are two types of respiration of yeast. R. N. C.

Action of 2:4-dinitrophenol on washed yeast. J. FIELD and A. W. MARTIN (Compt. rend. Soc. Biol., 1935, 119, 458—461).—Washing the yeast in distilled H<sub>2</sub>O or PO<sub>4</sub><sup>'''</sup> buffer has no effect on the stimulation of respiration by 2:4-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>·OH.

H. G. R.

Action of dinitrocresol on yeast fermentation and oxidation. M. E. KRAHL and G. H. A. CLOWES (J. Amer. Chem. Soc., 1935, 57, 1144).—4: 6-Dinitro-o-cresol at optimum concn.  $(10^{-5}M)$  increases the rate of anaërobic CO<sub>2</sub> and EtOH production, to a smaller extent the (aërobic) consumption of O<sub>2</sub>, and the total amount of glucose consumed by yeast cells, but not the rate of growth of the cells. Higher concns. cause abnormally low activity. R. S. C.

Action of top yeast on levosin in solution and during the process of bread-making. R. GEOF-FROY (Bull. Soc. Chim. biol., 1935, 17, 848—851).— Free levosin (I) extracted from wheat flour is not fermented by top yeast. During the process of bread-making, however, the (I) in the flour is fermented, although much more slowly than sucrose and maltose. A. L.

Precipitinogenic properties of "radium" strains of Zygosaccharomyces mandshuricus, Saito. J. M. OLENOV (Bot. Arch., 1935, 37, 140— 149).—New strains produced by repeated irradiation of cultures show successive changes in the serological reactions of their proteins. A. G. P.

Permeability of Amæba proteus to water. S. O. MAST and C. FOWLER (J. Cell. Comp. Physiol., 1935, 16, 151—167).—Permeability data in Ringer's solution containing lactose are recorded. Permeability is not influenced by the thickness of the plasmagel, but is probably regulated by the plasma-lemma.

A. G. P.

Growth of Chilomonas paramecium in inorganic media. J. B. LOEFER and R. P. HALL (Science, 1935, 81, 486).—The strain used appeared incapable of synthesising protoplasm from  $NH_4$  and other inorg. salts. L. S. T.

Auxogenic action of vitamin- $B_1$  on a microorganism. W. H. SCHOPFER (Compt. rend., 1935, **200**, 1965—1967).—The effects of a no. of cryst. preps. of vitamin- $B_1$  on the growth of *Phycomyces* are practically identical, and confirm the essential character of  $-B_1$  for the synthesis of growth-substance by the organism. A. G. P.

Acid-producing power as a means of characterising strains of Aspergillus niger. G. VAS-SILIEV (Biochem. Z., 1935, 278, 226–234).—The production and accumulation of citric and gluconic acids by different strains of A. niger (on a medium containing sugar) is specifically influenced by 0.01%ZnSO<sub>4</sub>, which restricts these activities in some cases, but stimulates them in others. ZnSO<sub>4</sub> also affects the respiration of the mould and its power to consume sugar. W. McC.

Formation of intermediate products in the growth of Aspergillus niger as a function of the age of the mycelium. R. BONNET and R. JACQUOT (Compt. rend., 1935, 200, 1968—1970).—Formation of  $H_2C_2O_4$  in cultures of A. niger increases with the age of the culture in media containing  $KNO_3$ , but none is formed in those containing  $NH_4$  salts.  $H_2C_2O_4$  is an unutilisable by-product, and its production is related to the maintenance of an appropriate energy balance in the culture. Citric acid is formed from spores and is subsequently utilised during the growth of mycelium. In older cultures autolysis of mycelium results in a further accumulation of citric acid in the medium. A. G. P.

Can excess of a metal correct insufficiency of potassium in the development of Aspergillus niger? C. PONTILLON (Compt. rend. Soc. Biol., 1935, 119, 349—350).—K can be replaced by Na, Mg, or Ca, but Fe and Al inhibit germination of the spores. R. N. C.

Thermochemical investigations of the energy balance during the growth of fungi. A. YAMA-MOTO and S. YAMAGATA (Acta Phytochim., 1935, 8, 245–254).—The formation of 1 g. of the substance  $C_{409}H_{717}O_{233}N_{46}$  of A. oryzæ from NH<sub>3</sub> and galactose is accompanied by evolution of 632.5 g.-cal. H. W.

Production of trimethylarsine by Penicillium brevicaule (Scopulariopsis brevicaulis). F. CHALLENGER and C. HIGGINBOTTOM (Biochem. J., 1935, 29, 1757-1778).-Bread cultures of P. brevicaule containing hydroxytrimethylarsonium nitrate (A., 1933, 266) or hydroxytri-n-propylarsine oxide (corresponding picrate) evolve AsMe3 and AsPra3, respectively; no odour of NMe3 is detected with NMe3CI.OH or NMe<sub>3</sub>O. Na arsenate affords AsMe<sub>3</sub> but no gaseous product giving a ppt. with 2:4-dinitrophenyl-hydrazine. Neither Na nor Ca  $\beta$ -hydroxyethylarsinate yields AsMe3. Addition of propionates or butyrates to cultures (normal or grown with  $EtCO_2Na$ or  $PrCO_2Na$  as sole source of C) containing  $As_2O_3$ yield always pure AsMe3, contrary to the theory of formation of methylarsinic acid from AcOH; also arsinoacetic acid affords only traces of AsMe3 (due to hydrolysis). With glycine or alanine, NH<sub>3</sub> but not betaine is formed in absence of As<sub>2</sub>O<sub>3</sub>, whilst in presence of  $As_2O_3$  the yield of  $AsMe_3$  is  $\Rightarrow$  normal. Yields of AsMe<sub>3</sub> with fructose, xylose, glycerol, etc. as source of C and with addition of MeOH, EtOH,  $HCO_2Na$ ,  $CH_2O$ ,  $(CH_2O)_3$ ,  $(CH_2)_6N_4$ , or Na formaldehydesulphoxylate are tabulated. Reactions between choline chloride or betaine and arsenite, selenite, and tellurite indicate the possibility of elimination of Me from methylated bases. No active enzyme prep. could be isolated from the mould. The data indicate a reducing action by *P. brevicaule* on As<sup>v</sup> derivatives; reduction of OH·CH<sub>2</sub>·PO<sub>3</sub>H<sub>2</sub> to a volatile phosphine or MePO<sub>3</sub>H<sub>2</sub>, however, could not be achieved. The bearing of the results on the mechanism of methylation by moulds is discussed.

F. O. H.

Biochemistry of micro-organisms. XLVI. *i*-Erythritol, a metabolic product of *Penicillium brevi-compactum*, Dierckx, and *P. cyclopium*, Westling. A. E. OXFORD and H. RAISTRICK (Biochem. J., 1935, 29, 1599—1601).—*i*-Erythritol (I) is isolated in small yields together with mannitol from the mycelium and the metabolism solution of *P. brevi-compactum* and *P. cyclopium* when grown on media containing glucose and tartaric acid, growth being stopped before all the sugar has disappeared. With *P. cyclopium* the presence of tartaric acid is not essential for its formation. (I) is present in the mycelium in the largest amounts in the earlier stages of growth, and may disappear from the mycelium before disappearing from the medium. P. W. C.

Protein synthesis by the genus Azotobacter. R. A. GREENE (Soil Sci., 1935, 39, 327–336).—Proteins occurring in the organisms were principally globulins, glutelins, and albumins. Arginine and lysine were the chief  $\rm NH_2$ -acids; tyrosine, tryptophan, cystine, and histidine were found in smaller amounts. Approx. 40% of the total N occurred in the non-basic fraction. A S-containing substance (possibly glutathione) was also detected. A close similarity is shown between the composition of A. vinelandii and A. agilis, and between A. chröococcum and A. Beijerinckii. A. G. P.

Formation of hydrogen from glucose and formic acid by "resting" B. coli. I. A. TASMAN and A. W. POT (Biochem. J., 1935, 29, 1749— 1756).—Differentiation between the formation of mol.  $H_2$  from glucose (by glucose hydrogenlyase) and from HCO<sub>2</sub>H (by formic hydrogenlyase) by "resting" B. coli could not be confirmed (cf. A., 1930, 251; 1932, 880; 1933, 1333). Production of  $H_2$  by growing and "resting" B. coli generally has HCO<sub>2</sub>H, and in a few cases AcCO<sub>2</sub>H, as an intermediary. F. O. H.

Volume increase of bacteria from X-ray irradiation. T. J. DIETZ (Radiology, 1935, 24, 31-38).—The increased vol. per normal bacterium  $(E. \ coli)$  following irradiation comprises an increased protoplasmic vol. due to stimulation and additional swelling caused by  $H_2O$  absorbed from the medium.

CH. ABS. (p)

Chemistry of the diphtheria bacillus. Fractional extraction of the lipins; separation of the hapten fraction; presence of soap in the bacterial cell. M. A. MACHEBGEUF and H. CAS-SAGNE (Compt. rend., 1935, 200, 1988—1990).—The hapten of the diphtheria bacillus closely resembles that of the tubercle bacillus. It occurs only in the P-rich fraction of the lipin sol. in COMe<sub>2</sub>. It is possibly free and not in the form of an antigenic protein complex. The MeOH extract of the diphtheria bacillus contains appreciable amounts of Na palmitate. A. G. P.

Purification of diphtheria toxoid. P. J. MOLONEY and M. D. ORR (Biochem. J., 1935, 29, 1525-1531).—The toxoid is pptd. from its crude solutions by FeCl<sub>3</sub> or COMe<sub>2</sub>, or by adsorption on FePO<sub>4</sub>. The yields (70-100%) and degrees of purification are the same for the three methods. J. N. A.

Purification and concentration of diphtheria toxin and anatoxin with sodium  $\beta$ -naphthylamine-3:6:8-trisulphonate. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 119, 518—520).—The toxin or anatoxin can be pptd. with the Na salt and citric acid at  $p_{\text{II}}$  4 and redissolved in physiological salt solution. H. G. R.

Serological analysis of the different lipoid fractions of BCG. E. CHARGAFF and W. SCHAEFER (Ann. Inst. Pasteur, 1935, 54, 708—714).—Only the phosphatide fraction of BCG shows antigenic activity in vitro and in vivo. It acts in a dose of 0.0003 mg. M. T.

Fluorescence of phthiocol, the pigment of the human tubercle bacillus. C. DHERE (Compt. rend. Soc. Biol., 1935, 119, 780—782).—Phthiocol is not fluorescente in the usual org. solvents, but shows a violet fluorescence in ultra-violet light, after treatment in  $Et_2O$  solution with aq.  $Na_2SO_4$ . The orange and red bands of the ultra-violet fluorescence spectrum of cultures of *B. tuberculosis* are not due to the presence of phthiocol. H. G. R.

Methylene-blue reduction by B. tuberculosis R and S. T. GUTHE (Compt. rend. Soc. Biol., 1935, 119, 694—697).—Methylene-blue is reduced by avian and mammalian strains of B. tuberculosis R and S. Reduction is more rapid with the mammalian than with the avian strains of the S variety. R. N. C.

Oxidation of amino-acids by resting Bacillus proteus. F. BERNHEIM, M. L. C. BERNHEIM, and M. D. WEBSTER (J. Biol. Chem., 1935, 110, 165-172).—At  $p_{\rm H}$  7.8 in presence of the resting bacillus, leucine, phenylalanine, and methionine are rapidly oxidised utilising 1 O per mol. Serine (I), alanine (II), and proline (III) utilise, respectively, 3, 4, and 7 0 per mol. Tyrosine and tryptophan (IV), which utilise, respectively, 2 and 3 0, are oxidised more slowly. Glycine is completely oxidised to  $CO_2$ ,  $H_2O$ , and  $NH_3$ , but valine (V), isoleucine (VI), hydroxyproline, and histidine are only very slowly oxidised. Except with (I) and (II), both forms of which are oxidised, only the naturally occurring optical isomerides are oxidised. In dl-mixtures non-natural isomerides of (V) and (VI) restrict the oxidation of the natural isomerides. The oxidations are completely inhibited by 0.005M-KCN. Except with (V) the extent of deamination corresponds with the O<sub>2</sub> uptake. Only (I)—(V) are decarboxylated. Methylene-blue, in the presence of the bacillus, is reduced by the acids at varying rates not correlated with the rates of O<sub>2</sub> uptake during oxidation.

W. McC.

Action of intestinal bacteria on æsculin-gelatin. L. JAME, R. CROSNIER, and F. MOREL (Compt. rend. Soc. Biol., 1935, 119, 849-850).—The blackening offects on an æsculin-gelatin medium by various intestinal bacteria are tabulated. H. G. R.

Fermentation of sugars by the group [Salmonella] pullorum-gallinarum. G. PACHECO and C. RODRIGUES (Compt. rend. Soc. Biol., 1935, 119, 889—890).—The group can be identified by differential fermentation reactions. H. G. R.

Physiology of the respiration of bacteria. II. Intracellular indophenol reaction of bacteria. S. YAMAGUTCHI (Acta Phytochim., 1935, 8, 263-284). -In normal cells respiration is due to the oxygenated cytochrome system, and in such cells the intracellar oxidation of the "Nadi" reagent in presence of indophenolase (I) is carried on by mol.  $O_2$  transferred by this system. In considering poisoning, the effect on (I) and the system must be considered separately. The "Nadi" oxidation of Micrococcus ochraceus and 4 Pseudomonas type is either not restricted or accelerated by 90% CO, which does not hamper the  $O_2$  respir-ation of these bacteria. The indophenol reaction occurs also without aid of the cytochrome oxidation. On the other hand, the indophenol reaction of B. mycoides, B. xylinum, B. subtilis, and B. mesentericus vulgatus, in which respiration is rendered possible by the cytochrome system, is hampered by CO, and the restriction is removed by irradiation, as is the case with respiration, so that the action of (I) is more or less dependent on the cytochrome-O. Indophenolase reaction is not observed with Escherichia, Proteus, and Staphylococcus types in which respiration is restricted by CO. The indophenol reaction of all bacteria examined is remarkably restricted by HCN; "Nadi" oxidation of M. ochraceus, the  $O_2$  respiration of which is resistant to HCN, is greatly hindered. Generally, HCN affects the indophenol reaction of bacteria at concn. so small that the respiration is unaltered. HCN exerts therefore a twofold action: the damaging of (I) and the restriction of cytochrome activity. No parallelism appears between the occurr-ence of cytochrome and (I) in bacteria. With the exceptions of B. mycoides and B. abortus equi (I) is not present in bacteria free from cytochrome-c. In all types of bacteria containing (I) the c-component of cytochrome is present, although in certain bases the "Nadi" reaction is not observed. H. W.

Bacterium tumefaciens, Smith and Townsend: biochemistry of two varieties of different pathogenicity. G. AMOUREUX (Ann. Inst. Pasteur, 1935, 54, 730—763).—The two species display some differences in their action on sugars,  $AcCO_2H$ , and peptone. They have similar actions on starch, *l*aspartic acid, asparagine, and urea. The action of *B. tumefaciens* on substrates containing sucrose is probably due to the enzymic action of invertase. There are probably four enzymes in *B. tumefaciens*, viz., dextrinase, amylase, invertase, and urease, all being endocellular. No action on ovalbumin and gelatin and no coagulation of milk or gelification of pectin could be demonstrated. M. T.

Mechanism of the acetic acid fermentation. A. JANKE and S. KROPACSY (Biochem. Z., 1935, 278, 37-59).—The oxidation of EtOH to AcOH by resting cultures of *B. ascendens* is followed using the authors' methods (see this vol., 1044). The further oxidation of AcOH to  $CO_2$ , supposed to take place with proliferating organisms, does not occur. Curves show the influence of  $p_{\rm H}$  on the  $O_2$ -utilisation curves. The dismutation process ceases as soon as a relatively small amount of acid has accumulated in the fermentation liquid. Very different  $p_{\rm H}$  optima are obtained for the two dehydrogenation processes on the one hand and for the dismutation process on the other. With the same suspension of organisms, the  $O_2$  utilisation for both dehydrogenation processes depends on the  $p_{\rm H}$  and on the age of the culture. The velocity of the dismutation process in acid solution is so small that in the technical AcOH process it can play no significant part. P. W. C.

Physiology of acetic bacteria. II. Oxidation of organic acids in presence of acetic bacteria. K. TANAKA (Acta Phytochim., 1935, 8, 285-313).-AcOH, (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, AcCO<sub>2</sub>H, malie (I) and fumaric acid (II) are degraded in presence of B. aceti with absorption of  $O_2$  and evolution of  $CO_2$ ; the quotients  $CO_2/O_2$  are in harmony with the vals. calc. for complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O.  $HCO_2H$ ,  $EtCO_2H$ ,  $H_2C_2O_4$ ,  $OH \cdot CH_2 \cdot CO_2H$ , glutaric, tartaric, and citric acids are unaffected. Max. activity of the bacteria is observed at  $p_{\rm H}$  5 with substrate concn. 0.03-0.1M. If any two of the above acids are present simultaneously, a summation effect with respect to absorption of  $O_2$  is never observed; the mechanism of degradation of the various acids is therefore closely similar. The oxidising power of the bacteria towards AcOH and  $(\cdot CH_2 \cdot CO_2 H)_2$  is most affected by rise in temp. and towards  $AcCO_2 H$  least. Aldehydrase is far more stable than alcohol-dehydrase and the activities can be separated by this means. In the dehydrogen-ation of these acids the bacteria cannot utilise benzoquinone or methylene-blue as H acceptor. Addition of PhMe greatly retards the dehydrogenation of acids; the activity of the bacteria towards (I) and (II) is restored by thorough washing, but towards other acids is mostly or completely lost.  $CH_2I \cdot CO_2H$  at very low concn. restricts the absorption of  $O_2$ . All aerobic oxidations except that of AcCO<sub>2</sub>H are greatly retarded by minute amounts of HCN. CO also restricts oxidation; prevention of this inhibition by light is somewhat indistinctly observed. The powerful inhibitory action of benzoquinone is irreversible.

H. W. Bacterial metabolism. I. Reduction of propaldehyde and propionic acid by Clostridium acetobutylicum. K. C. BLANCHARD and J. MAC-DONALD (J. Biol. Chem., 1935, 110, 145—150). Since fermenting cultures of the bacteria convert EtCHO and EtCO<sub>2</sub>H into  $Pr^{\alpha}OH$  (EtCO<sub>2</sub>H first into EtCHO) without accompanying production of any other end-products (e.g., aldols or their transformation products) not normally produced by the bacteria in the fermentation of carbohydrates, it is improbable that intermediate production of aldol occurs during the production of  $Pr^{\alpha}CO_{2}H$  and  $Bu^{\alpha}OH$  from carbohydrates by these bacteria. W. McC.

Activator of the metabolism of Bacterium propionicum. P. CHAISE and C. FROMAGEOT (Bull. Soc. Chim. biol., 1935, 17, 874—892; cf. A., 1934, 330).—The accelerating action of potato extract on the growth of *B. propionicum* (I) on a boiled maize medium containing glucose is confirmed using a conc. prep. of potato extract made by treatment with  $Hg(OAc)_2$  in aq.  $Na_2CO_3$  and  $H_2S$ . When lactic acid is substituted for glucose in the medium no activation occurs. Determinations of the amount of fermentation taking place with small quantities of (I) indicate that with glucose as substrate there is a threshold for the amount of (I) below which no growth takes place in the absence of the activator. By the action of the activator the threshold is lowered. With lactic acid as substrate the phenomenon is not so marked. A. L.

Behaviour of bacteria and infectious lysin in the ultra-violet spectrum. C. HALLAUER (Z. Hyg. Infektionskrankh., 1935, 117, 18—25).—Lysins agree approx. with the organisms that produce them with regard to resistance to ultra-violet radiations, formation of max. of sensitivity, and the spectral range of radio-sensitivity. R. N. C.

Ultrafiltration of the virus of vesicular stomatitis. J. H. BAUER and H. R. Cox (Proc. Soc. Exp. Biol. Mcd., 1935, 32, 567—570).—The filtration endpoint of the virus is independent of the source or serological type, and is approx. 140 m $\mu$ . R. N. C.

Formation of the Forssman antigen by a strain of *B. dysenteriæ*, Shiga, in different nutrients. M. EISLER and A. HOWARD (Z. Hyg. Infektionskrankh., 1935, **117**, 56—65).—The antigen is not produced when *B. dysenteriæ*, Shiga, *L* is grown in media containing asparagine, leucine, and cystine as N source, and lactate, mannitol, and glycerol as C source. The agglutinability is fundamentally altered. If glycyl-glycine or -leucine is added, these effects do not occur. This behaviour is sp. for the *L* strain.

R. N. C.

Paradoxical relation between  $\zeta$ -potential and suspension stability in S and R variants of intestinal bacteria. E. W. JOFFE and S. MUDD (J. Gen. Physiol., 1935, 18, 599-613).—Determinations of electrokinetic potentials and suspension stability of 4 strains of non-flagellate intestinal bacteria indicate that the S (smooth) variants have  $\zeta$ -potentials of approx. zero over a wide range of  $p_{\rm H}$ and electrolyte concn., yet form stable suspensions by virtue of hydrophobic constituents. R (rough) variants have potentials varying with  $p_{\rm H}$  and electrolyte concn. in the normal way, whilst the vals. of potential are crit. for suspension stability.

F. O. H.

Physico-chemical difference in antibodies against S and R variants of a single bacterial strain. E. W. JOFFE (J. Gen. Physiol., 1935, 18, 615-625).—The antibodies against R and S variants of B. typhosum, when studied as deposits on maximally sensitised bacterial surface, differ in isoelectric point and  $\zeta$ -potential. With increasing time of immunisation (rabbit), the isoelectric point moves to the alkaline side, but the agglutination titre does not change in a parallel manner. Rabbits immunised with single cell strains of R slowly develop antibodies for S and vice versa. F. O. H. Bactericidal substances of human serum, particularly in fever. F. WULFF (Compt. rend. Soc. Biol., 1935, 119, 424-426).—Some properties of the anti-typhoid and anti-meningococcal substances of febrile serum are described. R. N. C.

Action of gastric juice on typhoid bacilli. K. TODOROVITCH (Compt. rend. Soc. Biol., 1935, 119, 638-639).—The resistance of the bacilli to gastric juice falls as total acidity increases. R. N. C.

Antagonistic action of sterile broth extract of *B. prodigiosus*. M. EISLER and I. JACOBSOHN (Z. Hyg. Infektionskrankh., 1935, 117, 76-91).—A thermostable substance that inhibits growth of diphtheria bacilli, gonococci, and certain other types is present in sterilised broth in which *B. prodigiosus* has been grown. Its action is associated with its adsorption on the bacilli and is > that of pyocyanase. R. N. C.

Resistance to drugs and chemical tolerance of trypanosomes. E. SINGER and V. FISCHL (Z. Hyg. Infektionskrankh., 1935, 116, 683—687).—Strains of T. nagana exposed temporarily to non-trypanocidal atebrin or rivanol afterwards absorb considerably more of these drugs than untreated strains; hence chemical tolerance is fundamentally different from resistivity to drugs. Spontaneously resistant T. lewisi is not affected either positively or negatively by solu-salvarsan. R. N. C.

Chemotherapy of rat trypanosomiasis. V. FISCHL and E. SINGER (Z. Hyg. Infektionskrankh., 1935, 116, 652—659).—Many arsenicals and other substances, including normal and syphilitic human serum, were without therapeutic effect on rats infected with T. lewisi. Storage and activity were parallel only in the case of arsenicals, Au compounds being stored in considerable quantities in spite of their inactivity.

R. N. C.

Antagonism of the actions of chemotherapeutic agents. II. A. HASSKÓ (Z. Hyg. Infektionskrankh., 1935, 116, 669—671).—Me- and Et-violet and pyocyanine reduce the absorptivity for trypaflavin of the flagellæ of T. nagana in rats. Brilliant-green exerts the same effect through its high toxicity when injected intraperitoneally, but not subcutaneously. Trypanred and -blue are both absorbed by trypanosomes, and reduce absorptivity to a min. There is no great difference between the dye contents of the parasites and the serum. R. N. C.

Mode of action of chemotherapeutic agents. I. A. HASSKÓ (Z. Hyg. Infektionskrankh., 1935, 116, 660—668).—Inoculation into normal mice of trypanosomes treated with trypaflavin or neosalvarsan (I) results in a retarded increase of trypanosomes; the retardation  $\infty$  the quantity, therapeutic index, and time of action of the drug, which affects the vitality of the flagellates. Their disappearance from the bloodstream inversely  $\infty$  the dye content. Parafuchsin has scarcely any effect on trypanosomes. (I) cannot be detected in them, the active agent being formed from (I) by the animal body. The therapeutic effect of tartar emetic is reduced by exclusion of reticuloendothelial cells. R. N. C. Action of alkaloids on pure cultures of *B.* radicicola. G. MEZZADROLI and L. SGARZI (Atti R. Accad. Lincei, 1935, [vi], 21, 105–110).—With liquid cultures (containing glucose,  $K_2HPO_4$ , and  $KNO_3$ ) of *B. radicicola*, caffeine increases growth in concns. of 0.005–0.025%, depresses it at 0.11%, and is toxic at 0.15%. Quinine and, to a greater extent, strychnine give corresponding lower vals. The effects are less marked in solid (agar) nutrients. F. O. H.

Effect of dyes on colonies of certain pathogenic fungi. III. J. W. WILLIAMS and L. GREEN (Proc. Soc. Exp. Biol. Med., 1935, 32, 625-628).—The effects of certain dyes on a no. of fungi are given. In general, growth is more profuse and more frequently coloured on acid than on basic dyes.

R. N. C.

Bactericidal and sterilising powers of aminobenzoic esters. A. MOREL, A. ROCHAIN, and H. DELABORDE (Compt. rend. Soc. Biol., 1935, 119, 612-615).—The bactericidal and sterilising powers of a no. of aminobenzoic esters on different organisms are given. They are < those of vegetable essences. They are not very different from those of the corresponding hydroxybenzoic esters. Sterilising power is not affected by the position of the NH<sub>2</sub>; it is reduced by introduction of Me, but increased by Bu, in the NH<sub>2</sub>. R. N. C.

Bactericidal and fungicidal action of homologous halogenophenol derivatives and its "quasi-specific " character. II. Derivatives of o-chlorophenol. Chlorine-free alkylphenol derivatives. E. KLARMAN, V. A. SHTERNOV, and L. W. GATES (J. Lab. Clin. Med., 1934, 20, 40-47; cf. A., 1934, 68) .- Aliphatic and aromatic derivatives of  $o - C_6 H_4 Cl \cdot OH$  (I) show similar relationships between mol. wt. and bactericidal and fungicidal properties, as do corresponding p-derivatives of p- $C_6H_4Cl$ ·OH, although their action is less effective. Higher homologues of (I) and the p-alkyl derivatives of PhOH (Cl-free) have a selective or "quasi-sp." action on Gram-positive organisms. The microbiological potency increases, and toxicity to animals decreases, with increasing mol. wt. of the substituting radical. Introduction of Cl into the nucleus of palkylphenols decreases their toxicity. CH. Abs. (p)

Stimulatory and inhibitory effects of silver and formaldehyde on bacterial growth: growth curves. W. OETTEL (Arch. Hyg. Bakt., 1934, 113, 71-91; Chem. Zentr., 1935, i, 424).—In sub-lethal concess. solutions of colloidal Ag and of  $CH_2O$  produce periodically alternating stimulatory and inhibitory effects on the growth of *B. coli* and of staphylococci. The nature and extent of these effects vary with the conce. of antiseptic applied. A. G. P.

Sterilisation of hydatic sand by formolised and by iodised solutions. F. DEVE (Compt. rend. Soc. Biol., 1935, 119, 352–354).—Hydatic gravel is sterilised by 1% aq. CH<sub>2</sub>O, by Lugol's I solution, whether freshly prepared or after 4 months' storage, and by 0.1% I in EtOH. R. N. C.

Culture of micro-organisms on Cellophane membranes. T. R. BHASKARAN, M. SREENIVASAYA, and V. SUBRAHMANYAN (Current Sci., 1935, 3, 484).— Cellophane, closely applied to the surface of a culture medium, permits the ready growth of bacteria, which are thereby obtained free from the solid constituents of the medium. J. L. D.

Adrenal cortex and resorption of fat. F. VERZAR and L. LASZT (Biochem. Z., 1935, 278, 396— 400; cf. this vol., 524).—In rats, the inability to resorb fats caused by extirpation of the adrenals is counteracted (up to 77% of administered olive oil resorbed) by subcutaneous injection of the hormone ("eucortone") of the adrenal cortex. Adrenaline and/or ascorbic acid have no such effect. The hormone acts by controlling phosphorylations.

W. McC.

Variations of blood-sugar in the course of continuous intravenous injection of adrenaline. J. MALMEJAC and V. DONNET (Compt. rend. Soc. Biol., 1935, 119, 734-736).—Continuous intravenous injection of adrenaline (I) at the rate of 0.05 mg. per kg. per hr. in dogs produces an increase of bloodsugar, which reaches its max. in  $\frac{1}{2}$  hr., and then returns to normal. This fall is due to increased secretion of insulin and to suppression of (I) secretion. R. N. C.

Blood-vessels, blood-pressure, and adrenaline. D. P. ORAHOVATS and T. GOTSER (Pflüger's Archiv, 1935, 235, 367—376).—Adrenaline (I) produces a vaso-dilatation of the intestinal blood-vessels in the dog more often than a vaso-constriction, whilst the effect on the vessels of the extremities varies. (I) injected into the mesenteric artery causes contraction of the blood-vessels. The effects are independent of the quantity of (I) injected, and are not affected by  $p_{\rm H}$  changes, spinal or vagal section, atropine, asphyxia, or hyperventilation. R. N. C.

Effect of adrenaline on the metabolism of isolated muscle. D. NACHMANSOHN, J. WAJZER, and R. LIPPMANN (Compt. rend., 1935, 200, 1981— 1982).—The action of adrenaline on the energy metabolism of muscle consists only of a sp. acceleration of lactic acid production. A. G. P.

Hypoglycæmia provoked by insulin before and after nephrectomy. E. GAUJOUX, M. RECORDIER, and M. ANDRAC (Compt. rend. Soc. Biol., 1935, 119, 745—746).—The max. fall in blood-sugar provoked by insulin in rabbits varies after nephrectomy; in some cases after double nephrectomy it is < after single nephrectomy. Blood-sugar remains low for a longer period in nephrectomised rabbits. R. N. C.

Effect of the state of the kidney on the activity of insulin. E. GAUJOUX, M. RECORDIER, and M. ANDRAC (Compt. rend. Soc. Biol., 1935, 119, 747— 748).—The max. fall of blood-sugar provoked by insulin is independent of blood-N. R. N. C.

Can glycogen accumulate in the liver of a totally depancreatised dog under the influence of an insulin deprived of vagotonising action ? L. HÉDON and A. LOUBATIERES (Compt. rend. Soc. Biol., 1935, 119, 358-360).—Vagotonin-free insulin provokes glycogen deposition similarly to the commercial product. R. N. C.

Pituitary growth-hormone and glutathione concentration : does the hormone influence the

concentration concurrently with the stimulation of increase in weight? P. W. GREGORY and H. Goss (J. Exp. Zoöl., 1934, 69, 13-35).—The livers and muscles of rats killed after a period of growth induced by anterior pituitary injections show an increased content of I-reducing substances. This is not due to ascorbic acid, which remains the same as in controls. It is attributed to an increase of glutathione compounds during the induced growth.

## NUTR. ABS. (b)

Effects of antuitrin-S and pituitary extract on the armadillo ovary. G. W. D. HAMLETT (Anat. Rec., 1935, 62, 201—207).—Human pregnancy urine extract and whole pituitary extract stimulate cystic and luteinised follicle production, and in some cases corpus luteum formation. The urine extract, but not the pituitary extract, causes resorption of the unimplanted blastocyst. R. N. C.

Concentration of the antidiuretic factor of the anterior lobe of the pituitary. H. R. DOWNES and L. RICHARDS (J. Biol. Chem., 1935, 110, 81— 90).—Dried pituitary gland is extracted with aq. AcOH and the antidiuretic factor is separated from the extract by dialysis; impurities are removed from the dialysate by pptn. with  $COMe_2$ . Biological assays indicate that the treatment removes vasopressin, most of the oxytocin, thyrotropin, intermedin, and the gonad-stimulating hormone. The antidiuretic factor occurs chiefly in the posterior lobe and the pars intermedia. H. D.

Effect of the thyrotropic hormone on carbohydrate metabolism. V. Jonáš (Z. ges. exp. Med., 1934, 94, 495-503).-Repeated injection of thyrotropic hormone (I) had no effect on the fasting bloodsugar (II) of healthy subjects or patients with Graves' disease, but caused a higher and more prolonged curve after the ingestion of glucose, usually with glycosuria. In two cases of Graves' disease with disturbances of carbohydrate metabolism these became more marked. In a patient with myxœdema (II) rose and approached normal; the alteration in carbohydrate metabolism, which resembled that occurring in Graves' disease, generally occurred later than the increase in basal metabolism. In one patient with Graves' disease, who showed galactosuria after galactose, administration of (I) caused a higher and more prolonged (II) curve and a greater degree of galactosuria. The disturbances in carbohydrate metabolism occurring in Graves' disease are directly related to altered NUTR. ABS. (m) thyroid function.

Seasonal changes in the thyroid gland of the thirteen-lined ground-squirrel (*Citellus tridecemlineatus*) with particular reference to its sexual cycle. M. ZALESKY (Anat. Rec., 1935, 62, 109–137).—Thyroid activity falls during hibernation, but can be stimulated to levels > the summer level by anterior pituitary extract. In the female the max. activity coincides with pregnancy and lactation. Activity is not affected by castration, sex hormones, or pregnancy urine extracts. R. N. C.

Action of thyroid secretion on the variations of the chromic residual index of the bloodplasma. M. POLONOVSKI, H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 119, 585—586).—Thyroxine reduces the index in cases of diabetes and cancer when this is initially high, but does not affect it when it is initially normal or low. R. N. C.

Diuresis of hyperthyroidism. A. S. DIX, J. M. ROGOFF, and B. O. BARNES (Proc. Soc. Exp. Biol. Med., 1935, 32, 616-618).—Thyroid administration produces diuresis in normal, but not in depancreatised, dogs, although it increases the metabolic rate in the latter. R. N. C.

Gonadotropic hormones from various organs. S. SZARKA (Orvosi Hetilap, 1934, 78, 1009–1012).— Luteocrescin (I) differs in biological action from gonadotropic hormones from urine or anterior pituitary. The luteinising and ovary-stimulating effect of (I) is much > that of hormones from the named sources. CH. ABS. (p)

Differential effect of some gonadotropic substances on development of cyclic sex characteristics in the English sparrow. E. WITSCHI and W. N. KECK (Proc. Soc. Exp. Biol. Med., 1935, 32, 598-603).—The hormone of the pituitary, but not that of pregnancy urine, accelerates the development of the sex glands. R. N. C.

Colour reaction of the sex hormones and its application to colorimetric determination. W. ZIMMERMANN (Z. physiol. Chem., 1935, 233, 257— 264).—Alkaline m-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> gives a coloration with the ·CO·CH<sub>2</sub>· group. It detects androsterone, follicular hormone, luteosterone, and pregnandione in amounts of 0.01, 0.02, 0.05, and 0.025 mg., respectively, and may be used for the determination of these hormones. J. H. B.

Constitution of equol. G. F. MARRIAN and D. BEALL (Biochem. J., 1935, 29, 1586–1588).—Equol (A., 1932, 1156) is isolated from the Et<sub>2</sub>O-sol. phenolic fraction of the PhMe extract of urine of both pregnant and non-pregnant mares and stallions by crystallisation from CHCl<sub>3</sub>. The yields varied seasonally, becoming zero in winter. Mild KOH fusion yielded 2:4- $(OH)_2C_6H_3$ ·CO<sub>2</sub>H, resorcinol (I), and a trihydric phenol which gave a Me<sub>2</sub> ether with CH<sub>2</sub>N<sub>2</sub>. More vigorous fusion gave (I), p-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, and p-C<sub>6</sub>H<sub>4</sub>Et·OH. On the basis of these facts three formulæ are suggested for the constitution of equol: 7-hydroxy-2-, 7-hydroxy-3-(4'-hydroxyphenyl)-chroman, and 6-hydroxy-2-(4'-hydroxybenzyl)-coumaran. H. D.

Presence of testicle hormones in the blood. L. PTASZEK (Soc. biol. Lwow, 1933, May 8th).— Resection of the vas deferens causes an increase in the male sexual hormone in blood. CH. ABS. (p)

Male hormone. VI. Male hormone from boar testes. New crystalline male hormone. VII. Test of the male hormone by measurement of increase in weight of seminal vesicles of castrated rats. New rat unit. A. OGATA and S. HIRANO (J. Pharm. Soc. Japan, 1934, 54, 1010– 1019).—VI. The cryst. hormone, m.p. 129–130°, is N-free and more active than other testicular preps. Its activity is not destroyed by boiling with KOH-EtOH.

VII. A new technique is described. CH. ABS. (p)

Quantitative studies on the response of the capon's comb to androsterone. A. W. GREEN-WOOD, J. S. S. BLYTH, and R. K. CALLOW (Biochem. J., 1935, 29, 1400-1413).-For the study of the response of the comb of the brown Leghorn capon to cryst. androsterone (I), groups of five kinds of similar initial comb-size and body-wt. are used and the technique of comb measurement is carefully standardised. Daily injections are made for 5 days and the response is measured in terms of increase of max. length + height of comb. The response  $\infty$ the log of the dose between the limits of 0.5 and 8 mg. The results, which imply a standard error of about  $\pm 18\%$  in the determination of the dose, are considered in relation to the formulation of a technique for the assay of male hormone. The amount and nature of the solvent influence the response, the latter being the same for groups of birds of different ages (4 months to 6 years) and for both subcutaneous and intramuscular injection. As a precautionary measure, birds should not be used earlier than 12 months after castration. No relationship was detected between body-wt. and comb response. Birds should not be used for a new series of doses until 1 month after the previous doses. The activity of (I) is unaffected by heating the solution in arachis oil at 150° for 24 hr.

P. W. C.

Growth and maintenance of the fowl's comb by administration of androsterone. R. K. CALLOW and A. S. PARKES (Biochem. J., 1935, 29, 1414-1423).--Very rapid growth of the combs of capons with complete restoration to normal size in the course of a few weeks can be induced by injections of cryst. androsterone (I) in doses of the order of 2.5-5 mg. daily. The comb can be maintained at the normal level by daily doses of 1 mg. of (I). This requirement is not inconsistent with the view that secretion of (I) accounts for the whole androkinetic activity of the testes of the cock. Observations are made also on the restoration of the vas deferens. The comb of the Leghorn capon is several times more sensitive to (I) than is that of the Plymouth Rock capon. The comb of the hen is much less responsive than is that of the capon. P. Ŵ. C.

Effect of androsterone and of male hormone concentrates on the accessory reproductive organs of castrated rats, mice, and guinea-pigs. R. K. CALLOW and R. DEANESLY (Biochem. J., 1935, 29, 1424-1445).-Androsterone (I) is injected into groups of adult rats for 14 days, beginning on the day of castration. 1 mg. daily maintained the growth and normal structure in the prostate of 140-160g. rats, but > 2 mg. daily were required for maintenance of seminal vesicles. Larger rats receiving 3 mg. (I) had prostate larger than and seminal vesicles of normal size. With mice 1-2 mg. daily of (I) failed to maintain completely the seminal vesicles or the cranial lobes of the prostate. A comparison of different urine concentrates showed that in two urines the effect per capon unit on the accessory glands of rats is much the same as that produced per capon unit of cryst. (I), whilst in a third urine, the activity on rats was 3-4 times as great. The activity of the most effective urine concentrate cannot be reproduced by combined administration of œstrone and (I), which gave results little if any better than (I) alone. Some urine concentrates may contain a male hormone other than (I) with much greater activity on the accessory glands of mammals. P. W. C.

Crystalline male hormone from testes (testosterone), more active than androsterone prepared from urine or from cholesterol. K. DAVID, E. DINGEMANSE, J. FREUD, and E. LAQUEUR (Z. physiol. Chem., 1935, 233, 281-282).—A hormone from testis extract, testosterone (I), m.p. 154-154.5°,  $[\alpha]_{\rm D}$  +109° in EtOH, has an activity of 1 capon unit in 10<sup>-5</sup> g. An activator present in inactive testis extract or urine is necessary to enable (I) to exert its full growth-promoting power on the seminal vesicles of the infantile castrated rat. J. H. B.

Androsterone. IV. Degradation of stigmasterol to isoandrosterone and androstanedione. Relationship between hormone of the corpus luteum, allopregnanolone, and androsterone. A. BUTENANDT and H. COBLER. V. Androstanediol, a physiologically active reduction product of androsterone. A. BUTENANDT and K. TSCHERN-ING (Z. physiol. Chem., 1935, 234, 218-223, 224-234).—IV. alloPregnanolone (1 g. from 17 g. of stigmasterol) with MeMgI gives a carbinol (I),  $C_{22}H_{38}O_{2}$ .m.p.182-186°, which loses  $H_2O$  when heated with AcOH and  $Ac_2O$ , giving the acctate (II), m.p. 144°, of the unsaturated alcohol,  $C_{22}H_{36}O$ , and an isomeride, m.p. 111-112°. A second isomeride, m.p.  $64\cdot0-64\cdot5^{\circ}$ , is obtained from the mother-liquors of (I) by acetylation. Oxidation of (II) with  $O_3$  gives the acetate, m.p. 96-97°, of isoandrosterone (III) (3-hydroxyætioallocholanone-17), which differs from androsterone (IV) only in the spatial position of the OH. (III), like (IV), yields androstanedione on oxidation with CrO<sub>3</sub>.

V. Reduction of (IV) with Na and Pr<sup> $\circ$ </sup>OH gives a mixture of which the chief constituent is androstanediol (V), m.p. 221°,  $[\alpha]_{22}^{32}$  +12.6° [diacetate (VI) m.p. 159—160°]. (V) and (VI), which are identical with the corresponding substances described by Ruzicka *et al.* (this vol., 346), are about three times as active as (IV), the effects of (VI) being more protracted and its max, effect being attained later.

W. McC.

Use of albino rats for assay of the male sex hormone. Y. WANG and H. WU (Chinese J. Physiol., 1935, 9, 149—163).—The rats are castrated at 4 weeks and given 2 daily injections at 8 weeks; 48 hr. later the preputial glands are dissected and weighed. 1 rat unit corresponds with a 50% increase in wt. over that of the control. The effect of the same amount of hormone in 2 daily injections is > that of a single injection. H. G. R.

Chemistry of œstrogenic substances. E. FRIEDMANN (Nature, 1935, 135, 622-623).—A discussion of the mol. structures which give rise to œstrogenic activity. It is claimed that benzylideneand (to a greater extent) furfurylidene-pyruvic acid are active.

Chemistry of œstrogenic substances. J. W. COOK and E. C. DODDS (Nature, 1935, 135, 793, 959).—Friedmann's views (see above) are criticised. No œstrogenic activity of benzylidene- or furfurylidene-pyruvic acid or their Na salts could be detected when injected in amounts of 100 mg. per rat.

L. S. T.

Effect of progynon on regeneration of erythrocytes. T. MINOUCHI and H. SCHWALM (Klin. Woch., 1934, 13, 1565—1568; Chem. Zentr., 1935, i, 586).— Progynon (I) has only a slight effect on the red-cell count in normal or castrated female rabbits. After venesection in normal animals, (I) increases the reticulocyte count; the effect does not appear in castrated animals. R. N. C.

Does folliculin provoke the interruption of gestation by arrest of the function of the corpus luteum? S. SKOWRON and A. PERAUS (Compt. rend. Soc. Biol., 1935, 119, 772—774).—The abortive action of folliculin in rabbits is not related to arrest and regression of the corpus luteum, and is not checked by progestin. R. N. C.

Action of ovarian hormone on lachrymal elimination of sodium chloride. D. MICHAIL and P. VANCEA (Compt. rend. Soc. Biol., 1935, 119, 447).— Lachrymal NaCl is increased by injection of ovarian hormone, reaching its max. 1 hr. after injection. The effect is the same in both sexes. R. N. C.

Colorimetric determination of œstrin in the urine of non-pregnant women. G. F. MARRIAN and S. L. COHEN (Nature, 1935, 135, 1072).—The method described for pregnancy urine (A., 1934, 1269) is of little val. for the determination of the much smaller amounts of œstrin present in the urine of non-pregnant women. L. S. T.

Hydrolysis of combined forms of æstrone and æstriol in human pregnancy urine. S. L. COHEN and G. F. MARRIAN (Biochem. J., 1935, 29, 1577— 1585).—The optimum conditions for the hydrolysis of human pregnancy urine previous to the determination of æstrone (I) and æstriol (II) (A., 1934, 1269) are a [H<sup>-</sup>] such that the final  $p_{\rm H} < 1$ , and autoclaving at 120° for 2 hr. Destruction of both (I) and (II) occurs on heating in alkaline or acid solution in presence of O<sub>2</sub>. Heating urine with alkali causes only about 50% hydrolysis; subsequent treatment with HCl completes the process. H. D.

New agent produced from urine of pregnant women and its biological effects. J. BAUMANN (Orvosi Hetilap, 1934, 78, 1138—1141).—The new substance affects the ovaries of mature but not of infantile rats, and differs from the cestrus hormone and from gonadotropic agents. CH. ABS. (p)

"Anti-hormones." T. MARTINS (Compt. rend. Soc. Biol., 1935, 119, 753-755).—Theoretical.

R. N. C.

Relations between hormones and vitamins. Mechanism of the action of the antirachitic vitamin in the organism with reference to the physio-pathology of the thymus. M. MESSINI and M. COPPO (Arch. Ist. Biochim. Ital., 1935, 8, 195—232).—The toxic action of vitamin-D (I) in thymectomised rabbits is < in normal rabbits; blood-Ca is not increased, nor bone decalcification compensated by (I), and calcification of fractures is not affected as in parathyroidectomised animals. (I) increases bone Ca and ash, but scarcely affects P,  $H_2O$ , and dry residue. The action of (I) on the normal calcification process is obstructed in thymectomised animals by the acid reaction, which prevents its catalysis of the formation of the Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-saline complex. A sp. thymus function, possibly hormonal, is hence probably involved in the regulation of the action of (I) on Ca. R. N. C.

Rôle of vitamin-A in nutrition. М. В. RICHARDS (Brit. Med. J., 1935, 1, 99—102).—А review. Сн. Авѕ. (p)

Vitamin-A and cholesterol metabolism. J. A. COLAZZO, I. TORRES, and SANCHEZ-RODRIGUEZ (Klin. Woch., 1934, 13, 1678—1682; Chem. Zentr., 1935, i, 429).—The level of cholesterol in serum and organs of rats was considerably lowered in avitaminosis-A and increased (especially in the central nervous system) in hypervitaminosis-A. A. G. P.

Effect of vitamin-A on the serum-cholesterol in man. F. LASCH (Klin. Woch., 1934, 13, 1534— 1536; Chem. Zentr., 1935, i, 429).—Increased serum-cholesterol following administration of vitamin-A is primarily due to the increased proportion of cholestervl esters. A. G. P.

Influence exerted by the nervous system on the vitamin-A content of the blood. A. CHEVAL-LIER, J. MALMEJAC, and Y. CHORON (Compt. rend. Soc. Biol., 1935, 119, 739-740).—Blood-vitamin-A is increased by excitation of the central ending of the pneumogastric, and of the peripheral ending of the splanchnic. R. N. C.

Chemical composition of the white rat during the course of avitaminosis-A. L. EMERIQUE (Bull. Soc. Chim. biol., 1935, 17, 612—619).—The tissues of white rats undergoing progressive avitaminosis-A show first a deficiency in the protoplasmic constituents, then in the reserve fatty matter, and finally, when the avitaminosis has reached an advanced state, in the calcification of the bones. Under normal conditions there may therefore be an equilibrium between vitamin-A and -D. A. L.

Discrepancy between biological assays and other methods of determining vitamin-A. I. R.S. MORGAN, J. R. EDISBURY, and R. A. MORTON (Biochem. J., 1935, 29, 1645-1660).-Biological assays for vitamin-A (I), Lovibond blue vals., and spectroscopic estimates of the % of (I)  $(C_{20}H_{29} OH)$  present are given for 22 oils and concentrates covering a range of potency of 530-1,290,000 international units per g., and the results are examined statistically. Accepting the characteristics of the rich Carr and Jewell concentrate as those of the pure (I), the assays are extrapolated to pure (I) and give vals. varying from 1.23 to  $3.38(\times 10^6)$  units per g. (mean 1.77) when calc. from the blue vals. and from 1.08 to  $2.9(\times 10^6)$ units per g. (mean 1.73) calc. from the spectroscopic estimates. This variation is > can be accounted for by the known error of the assays. Generally the highest vals. are given by cod-liver oils of medicinal grade. Accepting the unit of (I) as the activity of  $0.6 \times 10^{-6}$  g. of  $\beta$ -carotene (II), it is calc. that if (II) is efficiently converted into (I) at the levels of dosage used in the assays, the potency of pure (I) would be  $1.56 \times 10^6$  units per g. Vals. < this might be accounted for by the presence of biologically inactive material showing selective absorption and chromogenic power, whilst vals. significantly higher suggest the existence of a biologically active material without selective absorption or chromogenic power, or with these characteristics much weaker than in (I).

P. W. C.

Modification of Sherman and Smith's vitamin-A-deficient ration for rats. H. C. Hou (Chinese J. Physiol., 1935, 9, 197—205).—By substituting soya-bean protein for casein, a shorter depletion period and a better wt. increase were observed. Substitution of potato- for corn-starch gave the shortest depletion period and the best wt. increase. H. G. R.

Syntheses in the vitamin-A field.—See this vol., 978, 979, 983.

Effect of type of carbohydrate on vitamin-B synthesis in the digestive tract of the rat. N. B. GUERRANT, R. A. DUTCHER, and L. F. TOMEY (J. Biol. Chem., 1935, 110, 233—243).—The vitiating effect of coprophagy on vitamin-B (I) assay is most serious when the experimental diet contains dextrinised maize-starch (II) as the source of carbohydrate. Animals fed on such a diet have an unusually large cæcum, which contains an enormous no. of live yeast cells and incompletely digested (II). It is suggested that under these conditions (I) is synthesised, and coprophagy enables animals fed on a (I)-free diet to maintain their normal growth curve. E. A. H. R.

Relationship between nutrition and the enzymic activity of the blood-serum. K. ARIMOTO (Sei-i-kwai Med. J., 1933, 52, No. 10, 103—107).— Feeding albino rats with excess of vitamin-*B* causes no appreciable increase in blood-amylase (I) unless excess of carbohydrate is also supplied, when (I) decreases. CH. ABS. (p)

Vitamin- $B_1$  content of foods. A. Z. BAKER and M. D. WRIGHT (Biochem. J., 1935, 29, 1802—1807).— The trustworthiness of the cure of bradycardia as a method of determining vitamin- $B_1$  (A., 1934, 705) is confirmed. The contents (in international units) of various foods thus determined are tabulated.

F. O. H. Crystalline vitamin- $B_1$ . VII. Relation to pathological states. R. R. WILLIAMS, R. E. WATERMAN, and J. C. KERESZTESY (Science, 1935, 81, 535-536).—The antineuritic activity of the crystals towards human beri-beri has been confirmed. Rats fed on a vitamin- $B_1$ -free diet show complete freedom from polyneuritis with only  $1-2 \times 10^6$  g. of the crystals per day, but growth is slight. Marked insufficiency of  $B_1$  may be possible without manifestations of polyneuritis. L. S. T.

**Tissue respiration in avitaminosis-B**<sub>1</sub>. H.G.K. WESTENBRINK (Arch. neerl. Physiol., 1935, **20**, 175– 176).—A reply to Abderhalden and Wertheimer (cf. this vol., 669). R. N. C.

Crystalline vitamin-B<sub>1</sub>. VIII. Sulphite cleavage. II. Acidic product. R. R. WILLIAMS, E. R. BUCHMAN, and A. E. RUEHLE (J. Amer. Chem. 3 z

Soc., 1935, 57, 1093-1095; cf. this vol., 668).-The "aminosulphonic acid" (I), C<sub>6</sub>H<sub>9</sub>O<sub>3</sub>N<sub>3</sub>S, obtained from vitamin- $B_1$ , is probably a 6-aminopyrimidine. It chars slowly > 400°, melts > 440°, is sol. in dil. alkali or NH<sub>3</sub>, conc. HNO<sub>3</sub>, or H<sub>2</sub>SO<sub>4</sub> (with which it does not react), has  $p_{\rm H}$  5·2 in saturated aq. solution, does not react with p-SO<sub>3</sub>H·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl (II), moist NaOH at 135°, NH<sub>3</sub>, or HCl at 100°, is pptd. by AgNO<sub>3</sub> at  $p_{\rm H}$  8.9 but not by phosphotungstic acid, gives much SO3" with NaOH at 185° and SO4" with H<sub>2</sub>O at 200°, and with conc. HCl at 150° gives a 96% yield of a "hydroxysulphonic acid" (III), C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub>S, m.p. 360°, which gives no colour with p-SO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl, resists hydrolysis, and is probably a 6-hydroxypyrimidine. (I) and (III) resemble also the 2-substituted pyrimidines chemically, but differ therefrom in absorption spectra and in that 2-hydroxy-4: 6-dimethylpyrimidine gives a strong colour with (II). The absorption spectra of 6-aminoand 6-hydroxy-2: 4-dimethylpyrimidine resemble those

Characteristics of avitaminosis in rats caused by lack of skin factors in the diet. H. VON EULER and M. MALMBERG (Biochem. Z., 1935, 278, 351--363).—Some of the symptoms (e.g., loss of hair and skin) of pellagra are caused by lack of lactoflavin (I) in the diet. At least partial cure (florid dermatitis cured) is achieved by administration of (I) with supplement (yeast juice). Basal diets containing in addition (I) and supplement lack components present in a normal mixed diet. Healthy skin can readily be distinguished histologically from skin of rats deprived of (I) even when external symptoms of pellagra are absent. W. McC.

of (I) and (III), respectively.

Determination of vitamin- $B_2$  by measurement of fluorescence. F. H. COHEN (Arch. néerl. Physiol., 1935, 20, 167—174).—The fluorescence of pure vitamin- $B_2$  (I) in aq. EtOH increases linearly with the concn. up to  $10^{-6}$  g. per c.c.; at higher concns. the rate of increase slackens. Fluorescence falls with  $p_{\rm H}$ ; it varies slightly with the solvent, max. occurring in  $C_5H_5N$ , and min. in  $H_2O$ , at the same concn. The adsorption of (I) on franconite and subsequent elution are quant. Plant extracts after irradiation show a residual fluorescence. Pure (I) added to the extracts cannot always be recovered quantitatively. The (I) content of carrot extracts is determined from the difference of intensities of fluorescence before and after exhaustive irradiation. R. N. C.

Enzymic esterification of lactoflavin with phosphoric acid. H. RUDY (Naturwiss., 1935, 23, 286-287).—The glycerol extract of the enzyme of the small intestine of rats, in 0.01M-PO<sub>4</sub><sup>'''</sup> at  $p_{\rm H}$  7·2 and 37°, converts lactoflavin quantitatively into a phosphoric ester. The vitamin-B<sub>2</sub> phosphoric ester so obtained, like that obtained by means of POCl<sub>3</sub> (this vol., 545), gives readily sol. Ca and Ba salts. No esterification occurs when the phosphatase solution is deactivated by heating for a short time. It is probable that those flavins which cannot be esterified with H<sub>3</sub>PO<sub>4</sub> in the animal body cannot show any growth-promoting action. H. G. M.

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R. S. C.

Constitution and biological activity of flavins. --See this vol., 993.

Ascorbic acid of the adrenals and mortification. G. MOURIQUAND and A. COEUR (Compt. rend. Soc. Biol., 1935, 119, 615—616).—The Giroud-Leblond  $AgNO_3$  reaction is positive in normal guineapig adrenals 96 hr. after death. It remains negative after this time in scorbutic animals. R. N. C.

Histochemistry of adrenal gland. I. Distribution of vitamin-C. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1935, 110, 1-7).—Ox adrenals were sectioned by the method of Linderstrom-Lang (A., 1934, 1260) and the vitamin-C (I) in the different sections was determined (this vol., 793); the (I) content is plotted against distance from the surface of the gland. The no. of cells per slice of tissue was counted and hence the quantity of (I) per cell was plotted as above. The highest peak in the curve occurs in the fascicular region. H. D.

Behaviour of *l*-ascorbic acid and chemically related compounds in the animal body. Antiscorbutic activity in relation to retention by the organism. S. S. ZILVA (Biochem. J., 1935, 29, 1612—1616).—When the animal organism (guineapig) was exhausted of *l*-ascorbic acid and a variety of substances administered (*e.g.*, *l*-arabo-, *l*-glucoascorbic acid, which are antiscorbutically active to different extents; *d*-ascorbic, *d*-gluco- and *d*-galactoascorbic acid, which are inactive) the degree of "fixation" by the tissues, especially by the adrenals, anterior lobe of pituitary, and intestine, appeared to vary directly with the degree of antiscorbutic activity, and the kidney excreted these compounds in amounts which varied inversely with the potency. P. W. C.

Effect of vitamin-C (ascorbic acid) on the growth of plants. S. VON HAUSEN (Suomen Kem., 1935, 8, B, 27–28; cf. A., 1933, 757; 1934, 225).— Ascorbic acid (I) causes an increased development of plants grown in sterile cultures. (I) is stored by the plant. J. L. D.

Diphtheria toxin and vitamin-C. D. M. CAR-DOSO (Compt. rend. Soc. Biol., 1935, 119, 749-750). —Diphtheria toxin destroys vitamin-C in the adrenals of guinea-pigs. R. N. C.

Action of different biological agents on vitamin-C. I. Penicillium digitatum (Pers.), Sacc. M. BIFANO and O. SERVAZZI (Arch. Ist. Biochim. Ital., 1935, 8, 151—156).—The vitamin-C content of lemon-juice is not appreciably decreased by experimental infection of the lemons with P. digitatum. R. N. C.

Vitamin-C content of some Indian plant materials. M. DAMODARAN and M. SRINIVASAN (Current Sci., 1935, 3, 553).—The ascorbic acid content of *Phyllanthus emblica*, L., *Moringa oleifera*, Lamk., *Sesbania grandiflora*, Pers., *Capsicum frutescans*, L., and *Anacardium occidentale*, L., is 1—4 mg. per g. of fresh material. Extracts from the first and last are stable, the former even for a week; the others undergo oxidation rapidly. After pptn. by Hg salts, or treatment with Pb(OAc)<sub>2</sub> or CCl<sub>3</sub>·CO<sub>2</sub>H, the extracts are readily autoxidisable: the presence of protective substance(s) in *P. emblica* and *A. occidentale* is therefore deduced. Ascorbic acid in C. frutescans reaches a max. at a certain stage of ripeness. E. W. W.

Interfering action of glutathione in the silver nitrate test for ascorbic acid. J. L. SVIRBELY (Biochem. J., 1935, 29, 1547—1551).—The  $\rm NH_3$ -AgNO<sub>3</sub> test for ascorbic acid (I) depends on the amounts of (I) and glutathione (II) present. If (II) is absent, the limit of sensitivity is 0.015 mg. of (I). Adrenaline, glycogen, lactose, gelatin, and starch do not interfere. With increasing amounts of (II) the test is less sensitive, and is not as definite as titration with dibromophenol-indophenol-blue. J. N. A.

Determination of vitamin-C in brain, cerebrospinal fluid, and serum. F. PLAUT, M. BULOW, and F. PRUCKNER (Z. physiol. Chem., 1935, 234, 131— 145).—The determination of the ascorbic acid (I) contents of these materials by a spectrographic method described is frequently possible (often impossible with human blood-serum), and the results agree well with those obtained by titration. Complete removal of interfering substances is sometimes impossible and undesired oxidation of (I) cannot always be avoided. W. McC.

Vitamin-D content of vegetable oils. T. BER-ZACZY and K. RUPLIUS (Wien. klin. Woch., 1934, 47, 1449—1450; Chem. Zentr., 1935, i, 431).—Crude olive oil, in contrast to the commercial oil, has antirachitic activity. The activity is dependent on the harvesting time, winter-gathered fruit supplying the most active oil. The activity is increased by ultraviolet irradiation, with or without addition of Fe<sup>\*\*</sup>. R. N. C.

Seasonal variations in the vitamin-D potency of pilchard oil. B. E. BAILEY (Pacific Biol. Sta. Nanaimo, Prog. Dept. 1934, No. 19, 5-6).—The vitamin-D potency of the oil probably  $\propto$  the oil content of the fish. CH. ABS. (p)

Calcium and phosphorus. X. Effect of variation of calcium, phosphorus, and vitamin-D in the diet on iron retention in rats. D. H. SHELLING and H. W. JOSEPHS. XI. Effect of prophylactic and curative doses of standardised viosterol on human tissues; necropsy report of thirteen cases showing no tissue damage. D. H. SHELLING and D. A. JACKSON (Bull. Johns Hopkins Hosp., 1934, 55, 309-313, 313-334; cf. this vol., 409).—X. A high-Ca, low-P diet causes abnormally low hæmoglobin vals. in rats, whether viosterol (I) is given or not. Fe retention is similarly lowered and is < that of animals fed on low-Fe milk. (I) increases Fe retention in rats receiving a high-P diet, but does not affect those on a high-Ca diet.

XI. Administration of (I) had no ill-effects on the soft tissues or skeletons of infants. CH. ABS. (p)

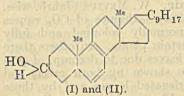
Calcifying factors in the diet of salamander larvæ. E. M. PATCH (Science, 1935, 81, 494).— Salamander larvæ do not differ widely from higher animal forms in their responses to calcification factors in the diet. They should form a suitable means for the biological assay of calcifying agents. L. S. T.

Ring structure of calciferol. I. M. HEILBRON, K. M. SAMANT, and F. S. SPRING (Nature, 1935, 135, 1072).—With CrO<sub>3</sub> or KMnO<sub>4</sub> calciferol (I) and calci-

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feryl acetate yield an oily aldehyde. C21H34O (semicarbazone, m.p. 242°). A three-ring formula is sug-gested for (I) and the probable positions of the ethylenic linkings are indicated. L. S. T.

Vitamin-D and its thermal and photochemical reaction products. M. MÜLLER (Z. physiol. Chem., 1935, 233, 223-234).—Se dehydrogenation of the mol. compound isopyrovitamin (I)-pyrocalciferol (II) yields methylcyclopentenophenanthrene. Thus ringclosure on heating the vitamin (III) occurs at the same place as the photochemical fission. The acetate of (I) (dinitrobenzoate, m.p. 171–172°,  $[\alpha]_{\rm D}$  +281° in CHCl<sub>3</sub>) with conc. HNO<sub>3</sub> affords 1 : 2 : 3 : 4 : 5-C<sub>6</sub>HMe(CO<sub>2</sub>H)<sub>4</sub> (IV) (isolated as the Me<sub>4</sub> ester), and condenses with maleic anhydride giving a product  $C_{34}H_{48}O_5$ , m.p. 203—204°. The H<sub>2</sub> uptake of the acetate is 3 mols. (II) (acetate, m.p. 81—82°,  $[\alpha]_D$  +403° in CHCl<sub>3</sub>) with HNO<sub>3</sub> also affords (IV). The acetate with maleic



anhydride gives a pro--C<sub>9</sub>H<sub>17</sub> duct, m.p. 161-162°, and takes up 2H2. These properties are expressed by the annexed constitution.

(I) and (II) probably differ only in

the steric arrangement of the substituents at

 $C_5$  and  $C_{10}$ . Se or Pt dehydrogenation of suprasterol-I (V) or -II (VI) gave non-cryst. products. (V) absorbs (Pt) 3H<sub>2</sub> (2 quickly), (VI) absorbs about 3.5H<sub>2</sub> (oxalate  $6.6H_2$ ). Ring-closure must have occurred in (V), but is doubtful in (VI). The constitution of the products derived from (III) is discussed. J. H. B.

Vitamin-E. I, II. Measurement of absorp-tion band. S. UENO, Y. OTA, S. YOKOYAMA, and S. MATSUDA (J. Soc. Chem. Ind. Japan, 1935, 38, 190-192B, 192-195B).-I. From the unsaponifiable matter of rice oil a fraction, b.p. 200-250°/1 mm., has been obtained which closely resembles the vitamin-E fraction isolated from wheat-germ oil by Evans and Burr. Constituents of the unsaponifiable matter vary with the mode of manufacture of the oil.

II. The absorption spectra of rice oil and some of its components have been measured. The fraction of b.p. 200-250°/1 mm. has an absorption band at about 260 mµ (cf. A., 1933, 987). H. G. M.

Rate of absorption of ammonium- and nitratenitrogen from culture solutions by ten-day-old tomato seedlings at two  $p_{\rm H}$  levels. L. B. ARRING-TON and J. W. SHIVE (Soil. Sci., 1935, 39, 431-435; cf. B., 1934, 468, 776).—The rate of absorption of  $NO_3$ -N was much > that of  $NH_4$ -N at  $p_{II}$  4 and 7. Intake of  $NH_4$ -N at  $p_{\rm H}$  7 was > that at  $p_{\rm H}$  4, whereas that of  $NO_3 N$  was somewhat higher at  $p_{\rm H} 4$ . The influence of the reaction of the medium on N absorption was more marked in the case of NO<sub>3</sub>-N than of NH<sub>4</sub>-N.

A. G. P.

Absorption of ions by living cells. H. LUNDE-GARDH (Naturwiss., 1935, 23, 313-318).-The role of adsorption, hydration, dissociation, etc. in the absorption of ions by plant cells is discussed (cf. A., 1933, 874). A scheme is advanced depending on the p.d. existing between the sides of a cell membrane, a negatively-charged colloid participating in the transport of cations, whilst the anions are primarily carried by positively-charged protoplasmic micelles, the complex being oxidatively (aerobic or anaerobic) decomposed to CO<sub>2</sub> and the acid corresponding with the anion.

F. O. H.

Water relationships of tomato plants. I. W. SELMAN (Cheshunt Exp. Sta. Ann. Rept., 1934, 89-95).-The suction force of tomato leaf-cells increases during the day in summer, probably as the result of increased osmotic pressure of the cell contents. The phenomenon does not occur in winter. Loss of  $H_2O$  per unit leaf area by transpiration is highest in embryonic and least in fully expanded leaves. Differences in permeability of leaf cells to H<sub>2</sub>O are indicated. Increases in leaf area during the night are closely correlated with the H<sub>o</sub>O deficit of the cells.

A. G. P.

Nutrient intake of plants from flowing and stationary nutrient solutions. II. E. UNGERER (Z. Pflanz. Düng., 1935, 39, 15-23; cf. this vol., 131). -The poorer growth of plants in dil. but flowing media as compared with that in conc. stationary media results from inability to take up sufficient K and N in the early stages of growth from solutions of low osmotic pressure. It is unlikely that plants can grow to maturity in nutrients as dil. as the soil solution.

A. G. P.

Assimilation of inorganic nitrogenous salts, including sodium nitrite, by the grass plant. W. G. E. EGGLETON (Biochem. J., 1935, 29, 1389-1397).—The transformation of various forms of inorg. N applied to the soil into org. N in the plant is investigated, determinations of  $\rm NH_2$ -, pepsin-HCl-sol, true protein-, total,  $\rm NH_3$ -,  $\rm NO_2$ -, and  $\rm NO_3$ -N being carried out (the last three determinations also on the corresponding soil extracts). Inorg. N was detected in substantial amounts in the herbage only 2 hr. after application to the soil. In early spring, synthetic processes in the leaf are slow enough to permit accumulation of simple org. and inorg. compounds. This margin of partly elaborated N rapidly disappears, but at a diminished rate, when inorg. N salts are applied to the soil.  $NO_2'$  occurs naturally in spring grass, and the amount is increased when the grass is treated with  $(NH_4)_2SO_4$ or NaNO3 at this time. Grass treated with NaNO2 at the rate of 3 cwt. per acre shows no visible signs of distress, although some metabolic disturbances do occur. The possible significance of  $NO_2'$  in the synthesis of protein is discussed and it is suggested that nitrites play a part in the "grass tetany" of cattle. P. W. C.

Absorption of nitrates by corn in the dark. P. L. GILE (Science, 1935, 81, 520-521).-Maize grown under alternating periods of light and dark assimilates  $NO_3'$  as well in darkness as in light. Practically all the N needed can be taken up in complete darkness. L. S. T.

Nitrogenous nutrition of the flower. R. COMBES (Compt. rend., 1935, 200, 1970-1972; cf. this vol., 552).-The protein content of the calyx and corolla of Lilium croceum increases rapidly with growth until the flower begins to open, when vigorous proteo-lysis and translocation ensue. The protein content of the andræcium declines steadily from the "button" stage until full expansion. In the gynæcium protein increases throughout, but the major portion of the N leaving the perianth is translocated to the stem.

A. G. P.

Zinc and cadmium as stimulators of oxidation processes in certain plant-seed extracts. T. THUNBERG (Skand. Arch. Physiol., 1934, 69, 247— 254; Chem. Zentr., 1935, i, 733).—Zn and Cd activate the decolorisation of redox indicators in plant extracts. A. G. P.

Restoration of potassium effect by action currents. W. J. V. OSTERHOUT and S. E. HILL (J. Gen. Physiol., 1935, 18, 681—686).—Treatment of *Nitella* cells with distilled H<sub>2</sub>O removes the ability to give p.d. (approx. 80 mv.) between 0.01M-KCl and NaCl["K effect"]; this effect, however, is restored by action currents following application of a p.d. of 500 mv. It appears to be due to a substance or mixture, substance R. F. O. H.

Mechanical restoration of irritability and of potassium effect. S. E. HILL and W. J. V. OSTER-HOUT (J. Gen. Physiol., 1935, 18, 687–694).—The irritability and "K effect" of Nitella cells, lost on treatment with distilled  $H_2O$ , are restored by the mechanical forcing of sap (containing substance R) into the protoplasm (cf. preceding abstract). F. O. H.

Photosynthetic behaviour of leaves with variations in temperature. B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 1, B, 736— 753).—With normal atm.  $[CO_2]$  the assimilation of radish leaves increases with rise of temp. to a max. at 30°. Above this assimilation has the same initial rate as at 30°, but this declines with time. The hourly decrease in assimilation is very marked at 37°. Increased  $[CO_2]$  at 29° causes a higher rate of assimilation. Assimilation commences at  $< 12.6^\circ$  and ceases at 47.4°. A. G. P.

Effect of light on growth and differentiation in tomato seedlings, variety E.S.I. B. D. BOLAS and I. W. SELMAN (Cheshunt Exp. Sta. Ann. Rept., 1934, 86—89).—The curve representing the wt. per plant at the seventh leaf stage at different periods of the year closely resembles that for the total illumination per day or for day length, but is displaced several weeks forward. Although illumination ceases to limit assimilation after about April (greenhouse), it affects growth and leaf differentiation throughout the summer months. A. G. P.

Reaction of the assimilatory system to alterations of light intensity. B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 1, B, 754— 762).—The assimilation rate of radish leaves increases with light intensity up to 68,000 m.-candles under normal atm. conditions and up to somewhat higher vals. when  $[CO_2]$  is artificially increased. A time factor is apparent at 180,000 m.-candles. The depression in photosynthetic activity at high light intensities is related to a reversible inactivation of chloroplasts. The threshold val. for this activity is approx. 4000 m.-candles. A. G. P.

Nature of the photoperiodic effect (induction), and the effect of length of day on the activity of [plant] oxidising enzymes. M. C. TSCHAILACHIAN and V. A. ALEXANDROVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 161—166).—"Short-day" plants (millet) exhibited no "long-day" photoperiodic after-effects, and vice versa. Induction effects in millet and barley occurred when the causative factor accelerated the fruiting process and the development of the plants. The peroxidase (I) of millet was higher under long-day conditions, and that of barley (a "long-day" plant) under short-day conditions. Temporary (6-day) exposure of plants to an altered day period affected (I) in the direction in which the new photoperiod acted. In soya bean and *Phaseolus*, (I) was more active under short-day conditions when growth processes were retarded. Tomato leaves contained no (I). The catalase activity of plant leaves was practically unchanged throughout the experiment. A. G. P.

Behaviour of illuminated [plant] leaves in carbon dioxide-free air. W. MEVIUS (Jahrb. wiss. Bot., 1935, 81, 327—382).—Absence of CO<sub>2</sub> causes rapid defoliation of normally coloured and fully turgescent leaves in certain plants. In others there is a slow yellowing of leaves due to decomp. of proteins. The effects are shown by both green and colourless areas of variegated leaves and by those screened with tinfoil. Plants which normally bear anthocyanin pigments in leaves and stems cease to produce pigment in newly developing leaves, when deprived of CO<sub>2</sub>. This effect is accentuated if the supply of NO<sub>3</sub> is maintained. The formation and destruction of these pigments are photosynthetic processes, and are closely related to the carbohydrate and N economy of the plants. A. G. P.

Chlorophyll fluorescence and assimilation of carbonic acid. IV. Effect of oxygen on fluorescence in living leaves. H. KAUTSKY and A. HIRSCH (Biochem. Z., 1935, 278, 373–385; cf. this vol., 794).—The usual course of the fluorescence on irradiation of green leaves is a consequence of interaction between  $O_2$  (bound in dissociable form to the chloroplast) and stimulated chlorophyll. Leaves irradiated in an atm. free from  $O_2$  fluoresce from the beginning with max. unchanging intensity until liberated or added  $O_2$  restores the normal behaviour. W. McC.

Growth-stimulating substance in indigenous plants. II. Physiology. F. BOAS (Ber. deut. bot. Ges., 1935, 53, 495-511).—The presence is recorded of widely varying amounts of yeast growthpromoting substance in numerous plants and in cattle manure. Notably large amounts occur in mistletoe and in camomile. The proportion of this substance in *Phaseolus* varies with the  $\lambda$  of light to which the plant is exposed. A. G. P.

Artificially induced root formation by means of growth-substance paste. F. LAIBACH and O. FISCHNICH (Ber. deut. bot. Ges., 1935, 53, 528–539). —The growth-promoting effects of the treatment of intact *Coleus* stems with  $\beta$ -indolylacetic acid paste are described. A. G. P.

Inhibition of the action of growth-substance by parts of living plants. P. KORNMANN (Ber. deut. bot. Ges., 1935, 53, 523-527).—The activity of agar block preps. of the growth-promoting substance of maize-gluten meal was counteracted by placing on the block tips of, or rings from, the base of the coleoptile of oats, but not the coleoptile tips of maize. Agar-oat flake preps. were not affected by oat tips; their activity was increased by maize tips but decreased by basal rings of oats. Maize tip-agar blocks were unactivated by oat tips. The presence of a growth-inhibiting substance in the older parts of a no. of plants is indicated. A. G. P.

Method for determining the callus-forming action of pastes containing growth-promoting substance. F. LAIBACH and O. FISCHNICH (Ber. deut. bot. Ges., 1935, 53, 469-477) .- The activity of growth-promoting substance is determined by the rate of callus formation on decapitated epicotyls of Vicia faba in comparison with that of a standard prep. of  $\beta$ -indolylacetic acid (73×10<sup>-6</sup> g. per g. of A. G. P. lanolin paste).

Action of growth-substance in parallelotropic plant organs. A. T. CZAJA (Ber. deut. bot. Ges., 1935, 53, 478-490).—Application of growth-substance parallel to the direction of the growth-substance stream in decapitated stems etc. causes lengthening but no thickening of the stem. Transverse applications cause thickening below the point of application. Cell elongation due to the growth-substance is unaccompanied by cell division. The latter occurs as a secondary effect of the disturbed polarity, following transverse treatment of stems with growth-substance. A. G. P.

Vitamins and growth-factors in plants. Growth-factor content of spores of Phycomyces. W. H. SCHOPFER (Ber. deut. bot. Ges., 1935, 53, 466-468).-The heterotrophic character (in respect of growth-factors) of *Phycomyces* is established. Spores contain enough growth-factors for germination, but external supplies of vitamin- $B_1$  or extracts of cultures on vitamin-containing media are necessary for further development. A. G. P.

Growth-hormone of plants. VII. Fate of growth-substance in the plant and nature of growth process. J. BONNER and K. V. THIMANN (J. Gen. Physiol., 1935, 18, 649-658; cf. A., 1934, 1272).—Removal of hormone-producing tips of Avena coleoptiles is followed by a decrease in growth (and hence in hormone) to approx. 50% in 2 hr. and then by a return to normal levels after 3 hr. Immediate increase in growth follows application of hormonecontaining agar blocks. The hormone is inactivated in the plant to an extent either = or, when conditions are unfavourable for growth, > the proportionate amount of growth. Inactivation of the hormone, which appears to be irreversible, is not affected by HCN. The process of growth is discussed.

F. O. H.

Growth-hormone and dwarf type of growth in maize. J. VAN OVERBEEK (Proc. Nat. Acad. Sci., 1935, 21, 292–299).—Auxin destruction, which may be due to oxidation-reduction changes, is greater in nana maize than in normal, and this causes the dwarf type of growth. Another growth-factor (cell-extension material) is present in coleoptiles of maize.

M. S.

Auxins. A. J. H. SMIT (Chem. Weekblad, 1935, 32, 398-403).-A lecture.

Effect of cestrogenic substances on plants. IV. W. SCHOELLER and H. GOEBEL (Biochem. Z., 1935, 278, 298-311; cf. A., 1934, 1145).-Follicular hormone (cryst. but not quite pure) supplied in H<sub>2</sub>O during early stages of growth to plants (primula, fuchsia, pink, chrysanthemum, violet, forget-me-not, cyclamen, tomato) growing in soil has a powerful general and sp. effect on the growth, the no. of blossoms and fruit being very greatly increased. The amount of hormone required for optimal effect varies from species to species of plant. W. McC.

Flower development and hormone action. R. HARDER and I. STORMER (Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl., VI, 1934, 1, 11-16; Chem. Zentr., 1935, i, 737) .- Contrary to the results of Schoeller and Goebel (A., 1934, 1145), neither cryst.  $\alpha$ -folliculin nor progynon affects the flowering of a A. G. P. no. of plants.

Growth and metabolism of plants with mineral salt nutrition. III. Sugar content of the pressjuice of tobacco leaves in relationship to the mineral salt nutrition of plants. K. BÖNING and E. BÖNING-SEUBERT (Biochem. Z., 1935, 278, 71-88).-Increase of the mineral salts administered to the plant decreases, and decrease of salts increases, the sugar content of the leaf press-juice, the effect of the anions and cations being in the order PO<sub>4</sub>< SO4 < NO3 < Cl and Ca < Na < K. Thus the more readily permeable ions have the largest decreasing effect on the leaf-sugar content, whilst the less permeable either have little effect on or may increase the P. W. C. sugar content.

Structure of cell-wall of coffee[-bean]. K. TAUFEL and H. THALER (Z. Unters. Lebensm., 1935, 69, 152-158).-A sample of coffee contained 52.6% of cell-wall (i.e., residue after extraction with Et<sub>2</sub>O and  $H_2O$ ), of which 47.0% consisted of the glucose fraction (mannan 15.3, xylan 1.8, cellulose 29.9%) and 5.6% of material rendered sol. by treatment with aq. ČlO<sub>2</sub> (cf. A., 1931, 1101). E. C. S.

Influence of the pyrrole nucleus on the formation of chlorophyll. G. POLLACCI (Ber. deut. bot. Ges., 1935, 53, 540-542).-The growth of Chlorella vulgaris and other algæ is not injured if Mg is supplied in the form of Mg pyrrole-2carboxylate (I). Replacement of (I) by MgSO4 in Fe-free media results in new growth containing high leucoplast but no chloroplast contents. Re-addition of (I) causes normal green growth. The function of Fe in the cells is purely catalytic. It is probably concerned in the formation of the pyrrole compounds. A. G. P.

Leaf, flower, and fruit characters of the Santra orange (Citrus nobilis var. deliciosa). S. S. BHAT (Poona Agric. Coll. Mag., 1934, 26, 116– 124).—Analytical data are given.  $CaC_2O_4$  was de-posited in leaves as cystoliths below the upper epidermis; it also occurred in leaves of Citrus sincensis, Swingh. CH. ABS. (p)

Distribution of constituents of the beech (Fagus silvatica, L.). E. GAUMANN (Ber. deut. bot. Ges., 1935, 53, 366–377).—The fat, protein, and carbohydrate contents of the various organs of the beech at different growth periods are examined. A. G. P.

Chemical genetics of barley mutants. Chlorophyll and gramine contents of the mutants. H. von EULER, H. HELLSTROM, and N. LOFGREN (Z. physiol. Chem., 1935, 234, 151–164; cf. A., 1934, 1419).—The chlorophyll and gramine (I) contents of normal and chlorophyll-defective barley mutants are recorded. (I),  $C_8H_6N\cdot CH_2\cdot NMe_2$ , which occurs chiefly in the roots (not in the coleoptile), on heating for 3 hr. at 80° with 0·1*N*-HCl gives a substance exhibiting max. absorption at 330 mµ and identical with "phenyl-X," the product of spontaneous transformation. The transformation probably consists in addition of H<sub>2</sub>O to a pyrrole double linking. The product of transformation is accompanied by another substance having absorption max. at 270 mµ.

## W. McC.

Identity of calycopterin and thapsin. W. KARRER and K. VENKATARAMAN (Nature, 1935, 135, 878).—The yellow colouring matter from the leaves of *Calycopteris floribunda*, Lamk (this vol., 246), and the thapsin obtained from a Spanish *Digitalis (ibid.*, 91) are identical. The name "calycopterin" should be retained for the flavone constituents of these two plants. L. S. T.

Carotene and xanthophyll in pineapples. O. C. MAGISTAD (Plant Physiol., 1935, 10, 187—191).— The yellow colour in pineapples is due principally to carotene (I) (0.1-0.25 mg. per 100 g. of flesh) and xanthophyll (II). The ratio (I): (II) averages 8— 13:1. A. G. P.

Pigments of pink grapefruits, Citrus grandis, L., Osbeck. M. B. MATLACK (J. Biol. Chem., 1935, 110, 249—253).—The dried flesh of the Foster and the Marsh pink grapefruits was extracted with  $CS_2$ , and after a preliminary purification, the pigments were separated and isolated by the Tswett chromatographic method. The separated pigments were identified spectroscopically as lycopene (I) and  $\beta$ -carotene (II). (I) predominates in Foster and (II) in Marsh variety. E. A. H. R.

Carotenoids. I. Carotenoids of Diospyros fruits. II. Carotenoids of Arbutus fruits. K. SCHON (Biochem. J., 1935, 29, 1779–1782, 1782– 1785).—The fruits of D. costata and A. unedo contain  $\alpha$ - and  $\beta$ -carotene, lycopene, cryptoxanthin, zeaxanthin, and violaxanthin (I). Approx. 80% of the total pigment of A. unedo is (I), m.p. 203° (corr.). F. O. H.

[Chemistry of] algæ. I. Lipochromes of Fucus vesiculosus. I. M. HEILBRON and R. F. PHIPERS. II. Relationship between certain algal constituents. III. Isolation of lactoflavin. I. M. HEILBRON, E. G. PARRY, and R. F. PHIPERS (Biochem. J., 1935, 29, 1369—1375, 1376— 1381, 1382—1383).—I. Dead material from *F. vesi*culosus (I) contains  $\beta$ -carotene (II) and zeaxanthin, whilst the living plant contains (II) and fucoxanthin (III) but no xanthophylls usually associated with higher plants. (III), C<sub>40</sub>H<sub>60</sub>O<sub>6</sub>, m.p. 166—168° (uncorr.), [ $\alpha$ ] 0° (cf. A., 1931, 733), which yields a substance  $C_{40}H_{78}O_2$ , m.p. 63-64°, on complete hydrogenation under pressure, appears to be a dihydroxycapsorubin (this vol., 233).

II. Examination of the unsaponifiable fractions from Cladophora sauteri, Nitella opaca, Oedogonium, and Rhodymenia palmata indicates the lipins to be characteristic for each species and related to their habitat. All contain lutein, taraxanthin, (II), and small amounts of hentriacontane (A., 1934, 1347), whilst C. sauteri contains  $\alpha$ -carotene. N. opaca and Oedogonium yield a phytosterolin, C<sub>35</sub>H<sub>66</sub>O<sub>6</sub>, m.p. 283-285° (cf. A., 1934, 637).

III. Lactoflavin was isolated from aq. extracts of C. sauteri by direct adsorption and lumilactoflavin from irradiated alkaline extracts of (I).

F. O. H. r plants an

Occurrence of cytochrome in higher plants and algæ. E. YAKUSHIJI (Acta Phytochim., 1935, 8, 325-329).—Cytochrome is detected in the seeds of Soja hispida, the roots of Raphanus macropoda, Brassica campestris, in Sagittaria trifolia, apple, and in Allium cepa, in cabbage-leaves (after removal of chlorophyll by COMe.) and in Sargassum Thunbergii, S. piluliferum, S. serratifolium, Cystophyllum sisymbrioides, Endarachne Binghamiæ, Myeloplycus cæspitosus, Ishige Okamurai, Gelidium Amansii, Gymnogongrus flabelliformis, Porphyra tenera, Enteromorpha Linza, and Ulva types. H. W.

Chemistry of pigments of pepper. Red pigment in the perfection pimento (*Capsicum annuum*). W. L. BROWN (J. Biol. Chem., 1935, 110, 91-94; cf. Zechmeister *et al.*, A., 1934, 657).—The pigment is identical with the capsanthin of Hungarian paprika. W. McC.

Saponins of Chenopodium ambrosioides, L. S. GREIFINGER (Wiad. farm., 1934, 61, 275-277, 289-291; Chem. Zentr., 1935, i, 746).—Saponins occur in largest amounts in roots (2.5%). The amount increases with age and is influenced by soil type and manuring. The pure saponin is amorphous, m.p. 196-200°, and has a mild hæmolytic action.

A. G. P.

Presence of saponins in tobacco; an accompanying substance. (FRL.) M. KOBEL and C. NEUBERG (J. pr. Chem., 1935, [ii], 143, 29–41).— Freshly plucked and chopped tobacco leaves heated to stop fermentation, and extracted with boiling EtOH, yield a product containing saponins. The haemolytic action of various fractions (from aq. EtOH and/or  $Et_2O$ ) is measured; it is arrested by cholesterol. Rutin is also present, with nicotine, and material hydrolysed to a product containing uronic acids and a sugar. E. W. W.

Alkaloid content and activity of saprophytic ergot cultures. R. JARETZKY (Arch. Pharm., 1935, 273, 348—357).—Ergot grown on maltosepeptone-agar contains more alkaloids than if grown on other media, as shown by colorimetric determination by p-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO and by biological tests on the rabbit's isolated uterus. R. S. C.

Protein of healthy potato tubers. H. KAHO (Biochem. Z., 1935, 278, 235-239).—The H<sub>2</sub>O-sol. protein of potatoes is pptd. by salts only when their concn. is high (6N to saturation). The degree of stimulation of heat-coagulation of the protein by anions and cations varies in accordance with the reversed lyotropic series, and provides a means of distinguishing between different sorts of potatoes. The protein occurs in potatoes combined with an acid (possibly  $H_2C_2O_4$ ). W. McC.

Organic nitrogenous and non-nitrogenous compounds occurring in the Alaska pea. II. Isolation of pyrrolidonecarboxylic acid, tyrosine, and diamino-acids from the non-proteins thereof. S. L. JODIDI (J. Amer. Chem. Soc., 1935, 57, 1142; cf. B., 1934, 852).—An EtOH extract of defatted Alaska peas gives with  $K_2Cr_2O_7$ -H<sub>2</sub>SO<sub>4</sub> pyrrolidonecarboxylic acid. The peas yield arginine (0.7%) and give colour reactions for histidine and tyrosine. R. S. C.

Betaine in wheat bran. F. E. NOTTBOHM and F. MAYER (Z. Unters. Lebensm., 1935, 69, 289— 300; cf. A., 1934, 571).—The aq. Mg(OH)<sub>2</sub> extract of wheat bran consists largely of betaine (I), which constitutes 0.35% approx. of the bran. The composition and properties of phosphatide (II) from wheat bran and oats (cf. A., 1911, ii, 426) are described. Both contain (I), but it is present as an impurity, probably in combination with sugar. The P.-L. no. (cf. B., 1934, 425) of wheat-bran-(II)=3.44; that of seeds  $\infty$  the % of N in the fat-free material. E. C. S.

Presence of 2-hydroxy-5-methoxyacetophenone in extracts of rhizomes of *Primula acaulis*. A. GORIS and H. CANAL (Compt. rend., 1935, 200, 1990—1992).—The isolation and characterisation of the compound are described. A. G. P.

Resin of wheat straw. L. MARION (Canad. J. Res., 1935, 12, 554–563).—MeOH–C<sub>6</sub>H<sub>6</sub> (1:1) extracts from wheat-straw lignin (4·72%) and a resin (1·5%), which contains free fatty acids [including palmitic (I), stearic (II), and lignoceric], glycerides [yielding (I), (II), linolenic and oleic acids], ceryl cerotate, m.p. 70°, much wax [containing a little P and yielding ceryl alcohol, sitosterol, m.p. 137°, (I), and cerotic acid], a sterol ester [giving a sterol,  $C_{27}H_{46}O$  (Ac derivative, m.p. 134–135°)], a phytosterolin,  $C_{33}H_{56}O_6$ , m.p. 291–292° (Ac derivative, m.p. 137°, and glucose) (cf. A., 1934, 1276), KNO<sub>3</sub>, and *i*-inositol. R. S. C.

2:4:5-Trimethoxy-1-allylbenzene. Asarone (allyl). B. S. RAO and K. S. SUBRAMANIAN (Current Sci., 1935, 3, 552).—The "asarone" obtained from calamus roots (A., 1934, 529), when treated with  $H_2SeO_3$  and distilled from Na, is a liquid, b.p. 283°/685 mm., identified as 2:4:5-trimethoxy-1-allylbenzene, and named "asarone (allyl)." When heated with KOH, this gives ordinary asarone ["asarone (propenyl)"]. E. W. W.

Constituents of Verbena officinalis, L. I. Identity of verbenalin and cornin. B. REICHERT (Arch. Pharm., 1935, 273, 357-360).—Verbenalin from V. officinalis (A., 1908, i, 197) and cornin from Cornus florida, L. (A., 1928, 1137), are identical.

R. S. C. Composition of Bourdaine bark. III. Isolation of frangularoside and its hydrolysis product frangularol. IV. Water-soluble complex purgative hydrolysed by rhamnodiastase. M. BRIDEL and C. CHARAUX (Bull. Soc. Chim. biol., 1935, **17**, 780—792, 793—816).—III. The fresh bark, in contrast with the commercial product, gives on autolysis a rhamnoside, *frangularoside*,  $C_{21}H_{24}O_{9}$ , m.p. 234°. This on hydrolysis with aq.  $H_2SO_4$  and  $HCO_2H$  yields *frangularol*,  $C_{15}H_{14}O_5$ , m.p. 301°, and rhamnose.

IV. The active principle of Bourdaine bark, extracted with 95% aq. EtOH and pptd. with COMe<sub>2</sub>, gives on hydrolysis with 5% aq.  $H_2SO_4$  40% of emodol, 43% (2 mols.) of glucose, and 16% (1 mol.) of rhamnose. It is partly hydrolysed by rhamnodiastase with the formation of franguloside and glucose with small quantities of emodol and an unidentified anthraquinone derivative, m.p. 160°. It may consist of a compound of 1 mol. of franguloside with 2 mols. of glucose. A. L.

Sophoricoside, a heteroside of the fruits of Sophora japonica, L. C. CHARAUX and J. RABATÉ (J. Pharm. Chim., 1935, [viii], 21, 546–554).— From the boiling 80% EtOH extract of the pods of S. japonica, L., is isolated (1.5% yield) a  $\beta$ -glucoside sophoricoside, m.p. 297.5° (block),  $[\alpha]_{\rm D} - 32.2°$  in  $C_5H_5N-10\%$  H<sub>2</sub>O, hydrolysed by boiling AcOH-6% H<sub>2</sub>SO<sub>4</sub> or by emulsin to glucose and genistein, previously isolated from Genista tinctoria (Perkin et al., J.C.S., 1899, 75, 830; 1900, 77, 1310).

J. W. B.

Kuromamin, the colouring matter of "Kuromame." III. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1935, 11, 189—191; cf. A., 1934, 229).—Kuromamin is identical with cyanidin 3-monoglucoside (cf. A., 1931, 1423). J. L. D.

Phytosterol and phytosterolin from the sweet potato. M. B. MATLACK (Science, 1935, 81, 536).— A phytosterol, consisting mainly of sitosterol, and a phytosterolin, sitosterol glucoside, have been isolated from *Ipomæa batatas*, Poir. L. S. T.

Production of sterols by plants. The "oily chloroplasts" described by Savelli in cacti. J. MANUEL (Compt. rend. Soc. Biol., 1935, 119, 480— 482).—The properties of these chloroplasts from *Echinocereus procumbens* and *Cephalocereus senilis* are described. H. G. R.

Unsaturated acids of natural oils. II. Highly unsaturated acids of the kernels of Parinarium laurinum. E. H. FARMER and E. SUNDERLAND. III. Highly unsaturated acid of the kernels of *P. macrophyllum*. W. B. BROWN and E. H. FARMER (J.C.S., 1935, 759-761, 761-763; cf. B., 1933, 476).—II. Kernels of *P. laurinum* gave 44% of fat  $(n_p^{-5} \ 1.5565)$  on extraction with petroleum. 10 g. of fat gave with KOH-EtOH  $2 \cdot 5 - 3$  g. of unsaturated acid, m.p. 83.5°, which is attacked by atm. O<sub>2</sub>; with alkaline KMnO<sub>4</sub> it gave EtCO<sub>2</sub>H and azelaic acid, and on Pt hydrogenation stearic acid. The structure Et·[CH:CH]<sub>4</sub>·[CH<sub>2</sub>]<sub>7</sub>·CO<sub>2</sub>H is ascribed. III. Kernels of nuts of *P. macrophyllum* or *P.* 

111. Kernels of nuts of *P. macrophyllum* or *P. Senegalense* (Rosaceæ, tropical Africa) gave 70% of drying oil (4% on nuts). The unsaturated acid from the oil is shown to be  $\alpha$ -elæostearic acid. The

unsaturated acid, m.p. 73°, described by Steger and van Loon (B., 1934, 369) may be  $\beta$ -elæostearic acid formed from  $\beta$ -elæostearin resulting from irradiation of  $\alpha$ -elæostearin in the oil. P. G. C.

Biochemistry of the Salicaceæ. X. Leaf enzymes of S. purpurea. XI. Hydrolysis of salicoside by leaf enzyme preparation. XII. Oxidation of salicoside by leaf enzyme preparation. J. RABATÉ (Bull. Soc. Chim. biol., 1935, 17, 561— 571, 572—601, 602—611).—X. Whereas the enzyme from the leaves of S. purpurea hydrolyses rapidly phenolic glucosides such as salicoside (I), piceoside (II), helicoside, chloropiceoside, and  $\beta$ -phenylglucoside, the hydrolysis of  $\beta$ -methylglucoside (III), benzylglucoside, amygdalin, and aucuboside proceeds slowly.

XI. Under the action of the enzyme prep. (IV) from the leaves of S. purpurea, the hydrolysis of (I) leads to the formation of some  $\beta$ -salicylglucoside. Starting with MeOH and glucose, no synthesis takes place with (IV), although with emulsin (V) there is considerable synthesis. When, however, the hydrolysis of (II) by (IV) is carried out in the presence of 3% MeOH, 57% of the glucose liberated is converted into (III) compared with 6% when (V) is used. Addition of (V) in this reaction does not prevent the synthesis, which can take place only if the glucose is liberated in the presence of the alcohol. The glucose when liberated is probably in an active form.

XII. The oxidation of saligenol is 3 times as rapid as, and is brought about with less  $CO_2$  formation than, that of pyrocatechol (VI). It is believed therefore that the action of the oxidase responsible for the blackening of the leaves of *Salix* does not lead to the intermediate formation of (VI). A. L.

Alleged autohydrolysis of vegetable ivory. D. MELNICK and G. R. COWGILL (Biochem. J., 1935, 29, 1515—1518).—Paton's statement (A., 1924, i, 801) that a mannanase exists in *Phytelephas macrocarpa* is disproved by incubation experiments; failure to obtain reducing substances from the ivory after heating at 100° and washing is due to the removal of these substances by this treatment and not to the inactivation of an enzyme. A reducing substance is pptd. from an aq. extract of the ivory with AcOH which on hydrolysis is converted into mannose. Albumin and globulin fractions showing no enzymic activity are prepared. H. D.

Hemicelluloses extracted from mesquite wood after chlorination. L. SANDS and P. NUTTER (J. Biol. Chem., 1935, 110, 17–22).—Mesquite sawdust was extracted as before (A., 1933, 989), treated with  $Cl_2$  and aq. NH<sub>3</sub>, and the hemicelluloses (I) were removed by aq. NaOH. By successive extractions four fractions were obtained. The pentosan content increased as the delignification proceeded. Hydrolysis of (I) gave xylose in three fractions and glucose in one. No free uronic acid was found in the hydrolysates, 2 mols. of pentose being associated with the acid. H. D.

Analysis of carbohydrates of the cell-wall of plants. I. Relation between uronic anhydride content and furfuraldehyde. F. W. NORRIS and C. E. RESCH (Biochem. J., 1935, 29, 1590-1596).----The determination of the products of distillation of the cell-wall with 12% HCl is investigated. The relation between uronic acid (I) concn. and the CO<sub>2</sub> produced by the decarboxylation method of Dixon (A., 1930, 453) in pure specimens of galacturonic, pectolic, and euxanthic acids is determined. Furfuraldehyde (II) is pptd. from the reaction products as the phloroglucide and weighed as such and the relation between (II) produced and (I) concn. is determined for the same acids. H. D.

Liberation of methyl sulphide by seaweed. P. HAAS (Biochem. J., 1935, 29, 1297—1299).—The identity of the gaseous odoriferous principle evolved by *Polysiphonia fastigiata* and *P. nigreonus* with MeSH has been confirmed. P. W. C.

Amount of hydrocyanic acid in blue couch grass (Cynodon incompletus, Nees). H. FINNE-MORE and A. B. JAFFRAY (J. Counc. Sci. Ind. Res. Australia, 1935, 8, 136—138).—The decrease in HCN content of the grass (determined after complete decomp. of glucoside by enzyme) during drying and subsequent storage was much < that in cases recorded by Seddon and King (A., 1930, 812). A. G. P.

Iodine content of tea. A. ITANO and Y. TUZI (Proc. Imp. Acad. Tokyo, 1935, 11, 141—143).— Japanese tea contains 0.45— $1.20 \times 10^{-6}$  g. of I per g. of dried leaves, of which 33—75% is extracted by hot H<sub>2</sub>O. More I is contained in younger leaves.

H. G. R.

Constituent of Pertusaria dealbata, Ach., Nyl. G. KOLLER and H. HAMBURG (Monatsh., 1935, 65, 375—379).—This lichen when extracted with Et<sub>2</sub>O gives a substance  $C_{19}H_{16}O_{11}$ , decomp. 223° (in evacuated tube), which is considered to be thamnolic acid (A., 1929, 818; 1932, 275), since it contains OMe, decomposes to form an atranol-like substance, with orcinol Me<sub>1</sub> ether, and is converted by MeOH into Me evernate and a resin, and by HCO<sub>2</sub>H into thamnol, and since the acid  $C_{10}H_{10}O_6$ , m.p. 207°, which it gives on treatment with KHCO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub>, is methylated to Me 3:5-dimethoxytoluene-1:4-dicarboxylate (A., 1929, 1460). E. W. W.

Chemical characteristics of fungi. G. REIF and G. BORRIES (Biochem. Z., 1935, 277, 329–336). —A table summarises the colours obtained when aq. extracts of the dried, finely powdered,  $Et_2O$ -extracted tissues of a variety of fungi were treated with *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO-H<sub>2</sub>SO<sub>4</sub> reagent. P. W. C.

"Blackfellow's bread," the sclerotium of the fungus Polyporus mylittæ, Cke. and Mass. J. C. EARL and G. H. McGREGOR (J. Proc. Roy. Soc. New South Wales, 1935, 68, 149—152).—The principal constituent of the sclerotium of *P. mylittæ* is closely allied to fibre cellulose, containing a polyfructosan (?) in admixture with the main polyglucosan constituent. Fats and proteins are absent. F. N. W.

Histological characteristics of plants grown in toxic concentrations of boron. I. E. WEBBER (J. Agric. Res., 1935, 50, 189—194).—Histological abnormalities in B-injured stems and leaves of prune, peach, and apricot are most marked in tissues in which accumulation of B is relatively large. No sp. reaction of the plant to B is observed. A. G. P. Physiology of germination of sugar heet. E. W. SCHMIDT (Z. Wirts. Zuckerind., 1935, 85, 303– 315).—Seedling injury, closely resembling in appearance that of mosaic virus, is produced by dil. solutions of HgCl<sub>2</sub>, TlSO<sub>4</sub>, KI, and Na<sub>3</sub>AsO<sub>3</sub>, HgCl<sub>2</sub> being the most active in this respect. Solutions of KClO<sub>3</sub> caused general destruction of the chlorophyll apparatus of the leaves. Root injury by KClO<sub>3</sub> is intermediate in severity between that by Na<sub>3</sub>AsO<sub>3</sub> and KI, and is < that by HgCl<sub>2</sub> and TlSO<sub>4</sub>. A. G. P.

Composition of mineral matter in wartresistant and -susceptible varieties of potato. A. NEMEC (Phosphorsäure, 1934, 4, 352—357; Chem. Zentr., 1935, i, 812).—Resistant varieties have higher Mg and usually Mn contents, but less Ca, than susceptible kinds. The Mg: Ca ratio in the former varies from 2.4 to 4.4 and that in the latter from 1.5 to 3.2. Infected tubers and also the warts have a low ash content and the warts contain much Ca and SiO<sub>2</sub> and little Mg. A. G. P.

Diseases of potatoes. II. E. PFANKUCH and G. LINDAU (Biochem. Z., 1935, 277, 129–138).— Acceleration of oxido-reduction reactions appears to be the most important metabolic disturbance in diseased tubers, but this is not a const. change in the press juice. The phenolase activity is at first greater but the difference disappears after a time. The determination of phenolase activity is best carried out in a buffered solution of quinol-*iso*vitamin-C.

P. W. C.

Chemistry of white rots of wood. IV. Effect on wood substance of Ustulina vulgaris, Tul. W. G. CAMPBELL and J. WIERTELAK (Biochem. J., 1935, 29, 1318—1321).—U. vulgaris produces in lime (Tilia vulgaris, Hayne) wood a typical white rot, both the carbohydrates (cellulose etc.) and lignin being attacked and the alkali-solubility when calc. as % of sound wood decreasing steadily as decay proceeds. The organism also attacks beech wood (Fagus sylvatica, L.) but more slowly, the attack being conc. as before on the cellulose. The fungus has a pronounced detrimental effect on the mechanical properties of the wood. P. W. C.

Properties of the curly top virus [of sugar beet]. C. W. BENNETT (J. Agric. Res., 1935, 50, 211—241).—Isolation of the virus is described. Its resistance to ageing and to desiccation is influenced by the nature of the medium in which it is preserved. Acid media ( $p_{\rm H}$  2.9) caused rapid inactivation, but alkaline media ( $p_{\rm H}$  7.9) are not deleterious. Preps. in 75% EtOH or COMe<sub>2</sub> retain considerable activity after 56 days. The virus is notably resistant to CuSO<sub>4</sub> (1 in 200), HgCl<sub>2</sub> (1 in 50), CH<sub>2</sub>O (1 in 100), and PhOH (1 in 25) but is inactivated by exposure to the expressed juice of beet or other plants. A. G. P.

Statistical aspect of the production of primary lesions by plant viruses. J. G. BALD (Nature, 1935, 135, 996). W. J. YOUDEN (*ibid.*, 1075). L. S. T.

"Iron-stain" disease of potatoes. G. EHRKE (Biochem. Z., 1935, 278, 195-225).—As compared with the healthy parts of potatoes the brown ("ironstained") parts have high salt and  $H_2O$  contents, reduced catalase and increased oxidase and peroxidase activity, increased  $O_2$  consumption, increased fermenting power, usually decreased  $NH_2$ -acid content, increased diastase activity, increased content of reducing substances (glutathione, ascorbic acid), and increased Fe and Mn contents. These characteristics are especially pronounced in the starch-free parts of the diseased tissue. W. McC.

Spectrochemistry of algæ. C. DHERÉ and A. RAFFY (Compt. rend. Soc. Biol., 1935, 119, 232— 235; cf. A., 1931, 884).—The fluorescence spectra of Ulva lactuca, Fucus serratus, and the phycocyanin of Aphanizomenon flos aquæ have been examined using plates especially sensitive to infra-red. H. G. R.

Intake of fluorescent substances by living plant cells. H. DORING (Ber. deut. bot. Ges., 1935, 53, 415-437).—Applications of fluorescence microscopy are described and factors affecting the absorption of luminescent substances are examined. A. G. P.

Use of methylal for inclusions in paraffin. J. DUFRENOV (Compt. rend. Soc. Biol., 1935, 119, 375-376).—Methylal, being sol. in  $H_2O$  and paraffin, can be used as an intermediary in the replacement of  $H_2O$  in tissues by paraffin. R. N. C.

Reactions of dyes with cell-substances. I. Staining of isolated nuclear substances. II. Differential staining of nucleoprotein and mucin by thionine and similar dyes. E. G. KELLEY and E. G. MULLER, jun. III. Apparatus for the definition of colour in stained histological sections. E. G. KELLEY (J. Biol. Chem., 1935, 110, 113-118, 119-140, 141-144).-I. In histological staining (e.g., of  $\beta$ -nucleohistone,  $\alpha$ -nucleoprotein, nucleic acid, histone, metaprotein, thymus) the changes in colour produced by varying the  $p_{\rm H}$ , type of dye, and type of fixative are adequately explained by supposing that salt formation occurs, but adsorption may also take place. With unmordanted hæmatoxylin the histological metachromasy appears to depend directly on [H']

II. Dyes which, on dilution, exhibit a shift towards longer  $\lambda\lambda$  in the position of max. absorption stain mucins and nucleoproteins differently, the mucins being coloured chiefly by the form of the dye which occurs in conc. solution, the nucleoproteins chiefly by that which occurs in dil. solution. The difference does not depend on [H<sup>\*</sup>].

III. An instrument similar to the Nutting monochromatic colorimeter is described. W. McC.

Mechanism for controlled continuous flow of nutrient solutions. F. P. MEHRLICH (Plant Physiol., 1935, 10, 169–177).—Apparatus is described.

A. G. P. Determination of hydrogen exponent by means of the step-photometer. A. JANKE and F. SEKERA (Biochem. Z., 1935, 277, 452).—A correction of the author's paper (A., 1932, 471). The indicator, 2:4dinitrophenol, is used in a concn. not of 0.01M but of 0.002M. P. W. C.

Use of quinhydrone and antimony electrodes for determining the  $p_{\rm H}$  of solid culture media. P. E. TILFORD (Phytopath., 1935, 25, 362—367).— Suitable technique is described. In the  $p_{\rm H}$  range  $2 \cdot 0 - 7 \cdot 1$  the quinhydrone electrode gave results in closer agreement with colorimetric tests than did the Sb electrode. In alkaline ranges both electrodes recorded unduly low vals. The former is more generally satisfactory than colorimetric tests. A. G. P.

Spectroscopically pure  $\gamma$ -ferric oxide in colloidal aggregation as a biological indicator.—See this vol., 834.

Reagents for analysis of plant sections. E. STEIMETZ (Bull. Soc. bot. France, 1934, 81, 296— 297; Chem. Zentr., 1935, i, 446).—A solution for the differential staining of cell constituents is described.

H. N. R.

**Deproteinising agent.** R. VLADESCO (Compt. rend. Soc. Biol., 1935, 119, 768-770).—Saturated solutions of  $CuSO_4$  and  $K_4Fe(CN)_6$  together form a good general deproteinising agent through pptn. of  $Cu_2Fe(CN)_6$ . It removes none of the normal determinable constituents from blood and milk, except uric acid. R. N. C.

Destruction of organic matter in plant material by nitric and perchloric acids. J. E. GIESEKING, H. J. SNIDER, and C. A. GETZ (Ind. Eng. Chem. [Anal.], 1935, 7, 185–186).—Wet ashing with boiling  $HNO_3$ -HClO<sub>4</sub> gives good recovery for Ca, Mg, K, and P. The analytical results are uniformly > after dry ashing procedures. J. L. D.

Micro- and submicro-determination of methyl alcohol. Determination in blood and tissues. M. NICLOUX (Bull. Soc. Chim. biol., 1935, 17, 194–202).—The author's earlier method for determination of EtOH by complete oxidation with  $K_2Cr_2O_7$  and determination of  $K_2Cr_2O_7$  disappearing can be applied also to MeOH with the same degree of accuracy.

P. W. C.

Determination of ethyl alcohol and its oxidation products in biological substrates. A. JANKE and S. KROPACSY (Biochem. Z., 1935, 278, 30—36).—The oxidation is stopped by addition of  $Ag_2SO_4$ , the EtOH+MeCHO determined by oxidation with  $CrO_3-H_2SO_4$  mixture, the MeCHO alone by a modified H sulphite method, and the AcOH by steamdistillation of the solution after acidification with  $H_3PO_4$  and titration of the distillate. P. W. C.

Determination of total cholesterol with digitonin. R. GOFFINET (Compt. rend. Soc. Biol., 1935, 119, 330-331).—After saponification and acidification with HCl, cholesterol is pptd. with digitonin.

H. G. R.

Application to the colorimeter of the Schoenheimer and Sperry method for determination of total and free cholesterol. F. FITZ (J. Biol. Chem., 1935, 109, 525—527).—The Schoenheimer-Sperry determination of cholesterol (A., 1934, 1240) is adapted to the colorimeter; samples of serum extracts must contain > 0.05 mg. of cholesterol, and a fresh quantity of the standard solution must be used for each determination. H. D.

Colorimetric determination of amino-acid function by triketohydrindene hydrate (ninhydrin). M. POLONOVSKI and F. MORENO-MARTIN (Compt. rend. Soc. Biol., 1935, 119, 583—585).— The blue compound of  $\alpha$ -NH<sub>2</sub>-acids and ninhydrin is separated from photosensitising yellow substances by extraction with  $CHCl_3$ , followed by re-extraction from the  $CHCl_3$  with 0.01N-NaOH, and can then be used for colorimetric determination. R. N. C.

Simple modification of Nessler colorimetry for determination of total, residual, and polypeptidenitrogen and of urea. E. HERZFELD (Mikrochem., 1935, 17, 155—164).—1 c.c. of serum is deproteinised at 100° with 20 c.c. of EtOH containing 5 drops of 1% aq. AcOH. EtOH is evaporated from the filtered liquid,  $H_2SO_4$  is added, and the residue oxidised with  $H_2O_2$ . The liquid is diluted, made alkaline, and Nessler solution + 5 c.c. of 1% gelatin added. Albumoses and peptones are similarly determined after degradation with pepsin. Urea is determined by deproteinising with AcOH and hydrolysing with urease. J. S. A.

Composition of tissue-proteins. I. Determination of purines in tissues. S. GRAFF and A. MACULLA (J. Biol. Chem., 1935, 110, 71-80).—The composition of the tissue-proteins in relation to the anatomy and physiology of the cell is investigated. Purines (I) are determined in microtome slices of the frozen tissue by extraction with EtOH, EtOH- $Et_2O$  (1:1), and COMe<sub>2</sub>. The extract is hydrolysed by a 10N-HCO<sub>2</sub>H-N-HCl mixture, which does not destroy (I). (I) are pptd. with Cu<sub>2</sub>O twice under controlled conditions, and after dissolving the Cu complex in H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> total N is determined. H. D.

Determination of carbon dioxide in culture solutions. L. B. ARRINGTON, C. H. WADLEIGH, and J. W. SHIVE (Soil. Sci., 1935, 39, 437–441).— Apparatus is described. A. G. P.

Micro-volumetric determination of sodium in blood. S. RASEJA (Bull. Soc. Chim. biol., 1935, 17, 817—830).—The material is oxidised with  $HNO_3$ and  $HClO_4$ ,  $PO_4^{\prime\prime\prime}$  removed with CaO, and Na pptd. as  $NaMg(UO_2)_3(OAc)_9$ . The ppt. is reduced with Zn-Hg for 3 hr. at 80°, and the U<sup>IV</sup> titrated with aq. KMnO<sub>4</sub>. By this method Na in normal human bloodcorpuseles and plasma is 0.6954 and 3.3843 mg. per c.c., respectively, and the ratio Na : Cl of the plasma 1.097. A. L.

Micro-determination of sodium. A. P. WEIN-BACH (J. Biol. Chem., 1935, 110, 95–99).—Na is determined (e.g., in 0·1 c.c. of serum, plasma, or whole blood) by a volumetric modification of the method of Barber et al. (A., 1932, 52). W. McC.

Digesting biological materials for calcium and phosphorus analysis. H. W. GERRITZ (Ind. Eng. Chem. [Anal.], 1935, 7, 167–168).—Digests of biological materials with boiling  $HNO_3-70\%$  HClO<sub>4</sub> are suitable for the determination of elements which do not form insol. perchlorates. J. L. D.

Microchemical detection of aluminium and its presence in the plant world. Y. YOSHH and T. JIMBO (Sci. Rep. Tôhoku, 1932, [iv], 7, 65-77; Bied. Zentr., 1934, A, 5, 261).—Alizarin-S is used for detecting Al in plant materials. Marked accumulation of Al occurs in leaves of nearly all members of the afmilies, Symplocaceæ, Diapensiaceæ, Theaceæ, Cytheaceæ, Gleicheniaceæ, and Lycopodiaceæ.

A. G. P.