

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JANUARY, 1935.

### General, Physical, and Inorganic Chemistry.

**Isotope effect in the Lyman series of hydrogen.** S. S. BALLARD and H. E. WHITE (Physical Rev., 1933, [ii], 43, 941).—Using  $H_2O$  containing a high  $[H^2]$ , six members of the Lyman series of H have been observed as close doublets. In agreement with the theory of broadening of lines due to the Doppler effect, the  $H^1$  component is broader than the  $H^2$ .

L. S. T.

**Spin of hydrogen isotope.** G. N. LEWIS and M. F. ASHLEY (Physical Rev., 1933, [ii], 43, 837).—The emission spectrum of mol.  $H_2$  containing approx. 25%  $H_2$ , 50%  $H^1H^2$ , and 25%  $H_2^2$  shows that the spin of  $H^2$  is neither 0, 1/2, nor 3/2; it is, in all probability, 2/2.

L. S. T.

**Band spectrum of the  $H^1H^2$  molecule.** M. F. ASHLEY (Physical Rev., 1933, [ii], 43, 770).—An electronic isotopic shift of approx. 2.4 wave-nos. has been observed.

L. S. T.

**He fluorescence and collisions of the second kind of excited He atoms.** W. MAURER and R. WOLF (Z. Physik, 1934, 92, 100—115).

A. B. D. C.

**Partial resolution of the Be I line 4572.69 Å. and probable spin of the  $Be^9$  nucleus.** A. E. PARKER (Physical Rev., 1933, [ii], 43, 1035—1036).—There is a separation of  $0.033 \pm 0.005$  cm.<sup>-1</sup> between the two components of the Be I line 4572.69 Å. The weaker component, a  $2^1P_1-3^1D_2$  transition, contains  $36 \pm 4\%$  of the total intensity, which indicates a nuclear spin of 1/2 for  $Be^9$ .

L. S. T.

**Metastable  $^2D$  level of the nitrogen atom.** H. STÜCKLEN and E. P. CARR (Physical Rev., 1933, [ii], 43, 944—945).

L. S. T.

**Intensity measurements in the first positive bands of nitrogen.** A. ELLIOTT and W. H. B. CAMERON (Proc. Physical Soc., 1934, 46, 801—804).—Integrated intensities measured by photographic photometry, using as sources the high-frequency discharge, the d.c. discharge, and the afterglow of active N, show that the probability of transition between two vibrational levels is independent of excitation conditions.

N. M. B.

**Wave-lengths and terms of the fluorine spectrum, F IV.** B. EDLÉN (Z. Physik, 1934, 91, 19—26).

A. B. D. C.

**Moving striations in neon.** (FRL.) B. VAN MANEN (Physica, 1934, 1, 967—978).—In the positive column with moving striations for Ne at 3.2 mm. pressure, the difference between the max. and min. potentials of a striation falls with increasing

column current for a W cathode. For an oxide cathode the p.d. depends on the no. of striations, but the results are not reproducible.

M. S. B.

**Transition probabilities in the sharp and diffuse series of the alkalis.** L. S. ORNSTEIN and J. KEY (Physica, 1934, 1, 945—952).—The transition probability for  $p-d$  and  $s-p$  lines in Na and K has been determined using the a.c. arc. It has also been calc. for Rb and Cs from previous data.

M. S. B.

**Starting potential of the glow discharge in neon-argon mixtures between large parallel plates. I. Results.** F. M. PENNING and C. C. J. ADDINK. II. Ionisation and excitation by electrons and metastable atoms. F. M. PENNING (Physica, 1934, 1, 1007—1027, 1028—1044).—I. Measurements previously made with pure Ne have been extended to pure A and mixtures of A and Ne.

II. Calculations have been made of: the relation between  $V_c$ , the starting potential of the corona discharge between infinite parallel plates, and  $\eta_2$ , the ionisation coeff. for A (A in mixture  $< 0.01\%$ ); the ionisation coeff.  $\eta_{2e}$  due to direct ionisation of A atoms by electrons; the relation between  $\eta_2$  and the ionisation by metastable Ne atoms; the influence of the energy loss of the electrons in elastic collisions; the relation of  $V_c$  to the proportion of A and the gas  $d$ .

M. S. B.

**Effect of mercury vapour on the high [spectral] terms of the alkali [metals].** B. PONTECORVO (Atti R. Accad. Lincei, 1934, [vi], 20, 105—109).—Hg vapour has a very weak effect in displacing the limits of the series of Na and K.

O. J. W.

**Paschen-Back effect and the polarisation of resonance radiation. Sodium ( $5^2P_{1/2,3/2}-3^2S_{1/2}$ ).** N. P. HEYDENBURG (Physical Rev., 1933, [ii], 43, 1045).—Preliminary data are given.

L. S. T.

**Zeeman effect and the magnetic quenching of the fluorescence of  $S_2$  and  $Te_2$ .** I. I. AGARBICEANU (Compt. rend., 1934, 199, 1036—1038; cf. A., 1933, 1095; 1934, 1, 353).—The decrease in the fluorescence of  $S_2$  and  $Te_2$  vapours under a magnetic field is explained by the Zeeman and Paschen-Back effects.

J. W. S.

**Additional bands in the band system of sulphur.** R. K. ASUNDI (Current Sci., 1934, 3, 154; cf. A., 1931, 996).

L. S. T.

**Spectra of potassium, K IV and K V, and of calcium, Ca V and Ca VI.** I. S. BOWEN (Physical Rev., 1934, [ii], 46, 791—792).—Data and classifications



for 19 new lines of K IV, 26 of K V, 36 of Ca V, and 31 of Ca VI, including singlet and intercombination lines, below 650 Å., are tabulated. The presence in nebulae of lines due to the forbidden  $^3P-^1D$  transitions in Si I, Cl II, A III, K IV, and Ca V is discussed.

N. M. B.

**Highly ionised potassium and calcium spectra.** A. E. WHITFORD (Physical Rev., 1934, [ii], 46, 793).—Classifications of 75 lines of K VI, K VII, K VIII, K IX, Ca VII, and Ca VIII, and term vals. are tabulated.

N. M. B.

**Nuclear moment of scandium (Sc<sup>45</sup>).** H. SCHÜLER and T. SCHMIDT (Naturwiss., 1934, 22, 758—759).—The hyperfine structure of the Sc spectrum between 4700 and 6500 Å. was investigated. The nuclear moment is  $7/2$ .

A. J. M.

**Nuclear moment of scandium.** H. KOPFERMANN and E. RASMUSSEN (Z. Physik, 1934, 92, 82—86).—The moment is  $7/2$ .

A. B. D. C.

**Hyperfine structure and nuclear moment of cobalt.** N. S. GRACE (Physical Rev., 1933, [ii], 43, 762).—Examination of the hyperfine structure of the spectrum of Co I indicates that the nuclear moment of Co is  $\approx 5/2$  and  $\approx 9/2$ .

L. S. T.

**Absorption measurements in the band spectra of zinc and cadmium vapours.** S. MROZOWSKI (Z. Physik, 1934, 91, 600—608).

A. B. D. C.

**Intensity measurements in a fine structure multiplet of As II.** S. TOLANSKY and J. F. HEARD (Proc. Roy. Soc., 1934, A, 146, 818—824).—The mean vals. of the intensity ratios in the fine structure triplet of As II  $\lambda 5231$  ( $5s^3P_1-5p^3P_0$ ) are 0.98 : 2 : 2.99, in agreement with the theoretical vals. 1 : 2 : 3. The quantum wts. of the fine structure levels in the  $5s^3P_1$  term thus  $\propto 2F+1$ .

L. L. B.

**I. Complexity of the resonance spectrum of selenium. II. Influence of nitrogen on the fluorescence spectrum of selenium.** S. GAWRONSKI (J. Phys. Radium, 1934, [vii], 5, 533—534, 535—537).—I. The complexity of the fluorescence spectrum of Se, excited by the Hg 4359 and 4047 Å. lines, using a low-pressure cooled Hg lamp, showed no difference if excited by broad or narrow Hg lines, and was uninfluenced by the temp. of the Se vapour or the mol. kinetic energy. The complexity is attributed to the existence of a large no. of isotopes.

II. Addition of N<sub>2</sub> extinguished the multiplets and slightly weakened the characteristic rotation doublets. With increasing pressure of N<sub>2</sub> the multiplets disappeared, giving place to band fluorescence, which in turn disappeared, passing to the continuous glow with only the rotation doublets visible.

N. M. B.

**Lack of observed hyperfine structure in strontium.** A. N. BENSON and R. A. SAWYER (Physical Rev., 1933, [ii], 43, 766—767).—Forty lines of Sr I and Sr II in the region 5600—4000 Å. gave no evidence of hyperfine structure. Sr has no nuclear spin or isotope shift  $> 0.050$  cm.<sup>-1</sup>

L. S. T.

**Nuclear moments of niobium from hyperfine structure.** S. S. BALLARD (Physical Rev., 1934, [ii], 46, 806—811).—The observed hyperfine structure in the arc spectrum can be accounted for by attribut-

ing mechanical and magnetic moments to the nucleus. The nuclear spin is  $9/2$ . The approx. nuclear  $g$ -factor is 0.83, giving a magnetic moment of 3.7 nuclear magnetons.

N. M. B.

**Excitation of atomic lines in the molecular absorption in Cd vapour.** E. KALINOWSKA (Acta phys. polon., 1933, 2, 111—117; Chem. Zentr., 1934, ii, 19).—From the dependence of the intensity of the fluorescence on that of the exciting light it is shown that excitation of Cd atom to the  $2^3S_1$  state at approx. 600° requires two absorption processes by the Cd mol. At approx. 900° only one is needed.

H. J. E.

**Polarisation of the fluorescence of Cd vapour.** L. SOSNOWSKI (Acta phys. polon., 1932, 1, 327—332; Chem. Zentr., 1934, ii, 19).—Data are recorded.

H. J. E.

**Fluorescence of mixtures of Cd and Zn vapours.** F. SPIEWANKIEWICZ (Acta phys. polon., 1932, 1, 345—350; Chem. Zentr., 1934, ii, 19—20).—Light between 2300 and 2150 Å. excites a band at 4850—6400 Å. in the mixed vapours at 780°.

H. J. E.

**Extension of the platinum I-like isoelectric sequence to tellurium IV, lead V, and bismuth VI.** G. K. SCHOEFFLE (Physical Rev., 1933, [ii], 43, 374).

L. S. T.

**Fluorescence and absorption spectrum of I<sub>2</sub> vapour.** I. I. AGARBICEANU (Ann. Physique, 1934, [xi], 2, 347—447).—Six anti-Stokes lines of the fluorescence spectrum of I<sub>2</sub>, excited by the  $\lambda\lambda 5460, 5770, \text{ and } 5790$  Hg lines, have been observed for the first time, the excitation being independent of the width of the exciting line. An interpretation is proposed. New absorption bands are reported. Addition of O<sub>2</sub> or N<sub>2</sub> causes a broadening of the absorption lines, more marked in the case of O<sub>2</sub>, and increasing with pressure. From the broadening the active radius of the I<sub>2</sub> mol. is calc. A connexion between this broadening and the depolarisation of resonance lines is found. From photographs of fluorescence lines excited by Hg  $\lambda 5461$  it is shown that, for a normal and excited level, the resonance line is more affected by a perturbing factor than the corresponding absorption line under the same conditions, analogous to the effect of a magnetic field.

N. M. B.

**Molecular spectrum emitted from atomic iodine vapour.** O. OLDENBERG (Physical Rev., 1933, [ii], 43, 501).—The intensity of the continuous spectrum shown by I vapour at high temp. decreases with a decrease in pressure; it is emitted from a mol. just formed by a pair of atoms, one of which is excited (cf. A., 1924, ii, 579).

L. S. T.

**Light absorption of adsorbed caesium.** J. H. DE BOER, J. F. H. CUSTERS, and C. J. DIPPFL (Physica, 1934, 1, 935—944).—The absorption spectrum of Cs adsorbed by CaF<sub>2</sub> has been measured for different degrees of occupation of the adsorbed layer. For low occupation the spectra are due to Cs atoms adsorbed on active spots by electrostatic polarisation, and strong light absorption beyond 440 m $\mu$  is no longer observed. Polyat. layers, in which the atoms are bound by van der Waals



forces, give a spectrum almost the same as that of a thin film of Cs metal. The high photo-electric yield at a low degree of occupation, and the shift of the threshold towards longer wave-lengths, are correlated with the absorption spectra. M. S. B.

**Nuclear magnetic moment of caesium from the polarisation of resonance radiation.** N. P. HEYDENBURG (*Physical Rev.*, 1934, [ii], 46, 802—805; cf. A., 1934, 1279).—For a nuclear spin of  $7/2$  the hyperfine separation consts. for the  $6^2P_{3/2}$  and  $7^2P_{3/2}$  levels of Cs I are  $1.42 \times 10^{-3}$  and  $4.86 \times 10^{-4}$  cm.<sup>-1</sup>, respectively. The calc. nuclear magnetic moments are 2.40/1840 and 2.41/1840 Bohr magnetons, respectively, in agreement with the val. 2.52/1840 obtained from the splitting of the lower  $6^2S_{1/2}$  level. N. M. B.

**Isotopes of samarium.** H. SCHÜLER and T. SCHMIDT (*Z. Physik*, 1934, 92, 148—152).—Optical isotope separation for Sm 150 and 152 is twice that for Sm 152 and 154, indicating a definite nuclear structure change in passing from 150 to 152. A. B. D. C.

**Hyperfine structure and isotopic constitution of tungsten.** N. S. GRACE and H. E. WHITE (*Physical Rev.*, 1933, [ii], 43, 1039; cf. A., 1934, 339).—The arc spectrum of W shows patterns corresponding with only three components which are attributed to the isotopes of even no. A fourth isotope, possessing a magnetic and a mechanical nuclear moment, is indicated. L. S. T.

**Application of the mechanical interval recorder to the analysis of the spectrum of osmium I.** W. ALBERTSON (*Physical Rev.*, 1933, [ii], 43, 501; cf. A., 1934, 468).—Some energy levels of Os I have been found by means of the mechanical interval recorder. L. S. T.

**Band systems of mercury.** T. S. SUBBARAYA (*Proc. Indian Acad. Sci.*, 1934, 1, A, 166—177).—A theoretical survey of the band systems and an analysis of five of them. N. M. B.

**Explosion spectrum of mercury compared with arc spectra under ordinary pressure and in a vacuum.** H. NAGAOKA and T. FUTAGAMI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, 25, 111—126).—The spectrum (I) produced by exploding a thin stream of Hg by an electric discharge has been compared with spectra from Hg-vapour lamps working at approx. atm. pressure (II) and in a vac. Owing to the violence of the explosion no bands appear in (I), and there are many lines due to ionised Hg. In (II) structureless bands are conspicuous. R. S. B.

**Intensity distribution in the fluorescence bands of mercury vapour.** I. MROZOWSKA (*Acta phys. polon.*, 1933, 2, 81—89; *Chem. Zentr.*, 1934, ii, 18—19).—The effect of temp. and pressure on the intensity distribution in bands excited by the Zn line 2558 Å. was studied. H. J. E.

**Zeeman effect of the hyperfine structure of the Hg line 2536.** A. ŽVIRONAS (*Helv. phys. Acta*, 1933, 6, 273—276; *Chem. Zentr.*, 1934, ii, 18).—Data are recorded, agreeing with theory. H. J. E.

**Anomalous Zeeman effect of single hyperfine structure components of the mercury resonance line 2537 Å.** I. The  $\pi$  components. A. ŽVIRONAS (*Helv. phys. Acta*, 1934, 7, 224—256; *Chem. Zentr.*, 1934, i, 3026).—Data are recorded and discussed. H. J. E.

**Emitter of the bands near 2482.07 Å. in the mercury spectrum.** L. JOB (*Acta. phys. polon.*, 1933, 2, 31—37; *Chem. Zentr.*, 1934, ii, 398).—Fine structure measurements are recorded. The origin of the bands is discussed. H. J. E.

**Resonance series of lead vapour.** M. DOMA-NIEWSKA-KRÜGER (*Acta phys. polon.*, 1932, 1, 357—362; *Chem. Zentr.*, 1934, ii, 18).—Two resonance series excited at 900° by 4358.3 and 5461 Å. Hg lines are described. H. J. E.

**Emission spectrum of the night sky. I. Ultra-violet.** J. DUFAY. II. Ultra-violet extremity. J. GAUZIT (*J. Phys. Radium*, 1934, [vii], 5, 523—526, 527—532; cf. A., 1934, 232).—I. Data for 78 bands or lines in the region 4815—3000 Å. are tabulated. The spectrum differs from that of the polar aurora by the weak intensity of the negative N<sub>2</sub> bands and of the bands of the second positive group, and by the presence of numerous lines of unknown or doubtful origin. Data on relationships with the spectra of A, He, and those of comet nuclei are extended to the ultra-violet.

II. Data for about 110 emission lines are given, with possible identifications, and comparisons with the results of other investigators. Absorption by atm. O<sub>3</sub> was not found; the spectral intensity of the night sky decreased only slowly towards 3000 Å. N. M. B.

**Auroral spectrum and its interpretation.** L. VEGARD (*Trans. Amer. Geophys. Union*, 1933, 68—69).—A review. CH. ABS. (e)

**Electric furnace ionisation effect.** A. S. KING (*Physical Rev.*, 1933, [ii], 43, 214).—When a substance of moderate ionisation potential is vaporised in a C-tube furnace a temp. is found at which practically the whole neutral spectrum and the stronger lines of the ionised atom are given. When the furnace is subsequently run at the same temp. and total pressure with but little of the substance present, a spectrum in which the enhanced lines are relatively strong is obtained. This effect is marked for Ca, Ba, Sr, and Nd. L. S. T.

**Anode temperature and emission of X-rays.** F. HALLA and H. NOWOTNY (*Z. Physik*, 1934, 92, 76—81).—Rise in temp. increases emission with const. anode current. A. B. D. C.

**Natural X-ray line widths: correction for finite resolving power.** L. G. PARRATT (*Physical Rev.*, 1934, [ii], 46, 749—754).—The resolving power of the X-ray double-crystal spectrometer is increased 2—4 times by employing etched quartz crystals. The shapes of the K $\alpha$  lines of Mo, Cu, and Ti were observed in anti-parallel positions. Correction for finite resolving power was negligible. N. M. B.

**Weak X-ray lines of niobium and antimony.** P. A. ROSS and P. KIRKPATRICK (*Physical Rev.*,



1933, [ii], 43, 1036).—Data for new weak emission lines of the *K* series of these elements are recorded.

L. S. T.

**Absolute X-ray wave-lengths by refraction in quartz.** J. A. BEARDEN and C. H. SHAW (Physical Rev., 1934, [ii], 46, 759—763).—High-precision measurements, with X-rays incident both internally and externally, gave  $1-\mu=(8.553\pm 0.005)\times 10^{-6}$ . Abs. wave-lengths calc. from quantum theory and from revised data for photographic results confirmed the vals. found by the ruled grating.

N. M. B.

**$K\alpha$  X-ray lines of carbon and carbon compounds.** H. BROILL, R. GLOCKER, and H. KIESSIG (Z. Physik, 1934, 91, 27—41).

A. B. D. C.

**Self-ionisation of sodium and caesium at glowing tungsten and rhenium surfaces.** H. ALTERTHUM, K. KREBS, and R. ROMPE (Z. Physik, 1934, 92, 1—18).—Na and Cs are 20 and 50% ionised at Rh, and 8.5 and 54% at W, the temp. variation of Na (but not Cs) efficiencies obeying Langmuir's first formula.

A. B. D. C.

**Ionisation potentials and probabilities for the formation of multiply-charged ions in the alkali vapours and in krypton and xenon.** J. T. TATE and P. T. SMITH (Physical Rev., 1934, [ii], 46, 773—776; cf. A., 1931, 665).—Probability curves and ionisation potential data, obtained by mass-spectrograph analysis, are given for ions formed by electron impact in Na, K, Rb, and Cs vapours, and in Kr and Xe. Evidence of additional mechanisms of formation appear for  $K^+$  at 15.5 and 150, for  $Rb^+$  at 12.5, for Cs at 10, 17.5, and 60, and for  $Cs^{2+}$  at 80 volts.

N. M. B.

**Electrical point action with spherical conductors of atomic and sub-atomic dimensions.** A. UPMARK (Z. Physik, 1934, 91, 737—741).—Theoretical.

A. B. D. C.

**Electrical clean-up of gases at low pressures.** II. W. VON MEYEREN (Z. Physik, 1934, 91, 727—736; cf. A., 1933, 992).—Clean-up has been studied in He, A, and  $N_2$  between  $5\times 10^{-4}$  and  $1\times 10^{-7}$  mm.

A. B. D. C.

**Disappearance of hydrogen in presence of potassium and lithium ion sources.** C. H. KUNSMAN and R. A. NELSON (J. Chem. Physics, 1934, 2, 752—755; cf. A., 1932, 892).—The disappearance of  $H_2$  in a discharge tube containing an anode coated with either synthetic spodumene or an Fe-Al-K catalyst is shown to be completely accounted for by reaction with the anode material. No evidence of reaction in the gaseous phase was observed.

F. L. U.

**Ionic shell effect in gas discharges.** A. GÜNTHER-SCHULZE (Z. Physik, 1934, 91, 724—726).—Decrease of electron velocity increases negative ions in a mol. gas; this forms a space charge in wide tubes maintaining the discharge within a narrow space.

A. B. D. C.

**Photo-electric effect of caesium vapour.** J. KUNZ (Physical Rev., 1933, [ii], 43, 1052).—The min. in the ionisation efficiency curve has again been established even in vapour at room temp.

L. S. T.

**Photo-electric effect. I. External photo-electric effect of elements in the periodic table.** R. SCHULZE (Z. Physik, 1934, 92, 212—227).—The long-wave limit, defined as the wave-length at which the electron current falls below  $10^{-15}$  amp. for an incident light energy of 10 ergs per sec., follows the ionisation potential derived from series limits of the free atoms. The quantum efficiency is of the same order for atoms in one group of the periodic table.

A. B. D. C.

**Energy distribution of photo-electrons as a function of the thickness of a potassium film.** J. J. BRADY (Physical Rev., 1934, [ii], 46, 768—772; cf. A., 1932, 1184).—Current-voltage curves for 0.8, 2, 3, and 30 mol. layers, using 3650 and 4350 Å., and analysis curves by the theory of Du Bridge (cf. A., 1933, 657) are given. Max. retarding potentials at 0° abs. were found by three methods. The photo-current decreased after the formation of films < 3 mol. layers, but remained nearly const. for thicker layers, indicating that the K "dissolves" in the Ag more readily before than after the formation of a continuous film.

N. M. B.

**Radiation quantum and photographic threshold.** H. BROILL, R. GLOCKER, and H. LANGENDORFF (Z. Elektrochem., 1934, 40, 784—789).—A quant. relation is established.

E. S. H.

**Chemical registration of the diffraction of electric waves.** W. ARKADIEW (Compt. rend., 1934, 199, 848—849).—Detectors of the Branly coherer type, with electrodes of different metals, are arranged with the electrodes in contact with paper impregnated with an indicator. When irradiated with Herzian waves, colour changes occur where the rays have passed. The method can be applied to the detection of diffraction images of the source.

J. W. S.

**Born's theory of the electron.** J. FRENKEL (Proc. Roy. Soc., 1934, A, 146, 930—935).—Mathematical.

L. L. B.

**Dependence of the magnetic susceptibility of an electron gas on temperature.** K. F. NIESSEN (Physica, 1934, 1, 979—988).—Theoretical. A formula has been deduced showing that the magnetic susceptibility of an electron gas increases with rise of temp.

M. S. B.

**Electron diffusion.** M. J. DRUYVESTYEN (Physica, 1934, 1, 1003—1006).—An error in a previous communication on the positive column with moving striations (A., 1934, 468) is corr. The distribution of final velocities of the electrons in a homogeneous field has been calc. for the case when the electrons make elastic collisions only with the atoms of gas.

M. S. B.

**Secondary electron emission from tantalum.** C. L. UTTERBACK and E. A. WILLIAMS (Physical Rev., 1933, [ii], 43, 212).—The electron emission from Ta bombarded by  $Li^+$  has been measured.

L. S. T.

**Diffraction of electrons as a search for polarisation.** F. E. MYERS, J. F. BYRNE, and R. T. COX (Physical Rev., 1934, [ii], 46, 777—785).—Electrons accelerated by voltages 80—225 kv. passed through a thin homogeneous foil of polycryst. Au and formed



a diffraction pattern on a fluorescent screen, through a hole in which various rays of the diffracted beam fell on a second diffracting foil. The second diffraction pattern, obtained on a photographic plate, showed, on examination for asymmetry, no evidence (<10%, if any) of polarisation of the electron beam.

N. M. B.

**Effect of spin interaction in the diffraction and polarisation of electrons.** J. H. HOWEY (Physical Rev., 1933, [ii], 43, 499).

L. S. T.

**Electron transfer from metals to dielectrics.** N. KALABUCHOV (Z. Physik, 1934, 92, 143—147).—The work of transfer of electrons from Ag to mica is 0.5, to rock-salt 1.8, volts < that for transfer to vac.

A. B. D. C.

**Collisions of slow electrons with atoms.** IV. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1934, A, 146, 880—900).—The theory of electron exchange developed previously (cf. A., 1933, 613) is applied to a study of the angular distribution of electrons scattered inelastically by A and Ne atoms, and good agreement is obtained with experiment. The effect of the disturbance of the at. field by the incident electron waves on the elastic scattering is discussed. The theory is applied to the scattering by H<sub>2</sub> and He. Comparison with experiment shows that the excess of scattering at small angles above that given by Born's approximation is due to this polarisation effect.

L. L. B.

**Electron capture cross-sections.** L. A. YOUNG and N. E. BRADBURY (Physical Rev., 1933, [ii], 43, 1054).—Vals. calc. on certain assumptions are of the same order of magnitude as experimental vals. for electronegative gases such as O<sub>2</sub> and CO<sub>2</sub>.

L. S. T.

**Probability function for the production of He<sup>++</sup> by single electron impact.** W. BLEAKNEY (Physical Rev., 1933, [ii], 43, 378).—It is concluded that about 1% of the He ions produced by 330-volt electrons are originally doubly charged.

L. S. T.

**Collision of K<sup>+</sup> ions with inorganic and organic gas particles.** I. Elastic and inelastic collision. II. Mechanism of the collision process. O. SCHMIDT (Ann. Physik, 1934, [v], 21, 241—267, 268—273; cf. A., 1934, 863, 937).—I. The nature of the collision of K<sup>+</sup> ions with gas particles is indicated by the symmetry of the distribution curve. For the completely symmetrical curves, which are given by Hg, Kr, Xe, MeCl, CO<sub>2</sub>, and N<sub>2</sub>, there is pure scattering at 200 volts. The energy losses are small, and the collisions are elastic. All other gases give unsymmetrical curves, indicating energy losses on impact. Two groups may be recognised: (a) in which the asymmetry (I) decreases with increasing mass in a homologous series (inert gases), (b) in which (I) increases with decreasing mass (paraffins and olefines).

II. The occurrence of elastic and inelastic collisions between K<sup>+</sup> ions and gas particles (II) is due to difference in time of impact, which in turn depends on the deformability of (II).

A. J. M.

**Speed of positive ions in nitrogen.** J. H. MITCHELL and K. E. W. RIDLER (Proc. Roy. Soc.,

1934, A, 146, 911—921).—The mobility of the positive ions formed by a glow discharge in pure N<sub>2</sub> at 4—9 mm. pressure is 2.67 cm./sec./volt/cm. Evidence is adduced to prove that these ions are N<sub>2</sub><sup>+</sup>, and that their mobility is 7.5% < that appropriate to their mass owing to the phenomenon of electron exchange. Vals. of the mobilities of NH<sub>3</sub><sup>+</sup>, Kr<sup>+</sup>, Xe<sup>+</sup>, and Hg<sup>+</sup> in N<sub>2</sub> all lie on a smooth curve connecting the mobility of an ion with its mass. Evidence for electron capture is obtained indirectly from the study of the breakdown of Langevin's law (mobility × pressure = const.), when the velocity is increased above a certain val.

L. L. B.

**Ions in oxygen and hydrogen.** C. D. BOCK (Physical Rev., 1933, [ii], 43, 1053—1054).—The results of a study of aged ions in O<sub>2</sub> using a magnetic spectrometer with high-order focussing are recorded.

L. S. T.

**High-velocity mercury ions.** W. M. COATES and D. H. SLOAN (Physical Rev., 1933, [ii], 43, 212—213).—The method of successive acceleration of Hg ions has been developed to produce particles of 2.85 × 10<sup>6</sup> e.v. energy. Each ion striking a Mo target produces seven to ten secondary electrons.

L. S. T.

**Mass spectrum analysis of the products of ionisation by electron impact in nitrogen and acetylene.** J. T. TATE, P. T. SMITH, and A. L. VAUGHAN (Physical Rev., 1933, [ii], 43, 1054).—A comparison of the ionisation potentials (I) of N<sub>2</sub> and A gave for the former the val. 15.65 ± 0.02 e.v. Mass spectrum analysis of the products of ionisation by electron impact in C<sub>2</sub>H<sub>2</sub> at low pressure showed the formation of C<sub>2</sub>H<sub>2</sub><sup>+</sup> (11.2), C<sub>2</sub>H<sup>+</sup> (17.8), C<sub>2</sub><sup>+</sup> (23.8), CH<sup>+</sup> (22.2), C<sup>+</sup> (24.5), and H<sup>+</sup> (21.7 and 25.6). (I) in e.v. are given in parentheses. The efficiency of formation of the H<sup>+</sup> ion increased sharply at 25.6 ± 1.0 e.v. C<sup>13</sup>, forming an ion of mass 27, was found, but no negative ions.

L. S. T.

**Mass of Be<sup>9</sup> and the at. wt. of beryllium.** K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 367—368).—The vals. obtained by measurements of spectra for the mass of Be<sup>9</sup> are 9.0155 ± 0.0006 on the O<sup>16</sup>=16 scale and 9.0154 ± 0.0008 (Ne<sup>20</sup>=19.9967). It is improbable that the nucleus of Be<sup>9</sup> consists of two α-particles and one neutron, or of two α-particles, one proton, and one electron. The at. wt. of Be from the above is 9.0130 ± 0.0007 on the chemical scale and is < Hönigschmid and Birckenbach's val. of 9.0179 ± 0.0009. The packing fraction of Be<sup>9</sup> is +17.2. The mechanism of disintegration and γ-ray production from Be<sup>9</sup> is discussed.

L. S. T.

**At. wt. of protoactinium.** A. V. GROSSE (J. Amer. Chem. Soc., 1934, 56, 2501).—The mean val. 230.6 has been determined.

E. S. H.

**Measurement of the masses of He and H<sup>1</sup>, Ne<sup>20</sup>, Ne<sup>22</sup>, B<sup>11</sup>, Cl<sup>35</sup>, and Cl<sup>37</sup> with a mass spectrograph.** K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 378; cf. A., 1933, 203).—Referred to H<sup>1</sup>=1.00778, He=4.00218 ± 0.00004. Referred to O<sup>16</sup>, Cl<sup>35</sup>=34.9796 ± 0.0012, and Cl<sup>37</sup>=36.9777 ± 0.0019. For other vals. see A., 1933, 442.

L. S. T.

**Relative abundance of the neon isotopes.** W. BLEAKNEY (Physical Rev., 1933, [ii], 43, 1056).—



Intensities observed are  $^{20}\text{Ne}^+ : ^{22}\text{Ne}^+ : ^{21}\text{Ne}^+ = 100 : 8.2 : 0.28$  and  $^{20}\text{Ne}^{++} : ^{22}\text{Ne}^{++} : ^{21}\text{Ne}^{++} = 100 : 9.2 : 0.30$ . The existence of  $^{21}\text{Ne}^{++}$  thus appears to be established. No trace of ion of mass 23 could be detected (cf. A., 1933, 333). L. S. T.

**Mass spectra of neon fractionated by G. Hertz and the non-existence of  $\text{Ne}^{23}$ .** K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 1060).—No line corresponding with  $\text{Ne}^{23+}$  was observed in fractionated Ne containing  $\text{Ne}^{22}$  in the same abundance as  $\text{Ne}^{20}$ .  $\text{Ne}^{21}$  and  $\text{Ne}^{22}$  were enriched three and nine times their abundance in atm. Ne, and  $\text{Ne}^{23}$ , if present, would have been enriched 27 times in this fraction. Bleakney's result (cf. preceding abstract) is confirmed. L. S. T.

**Isotopic constitutions of krypton, mercury, selenium, cadmium, and germanium.** K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 1056).—Results for Kr, Se, and Cd confirm Aston's work. There is no evidence for 9% of  $\text{Se}^{81}$ .  $\text{Cd}^{108}$  and  $\text{Cd}^{118}$ , found in band spectra, have not yet been observed, probably owing to technical difficulties and to their relatively small abundance. Lines attributed by Aston to  $\text{Ge}^{71}$ ,  $\text{Ge}^{75}$ , and  $\text{Ge}^{77}$  are mainly, if not entirely, due to hydrides of  $\text{Ge}^{70}$ ,  $\text{Ge}^{74}$ , and  $\text{Ge}^{76}$ . L. S. T.

**Application of radioactive methods in chemistry.** O. HAHN (Ber., 1934, 67, [A], 150—163).—A lecture. H. W.

**New kind of radioactivity.** R. M. LANGER and R. W. RAITT (Physical Rev., 1933, [ii], 43, 585).—General considerations and quantum theory lead to the conclusion that  $\text{Be}^9$  should decompose spontaneously, giving off  $\alpha$ -particles and possibly a neutron. Ra-free Be has an  $\alpha$ -particle activity of 1 cm. range in air, and half-life period of  $10^{14}$  years in accord with the He content of certain beryls.  $\text{He}^5$  may be a product of the disintegration. This abnormal He content should not be explained in terms of the radioactivity of  $\text{Be}^8$ , the life-period of which is too short for this isotope to have played any part in the chemistry of Be. L. S. T.

**Attempt to observe a helium isotope.** J. T. TATE and P. T. SMITH (Physical Rev., 1933, [ii], 43, 672).—A mass-spectrographic analysis of the gas obtained by heating a crushed crystal of beryl after passage through a C-liquid air trap showed the presence of  $\text{He}^4$ .  $\text{He}^5$ , if present, was  $< 1$  in  $4 \times 10^4$  relative to  $\text{He}^4$  (cf. preceding abstract). L. S. T.

**Radioactivity of beryllium.** R. M. LANGER and R. W. RAITT (Physical Rev., 1933, [ii], 43, 1055).—The decomp. products of Be disintegration have a range about 1 cm. in air. The decay const. of Be is  $10^{-21}$  sec. $^{-1}$  Strutt's data for the Acworth beryls lead to a const. of the same order of magnitude. The failure of the Condon-Gurney-Gamow theory in this case again indicates that the light nuclei, at least, are not composed of  $\alpha$ -particles. L. S. T.

**Formation of branched tracks (due to  $\alpha$ -particle collisions) on photographic plates covered with a heavy layer of emulsion.** A. P. ZHDANOV (Trav. inst. étât radium, U.S.S.R., 1933, 2, 249—

265).— $\alpha$ -Particles from Po in air were studied by photographing their tracks on thickly-coated plates. Of 3000 tracks, 35 showed breaks and 11 showed branchings. CH. ABS. (e)

**Errors in  $\alpha$ -particle measurements.** I. E. STARIK and O. S. MELIKOVA (Trans. inst. étât radium, U.S.S.R., 1933, 2, 117—126). A discussion. Most of the variations and errors are due to the type of vessel used for holding the sample. CH. ABS. (e)

**Continuous  $\beta$ -ray spectrum.** A. BRAMLEY (Physical Rev., 1933, [ii], 43, 767; cf. A., 1933, 1100).—A discussion of the equivalence of mass and energy in  $\beta$ -particle disintegration processes. L. S. T.

**$\beta$ -Rays of radium-D.** H. O. W. RICHARDSON and A. LEIGH-SMITH (Nature, 1934, 134, 772).—Expansion chamber  $\beta$  tracks from Ra-D tetramethyl show that the typical disintegration of Ra-D consists of a 47,200-volt  $\gamma$ -transition accompanied by the emission of a nuclear electron of 0—3 mm. range in air. The high energy limit of the nuclear spectrum is probably near 10—12 kv.  $\beta$ -Rays between 10 and 30 kv. found in previous experiments are absent. They are identified as secondary electrons which had lost energy in the solid material on which the radioelement had previously been mounted. L. S. T.

**Molecular changes accompanying the radioactive transformation of radium-D.** R. A. MORTENSEN and P. A. LEIGHTON (J. Amer. Chem. Soc., 1934, 56, 2397—2398).—Evidence is adduced to show that Ra-D tetramethyl is not broken down completely by the radioactive transformation into Ra-E and Ra-F, but adjusts itself to the new valency conditions by losing Me and completing an electron pair by acquiring an electron from the surroundings. E. S. H.

**Diffusion of  $\gamma$ -rays.** E. STAHEL and H. KETELAAR (J. Phys. Radium, 1934, [vii], 5, 512—522).—Work previously reported (cf. A., 1933, 1224) is extended with improved technique. Investigation by diffusion by thick screens shows that Pb, Au, and W emit radiation of which the hardest component is the same for each, and has an absorption coeff.  $3.3 \times 10^{-25}$ , against  $1.9 \times 10^{-25}$  for that of the hardest components of the incident radiation. N. M. B.

**Supplementary radiations in the recoil from Th active deposit.** (MISS) C. CHAMÉ (Compt. rend., 1934, 199, 943—945).—The anomalies previously reported (cf. A., 1934, 5) in the decay curves of Th-C'' from Th-C disappear when the quantity of Th-C'' increases with time of exposure, and increase when the activation time diminishes. Steeper curves were obtained for activation times of fractions of a sec. The phenomenon was not observed for a brass collector not at a negative potential. It is suggested that the curves can be explained by the existence of unknown sources in the Th-C, or by a transmutation induced in the source by its own radiation. N. M. B.

**Photographic determination of the half-period of thorium-B.** T. R. WILKINS and S. D. BURDICK (Physical Rev., 1933, [ii], 43, 1059).—The val. determined by a photographic method is approx.



10.2 hr. as compared with the accepted val. of 10.6 hr., based on ionisation measurements. L. S. T.

**Radioactivity and nuclear synthesis.** H. J. WALKER (Phil. Mag., 1934, [vii], 18, 795—822).—Assuming a primary distribution of a gravitating gas "neutron" of zero at. no., and a const. no. of neutrons in the universe, a mechanism whereby the elements are formed by radioactive synthesis due to  $\beta$ -ray emission from missing isotopes is indicated.

F. L. U.

**Artificial activation of lead by  $\gamma$ -rays.** H. R. VON TRAUBENBERG and H. BARTELS (Naturwiss., 1934, 22, 758).—An artificial activation was induced in Pb by the action of  $\gamma$ -rays from Th emanation.

A. J. M.

**Atomic disintegration of light elements by H and He.** R. DÖPEL (Z. Physik, 1934, 91, 796—809). Data are given for disintegration of Li, Be, and B.

A. B. D. C.

**Separation of the isotopes of lithium and some nuclear transformations observed with them.** M. L. OLIPHANT, E. S. SHIRE, and B. M. CROWTHER (Proc. Roy. Soc., 1934, A, 146, 922—929).—A method for preparing pure specimens of the separated isotopes of Li in quantities of the order of  $10^{-6}$  g. is described. Targets of  $\text{Li}^6$  and  $\text{Li}^7$  were bombarded successively with protons and with deuterons at about 160 kv. energy.  $\text{Li}^6$  with protons gives  $\alpha$ -particles of 11.5 mm. range; with deuterons,  $\alpha$ -particles of 13.2 cm. range and protons of 30 cm. range.  $\text{Li}^7$  with protons gives  $\alpha$ -particles of 8.4 cm. range; with deuterons,  $\alpha$ -particles up to 8 cm. range, and neutrons.

L. L. B.

**Disintegration of lithium by protons.** J. R. OPPENHEIMER (Physical Rev., 1933, [ii], 43, 380; cf. A., 1933, 205).—Theoretical. The Gamow model is applicable to the case of Li.

L. S. T.

**Disintegration experiments on elements of medium atomic number.** M. A. TUVE, L. R. HAFSTAD, and O. DAHL (Physical Rev., 1933, [ii], 43, 942).—There is no evidence that disintegration protons or  $\alpha$ -particles of range  $> 16$  mm. are produced by bombardment of Al, Ni, and Ag by 600-kv. protons. Small effects observed are explained by the presence of 1/9000—1/100,000 of B impurities in the targets.

L. S. T.

**Disintegration of aluminium by swiftly-moving protons.** M. S. LIVINGSTON and E. O. LAWRENCE (Physical Rev., 1933, [ii], 43, 369).—The bombardment of Al by high-velocity protons produces radiations (I), presumed to be  $\alpha$ -particles, which penetrate approx. 8 cm. of air. The distribution of the ranges of (I) is continuous. The effective nuclear cross-section for disintegration becomes const. at proton energies  $> 8 \times 10^5$  volts.

L. S. T.

**Neutron of high velocity, and energy relations for nuclear disintegration by non-capture.** W. D. HARKINS, D. M. GANS, and H. W. NEWSON (Physical Rev., 1933, [ii], 43, 584—585; cf. A., 1934, 827).—The energy of a neutron from Be used in  $\text{N}^{14}$  disintegration experiments has been calc. as  $16 \times 10^6$  e.v. and the velocity  $5.6 \times 10^9$  cm. per sec. Disintegration by non-capture of the neutron in these experiments is discussed.

L. S. T.

**Secondary emission from elements bombarded with neutrons.** Z. OLLANO (Nature, 1934, 134, 735).—Measurements of the absorption of the radiations from Po+Be in different elements indicate that the abnormally low absorptions found for Sn and Sb are to be ascribed to more absorbable secondary radiations produced by the passage of the primary rays through these elements. These softer radiations are probably of the nature of  $\gamma$ -rays and arise from excitation of nuclear levels of elements near Sn in the periodic table.

L. S. T.

**Secondary emission from elements bombarded with neutrons.** M. L. OLIPHANT (Nature, 1934, 134, 735—736).—Strong ionising radiations are produced when Ag is placed in a beam of neutrons (I) formed by the bombardment of elements by accelerated  $\text{H}^2$  ions. The effects observed (cf. preceding abstract) are probably due to the (I) in the radiation from Po+Be.

L. S. T.

**Effective neutron collision radius.** I. I. RABI (Physical Rev., 1933, [ii], 43, 838).—Neutron collision radii calc. for ten elements from C to Pb vary from 1.08 to 1.54, average val.,  $1.31 \times 10^{-13}$  cm.

L. S. T.

**Nitrogen disintegration by a very fast neutron.** F. N. D. KURIE (Physical Rev., 1933, [ii], 43, 771).—Be bombarded by  $\alpha$ -particles from Po gave an unusually fast neutron of  $17 \times 10^6$  volts energy (see above). The recoiling nucleus,  $\text{B}^{11}$ , and the disintegration particle ( $\text{He}^4$ ) when  $\text{N}_2$  is bombarded by this neutron are of ordinary energies and the "loss" of  $13.6 \times 10^6$  volts may be accounted for by the formation of a  $\text{B}^{11}$  slightly heavier than that measured in the mass-spectrograph.

L. S. T.

**Transmutation of elements by neutrons.** L. MEITNER (Naturwiss., 1934, 22, 759).—In extension of the work of Szilard and Chalmers (A., 1934, 77) it is shown that the neutrons emitted by the action of Ra  $\gamma$ -rays on Be will cause transmutation of I, Ag, and Au, but not of Na, Al, or Si. It is supposed that these neutrons have less energy than those emitted from Be by  $\alpha$ -rays, and consequently can only effect certain nuclear changes.

A. J. M.

**High-speed electrons liberated from fluorine after bombardment by neutrons.** I. KURTSCHATOV, G. SCHTSCHEPKIN, and A. VIBE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 572—575).—Neutrons bombarding LiF liberated electrons of energy  $4-5 \times 10^6$  e.v., confirming predictions based on Fermi's work.

H. J. E.

**Fermi's element 93.** A. V. GROSSE and M. S. AGRUSS (Nature, 1934, 134, 773; cf. A., 1934, 826, 1284).—Repetition of Fermi's experiments with Pa shows that the 13-min. product from U is chemically identical with element 91. In the Re sulphide reaction with Pa as indicator the element 91 is pptd. to the extent of 40—60% with Re sulphide from 15% HCl. It is concluded that the products with the 13 and 90—100 min. periods are isotopes of eka-Ta, changing by  $\beta$ -emission into isotopes of U. Fermi's proof of the non-identity of his products with element 91 is inconclusive.

L. S. T.



**Periodic property of atomic nuclei.** G. MONOD-HERZEN (Compt. rend., 1934, **199**, 859—860).—A curve relating the at. no. ( $Z$ ) with the no. of nuclear types known between  $Z$  and  $Z+4$  shows a periodicity with marked minima at  $Z=26$  (Fe), 56 (Ba), and 86 (Rn), as well as sub-minima. The first group contains most of the common elements and shows only a relatively small no. of isotopes, agreeing with the view that the abundance of an element depends on its stability. J. W. S.

**Classification of atomic nuclei.** V. V. TSCHERDINTSEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 576—583).—Theoretical. Nuclear structures are discussed. H. J. E.

**Equilibrium theory of the abundance of the elements.** T. E. STERNE (Physical Rev., 1933, [ii], **43**, 585—586, 768).—If all nuclei are ultimately composed of electrons and protons, the most abundant element when equilibrium is established must usually be that of even mass no. and smallest packing fraction. L. S. T.

**Hemi-alpha groups in atomic nuclei as related to the energy of binding.** W. D. HARKINS (Physical Rev., 1933, [ii], **43**, 1059). L. S. T.

**Low states of the heaviest elements.** T. Y. WU and S. GOUDSMIT (Physical Rev., 1933, [ii], **43**, 496).—The energies of the  $5f$ ,  $6d$ ,  $7s$ , and  $7p$  states of the atoms and ions built on the radon core have been calc. They depend chiefly on the degree of ionisation and change little with a change of nuclear charge from 92 to 89. L. S. T.

**Positrons from  $\gamma$ -rays.** C. D. ANDERSON and S. H. NEDDERMEYER (Physical Rev., 1933, [ii], **43**, 1034; cf. A., 1933, 658).—In addition to the positrons (I) ejected from Pb by hard  $\gamma$ -rays (II), there is an occasional simultaneous appearance of paired tracks of one positive and one negative particle with a common point of origin. The energy distribution of these pairs and of positively-charged particles is discussed. The (I) observed by other workers using neutrons with accompanying (II) may be due only to the latter and not to neutrons. L. S. T.

**Annihilation of fast positrons by electrons in the  $K$ -shell.** H. J. BHABHA and H. R. HULME (Proc. Roy. Soc., 1934, **A**, **146**, 723—736).—Mathematical. The probability of a stimulated transition of an electron from the  $K$  shell to a state of negative energy is calc. for the condition where all the states of negative energy are unoccupied. From this is calc. the probability of the corresponding spontaneous transition when only certain of the negative energy states are unoccupied. The probability of annihilation is always very small compared with that by free electrons, where 2 quanta are emitted. L. L. B.

**New "annihilation" process of positive electrons.** J. BRUNINGS (Physica, 1934, **1**, 996—1002).—The probability that a positron, combining with a  $K$  electron, should be annihilated, whilst the energy set free is taken up by the other  $K$  electron, has been calc. M. S. B.

**Exchange of energy between a platinum surface and gas molecules.** W. B. MANN (Proc. Roy.

Soc., 1934, **A**, **146**, 776—791).—The following vals. have been obtained for the accommodation coeffs. of different gases impinging on a clean Pt wire: He, 0.03 at room temp. and 0.04 at 80° abs. for mean filament temp. ( $T$ ) 100—1000°; A, 0.55—0.35 at room temp.,  $T$  100—1000°; Hg vapour, about 1.0 at room temp.,  $T$  100° and 200°; H<sub>2</sub>, 0.11—0.08 at room temp.,  $T$  100—1000°; O<sub>2</sub>, 0.42—0.55 at room temp.,  $T$  100—1000°. The results indicate that the process of contamination is one of adsorption, and that it is chiefly dependent on the nature of the filament surface. A process analogous to etching causes marked changes in the adsorbing properties of the surface in He. With H<sub>2</sub>, the accommodation is increased at higher temp. by absorption. L. L. B.

**Variation of the  $K$  resonating strength with atomic number.** J. A. WHEELER and J. A. BEARDEN (Physical Rev., 1934, [ii], **46**, 755—758).—The effective no. of  $K$  electrons, calc. on an approx. theory using Hartree wave functions, agrees, for at. no. < 40, with results obtained by anomalous dispersion, and by absorption data and theory. N. M. B.

**Distribution of energy in the ultra-violet solar spectrum as inferred from the photochemical theory of the ozone equilibrium in the earth's atmosphere.** D. EROPKIN (Phil. Mag., 1934, [vii], **18**, 838—841).—A preliminary calculation indicates that the sun's ultra-violet spectrum corresponds with Planck's curve if the O<sub>3</sub> mean height is 20 km. F. L. U.

**Positively-charged component of cosmic rays.** L. ALVAREZ and A. H. COMPTON (Physical Rev., 1933, [ii], **43**, 835—836).—Evidence for the existence of such a component, probably positrons, is given. L. S. T.

**Nature of the primary cosmic radiation.** W. F. G. SWANN (Physical Rev., 1933, [iii], **43**, 945—946). L. S. T.

**Composition of cosmic rays.** A. H. COMPTON and H. A. BETHE (Nature, 1934, **134**, 734—735).—A discussion. L. S. T.

**Electric deflexion of cosmic ultra-radiation.** E. LENZ (Nature, 1934, **134**, 809). L. S. T.

**Rock-salt absorption of cosmic rays.** S. ZIEMECKI (Nature, 1934, **134**, 773).—Measurements of the absorption of cosmic rays (I) by powdered rock-salt indicate that it is the most transparent substance for (I) so far examined. L. S. T.

**Velocity of light.** R. T. BIRGE (Nature, 1934, **134**, 771—772).—The val.  $299,776 \pm 4$  km. per sec. is suggested as a final weighted average val. for  $c$ . L. S. T.

**Value of  $e/m$ .** R. T. BIRGE (Physical Rev., 1933, [ii], **43**, 211; cf. A., 1933, 1226; 1934, 580). L. S. T.

**Electromagnetic fields in the quantum theory.** I. L. GOLDSTEIN (J. Phys. Radium, 1934, [vii], **5**, 545—552).—Mathematical. Static fields of H-type atoms, neglecting electron spin, are considered non-relativistically. N. M. B.



**Diffusion theory of the normal zero gradient of inert gases.** G. ZIMMERMANN (Z. Physik, 1934, 91, 767—774; 92, 282).—This zero gradient observed between concentric electrodes with A and Ne is due to diffusion of electrons.  
A. B. D. C.

**Transport phenomena in an ionised gas.** R. C. MAJUMDAR (Z. Physik, 1934, 91, 706—716).—Quantum-mechanical methods developed for metal-physics are applied to this problem.  
A. B. D. C.

**Photon spin.** L. DE BROGLIE and J. WINTER (Compt. rend., 1934, 199, 813—816).—Mathematical.  
J. W. S.

**Waves, spin, and constants.** E. SEVIN (Compt. rend., 1934, 199, 937—939).—Mathematical.  
N. M. B.

**Atomic wave functions.** F. W. BROWN and C. G. DUNN (Physical Rev., 1933, [ii], 43, 1047).  
L. S. T.

**Continuous current amplifier for microphotometric registration.** M. MEUNIER and J. ANDRIOT (J. Phys. Radium, 1934, [vii], 5, 538—540).

**Photo-electric measurement of relative and absolute extinction.** G. KORTUM and H. VON HALBAN (Z. physikal. Chem., 1934, 170, 212—230).—The sources of error, and particularly the effect of using spectrally impure light, in the photo-electric method are examined. An improved form of the two-cell arrangement (A., 1922, ii, 332) is described, which, using either a rotating sector or polarisation prisms, permits the abs. determination of extinction coeffs. with a precision of 1—2% and the comparison of two extinctions with a precision of 0.01%. The possibilities of the apparatus are demonstrated by data for the absorption curve of the 2:4-dinitrophenoxide ion and its change with temp.  
R. C.

**Absorption due to added substances in alkali halide crystals.** M. BLAU (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 401—405; Chem. Zentr., 1934, i, 3034).—Passage of electrons into NaCl or KCl crystals containing Ag, Cu, Tl, or Pb produces new absorption spectra of unknown origin.  
H. J. E.

**Photochemistry of alkali halide crystals.** R. HILSCH and R. W. POHL (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 406—419; Chem. Zentr., 1934, i, 3034—3035).—The mechanism of photo-dissociation and the origin of the crystal coloration are discussed.  
H. J. E.

**Spectrum of the afterglow of sulphur dioxide.** A. G. GAYDON (Proc. Roy. Soc., 1934, A, 146, 901—910).—The conditions of the production of the afterglow of SO<sub>2</sub> and the effects of change of pressure and electrical excitation on the spectrum have been studied. The spectrum consists of a continuum from 2400 to 4500 Å., and a band system from 3828 to 4699 Å. The vals. of the wave-no. intervals indicate that the afterglow bands are produced by mols. of SO<sub>2</sub>. An examination of the spectrum of the exciting discharge leads to the conclusion that the afterglow is caused by the recombination of SO and O<sub>2</sub> in the form of a flame which gives the observed spectrum.  
L. L. B.

**Perturbations due to spin-orbit forces in carbon monoxide and other band spectra.** J. H. VAN VLECK (Physical Rev., 1933, [ii], 43, 1047—1048).  
L. S. T.

**Internal resonance in the carbon monoxide molecule.** G. H. DIEKE (Physical Rev., 1933, [ii], 43, 780; cf. A., 1933, 207).  
L. S. T.

**Vibrational analysis of the GeO emission band spectrum.** R. W. SHAW (Physical Rev., 1933, [ii], 43, 1043).—Fifteen band heads in the region 2990—2500 Å., given by an arc with electrodes of graphite rods cored with fused GeO<sub>2</sub>, have been measured.  
L. S. T.

**Band spectrum of arsenic oxide (AsO).** F. C. CONNELLY (Proc. Physical Soc., 1934, 46, 790—800).—Data and vibrational analysis are tabulated for 35 lines of a system in the range  $\lambda\lambda$  3450—2950, degraded towards the red, and 66 lines of a system in the range  $\lambda\lambda$  2800—2350, degraded away from the red. Both are doublet systems, arising from transitions between two excited <sup>2</sup> $\Sigma$  levels and a <sup>2</sup> $\Pi$  ground level having a separation of 1026 cm.<sup>-1</sup> between the  $\Pi$  components.  
N. M. B.

**Ultra-violet absorption spectrum of osmium tetroxide.** A. LANGSETH and B. QVILLER (Z. physikal. Chem., 1934, B, 27, 79—99; cf. A., 1930, 1089).—The absorption spectrum of OsO<sub>4</sub> vapour in the near ultra-violet between room temp. and 400° may be accounted for in terms of three electron transitions, each of which is probably in the Os atom. There is probably a fourth system of bands in the short-wave region, and a continuous absorption is superimposed on the whole spectrum. There are Raman frequencies of 568, 688, 917, and 1187 cm.<sup>-1</sup>, corresponding with a regular tetrahedral mol., a structure also supported by other evidence. The absorption spectra of solutions of OsO<sub>4</sub> in H<sub>2</sub>O, C<sub>6</sub>H<sub>14</sub>, and CCl<sub>4</sub> have been examined. The above observations confirm the rule that in the electron transition not all the characteristic frequencies appear in the initial and final states.  
R. C.

**Absorption spectra of aqueous solutions of hydrochloric acid and of various chlorides in the ultra-violet.** R. TREHIN (Compt. rend., 1934, 199, 1047—1049).—Measurements are given for aq. solutions of HCl, LiCl, NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, SrCl<sub>2</sub>, and BaCl<sub>2</sub>, between 2110 and 2500 Å., and at 20—90°. HCl solutions are the more transparent in the nearer ultra-violet, but less so at shorter  $\lambda$ . The density of absorption increases with the at. no. of the cation.  
J. W. S.

**Absorption spectra of bromine trifluoride, iodine pentafluoride, and cyanogen fluoride.** C. F. WHITE and C. F. GOODEVE (Trans. Faraday Soc., 1934, 30, 1149—1051).—The absorption by BrF<sub>3</sub> and IF<sub>5</sub> vapours is continuous and commences at approx. 2800 and 2400 Å., respectively. A band at 3000—3600 Å. (max. 3250) is attributed to BrF. CNF does not absorb at > 1840 Å.  
J. G. A. G.

**Band systems of calcium chloride.** R. K. ASUNDI (Current Sci., 1934, 3, 153—154).—The bands consist of (i) a red system due to the transition <sup>2</sup> $\Pi \rightarrow$  <sup>2</sup> $\Sigma$  and (ii) an orange system involving a  $\Sigma \rightarrow \Sigma$



transition. The heats of dissociation for the  ${}^2\Pi$  and  ${}^2\Sigma$  states are 4.60 and 3.46 volts, respectively, whilst those for the upper and lower states of (ii) are 1.53 and 1.52 volts, respectively. L. S. T.

**Absorption spectra, in aqueous solution, of co-ordination compounds of chromium and cobalt.** A. MEAD (Trans. Faraday Soc., 1934, **30**, 1052—1058).—The absorption has been determined between 3000 and 7000 Å. of  $10^{-2}$ — $10^{-3}M$ -chlorides, -sulphates, and -K salts of  $[M(C_2O_4)_3]^{3-}$ ,  $[Cr(en)(C_2O_4)_2]^-$ ,  $[M(en)_2(C_2O_4)]^-$ , and  $[M(en)_3]^{3+}$ , where M is  $Cr^{III}$  and  $Co^{III}$ . Each ion has strong continuous absorption at  $< 3000$  Å., and in the visible and near ultra-violet two broad bands of which the heads are in approx. const. relationship and probably represent two excitation states of the co-ordination electrons. The absorption max. of the  $Cr^{III}$  compounds are shifted regularly and the Co compounds less regularly towards the ultra-violet by progressive replacement of  $C_2O_4$  by en. The absorption bands are symmetrical on a scale of wave-lengths and are reproduced by the formula of Lowry and Hudson (A., 1933, 889). J. G. A. G.

**Absorption spectra of nitrates and nitrites in relation to their photo-dissociation.** K. S. KRISHNAN and A. C. GUHA (Proc. Indian Acad. Sci., 1934, **1**, A, 242—249).—The absorption bands of inorg. nitrates with long wave-length limits at 3500 and 2300 Å. are attributed to dissociation into the nitrite and an O atom in the normal ( ${}^3P$ ) and excited ( ${}^1D_2$ ) states, respectively. From these wave-length limits the heat of dissociation of  $O_2$  into two normal atoms is 114 kg.-cal. per mol., and the energy of excitation of O from the  ${}^3P$  to the  ${}^1D_2$  level is 43 kg.-cal. per mol., in agreement with previous spectroscopic data. The dichroism of these absorption bands is attributed to the variation in quantum efficiency of the photo-dissociations with change in the direction of polarisation of the exciting light. The absorption bands of nitrites at 4000 and 3600 Å. are also attributed to dissociation with liberation of O in the normal and excited state, respectively. J. W. S.

**Photochemical studies. XIX. Ultra-violet absorption spectrum of acetone vapour.** W. A. NOYES, jun., A. B. F. DUNCAN, and W. M. MANNING (J. Chem. Physics, 1934, **2**, 717—725).—Bands in the neighbourhood of  $\lambda$  3000 Å. and between 2000 and 1800 Å. have been measured and analysed. A third group between 1700 and 1300 Å. has been photographed. F. L. U.

**The carbonyl group of aldehydes and ketones compared with carbon monoxide.** V. HENRI (Compt. rend., 1934, **199**, 849—851).—From the ultra-violet and infra-red absorption spectra of aldehydes and ketones it is concluded that the CO group in these compounds is in the  ${}^3\Pi$  electronic state, corresponding with the first state of activation of the CO mol. When such mols. are activated, the CO group passes into the  ${}^3\Sigma$  state, and on thermal or photochemical decomp. involving liberation of the CO group, the latter passes into the  ${}^1\Sigma$  state, and a CO mol. is formed in the normal state. It is suggested that the difference in electronic state accounts for the fact that aldehydes and ketones have high electric moments and CO a low moment, as

theoretically the  ${}^3\Pi$  state of CO should have a high moment, and the normal  ${}^1\Sigma$  state none. J. W. S.

**Optical absorption of porphyrins.** A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1934, **170**, 337—350).—Absorption curves of solutions have been determined between 480 and 650 m $\mu$ . Solutions in dioxan (I) have four well-marked bands and a smaller band, the positions of which are not greatly altered by the most diverse substitutions, indicating the presence of a common porphin framework; introduction of a  $CO_2Me$  group into the latter, however, changes the whole form of the absorption curve. The curves indicate that  $\psi$ -verdoporphyrin  $Me_2$  ester and rhodoporphyrin  $Me_2$  ester are not isomeric. The spectra of solutions in 3*N*-HCl consist of two bands. With some isomeric porphyrins the absorption curves are indistinguishable in (I), but exhibit perceptible differences in HCl. Others exhibit detectable differences in (I). R. C.

**Absorption spectra of alkaloids of calumba root and of some derivatives of berberine.**—See this vol., 99.

**New method for calculating molecular vibration frequencies.** D. H. ANDREWS, V. DEITZ, and S. GOLDHEIM (Physical Rev., 1933, [ii], **43**, 373).—Theoretical. L. S. T.

**Infra-red rotation vibration spectrum of hydrogen sulphide.** A. D. SPRAGUE and H. H. NIELSEN (Physical Rev., 1933, [ii], **43**, 375; cf. A., 1933, 208).—The band at 1.9  $\mu$  has two max. at 1.93  $\mu$ , and 1.97  $\mu$ . A second max. of the 3.73  $\mu$  band occurs about 3.88  $\mu$ . L. S. T.

**Vibrational isotope effects in polyatomic molecules. II.** E. O. SALANT and J. E. ROSENTHAL (Physical Rev., 1933, [ii], **43**, 581—582; cf. A., 1933, 204).—Mathematical. L. S. T.

**Infra-red spectra of silica.** D. G. DRUMMOND (Nature, 1934, **134**, 739).—Absorption coeffs. and wave-lengths have been measured for various thicknesses of fused  $SiO_2$  (I) and cryst. quartz (II). New bands have been found in (II), but that at 2.72  $\mu$  (A., 1929, 236) is absent, as are several bands in (I) between 2 and 4  $\mu$  (A., 1929, 974). A band near 2.73  $\mu$  is probably due not to  $SiO_2$  but to dissolved  $CO_2$ . L. S. T.

**Rotation-vibration spectra in the photographic infra-red of molecules with the hydrogen isotope of mass 2. I. The  $C_2H^1H^2$  spectrum and the C-C and C-H separation in acetylene.** G. HERZBERG, F. PATAT, and J. W. T. SPINKS (Z. Physik, 1934, **92**, 87—99).—Bands were photographed at 0.784, 1.03, 1.09, and 1.19  $\mu$ . The moment of inertia is  $27.753 \times 10^{-40}$  when vibrationless, and  $27.899 \times 10^{-40}$  g.-cm.<sup>2</sup> in the ground state. The C-H distance is 1.058, and C-C 1.199 Å. The fundamentals of  $C_2H^1H^2$  are 1840, 2570, and 3330 cm.<sup>-1</sup> A. B. D. C.

**Vibration spectra and force constants of "heavy" acetylene.** G. B. B. M. SUTHERLAND (Nature, 1934, **134**, 775—776).—Interpretations of recent observations on the infra-red and Raman spectra of  $CH^2:CH^2$  and  $C_2H_2^2$  are discussed. L. S. T.

**Rotation-vibration band of hydrogen cyanide near 10,381 Å.** W. SCHEIB and K. HEDFELD (Z.



Physik, 1934, **91**, 792—795).—The moment of inertia of the lower state is  $20 \times 10^{-40}$ , and of the higher  $19.44 \times 10^{-40}$  g.-cm.<sup>2</sup>; the C-N separation is 1.1 Å.

A. B. D. C.

**Near infra-red absorption of calciferol.** E. SHELOW (Bull. Basic Sci. Res., 1933, **5**, 1—4).—Absorption bands of calciferol (I) occur at 1.55 and 2.05  $\mu$  and characterise the alcohol group. Transmission curves resemble that of ergosterol, with which (I) is probably isomeric.

CH. ABS. (p)

**Influence of dissolved electrolytes on the constitution of water.** C. S. RAO (Current Sci., 1934, **3**, 154—155; cf. A., 1931, 408).—The Raman band for H<sub>2</sub>O in solutions of electrolytes (I) is always sharper than for pure H<sub>2</sub>O, the max. of the band being nearly in the same position as that attributed to the (H<sub>2</sub>O)<sub>2</sub> mols. With aq. solutions of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, LiNO<sub>3</sub>, and LiCl the band becomes sharper with an increase in concn. of (I) and shifts towards a greater frequency. With HCl, however, the band is sharper at 8N than at 11.7N, and the shift of the max. is in the opposite direction. These results indicate the extreme stability of the (H<sub>2</sub>O)<sub>2</sub> mols. and the comparative instability of the H<sub>2</sub>O and (H<sub>2</sub>O)<sub>3</sub> mols. in solutions of (I).

L. S. T.

**Raman effect and complexity of mercurous and thalious ions.** L. A. WOODWARD (Phil. Mag., 1934, [vii], **18**, 823—827).—A strong Raman line 169 cm.<sup>-1</sup> observed in a sat. solution of Hg (ous) nitrate is ascribed to (Hg-Hg)<sup>++</sup>. There is no similar evidence for (Tl-Tl)<sup>++</sup> in TlNO<sub>3</sub> solution. The amount of Tl<sub>2</sub><sup>++</sup>, if it exists, is < 10% of the total Tl present.

F. L. U.

**Raman effect in selenic acid and some selenates.** A. S. GANESAN (Proc. Indian Acad. Sci., 1934, **1**, A, 156—162).—Data are given for aq. H<sub>2</sub>SeO<sub>4</sub> and the selenates of K, NH<sub>4</sub>, Mg in solution, and of Tl (cryst.). Results for the acid differ considerably from those of the salts, for which the four lines are: 835 (strong), 875 (faint), 345, and 415 cm.<sup>-1</sup> A tetrahedral structure for SeO<sub>4</sub> is indicated. Heats of dissociation of Se-O and S-O are calc.

N. M. B.

**Raman effect of triatomic molecules. V. Constitution of N<sub>3</sub>' and NCS' ions.** A. LANGSETH, J. R. NIELSEN, and J. U. SØRENSEN (Z. physikal. Chem., 1934, **B**, 27, 100—110; cf. A., 1934, 942).—The Raman spectra of the above ions have been examined and the state of polarisation of the stronger Raman lines has been measured. Using the principle of isosterism in conjunction with the Raman data it is deduced that N<sub>3</sub>' is linear and centro-symmetrical and NCS' linear, with the negative charge on the S atom, N<sup>+</sup>C-S'. R. C.

**Raman spectrum of trichlorobromomethane.** J. WOUTERS (Bull. Acad. roy. Belg., 1934, [v], **20**, 782—788).—The principal lines are at 195, 247, 295, 425, 715, and 774 cm.<sup>-1</sup>, frequencies intermediate between those of CBr<sub>4</sub> and CCl<sub>4</sub>. The Raman spectrum is compared with those of other compounds of similar structure.

H. F. G.

**Raman spectra of five higher alcohols.** P. L. BAYLEY (Physical Rev., 1933, [ii], **43**, 373—

374).—The Raman spectra of *n*-amyl to *n*-nonyl alcohol have been obtained. In heptyl, octyl, and nonyl alcohol only lines corresponding with the spectrum of EtOH were found. Comparison of the spectra of *n*- and *iso*-alcohols shows that the no. and relative positions of lines are determined almost entirely by the no. of C atoms in the chain. The broad line at  $\Delta\nu$  1450 is double in *iso*amyl and hexyl alcohols. The latter has a line beyond 1450, at 1657 Å.

L. S. T.

**Raman effect in some organic substances.** G. B. BONINO and M. ANSIDEI (Mem. R. Accad. Sci. Ist. Bologna, 1934, **12**, 3—7, 27—31).—Frequencies and intensities of Raman lines are recorded for 95 org. substances, including aromatic esters and aldehydes, phorone, alkyl sulphides, and derivatives of Ph<sub>2</sub>, C<sub>5</sub>H<sub>5</sub>N, picoline, quinoline, pyrrole, pyrazole, indole, indene, and thionaphthene.

O. J. W.

**Raman spectra of deca- and tetra-hydro-naphthalene.** S. K. MUKERJI (Nature, 1934, **134**, 811—812).—The results of Bonino and Cella (A., 1932, 7) are confirmed, in the main, and additional frequencies are recorded.

L. S. T.

**Intensity determinations with Raman lines.** K. HABERL (Ann. Physik, 1934, [v], **21**, 285—300).—The variation of the intensity of the Raman lines of cyclohexane with the frequency of the exciting light was determined. Frequencies at 2835, 2920, and 2953 cm.<sup>-1</sup> were excited by the light of  $\lambda$  3132, 3022, 2967, and 2652 Å., the intensities being given by Placzek's formula  $I=c(\nu-\Delta\nu)^4/(\nu_a^2-\nu^2)^2$  assuming ultra-violet absorption  $\nu_a=53,000$  cm.<sup>-1</sup> A. J. M.

**Fluorescence of cyclohexane.** K. HABERL (Ann. Physik, 1934, [v], **21**, 301—302).—Fluorescence of cyclohexane has been observed. The intensities of the max. vary with temp., but their positions do not.

A. J. M.

**Photo-electric photometry of light scattering in fluids.** R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1934, **1**, A, 201—211).—Data for C<sub>6</sub>H<sub>6</sub>, CS<sub>2</sub>, PhCl, AcOH, Et<sub>2</sub>O, MeOH, and EtOH, obtained by use of a photo-electric cell, are in agreement with previous measurements obtained visually.

J. W. S.

**Optical evidence for molecular clustering in fluids.** R. S. KRISHNAN (Proc. Indian Acad. Sci., 1934, **1**, A, 211—216).—A method for detection of mol. clusters of magnitude comparable with the wave-length of light is developed, based on the anomalous depolarisation of light scattered by a fluid. Pure AcOH, MeOH, COMe<sub>2</sub>, PhCl, *n*-C<sub>7</sub>H<sub>16</sub>, and CH<sub>2</sub>:CH:CH<sub>2</sub>:OH show no large mol. aggregates, but a mixture of CS<sub>2</sub> and MeOH shows such clusters between the crit. solution temp. (40.5°) and 61.5°.

J. W. S.

**Scattering of light by particles suspended in a medium of higher refractive index.** R. S. KRISHNAN (Proc. Indian Acad. Sci., 1934, **1**, A, 147—155).—Mathematical. Calculations are made for three sizes of particles such as air bubbles suspended in a medium, and for three different vals. of *n*.

N. M. B.



**Fluorescent radiation from nitrous oxide.** P. K. SEN-GUPTA (Proc. Roy. Soc., 1934, A, 146, 824—828).—The  $\beta$ -bands of NO were obtained in fluorescence when  $N_2O$  was illuminated by light of suitable wave-length. This indicates that NO, one of the products of photochemical dissociation of  $N_2O$ , is excited during the process. L. L. B.

**Influence of KI on polarisation of fluorescence of dyes present in solutions.** S. M. MITRA (Z. Physik, 1934, 91, 61—63).—KI steadily increases polarisation of fluorescent light due to fluorescein and rhodamine-B in  $H_2O$ , and in  $H_2O$ -glycerol and glycerol increases it to a max. A. B. D. C.

**Action of sera on the fluorescence of uranine solutions.** C. ACHARD, A. BOUTARIC, and J. BOUCHARD (Compt. rend., 1934, 199, 903—906).—The addition of various therapeutic and human sera, when fresh, to a dil. solution of uranine in NaCl had no effect on the fluorescence; in the case of sera kept for  $> 5$  days a progressive diminution of fluorescence was found, similar to that caused by catalysts which have a negative effect on oxidation processes. N. M. B.

**Fluorescence of some substances containing vitamin-A.** J. W. WOODROW and A. R. SCHMIDT (Physical Rev., 1933, [ii], 43, 379).—Cod-liver oil (I) has a narrow fluorescent band from 530 to 570  $m\mu$  and a wider band (II) from approx. 410 to 510  $m\mu$ . The intensity of (II) is much reduced for (I) which has lost most of its vitamin-A (III) potency. The same bands, although less intense, are obtained with butter fat. (II) is also obtained with spinach and tomato juice. The fluorescence appears to be connected with either the (III) or the carotene present. L. S. T.

**Fluorescence of solutions of chlorophyll-a.** H. V. KNORR and V. M. ALBERS (Physical Rev., 1933, [ii], 43, 379).—The fluorescence of solutions of chlorophyll-a in  $Et_2O$  (I),  $C_6H_6$  (II),  $COMe_2$  (III), and MeOH at 6°, excited by radiation from Hg arcs, consists of a main band with max. at 6718, 6767, 6720, and 6745 Å. for the respective solvents, and a second band with max. at 6330 Å. for (I), 6358 Å. for (II), and 6392 Å. for (III). L. S. T.

**Luminescence from solidified gases and its interpretation.** L. VEGARD (Physical Rev., 1933, [ii], 43, 1060). L. S. T.

**Electrostriction of gases.** J. JAUMANN and V. STIPA (Z. Physik, 1934, 91, 685—705).—A compensated microphone is used to measure pressure changes, and to determine electrostriction of  $O_2$ ,  $N_2$ ,  $CO_2$ ,  $SO_2$ ,  $H_2$ , He, and A between 1 and 10 atm. The electrostriction of the first four gases increases with increasing pressure more rapidly than the dielectric const. A. B. D. C.

**Effect of a small admixture of a foreign gas on the conductivity of a rare gas irradiated by its own resonance radiation.** O. S. DUFFENACK and R. W. SMITH (Physical Rev., 1933, [ii], 43, 374).—The effect of impurities on the conductivity (I) produced in Ne and in He at pressures from 1 to 10 mm. by irradiation with their own resonance

radiation (II) has been investigated. Addition of 0.001% of A or Kr increases (I), whilst that of Ne to He decreases it. Metastable atoms which are probably formed indirectly through absorption of (II) may suffer either ionising collisions, increased (I), or dissipative collisions, decreased (I), depending on the ionisation potential of the added foreign gas. L. S. T.

**Rectification phenomenon in a pyrolusite crystal.** S. R. KHASTGIR and A. K. D. GUPTA (Current Sci., 1934, 3, 153).—When a pyrolusite crystal (I) is dipped in Hg, a.c. is rectified to a large extent. Current-voltage curves are given. (I) had a large area of contact, so that the effect cannot be attributed to ordinary crystal-and-point rectification. Galena, Fe pyrites, bornite, magnetite, and molybdenite show no such effect. L. S. T.

**Ionisation potentials and energies of formation of halogen molecules.** J. SAVARD (Compt. rend., 1934, 199, 939—941).—Ionisation potentials calc. from a relation previously proposed (cf. A., 1934, 11) are in satisfactory agreement, for BrCl, ICl, IBr,  $F_2$ , and HF, with those given by Mulliken (cf. *ibid.*, 1288). N. M. B.

**Temperature variation of the photo-effect of pure and impure metal surfaces at low temperatures.** R. SUHRMANN and A. SCHALLAMACH (Z. Physik, 1934, 91, 775—791).—Photo-effect was investigated for Be, Bi, and Ag, and for Ag with K as impurity at room, liquid air, and liquid  $H_2$  temp. The emission potential remains const., and the intensity of emission decreases with fall of temp. in agreement with quantum theory. A. B. D. C.

**Effect of gases on photo-electric effect of platinum.** E. SCHAAFF (Z. physikal. Chem., 1934, B, 26, 413—427).—With continued heating, the red limiting wave-length shifts to longer wave-lengths and back again. The effect of heating in  $H_2$  and then in  $O_2$  suggests that H creates the active Pt atoms required for adsorption of O. The effects of other gases have also been examined. R. C.

**Effect of temperature on the electrical conductivity of a thin film of CuS.** H. DEVAUX and J. CAYREL (Compt. rend., 1934, 199, 912—914).—When thin films of CuS, obtained by the action of  $H_2S$  on the surface of  $Cu^{II}$  solutions, are heated to approx. 90° the conductivity increases rapidly to a max. and remains at this val. on cooling. The effect appears to be due to the elimination of gas or  $H_2O$  vapour occluded in the film. N. M. B.

**Weiss law for Rochelle salt.** H. MÜLLER (Physical Rev., 1933, [ii], 43, 500; cf. A., 1933, 342).— $\epsilon$  for the salt has been measured between 23° and 50°; between 34° and 50°, Weiss' law is satisfied. The Curie const. is 128.5 and the dielectric Curie point 24.9°. The calc. Lorenz-Lorentz factor is 2.315. Assuming that the dielectric effect is due to freely rotating mols. of the  $H_2O$  of crystallisation this factor must be 2.314. The max. val. of  $\epsilon$ , viz., 1540, is reached at the ferromagnetic Curie point 23.75°. L. S. T.

**Dipole moment and Raman effect of molecules with groups capable of free rotation.** S. MIZU-



SHIMA, Y. MORINO, and K. HIGASI (Physikal. Z., 1934, **35**, 905—911).—The limited rotation of the  $\text{CH}_2\text{Cl}$  groups in  $\text{C}_2\text{H}_4\text{Cl}_2$  has been investigated quantitatively. An expression for the mean moment at different temp., assuming the Maxwell-Boltzmann distribution, gives vals. in agreement with observation. The val. of the const.  $\beta$  in the expression for the mutual potential energy of the two groups,  $U = \beta(1 - \cos \phi)$ , where  $\phi$  is the angle of rotation, depends on the solvent. The dipole moments of  $\text{C}_2\text{H}_4\text{Br}_2$ ,  $m\text{-C}_6\text{H}_4(\text{CH}_2\text{Br})_2$ ,  $\text{C}_2\text{H}_4\text{ClBr}$ , and  $\text{C}_2\text{H}_4\text{I}_2$  in  $\text{C}_6\text{H}_{14}$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , and  $\text{CS}_2$  were determined. The mol. polarisation of these substances is the same in each solvent with the exception of  $\text{C}_6\text{H}_6$ , where it is much smaller, showing that in  $\text{C}_6\text{H}_6$  solution the probability of deviation from the *trans*-position is unexpectedly great. The intensity of the Raman lines of  $\text{C}_2\text{H}_4\text{Cl}_2$  in  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{Et}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{MeOH}$  was also investigated. The smaller is the dielectric const. of the solvent, the greater is the intensity ratio (I) of the two Raman lines 752 and 653  $\text{cm}^{-1}$ . The  $\text{C}_6\text{H}_6$  solution is again an exception. (I) increases with increasing no. of mols. in the *trans*-position. A. J. M.

**Vector analysis of dipole moments.** F. R. GOSS (J.C.S., 1934, 1467).—The validity of the vector analysis has been examined by calculating the moments of  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  from the valency angles on the assumption that the moment due to the C-Cl linking is const.; the vals. obtained are identical with those calc. from polarisation data. H. F. G.

**Determination of dipole moments in solution.** F. FAIRBROTHER (J.C.S., 1934, 1846—1849; cf. A., 1934, 1156).—Calculation of the equations to the graphs of  $P_2$  against  $(\epsilon - 1)/(\epsilon - 2)$  by the method of least squares gives an average val. for  $\mu$  of  $\text{PhNO}_2$  in decane and *p*-xylene of  $4.24 \times 10^{-18}$  e.s.u. The slopes of the curves very nearly  $\propto 1/\text{abs. temp.}$  A. J. M.

**Dipole moment of chloromethyl ether.** M. A. G. RAU and N. NARAYANASWAMY (Proc. Indian Acad. Sci., 1934, **1**, A, 217—223).—The electric moment of  $(\text{CH}_2\text{Cl})_2\text{O}$  is 1.88 and 1.82— $1.85 \times 10^{-18}$  e.s.u. in  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$  solutions, respectively. This indicates that either the  $\text{CH}_2\text{Cl}$  group possesses free rotation, or there is an equilibrium between the *cis*- and *trans*-forms of the mol. J. W. S.

**A. Association of nitrobenzene in solutions and its dipole moment.** **B. Dielectric constant of nitrobenzene and its moisture.** A. PIEKARA. **C. Temperature dependence of the dielectric constant of nitrobenzene.** A. PIEKARA and J. MAZUR (Acta phys. polon., 1932, **1**, 393—399, 405—409, 401—404; Chem. Zentr., 1934, ii, 401).—**A.** The Debye equation is valid for the temp. variation of the polarisation of  $\text{PhNO}_2$  in  $\text{C}_6\text{H}_{14}$  solution. The electric moment is  $4.0 \times 10^{-18}$ . The measurements disagree with the assumption of two-fold association.

**B.** Vals. for wet and dry  $\text{PhNO}_2$  are recorded. No anomaly was found at 9.6°.

**C.** Vals. between 8° and 11° show no discontinuity at 9.6°. H. J. E.

**Dipole moment of *s*-trinitrobenzene.** G. BRIEGLER and J. KAMBEITZ (Z. physikal. Chem., 1934, **B**, **27**, 11—14).—New determinations and a review of previous determinations indicate that the moment is very small, but fail to decide whether it is finite or not. R. C.

**Influence of a magnetic field on the dielectric constant of liquids.** A. PIEKARA and M. SCHÉRER (Compt. rend., 1934, **199**, 840—843).—At  $\lambda = 600$  m.,  $\epsilon$  for  $\text{C}_6\text{H}_{14}$ , cyclohexane, PhMe,  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{CS}_2$ , quinoline, and  $\text{PhNO}_2$  is increased by a magnetic field of 51,000 gauss parallel to the electric field, the effect being greatest for  $\text{PhNO}_2$  and least for  $\text{C}_6\text{H}_{14}$  ( $\Delta\epsilon = 250$  and 1.4, each  $\times 10^{-3}$ , respectively). The effect decreases rapidly with decreasing intensity of the magnetic field; it is undetectable below 25,000 gauss. As the effect is about 1000 times that predicted by theory for gases, it is suggested that under an intense magnetic field the frequency of oscillation of the mols. may approach that of the electric field. J. W. S.

**Dielectric behaviour of germanium tetrachloride.** J. G. MILLER (J. Amer. Chem. Soc., 1934, **56**, 2360—2362).—Measurements with pure  $\text{GeCl}_4$  and with solutions in  $\text{CCl}_4$  show a zero moment, suggesting a symmetrical tetragonal structure for the mol. E. S. H.

**Determination of dielectric constants of aqueous solutions of electrolytes at high frequency.** M. RÖVER (Ann. Physik, 1934, [v], **21**, 320—344).—The results of the determination of the dielectric consts. of dil. aq. solutions of  $\text{CuSO}_4$  and  $\text{MgSO}_4$  at high frequency agree with the theory of Debye and Falkenhagen over the range for which this may be expected to hold. A. J. M.

**Electrolytic solutions. XIV. Dielectric constant of solutions of electrolytes in benzene.** G. S. HOOPER and C. A. KRAUS (J. Amer. Chem. Soc., 1934, **56**, 2265—2268; A., 1934, 1176).—Results are recorded for solutions of tetra- and tri-isoamylammonium picrate, tetraisoamylammonium bromide, and  $\text{AgClO}_4$ , chiefly between  $10^{-4}$  and  $10^{-3}N$ . The limiting mol. polarisation of these compounds is about 10 times that of ordinary polar mols., 2400—2700 c.c. The mol. polarisation decreases rapidly with increasing concn. for salts with two electrically symmetrical ions and slowly for salts with unsymmetrical ions. E. S. H.

**Refraction and dispersion of gases and vapours. VIII. Molecular refraction of argon, krypton, and xenon.** G. DAMKÖHLER (Z. physikal. Chem., 1934, **B**, **27**, 130—144; cf. A., 1934, 348).—The mol. refraction for 5461 and 6563 Å. has been determined with a precision of 0.07%, the results for A alone agreeing well with those of Cuthbertson (A., 1910, ii, 561). The max. error attributable to impurities in the gases was  $\pm 0.02\%$ . The metal double chamber of the Haber-Loewe interferometer sorbs and desorbs appreciable quantities of gas. R. C.

**Refractive index and dispersion of normal and heavy water.** L. W. TILTON and J. K. TAYLOR (J. Res. Nat. Bur. Stand., 1934, **13**, 207—209).—



Vals. of  $n$  at  $25^\circ$  for  $\text{H}_2\text{O}$  of  $d$  1.001376, at 10 wavelengths, are recorded and compared with those of other observers. The additive law appears to be applicable to mixtures of  $\text{H}_2\text{O}$  and  $\text{H}_2^{18}\text{O}$ . H. F. G.

**Index of refraction of carbon dioxide as a function of the density.** F. L. BROWN (Physical Rev., 1933, [ii], 43, 373).—When plotted against  $d$  the inverse of the Lorenz-Lorentz function  $(\mu_2 - 1)/[(\mu^2 + 2)p]$  shows a marked increase at the higher vals. of  $d$ . Data for  $d > 0.8$  g. per c.c. and  $\mu > 1.19$  have been obtained. L. S. T.

**Optical activity of camphor in alcoholic solutions.** C. F. POE and E. M. PLEIN (J. Physical Chem., 1934, 38, 883—887).—Sp. rotations of camphor (I) in aq. EtOH have been determined. Curves showing the relation between  $[\alpha]$ ,  $[\text{EtOH}]$ , and  $[\alpha]$  are given. F. L. U.

**Rotatory power of quartz for rays perpendicular to the axis and its dispersion in the ultra-violet.** G. BRUHAT and P. GRIVET (Compt. rend., 1934, 199, 1034—1036).—It is confirmed that the ellipticity of the privileged vibrations in a sheet of  $\alpha$ -quartz cut parallel to the optical axis varies from  $14/2'$  for  $5893 \text{ \AA}$ . to  $38/2'$  for  $2537 \text{ \AA}$ . (cf. A., 1934, 1160). J. W. S.

**Rotations of the nitrophenyl esters of disubstituted acetic and propionic acids and of the corresponding free acids.** P. A. LEVENE, A. ROTHEN, and G. M. MEYER (J. Biol. Chem., 1934, 107, 555—565).—The rotatory dispersion curves, in the homogeneous state (I) and in heptane solution (II), of the *p*-nitrophenyl esters of  $\alpha$ -methyl-*n*-butyric, b.p.  $137^\circ/0.1$  mm., -valeric, b.p.  $130^\circ/0.01$  mm., -hexoic, b.p.  $138^\circ/0.01$  mm., and of  $\beta$ -methyl-valeric, -hexoic, b.p.  $138$ — $140^\circ/0.02$  mm., -heptoic, b.p.  $152^\circ/0.01$  mm., and -octoic acid, b.p.  $160^\circ/0.1$  mm., are tabulated and analysed to determine the partial rotation of the  $\text{-C}_6\text{H}_4\text{-NO}_2$ . In the series  $\text{CHRMc-CO}_2\text{H}$ , and in  $\text{CHRMc-CH}_2\text{-CO}_2\text{H}$  (III) in (I), esterification causes a shift in rotation to the left. In (II) the considerable shift to the left observed with the first member of (III) diminishes successively to zero in the third member, and then changes direction in the fourth and all higher members of the series, and an explanation based on the relative predominance of the first and second partial rotations is elaborated. Hence in two configuratively related substances the two partial rotations of which are of opposite sign, identical substitution may effect shifts of rotation in different directions. J. W. B.

**Walden inversion. XVIII. Analysis of rotatory dispersion curves of  $\alpha$ -substituted *n*-carboxylic acids.** P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1934, 107, 533—553).—The ultra-violet absorption curves and the rotatory dispersions of *d*-CHMeI-CO<sub>2</sub>H (I), *d*-CHMeBr-CO<sub>2</sub>H (II), *d*- $\alpha$ -bromo-*n*-hexoic (III), *d*-lactic (IV), and *l*- $\alpha$ -methoxypropionic acid (V), and of their Na salts, and the Et esters of (IV) and (V), are recorded. In (I), (II), and (III), and the Na salt of (I), the first contribution is the dextrorotation of the halogen, (I) being configuratively related to (IV) and to *l*-

$\alpha$ -azidopropionic acid. All the acids show normal dispersion, represented by a two-term Drude equation in which the dispersion const.  $\lambda_0$  of the first term corresponds with the head of the absorption band. J. W. B.

**Magnetic birefringence and the critical dissolution point.** A. PIEKARA (J. Phys. Radium, 1934, [vii], 5, 541—544).—The temp. coeff. of magnetic birefringence of solutions of  $\text{PhNO}_2$  in hexane and in  $\text{CCl}_4$  increases with concn. to an abnormal val. in the neighbourhood of the dissolution point. N. M. B.

**Magnetochemical properties of samarium.** P. W. SELWOOD (J. Amer. Chem. Soc., 1934, 56, 2392—2394).—The following sp. magnetic susceptibilities have been determined:  $\text{Sm}_2\text{O}_3$   $5.60 \times 10^{-6}$ ,  $\text{SmBr}_3$   $2.49 \times 10^{-6}$ ,  $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$   $2.34 \times 10^{-6}$ .  $\text{Sm}^{++}$  has a definite existence and its susceptibility and electronic configuration are identical with those of  $\text{Eu}^{++}$ . E. S. H.

**Magnetic susceptibilities of the anhydrous and hydrated sulphates and double sulphates of the magnetic metals: increased susceptibility produced by heating cobalt salts.** E. F. HERROUN (Proc. Physical Soc., 1934, 46, 872—881).—When  $\text{K}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  is substituted for  $\text{H}_2\text{O}$  of constitution in the sulphates of Fe, Co, and Ni, susceptibility of the active constituent and of the mol. increase and so persist in the fully hydrated double salts. A similar but smaller effect is found for the sulphates of Mn and Cr, but for  $\text{CuSO}_4$  a decrease is observed.  $\text{CoCl}_2$ ,  $\text{CoSO}_4$ ,  $\text{Co}_3(\text{PO}_4)_2$ , and  $\text{Co}_2\text{P}_2\text{O}_7$  show increased susceptibility after heating. N. M. B.

**Magnetic properties of organic vapours.** S. R. RAO and P. S. VARADACHARI (Nature, 1934, 134, 812).—A discussion. L. S. T.

**Diamagnetic susceptibilities and polarisabilities of ions.** G. W. BRINDLEY (Physical Rev., 1933, [ii], 43, 1030—1031).—Agreement between calc. and experimental vals. for the *g*-at. susceptibility indicates that the Kirkwood-Vinti equation connecting diamagnetic susceptibilities and ionic refractivities is valid. Calc. vals. for the polarisability of the inert gases and of certain ions are also compared with experimental vals. L. S. T.

**Paramagnetic properties of cerous salts in solution.** C. HAENNY and G. DUPOUY (Compt. rend., 1934, 199, 843—845).—Aq. solutions of  $\text{Ce}(\text{NO}_3)_3$ ,  $\text{CeCl}_3$ , and  $\text{Ce}(\text{OAc})_3$ , and EtOH solutions of  $\text{Ce}(\text{NO}_3)_3$  obey the Curie-Weiss law. The magnetic moment of the  $\text{Ce}^{+++}$  ion, calc. from the magnetic susceptibilities of these solutions, is 2.49 Bohr magnetons, in agreement with theory. J. W. S.

**Properties of Rochelle salt.** H. MÜLLER (Physical Rev., 1933, [ii], 44, 854—855).—The dielectric, optical, electro-optical, and pyroelectric properties of Na K tartrate from  $-50^\circ$  to  $50^\circ$ , which are summarised, can be explained by a generalisation of Weiss' theory of ferromagnetism. L. S. T.

**Molecular structure of ozone.** W. S. BENEDICT (Physical Rev., 1933, [ii], 43, 580—581).—A discussion. Further confirmation of the obtuse-angled



structure is given. Approx. mol. dimensions are apex half-angle  $61^\circ$  and O-O distance 1.29 Å.

L. S. T.

**Even and odd co-ordination numbers.** R. C. MENZIES (J.C.S., 1934, 1755—1758).—The stability of compounds of Os, Pt, Au, and Pb with effective at. nos. (I) in the neighbourhood of 86 was investigated with reference to their co-ordination nos. (II). Stability depends not only on the attainment of 86 for (I), but also on the occurrence of an even (II). Pb diacetylacetonone, having (I)=88 and (II)=4, has been prepared, but is readily hydrolysed. Pb Et<sub>3</sub> acetylacetonone, having (I)=88 and (II)=5, could not be obtained.

A. J. M.

**Electroaffinity scale, with data on valency states and on valency ionisation potentials and electron affinities.** R. S. MULLIKEN (J. Chem. Physics, 1934, 2, 782—793).—Theoretical. A new "abs." scale is put forward, in which electroaffinity = average of ionisation potential and electron affinity, calc. for suitable valency states of the positive and negative ion. Tables of these quantities are given.

F. L. U.

**Comparative chemistry. VI. Oxides.** I. N. LONGINESCU (Bul. Chim. Soc. Române, 1933, 36, 25—31).—Theoretical. More oxides of types MO, M<sub>2</sub>O<sub>3</sub>, and MO<sub>2</sub> exist than can be forecast from the periodic system, whilst M<sub>2</sub>O<sub>5</sub> and MO<sub>3</sub> types are about as numerous as can be forecast.

T. W. P.

**Transfer of vibrational energy between molecules.** H. O. KNESER (Physical Rev., 1933, [ii], 43, 1051).

L. S. T.

**Brownian movement of an ellipsoid. I. Dielectric dispersion for ellipsoidal molecules.** F. PERIN (J. Phys. Radium, 1934, [vii], 5, 497—511).—Mathematical.

N. M. B.

**Wave-mechanical treatment of the Li<sub>2</sub> molecule.** H. M. JAMES (J. Chem. Physics, 1934, 2, 794—810).—Mathematical.

F. L. U.

**Chemical forces in the light of quantum mechanics.** H. HELLMANN and W. JOST (Z. Elektrochem., 1934, 40, 806—814).—Theoretical.

E. S. H.

**Rotation of diatomic molecules.** H. CASIMIR (Physica, 1934, 1, 1073—1076).—The moments of inertia of a diat. mol. are calc. by adding the masses of the closed electron shells to the masses of the corresponding nuclei.

M. S. B.

**Potential energy of diatomic molecules.** N. ROSEN (Physical Rev., 1933, [ii], 43, 671; cf. A., 1933, 206).

L. S. T.

**Mathematical analysis of the single and double six-ring.** P. C. HENRIQUEZ (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 532—547).—Mathematical. A method, based on a const. angle between the directions of the valencies of each C atom, and the absence of "strain," gives the configuration of the "fixed" (chair) form of the C<sub>6</sub> ring and the characterising magnitudes of the infinite no. of positions of the "mobile" form. The possible "strainless" configurations of the C<sub>10</sub>H<sub>8</sub> ring system are deduced.

J. G. A. G.

**Normal vibrations of molecules having octahedral symmetry.** N. S. N. NATH (Proc. Indian Acad. Sci., 1934, 1, A, 250—259).—The theory developed is in agreement with experimental data for SF<sub>6</sub>.

J. W. S.

**Intramolecular rotation in organic compounds.** M. A. G. RAU (Current Sci., 1934, 3, 145—150).—A review.

**Probability of multiple processes of very high energies.** W. HEITLER and L. NORDHEIM (Physica, 1934, 1, 1059—1072).—Theoretical.

M. S. B.

**Approximations involved in calculations of atomic interaction and activation energies.** A. S. COOLIDGE and H. M. JAMES (J. Chem. Physics, 1934, 2, 811—817).—Mathematical. Any modification of the complete Heitler-London treatment may lead to errors comparable in magnitude with the quantity to be computed.

F. L. U.

**Interaction of electronic and nuclear motion for linear triatomic molecules.** R. RENNER (Z. Physik, 1934, 92, 172—193).—Theoretical.

A. B. D. C.

**Influence of inner shells on atomic interactions.** H. M. JAMES (Physical Rev., 1933, [ii], 43, 589; cf. A., 1932, 1).—The inner shells of Li<sub>2</sub> appear to be responsible for a repulsion between the atoms which is of importance in comparison with the total energy of binding. The effect of neglecting these inner shells in computations on the alkali mols. is discussed.

L. S. T.

**Surface tensions of ethyl alcohol and carbon disulphide at low temperatures.** T. TONOMURA and (MISS) K. ISHIHARA (Bull. Chem. Soc. Japan, 1934, 9, 439—441).—Employing the method of capillary rise EtOH has been examined from  $-93^\circ$  to  $30^\circ$  and CS<sub>2</sub> from  $-42.4^\circ$  to  $20^\circ$ . For EtOH  $\sigma(M/D)^{2/3} = 703.09 - 1.3901T + 0.0004318T^2$  and for CS<sub>2</sub> it is  $2.0007(\tau - 9.28)$ , where  $\tau$  is temp. measured from crit. temp.

W. R. A.

**Parachors of polycyclic compounds.** D. N. KURSANOV (J. Gen. Chem. Russ., 1934, 4, 598—602).—Mumford and Phillips' view that a simple relationship exists between intramol. strain (I) and parachor variations (A., 1929, 1219) is not sustained by the vals. found for the parachors (P) of fenchane, cyclofenchene, carane, *d*-pinene, *cis*- and *trans*-decahydronaphthalene, and dicyclopentyl; in spite of considerable variations in (I) in this group, the experimentally determined P agree within 1% with the vals. calc. on the basis of Mumford's consts.

R. T.

**Density and molecular structure of a pure normal liquid.** R. LAUTIÉ (Compt. rend., 1934, 199, 932—934).—Mathematical. Calculations are derived from the MacLeod-Sugden and Eötvös-Ramsay-Shields formulæ.

N. M. B.

**Application of Valouch's method of measuring the constants of crystal lattices to the precision method of Kunzl and Köppel.** F. BOUGHAL and V. DOLEJSEK (Compt. rend., 1934, 199, 1054—1056; cf. A., 1933, 450).—The lattice const. of quartz, determined by measurement of the difference between the



angles of reflexion of the same order for two different X-ray lines, is in good agreement with previous vals.

J. W. S.

**Theory of linear crystallisation velocity.** R. KAISCHEV and I. N. STRANSKI (Z. physikal. Chem., 1934, 170, 295—299).—Proceeding on the same lines as before (A., 1934, 946) an expression for the rate of linear crystallisation has been derived which differs from that of Volmer and Marder (A., 1931, 672) only in containing a factor  $1/\Delta T^2$ , where  $\Delta T$  is the supercooling. It is compared with existing experimental data.

R. C.

**Potassium models. Spatial representation of the saturation relations of potassium salts.** E. JANECKE (Z. Elektrochem., 1934, 40, 735—743).—A lecture.

E. S. H.

**Inner equilibrium in solid phases. II.** A. SMITS (Physikal. Z., 1934, 35, 914—918).—The conclusion of Clusius and Perlick (A., 1934, 354) that the phase change in solid  $\text{CH}_4$  at  $-252.8^\circ$  is one of the second kind, as defined by Ehrenfest (A., 1933, 569), is probably incorrect. For accurate results it is necessary to use very pure substances. Comparison is made with the  $\text{NH}_4\text{Cl}$  system (*ibid.*, 1119).

A. J. M.

**Inner equilibrium in solid phases.** K. CLUSIUS and A. PERLICK (Physikal. Z., 1934, 35, 918—919).—A reply to Smits (cf. preceding abstract). The effect noted was not due to impurities, and cannot be regarded as a phase change of the first order.

A. J. M.

[Inner equilibrium in solid phases.] A. SMITS (Physikal. Z., 1934, 35, 919).—A reply to Clusius and Perlick (cf. preceding abstract).

A. J. M.

**Intensities of X-ray spectra and the imperfections of crystals.** R. W. JAMES (Z. Krist., 1934, 89, 295—309).—A review of experimental facts about the angular range of reflexion of X-rays by existing crystals, and of ways of calculating the extinction which applies to the observed intensities.

B. W. R.

**Intensities of X-ray reflexions from powders.** G. W. BRINDLEY and F. W. SPIERS (Proc. Physical Soc., 1934, 46, 841—852).—An improved and accurate method of photographic determination, by measuring the intensities of X-ray reflexions from a plane stationary layer of powder, is described. It is illustrated by comparison of reflexions of widely different intensity of  $\text{Cu } K\alpha$  radiation from Cu powder, by comparison of intensities for  $\text{Cu } K\alpha$  from  $\text{KCl (420) + KCl (422) + Cu (220)}$ , and by the accuracy for large-angle reflexions from Al powder.

N. M. B.

**Atom scattering factor of beryllium.** W. EHRENBERG (Z. Krist., 1934, 89, 185—189).—The abs. intensities of X-ray reflexion are measured for Be powder and compared with Hartree curves for Be and  $\text{Be}^{++}$ . Better agreement is obtained with the former.

B. W. R.

**Effect of temperature on the reflexion of X-rays from bismuth crystals.** A. GOETZ and R. B. JACOBS (Physical Rev., 1933, [ii], 43, 213).—The Debye-Waller relation for the temp. effect does not hold.

L. S. T.

**Change in the width of X-ray interference lines of palladium when charged with hydrogen elec-**

**trolytically.** E. NÄHRING (Ann. Physik, 1934, [v], 21, 303—319).—There is a widening of the X-ray interference lines of Pd with the absorption of  $\text{H}_2$ , the Pd being made an electrode in an electrolysis apparatus. The cubic symmetry of the Pd lattice changes as the  $\text{H}_2$  is absorbed.

A. J. M.

**Broadening of X-ray lines of cold-worked aluminium.** L. THOMASSEN and J. E. WILSON (Physical Rev., 1933, [ii], 43, 763).—Broadening with Al cold-worked at  $-75^\circ$ , but not at room temp., is indicated (cf. A., 1928, 693).

L. S. T.

**Inner absorption in crystals of salts.** D. BALAREV (Z. Krist., 1934, 89, 268—281).—A summary chiefly of the author's work (cf. A., 1933, 364, 563), showing that impurities in a crystal are in general closely related to its mosaic structure. Real crystals are pictured as a "growth-conglomerate" and it is argued that thermodynamic equilibrium in the crystal state implies a macro-structure.

B. W. R.

**Lineage structure of crystals.** M. J. BUEGGER (Z. Krist., 1934, 89, 195—220).—"Lineages" indicate the filled-in dendritic structures which are supposed to occupy the interior of most crystals. These are exhibited optically with many examples, chosen from both single and poly-crystals. On the basis of the lineage structure the "mosaic" ideas of other authors (e.g., Adams, Coker, Straumanis) are developed, and X-ray extinction, electrical conductivity, gas absorption, plasticity, gliding, and Goetz' m.-p. phenomena are discussed.

B. W. R.

**Mosaic structures of crystals.** H. E. BUCKLEY (Z. Krist., 1934, 89, 221—241).—A detailed summary of existing theories of the internal macrostructure of crystals. The theories of Smekal and Zwicky are reviewed, with the conclusion that the ideas of neither have a trustworthy experimental basis. The facts of X-ray extinction and reflexion width are undisputed, and indicate a mosaic of the Darwin type. Serious difficulties against such a mosaic are summarised as follows: passage of  $\text{H}_2\text{O}$  through crystals, existence of extremely thin crystals, etch figures, difficulty of understanding the formation of the mosaic interior, and the high surface perfection and optical homogeneity of existing crystals.

B. W. R.

**Non-existence of a regular secondary structure in crystals.** M. J. BUEGGER (Z. Krist., 1934, 89, 242—267).—A criticism of the ideas of Zwicky and his co-workers. In particular the work of Goetz is examined; the markings seen by him on a Bi surface are ascribed to gliding stria. His evidence for "block phase" in liquids near the m.p. is otherwise explained, and the alleged difference between the optical and X-ray expansion coeffs. of Bi is attributed to impurities. The various weaknesses of crystals are not accounted for by a secondary structure, and the experimental facts have been misinterpreted. Zwicky's argument based on the tendency of individual crystal planes to contract is shown to be fallacious.

B. W. R.

**Transformations in homogeneous substances.** G. TAMMANN (Z. physikal. Chem., 1934, 170, 380—390).—Transformations in cryst. solids are of two



main types, according as the properties vary normally with the temp.,  $T$ , above and below the transition temp.,  $\tau$ , and at  $\tau$  change discontinuously owing to appearance of a second cryst. species, or as no recrystallisation occurs and the properties vary abnormally, but continuously, over a certain  $T$  range. Which type occurs depends on whether or not the changes occurring in the atom or mol. so alter the fields of force of the mols. that the original lattice ceases to be stable. Ehrenfest's views on phase change (A., 1933, 569) are criticised. R. C.

**Universal significance of cubic face-centred lattice structure for the causal comprehension of hitherto unknown relations.** R. REINICKE (Z. physikal. Chem., 1934, B, 27, 28—36).—The fitting together of equal cubes, edge to edge, necessarily leads to a face-centred arrangement of their centres of gravity, which are to be identified with the at. positions. If the NaCl lattice is regarded, not as a manifestation of a certain grouping of masses, but as the most symmetrical distribution of opposite charges, then, since many metals, as well as most of the inert gases, have a cubic face-centred lattice, it may be assumed that the metal atoms release their valency electrons and the latter occupy the positions occupied in the NaCl lattice by Cl'. The consequences of this conception are examined. R. C.

**Review of new structure determinations of compounds of the type  $AB_2$ .** W. NOWACKI (Z. Krist., 1934, 89, 85—88).—A condensed account of further data since the author's previous review (cf. A., 1932, 796). B. W. R.

**X-Ray study of the effect of heat on the structure of sputtered films of gold.** S. R. SWAMY (Proc. Physical Soc., 1934, 46, 739—744).—Debye-Scherrer photographs of sputtered Au films of various thicknesses heated at stages in the range 200—900° showed that, on heating, the crystals grew, and oriented with their (111) planes parallel to the surface of deposition. Degree of orientation and crystal size depended on both film thickness and temp. N. M. B.

**X-Ray investigation of the disperse structure of different kinds of graphite.** V. S. VESSELOVSKI and K. V. VASSILIEV (Z. Krist., 1934, 89, 156—174).—A systematic treatment of disperse structures is suggested, a disperse structure being regarded as the sum of a large no. of separate elementary bodies. It is illustrated by a survey of different forms of C from single-crystal graphite to soots and anthracites. Particular attention is given to the size and orientation of particles. B. W. R.

**Unit cell of uranium calculated from X-ray powder method data.** T. A. WILSON (Physical Rev., 1933, [ii], 43, 781—782).—The unit cell has equal face perpendiculars of 2.535 Å. arranged in space at angles of 64°, 67° 45', 67° 45', respectively. The vol. is 20.26 Å<sup>3</sup>, giving U an X-ray  $d$  of 19.32 compared with a previous val. of 18.68. L. S. T.

**Lattice structure of beryllium carbide,  $Be_2C$ .** M. VON STACKELBERG and F. QUATRAM (Z. physikal. Chem., 1934, B, 27, 50—52).— $Be_2C$  has an antifluorite

lattice, with a 4.33 Å.,  $d$  2.44. The distance Be—C is 1.87 and the distance C—C 3.06 Å. R. C.

**Crystal structure of aluminium carbide,  $Al_4C_3$ .** M. VON STACKELBERG and E. SCHNORRENBERG (Z. physikal. Chem., 1934, B, 27, 37—49).— $Al_4C_3$  has the space-group  $D_{3d}^5$  and a layer-lattice, each layer consisting of four Al atom planes with three interposed C atom planes. R. C.

**Structure of aluminium carbide,  $Al_4C_3$ .** M. VON STACKELBERG (Fortschr. Min., 1933, 18, 35—36; Chem. Zentr., 1934, i, 2713—2714).— $Al_4C_3$  has two modifications. The  $\beta$ -form (probably hexagonal-holohedral;  $a$  3.27,  $c$  21.6 Å.; 2.5 mols. in unit cell) is formed from the elements at approx. 1600°. The  $\alpha$ -form (rhombohedral;  $a$  3.32,  $c$  24.9 Å.; 1 mol. in unit cell; space-group  $D_{3d}^5$ ) is produced at > 1600°. H. J. E.

**Powder diagram of a new iron carbide.** G. HÄGG (Z. Krist., 1934, 89, 92—94).—Prolonged treatment of Fe or  $Fe_2O_3$  by CO at low temp. (225°) seems to produce a new carbide  $Fe_2C$ . The prep. gives powder lines hitherto unknown, which are listed but not analysed. B. W. R.

**Structural principles of carbides, silicides, nitrides, and phosphides of electropositive metals.** M. VON STACKELBERG (Z. physikal. Chem., 1934, B, 27, 53—57).—The lattices of these compounds are ionic and the anions form a lattice of closest-packed spheres in the tetrahedral or octahedral interstices of which are the cations. Such a lattice is possible only if the no. or size of the cations is not such as to break up the anion lattice. R. C.

**Redetermination of parameter for hauerite,  $MnS_2$ .** F. OFFNER (Z. Krist., 1934, 89, 182—184).—The unexpectedly large Mn—S distance in this compound (cf. A., 1934, 350) was confirmed by an accurate X-ray measurement. B. W. R.

**Crystal structure of tetradymite,  $Bi_2Te_2S$ .** D. HARKER (Z. Krist., 1934, 89, 175—181).—The cell is rhombohedral,  $a_0$  10.31 Å.,  $\alpha$  24° 10'. From intensity calculations the structure is found to be essentially metallic, adjacent layers containing one kind of atom only in the order S Bi Te Te Bi S Bi etc., forming a cubic close-packed lattice if the identity of the atoms be disregarded. B. W. R.

**Orientation of crystallites in the ignition products of  $Mg(OH)_2$  and  $Ca(OH)_2$ .** C. D. WEST (Amer. Mineral., 1934, 19, 281—283).—From X-ray measurements, the CaO crystallites are oriented only along a 3-fold axis, whilst MgO crystallites are oriented on both 2- and 3-fold axes. An ignited Fe-brucite fibre contains magnesioferrite with an orientation similar to that of MgO. CH. ABS. (e)

**Crystal structure of tetramethylammonium silicofluoride.** R. B. COREY (Z. Krist., 1934, 89, 10—17).— $(NMe_4)_2SiF_6$  has a tetragonal cell containing 2 mols.,  $a_0$  7.88,  $c_0$  11.19 Å., space-group  $C_{4v}^2$ . At. parameters were determined from intensity measurements on artificially shaped crystals. B. W. R.

**Crystal structure of sodium uranyl acetate.** I. FANKUCHEN (Physical Rev., 1933, [ii], 43, 1048).—Powder photographs show that Na U acetate is cubic,





$a$  10.69 Å., 4 mols. in unit cell. Rotation and oscillation photographs confirm the space-group  $T^4$  (cf. A., 1930, 1351). The structure is similar to that of  $\text{NaClO}_3$  with the  $\text{UO}_2$  corresponding with Cl and the OAc with the O. L. S. T.

**Crystallographic investigation of carbamide phosphate.** C. MATIGNON and M. DODÉ (Bull. Soc. franç. Minéral., 1934, 56, 351—357; Chem. Zentr., 1934, ii, 426).—The crystals are orthorhombic ( $a:b:c=0.831:1:0.981$ ). From solutions rich in  $\text{CO}(\text{NH}_2)_2$  tables separate, whilst with excess of  $\text{H}_3\text{PO}_4$  small orthorhombic octahedra form. The neutral salt could not be isolated. Solubility data are recorded. H. J. E.

**X-Ray study of the crystal structure of Rochelle salt and the effect of temperature.** B. E. WARREN and H. M. KRUTTER (Physical Rev., 1933, [ii], 43, 500).—Oscillation and rotation patterns give an orthorhombic unit cell containing 4 mols. of  $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  with  $a$  11.85,  $b$  14.25,  $c$  6.21 Å.; space-group  $V^3$ .  $\epsilon$  is unusually large between  $20^\circ$  and  $-20^\circ$ . Integrated intensities measured at  $-50^\circ$  and  $25^\circ$  showed for  $-50^\circ$  only the normal increase to be expected from the usual Debye temp. factor. L. S. T.

**Electron diffraction investigation of non-metallic halides.** P. O. BROCKWAY and F. T. WALL (J. Amer. Chem. Soc., 1934, 56, 2373—2379).—The mol. structures of  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{CF}_4$ ,  $\text{SiF}_4$ ,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{PF}_3$ , and  $\text{AsF}_3$  have been investigated. Deviations from additivity of the covalent radii are discussed in relation to ionic character of the linkings and the formation of double electron pair linkings. E. S. H.

**X-Ray patterns of crystalline urease and pepsin.** I. FANKUCHEN (J. Amer. Chem. Soc., 1934, 56, 2398).—The results show that probably neither compound contains straight chains of  $\text{NH}_2$ -acid residues. E. S. H.

**X-Ray diffraction patterns of cellulose particles and interpretation of cellulose diffraction data.** W. K. FARR and W. A. SISSON (Contr. Boyce Thompson Inst., 1934, 6, 315—321).—Diffraction phenomena hitherto explained by the supposed existence of a micellar structure may be accounted for by the visible particles of cellulose occurring as units in young fibres and subsequently united by non-cellulose cementing substances to form fibrils. In the latter the individual particles cannot be observed. A. G. P.

**X-Ray diffraction of liquid films.** K. LARK-HOROVITZ and E. P. MILLER (Physical Rev., 1933, [ii], 43, 1060).—Diffraction patterns of very thin films of glycerol, paraffin oil fractions, and commercial mineral oil obtained at different temp. are described. Even at liquid air temp. the structure of the glycerol film remains quasi-liquid and shows no sign of orientation or crystal formation. L. S. T.

**Conditions and limits of correct electron projection of images.** Electron paths in the cylindrical electrical field of a coarse crystalline glowing wire. H. SEEMANN (Z. Physik, 1934, 92, 253—273). A. B. D. C.

**Electron photographs of graphite.** G. AMINOFF and B. BROOMÉ (Z. Krist., 1934, 89, 80—85).—Two types of photograph may be obtained, the one analogous to the usual X-ray rotation photograph, the other showing straight bands (Kikuchi lines). Interpretation on the basis of the reciprocal lattice agrees with accepted X-ray data for graphite. B. W. R.

**Diffraction of electrons by single molecules.** L. R. MAXWELL, M. E. JEFFERSON, and V. M. MOSLEY (Physical Rev., 1933, [ii], 43, 777; cf. A., 1934, 17).—Diffraction rings for  $\text{CCl}_4$  vapour give vals. corresponding with 2.98 Å. for the Cl-Cl distance. L. S. T.

**Diffraction of electrons by oxide films on molten metals.** J. A. DARBYSHIRE and E. R. COOPER (Trans. Faraday Soc., 1934, 30, 1038—1048).—Oxide films removed from the surface of Cd, Mg, Al, Bi, and 1% Mg-99% Sb (I) have been investigated. The data are consistent with the configurations deduced from X-ray studies, but discrepancies between the calc. and observed intensity ratios and anomalies indicate the inadequacy of the present optical theory of electron diffraction. The  $\text{Al}_2\text{O}_3$  was in the face-centred cubic  $\gamma$ -form with  $a$  7.78 Å., which is < earlier vals.  $\text{Bi}_2\text{O}_3$  was, in general, in a body-centred tetragonal form with  $a$  10.85 and  $c$  11.28 Å. (I) afforded films of oriented MgO, whilst in the other films examined orientation was generally small. J. G. A. G.

**New electron diffraction rings in zinc oxide and their interpretation.** K. LARK-HOROVITZ and H. J. YEARIAN (Physical Rev., 1933, [ii], 43, 376—377).—The diffraction of ZnO powder deposited from an electric arc between Zn electrodes has been investigated with 6- to 20-kv. electrons. Besides the ordinary rings, rings of smaller intensity, interpreted by an inner potential of 4 volts for ZnO, occur. L. S. T.

**X-Ray investigation of the mode of vibration of piezo-electric quartz plates.** S. NISHIKAWA, Y. SAKISAKA, and I. SUMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 20—30). R. S. B.

**Change of resistance of cobalt in longitudinal magnetic fields.** M. S. ALAM (Current Sci., 1934, 3, 155—156).—Contrary to McCorkle (Physical Rev., 1923, [ii], 22, 271) the resistance of Co increases to a saturation val. at 1200—1300 gauss in longitudinal fields. Hysteresis also occurs. L. S. T.

**Magnetic study of the metallic state and the Fermi-Dirac statistics.** S. FREED and H. G. THODE (Nature, 1934, 134, 774—775).—Preliminary measurements of the at. susceptibility of Na in liquid  $\text{NH}_3$  are recorded. L. S. T.

**Longitudinal and transverse magneto-resistance and magnetic structure of ferromagnetic materials.** G. ALOCCO (Atti R. Ist. Veneto Sci., 1932—1933, 92, 1353—1371; Chem. Zentr., 1934, i, 3446).—Polycryst. sheet Ni resembles single Ni crystals in its magneto-resistance. The elementary moments are oriented. H. J. E.



**Magnetisation function for ferromagnetic substances applicable to all temperatures.** H. LUDLOFF (Z. Physik, 1934, 91, 742—764).—Theoretical.

A. B. D. C.

**Ferromagnetism of the iron-nickel alloys under hydrostatic pressure.** R. L. STEINBERGER (Physical Rev., 1933, [ii], 43, 502).—The application of pressure causes a relatively large change, usually diminution, in flux density, and an incomplete recovery when pressure is released. In pure Fe, 20 and 80% Ni, the change is negative and linear. Pure Ni and 40, 50, and 90% Ni alloys show varying amounts of pressure hysteresis. In the 30 and 60% Ni alloys the rate of change of flux decreases with increasing pressure, and in the former the alloy becomes non-magnetic under pressure.

L. S. T.

**Paramagnetism of metallic rhenium.** N. PERAKIS, L. KAPATOS, and P. KYRIAKIDIS (Praktika, 1933, 8, 163—168; Chem. Zentr., 1934, ii, 404).—From measurement between  $-79^{\circ}$  and  $20^{\circ}$  a val. of  $\chi = 68.7 \times 10^{-6}$  was found.

H. J. E.

**Magnetism of tin.** S. R. RAO (Proc. Indian Acad. Sci., 1934, 1, A, 123—142; cf. A., 1934, 1061).—The susceptibility of white Sn *en masse* is 0.360 and is const. up to  $220^{\circ}$ ; at the m.p. ( $233^{\circ}$ ) it decreases rapidly to  $-0.0455$ , and regains the val. 0.360 on cooling to  $30^{\circ}$ . Pure colloidal white Sn, after settling in PrOH and centrifuging, becomes diamagnetic, this diamagnetism increasing at smaller particle sizes. On melting and recrystallising, paramagnetism is regained. The at. susceptibility of grey Sn is approx.  $-41.54 \times 10^{-6}$ .

N. M. B.

**Vectorial properties of ferromagnetic substances and the magnetic structure of polycrystalline materials.** A. DRIGO (Atti R. Ist. Veneto Sci., 1932—1933, 92, 1373—1386; Chem. Zentr., 1934, i, 3446—3447).

H. J. E.

**Permeability of iron at ultra-radio frequencies.** W. ARKADIEW (Physical Rev., 1933, [ii], 43, 671—672).—The vals. obtained by other investigators (A., 1933, 117) are compared with those of the author.

L. S. T.

**Theory of magnetostriction.** T. HAYASI (Z. Physik, 1934, 91, 818—819).—A correction (cf. A., 1931, 1360).

A. B. D. C.

**Magnetostriction in bismuth single crystals.** A. WOLF and A. GOETZ (Physical Rev., 1933, [ii], 43, 213).—The magnetostriction of Bi single crystals has been measured in a longitudinal field of approx. 20,000 gauss in two different directions to the principal axis. The effect of impurities has been determined.

L. S. T.

**Dispersion of the sodium-potassium feldspars.** E. LEISEN (Z. Krist., 1934, 89, 49—79).—Optical data are obtained for different members of the plagioclase series, and are related to the crystallographic properties. Different types of dispersion are analysed relative to the anorthite content, and are illustrated by stereographic projection.

B. W. R.

**"Banded spectrum" method for measurement of dispersion of birefringence of a crystal plate.** H. BRASSEUR and J. PIÉRARD (Z. Krist., 1934, 89, 24—31).—A modified calculation is de-

scribed and applied to the measurement of birefringence of an (001) flake of  $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ .

B. W. R.

**Examination of anisotropic substances between crossed nicols [in reflected light].** M. BEREK (Z. Krist., 1934, 89, 125—143).—Previous descriptions (cf. A., 1931, 587, 703) of behaviour of anisotropic substances when viewed by reflected light through a nicol prism are extended to the use of two prisms. The following topics are discussed: use of monochromatic and of white light; significance of slight departures from the extinction positions; polarisation defects in the incident light; practical construction of opaque illuminators; and influence of the absorption in the substance examined.

B. W. R.

**Theory of examination of anisotropic substances between crossed nicols [in reflected light].** M. BEREK (Z. Krist., 1934, 89, 144—155).—A parallel commentary, in mathematical language, to the preceding paper (cf. preceding abstract).

B. W. R.

**Stability of ionic lattices.** G. STEENSHOLT (Z. Physik, 1934, 91, 765—766).—The NaCl type lattice is shown to be most stable for RbBr.

A. B. D. C.

**Photochemical properties of synthetic rock-salt crystals. Red displacement of colouring absorption bands by plastic deformation.** K. HELBIG (Z. Physik, 1934, 91, 573—592).—Plastic deformation disturbs the photochemical photo-electric equilibrium, increases rate of bleaching, and displaces the colouring absorption band towards the red.

A. B. D. C.

**Colour centres and plastic deformation of synthetic rock-salt crystals containing foreign atoms.** E. POSER (Z. Physik, 1934, 91, 593—599).—The photochemical elastic limit of synthetic rock-salt and the red displacement of its colouring bands are independent of the presence of foreign mols. ( $\text{SrCl}_2$ ) even though these vary with the mechanical strength.

A. B. D. C.

**Fundamentals of the theory of practical strength.** A. V. STEPANOV (Z. Physik, 1934, 91, 42—60).—Mechanical breakdown is brought about by changes due to plastic flow causing local strains within the crystal.

A. B. D. C.

**Plasticity of crystals.** F. ZWICKY (Physical Rev., 1933, [ii], 43, 765—766).—Polemical (cf. A., 1934, 559, 768, 1005).

L. S. T.

**Previous deformations of crystals.** W. F. BERG (Z. Krist., 1934, 89, 286—294).—By reflecting X-rays diverging from a suitable line focus from a crystal face, a photograph can be obtained which displays the past deformations of the lattice. The interpretation and use of such photographs are discussed.

B. W. R.

**Investigations with pure  $\alpha$ -,  $\beta$ -, and  $\gamma$ -manganese.** F. BRUNKE (Ann. Physik, 1934, [v], 21, 139—168).—The three Mn phases were prepared in a state of purity as follows:  $\alpha$ -Mn by vaporisation of pure Mn in vac.;  $\beta$ -Mn by quenching Mn melts from  $1100^{\circ}$ ;  $\gamma$ -Mn by electrolysis of an aq. solution of  $\text{MnCl}_2$  and  $\text{NH}_4\text{Cl}$ . Determination of the temp. coeff.



of electrical conductivity of each phase, and other electrical and magnetic properties indicate that  $\gamma$ -Mn is the pure metal, whilst  $\alpha$ - and  $\beta$ -Mn are mixed crystals of the  $\gamma$ -phase, and partake of the nature of alloys.

A. J. M.

#### Dimorphism of certain aliphatic compounds.

**V. *n*-Primary alcohols and their acetates.** J. W. C. PHILLIPS and S. A. MUMFORD (J.C.S., 1934, 1657—1665).—The f.p. and polymorphism of the *n*-alcohols and acetates from dodecyl to nonadecyl (with the exception of tridecyl) have been investigated. In alcohols, the m.p. of the  $\alpha$ -forms lie on a smooth curve, whilst the m.p. curve of the  $\beta$ -forms shows alternations. The two curves intersect at about  $C_{13}$ . The acetates of the even alcohols show monotropic dimorphism. The  $\alpha$ -form of the acetates of the odd alcohols changes first into an opaque  $\beta$ -form monotropically, and this, on cooling, changes into a  $\beta_2$ -form of higher m.p. The  $\alpha$ -f.p. of all the acetates lie on a smooth curve, which intersects the  $\beta$ -curve of the odd members between  $C_{15}$  and  $C_{17}$ , and the  $\beta_2$ -curve of the odd members, and the almost coincident  $\beta$ -curve of the even members somewhere above  $C_{20}$ . The alternation of properties in homologous series of aliphatic compounds is discussed.

A. J. M.

**Swarm theory of liquid crystals.** L. S. ORNSTEIN (Kolloid-Z., 1934, 69, 137—155).—A theoretical exposition (cf. A., 1934, 949) of the macroscopic properties, turbidity, X-ray diagrams, and influence of magnetic and electric fields.

E. S. H.

**Superconductivity.** A. J. RUTGERS (Physica, 1934, 1, 1055—1058).—An equation is deduced connecting the jump in sp. heat of a superconductive metal at the transition point with the derivative of the magnetic threshold val. with respect to temp.

M. S. B.

**Superconductors.** T. C. KEELEY, K. MENDELSOHN, and J. R. MOORE (Nature, 1934, 134, 773—774).—Further experiments with Hg, Sn, and Pb are recorded (cf. A., 1934, 492).

L. S. T.

**Superconductivity of tin at radio-frequencies.** F. B. SILSBEE, R. B. SCOTT, F. G. BRICKWEDDE, and J. W. COOK (Physical Rev., 1933, [ii], 43, 1050—1051).—The effective resistance of extruded Sn wire carrying radio-frequency currents at temp. slightly  $<$  the transition temp. ( $3.7^\circ$  abs.) is  $<$  1% of that at temp. slightly above.

L. S. T.

**Temperature coefficient of electrical conductivity in thin metal films.** R. DEAGLIO (Z. Physik, 1934, 91, 657—659).—Conductivity and temp. coeff. of thin anomalously conducting metal films are in agreement with Biltz' conclusions (A., 1924, ii, 515).

A. B. D. C.

**Conductivity of thin metal films and the surface conductivity of metals.** E. PERUCCA (Z. Physik, 1934, 91, 660—669).—Arguments are given supporting the hypothesis that metals normally have a surface layer of conductivity small compared with the bulk conductivity.

A. B. D. C.

**Electrical resistivities of single and optically mosaic zinc crystals.** W. J. PORRY (Physical Rev., 1934, [ii], 46, 815—821).—The Voigt-Thomson symmetry relation is confirmed for strain-free Zn

single crystals, and principal electrical resistivities are given. Effects of strain and complex effects of annealing are shown graphically. Optically mosaic specimens have abnormal resistivities, and are highly strain-sensitive.

N. M. B.

**Peltier and Thomson effects and entropy.** A. LIÉNARD (Compt. rend., 1934, 199, 838—840).—Mathematical.

J. W. S.

**Thermal resistance of bismuth single crystals at low temperatures.** W. J. DE HAAS and W. H. CAPEL (Physica, 1934, 1, 929—934).—The heat conductivity of single crystals of Bi has been determined at  $81.5^\circ$  and  $20-16.5^\circ$  abs. along the directions parallel to a binary axis and to a bisectrix between two binary axes, both perpendicular to the direction of the trigonal principal axis for which  $\lambda$  has been previously determined (A., 1934, 983). For the two perpendicular directions the thermal resistance-temp. curve has a min. The prep. of the crystals is described.

M. S. B.

**Velocity of sound in anisotropic media, particularly in quartz measured by piezo-electric excitation.** R. BECHMANN (Z. Physik, 1934, 91, 670—678).

A. B. D. C.

**Dispersion of ultrasonic waves in a liquid.** B. G. SCHPAKOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 588—594).—Data are recorded for  $H_2O$ , EtOH, benzine,  $PhNO_2$ , ethylene chloride, amylacetate, EtOAc, and  $COMe_2$ . Up to frequencies of  $10^6$  cycles per sec. the velocity of sound in these liquids at  $20-24^\circ$  was const.

H. J. E.

**Ultrasonic absorption and reflexion coefficients in air and in carbon dioxide.** R. W. CURTIS (Physical Rev., 1934, [ii], 46, 811—815).—Measurements were made using Hubbard's method (cf. *ibid.*, 1931, [ii], 38, 1011). In the frequency range 88—1000 kc. per sec. absorption in air increased with  $\lambda^2$ , but in  $CO_2$  gave a sharp max. at 98 kc. per sec. The reflexion coeff., for a brass reflector, decreased for both gases, to the order of 20% at higher frequencies, with increasing frequency.

N. M. B.

**Effect of dissolved air on the specific heat of water.** R. JESSEL (Proc. Physical Soc., 1934, 46, 747—763).—Data are tabulated and plotted for the temp. range  $12-80^\circ$ , as obtained by the continuous-flow electric method, for saturated and air-free distilled  $H_2O$ . In the latter case the vals. are lower. An explanation is proposed.

N. M. B.

**Preliminary calculation of the molecular heat  $c_v$  of sodium chloride and metals at high temperatures.** A. EUCKEN and W. DANNÖHL (Z. Elektrochem., 1934, 40, 789—792).—Theoretical.

E. S. H.

**Effect of temperature on the true specific heat of nickel.** E. AHRENS (Ann. Physik, 1934, [v], 21, 169—181).—A new differential method for the determination of true sp. heats is described. It has been used to determine the true sp. heat of Pt and Ni between  $20^\circ$  and  $460^\circ$ . The sp. heat of Ni attains a max. at  $349.5 \pm 0.5^\circ$ . There is a max. in the curve of temp. coeff. of resistance and temp. within  $1.5^\circ$  of the above val.

A. J. M.



**Specific heats of metals at high temperature.**  
**XVII. Calorimetric retardation phenomena of cerium and chromium.** F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 489—497; cf. A., 1934, 481).—The vals. of the sp. heat,  $C_p$ , of Ce in the range 296—551° depend on the preliminary thermal treatment.  $C_p$  is raised by keeping the sample at  $> 360^\circ$ , and subsequent cooling at room temp. diminishes the acquired high  $C_p$ . The results are attributed to the complexity of the metal. A transition temp. at 360—370° is inferred. Vals. of the  $C_p$  of Cr between 400° and 1066° are reproducible, but the rate of evolution of heat is related to the preliminary thermal treatment of the sample. J. G. A. G.

**Empirical heat capacity equations for simple gases.** H. M. SPENCER and J. L. JUSTICE (J. Amer. Chem. Soc., 1934, 56, 2311—2312).—The heat capacities of equilibrium  $\text{Cl}_2$ , equilibrium HCl, and  $\text{CO}_2$  between 300° and 1500° abs. have been calc. from published data. Empirical equations of the form  $C_p = a + bT + cT^2$  fit the theoretical vals. for  $\text{Cl}_2$ , HCl,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , CO, Br, HBr, and  $\text{H}_2\text{O}$  vapour with average deviations 0.18—0.76%. E. S. H.

**Specific heat, entropy, and free energy of gaseous nitric oxide computed from spectroscopic data.** E. E. WITMER (J. Amer. Chem. Soc., 1934, 56, 2229—2233).—The vals. have been calc. for the range 1—500° abs., and are compared with those published elsewhere. E. S. H.

**Heats of crystallisation of the ethyl esters of the monobasic aliphatic acids.** A. M. KING and W. E. GARNER (J.C.S., 1934, 1449—1456).—Data are recorded for the esters of the acids from  $n=14$  to  $n=30$ . The form stable at the m.p. has a vertical chain when  $n$  is  $> 20$  and a tilted chain when  $n$  is  $< 20$ . The heat of crystallisation of the vertical chain types is a linear function of  $n$ , but with tilted chains the curve changes slope at  $n=20$  owing probably to a change of orientation of the ester group. The vertical forms have a higher sp. heat than the tilted, and a lower heat of crystallisation, on account of the greater amplitude of oscillation of the chain. The higher m.p. of the vertical forms is attributed to the increased probability of attachment of the chains to the surface of the solid. H. F. G.

**Heat of vaporisation of acetone, and its saturated vapour pressure.** N. A. DE KOLOSOVSKI and A. ALMOV (J. Gen. Chem. Russ., 1934, 4, 710—712).—Empirical formulæ for the latent heat of vaporisation and v.p. of  $\text{COMe}_2$  at 0—80° are given. R. T.

**Effect of high electrostatic fields on the vaporisation of molybdenum.** G. B. ESTABROOK (Physical Rev., 1933, [ii], 43, 383). L. S. T.

**Effect of high electrostatic fields on the vaporisation of metals.** A. G. WORTHING (Physical Rev., 1933, [ii], 43, 383).—Theoretical. L. S. T.

**F.p. of platinum.** F. H. SCHOFIELD (Proc. Roy. Soc., 1934, A, 146, 792—817).—The f.p. of Pt on the International temp. scale has been determined by measuring the ratio of brightness, for a certain wavelength, of black-body radiators held at the f.p. of Pt

and Au. The mean val.  $1773.3 \pm 1^\circ$  is in good agreement with the only previous val. obtained by the same method (A., 1931, 1004). L. L. B.

**Surface energy of molecules and their physico-chemical properties. IV. Surface energy and b.p. in certain organic and inorganic homologous series. V. Surface energy and dissociation temperature of complex compounds.** S. G. MOKRUSCHIN (J. Gen. Chem. Russ., 1934, 4, 577—579, 580—586).—IV [with E. I. KRILOV]. The formulæ  $T = an + b$ , and  $T = cn + dn^2 + g$ , where  $T$  is the b.p. of a member of a homologous series containing  $n$  homologous groups, and  $a, b, c, d$ , and  $g$  are consts., are verified for a no. of series.

V. The formula  $T = k/(A/d)^{2/3}$ , where  $T$  is the dissociation temp.,  $A$  the at. wt. of the central atom, and  $d$  its density, is verified for compounds of the types  $[\text{M}(\text{NH}_3)_6]\text{X}_2$ ,  $[\text{M}(\text{NH}_3)_6]\text{SO}_4$ , and  $[\text{M}(\text{NH}_3)_4]\text{SO}_4$ , where  $\text{M} = \text{Ni, Fe, Cu, Mn, Zn, Cd, and Mg}$ , and  $\text{X} = \text{Cl, Br, and I}$ . R. T.

**Density of small crystals.** J. D. BERNAL and D. CROWFOOT (Nature, 1934, 134, 809—810).—The  $d$  of small amounts ( $> 0.05$  mg.) of minute crystals has been determined by finding a liquid of known  $d$  in which no movement of the crystals occurs on centrifuging for 1—2 min. at 2000—4000 r.p.m. Vals. found are vitamin- $B_1$  hydrochloride  $1.403 \pm 0.003$ ,  $\text{C}_{21}\text{H}_{16}$   $1.244 \pm 0.002$ ,  $\text{C}_{25}\text{H}_{24}$   $1.195 \pm 0.003$ ,  $\text{C}_{26}\text{H}_{26}$   $1.158 \pm 0.003$ , and  $\text{C}_{27}\text{H}_{28}$   $1.135 \pm 0.002$  (four hydrocarbons obtained respectively by Se-dehydrogenation of cholic acid, cholesterol, ergosterol, and phyosterols). L. S. T.

**Thermal expansion of bismuth single crystals.** T. L. HO and A. GOETZ (Physical Rev., 1933, [ii], 43, 213).—The thermal expansion of Bi crystals with known admixtures of electro-positive and -negative impurities in low concn. has been determined between room temp. and the m.p. The decrease in the coeff. before the m.p. has been verified. Admixtures bring about definite changes at temp. characteristic for the impurity present. L. S. T.

**Thermal expansion of alkali halides and metals at high temperatures.** A. EUCKEN and W. DANNÖHL (Z. Elektrochem., 1934, 40, 814—821).—The expansion coeffs. of Pb, Ag, Cu, Ni, NaCl, KCl, KBr, and KI have been measured over different ranges of temp. E. S. H.

**X-Ray measurements of the thermal expansion of sodium nitrate.** H. SAINI and A. MERCIER (Helv. phys. Acta, 1934, 7, 267—272; Chem. Zentr., 1934, i, 3833).—Data are recorded between 18° and 200°, and the expansion coeffs. deduced. H. J. E.

**Thermal expansion of calcite.** J. WEIGLE and H. SAINI (Helv. phys. Acta, 1934, 7, 257—266; Chem. Zentr., 1934, i, 3833).—Lattice const. measurements by the X-ray method are recorded for 18°, 100°, 200°, and 300°, and the expansion coeffs. deduced. H. J. E.

**Thermal expansion of Jena thermometer glass 2954<sup>III</sup>.** W. H. KEESOM and D. W. DOBORZYŃSKÓ (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 480—481).—The equation  $l = l_0[1 + 10^{-6}(545.89\tau + 19.55\tau^2 + 17.16\tau^3 + 27.99\tau^4 + 5.24\tau^5)]$ , where  $\tau = t/100$ , is



valid between 100° and -273°. The coeff. of thermal expansion of fused SiO<sub>2</sub> is zero near -273°.

J. G. A. G.

**Vapour density of sulphur dioxide.** W. W. STEWART and O. MAASS (Canad. J. Res., 1934, 11, 530—538).—The sensitivity of the apparatus previously employed (cf. A., 1931, 1117) for v.d. determinations has been increased by the addition of a 50-litre container. It is shown that the apparent mol. wt.-pressure isothermal for SO<sub>2</sub> is not a straight line. This is in agreement with the equation of state for gases at low pressures. The experimental data give mol. wt. of 64.075 for SO<sub>2</sub>.

M. S. B.

**Vapour pressure of homologues of benzene. New method of determining vapour pressure.** B. B. KUDRJAFTZEV (J. Gen. Chem. Russ., 1934, 4, 563—566).—The v.p. of PhMe, *m*-xylene, and cumene are determined by an ebullioscopic method at const. pressure (1—760 mm.). A manostat is described.

R. T.

**Phase equilibria in hydrocarbon systems. V. Pressure-volume-temperature relations and thermal properties of propane.** B. H. SAGE, J. G. SCHAAFSMA, and W. N. LACEY (Ind. Eng. Chem., 1934, 26, 1218—1224).—Measurements have been made at 21—104° and from atm. pressure to 3000 lb. per sq. in. in a steel vessel the vol. of which could be varied by pumping in Hg. Vals. of sp. vol., fugacity, heat content, and entropy are tabulated at various temp. and pressures. The crit. data are 643.3 lb. per sq. in., 100.1°, and 0.06896 cu. ft. per lb.

A. G.

**Vapour pressure of anabasine and nicotine.** S. V. GORBATSHEV (J. Appl. Chem. Russ., 1934, 7, 388—391).—The v.p. *P* of anabasine is given by  $\log P = \log T - 2586.6/T + 1.9143$ , and of nicotine by  $\log P = \log T - 2408.4/T + 1.9135$ .

R. T.

**Vapour pressure of calcium between 500° and 625°.** E. RUDBERG (Physical Rev., 1934, [ii], 46, 763—767).—Using the method of mol. effusion, v.-p. data were obtained as a function of temp. for solid Ca. The calc. chemical const. is  $4.53 \times 10^4$  g.-cal. per mol.

N. M. B.

**Physical constants of methyl ethyl ketone and an investigation of its additive compound with sodium iodide dihydrate.** W. A. FELSING, L. SHOFNER, and N. B. GARLOCK (J. Amer. Chem. Soc., 1934, 56, 2252—2254).—The following data are recorded: v.p. (-30° to 80°)  $\log_{10} p$  (mm.) =  $-2644.996/T - 313.0342 \times 10^{-2} \log_{10} T - 403.78573 \times 10^{-5} T + 19.778594$ ; b.p. 79.56°; *d* (-30° to 85°)  $1.0717 - 103.125 \times 10^{-5} T$ ; *n*<sub>D</sub> (15—35°)  $1.37799 - 0.000483(t - 20)$ . The heat and mol. entropy of vaporisation have been calc.

E. S. H.

**Joule-Thomson effect in argon.** J. R. ROEBUCK and H. OSTERBERG (Physical Rev., 1934, [ii], 46, 785—790).—Investigations previously reported for He (cf. A., 1934, 481) are extended to Ar. Data for the isenthalpic curves are tabulated and plotted. Vals. of the Joule-Thomson coeff. for the pressure range 1—200 atm. and temp. -150° to 300° are calc., and plotted as a function of temp. and pressure. Results resemble those for air and N<sub>2</sub>.

N. M. B.

**Properties of real gases according to the thermodynamic equation of state. II. Joule-Thomson effect for helium.** V. JACYNA (Z. Physik, 1934, 92, 204—211; cf. A., 1934, 1300).—*c<sub>p</sub>* data are used to determine the Joule effect and change in internal isothermal energy.

A. B. D. C.

**Viscosity.** J. M. BURGERS (Chem. Weekblad, 1934, 31, 582—584).—Viscosity is discussed in relation to plasticity, elasticity, and the behaviour of systems containing elastic and plastic components. Reference is made to the mechanism of laminar flow and the relation between temp. and viscosity, especially in the light of Andrade's work.

H. F. G.

**Viscosity and density of fused yellow phosphorus over the range 45—90°.** N. D. LITVINOV and I. E. FURMER (J. Appl. Chem. Russ., 1934, 7, 321—327).—For yellow P fused under H<sub>2</sub>O  $\eta = 0.03314 - 0.965 \times 10^{-3} T + 0.1279 \times 10^{-4} T^2 - 0.576 \times 10^{-7} T^3$ , and  $d = 1.782 - 0.0009 T$ , where *T* is temp.

R. T.

**Determination of viscosity of water vapour.** W. SCHILLER (Forsch. Ingenieurw., 1934, A, 5, 71—74; Chem. Zentr., 1934, ii, 393).—Measurements are recorded at 100—300° and 1—30 atm.

H. J. E.

**Connexion between rotatory and translatory viscosity.** J. L. SNOEK (Physikal. Z., 1934, 35, 911—914).—The ratio, *K*, of the viscosity of the solution to that of the solvent for solutions of dipole substances (PhNO<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, C<sub>5</sub>H<sub>11</sub>·NO<sub>2</sub>, C<sub>5</sub>H<sub>11</sub>·OAc, 1-C<sub>10</sub>H<sub>7</sub>Br, C<sub>5</sub>H<sub>5</sub>N) in non-polar solvents (CCl<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>) was determined. *K*-1 in C<sub>6</sub>H<sub>6</sub> is > in CCl<sub>4</sub>, due to the solvation of the solute by C<sub>6</sub>H<sub>6</sub>. Experiments with non-polar solutes which would be expected to have the same val. of *K*-1 in the two solvents give no such definite result.

A. J. M.

**Changes in the viscosity of liquids with temperature, pressure, and composition.**—See B., 1934, 992.

**Purity of zinc for which thermal diffusivity was recently reported.** R. H. FRAZIER (Physical Rev., 1933, [ii], 43, 762; cf. A., 1933, 217).

L. S. T.

**Solidification diagram for sodium-cæsium alloys.** E. RINCK (Compt. rend., 1934, 199, 1217—1219; cf. A., 1933, 771).—The equilibrium diagram has a eutectic at -30° (75% Cs) and a transition temp. at -8°; the compound Na<sub>2</sub>Cs is formed. K, Rb, and Cs dissolved in Na at its m.p. are present to the extent of 18, 22, and 64%, respectively, as diat. mols.

H. J. E.

**Phase diagram of the system copper-gallium.** F. WEIBKE (Z. anorg. Chem., 1934, 220, 293—311).—A close similarity is shown to exist between Cu-Al and Cu-Ga alloys. The compounds Cu<sub>2</sub>Ga and Cu<sub>3</sub>Ga<sub>4</sub> are formed.

M. S. B.

**Phase diagram of the system copper-indium.** F. WEIBKE and H. EGGERS (Z. anorg. Chem., 1934, 220, 273—292).—71 different alloys of Cu and In have been prepared and analysed by thermal, microscopical, and X-ray methods. The results are



combined in a phase diagram. Mixed crystals and solid solutions are formed and possible compounds are  $\text{Cu}_4\text{In}$  and  $\text{Cu}_2\text{In}$ . M. S. B.

**System copper-lead.** W. CLAUS (Metallwirts., 1934, 13, 226—227; Chem. Zentr., 1934, ii, 319).—Phase relations are discussed. H. J. E.

**System praseodymium-gold.** A. ROSSI (Gazzetta, 1934, 64, 748—757).—The f.-p. diagram shows the formation with marked heat evolution of 4 compounds between Au and Pr (99.5%, m.p. 950°), viz.,  $\text{AuPr}_2$  (transition point 710°),  $\text{AuPr}$  (m.p. 1350°),  $\text{Au}_2\text{Pr}$  (m.p. 1210°), and  $\text{Au}_4\text{Pr}$  (m.p. 1200°). The mutual solubility in the solid phase is very small. Continued heating at 600° of the alloys rich in Pr gives rise to a new cubic face-centred phase which is supposed to be a solid solution of  $\beta$ -Pr in small amounts of Au or in the impurities present (Si and C). The sp. heat of Pr in the range 20—100° is  $0.0486 \pm 0.0007$  (at. heat=6.85). O. J. W.

**Intermetallic compounds formed in mercury. V. Compounds in the Zn-Mn, Zn-Co, Zn-Ni, Al-Fe, Sn-Mn, and Sn-Co systems.** A. S. RUSSELL, T. R. KENNEDY, and R. P. LAWRENCE (J.C.S., 1934, 1750—1754).—Metallic systems which form binary compounds in Hg without inclusion of Hg itself have been investigated. These have been analysed chemically without removal from Hg (cf. A., 1932, 456). The empirical formulæ are in satisfactory agreement with those determined for the same systems by thermal and X-ray methods. The following compounds have been detected:  $\text{Zn}_7\text{Mn}$ ,  $\text{Zn}_4\text{Mn}$ ,  $\text{Zn}_3\text{Mn}$ ,  $\text{Zn}_{4.2}\text{Co}$ ,  $\text{Zn}_3\text{Co}$ ,  $\text{ZnCo}_4$ ,  $\text{Zn}_{4.2}\text{Ni}$ ,  $\text{Zn}_3\text{Ni}$ ,  $\text{ZnNi}$ ,  $\text{AlFe}$ ,  $\text{Al}_4\text{Fe}_9$ ,  $\text{AlFe}_3$ ,  $\text{Sn}_3\text{Mn}$ ,  $\text{Sn}_2\text{Mn}$ ,  $\text{SnMn}$ ,  $\text{SnMn}_2$ ,  $\text{Sn}_2\text{Co}$ , and  $\text{SnCo}_2$ . M. S. B.

**A manganese-silicon solution of A2 type.** F. LAVES (Z. Krist., 1934, 89, 189—191).—Confirming previous work,  $\text{Mn}_3\text{Si}$  has been found by X-rays to have the A2 structure (cubic space-centred lattice); it is regarded as a mixed crystal, not as a compound. B. W. R.

**Transformation processes in  $\beta$ -aluminium bronze.** G. WASSERMANN (Metallwirts., 1934, 13, 133—137; Chem. Zentr., 1934, i, 3914).—The  $\beta$  phase is stable above 570° (cubic body-centred structure). It passes on slow cooling into the stable  $\delta + \alpha$  phase. Rapid cooling yields the  $\beta'$  phase, which is stable at < 300° but at > 300° forms the  $\beta_1$  phase, which passes at higher temp. into  $\delta + \alpha$ . H. J. E.

**Further X-ray studies in the diffusion of the nickel-copper system.** C. MATANO (Mem. Coll. Sci. Kyoto, 1933, A, 16, 249—259).—The interdiffusion of Ni and Cu was investigated by the X-ray method with (a) a thin layer of Cu on Ni, (b) a thin layer of Ni on Cu, and (c) alternate layers of Ni and Cu, heated, in each case, at 500°, 650°, and 900°. The coeff. of diffusion is not const. as demanded by Fick's law, but varies with concn. It is given by  $D = Ae^{-\beta/T}$ , where  $A$  is a const. independent of  $T$ , but varying with concn., and  $\beta$  is a const. which differs for the two metals. A. J. M.

**Electrical conductivity and equilibrium diagram of binary alloys. XV. System lithium-lead.** G. GRUBE and H. KLAIBER. XVI. System

**lithium-tin.** G. GRUBE and E. MEYER (Z. Elektrochem., 1934, 40, 745—754, 771—777; cf. A., 1934, 1065).—XV. The compounds  $\text{LiPb}$  (m.p. 482°),  $\text{Li}_5\text{Pb}_2$ ,  $\text{Li}_3\text{Pb}$ ,  $\text{Li}_7\text{Pb}_2$  (m.p. 726°), and  $\text{Li}_4\text{Pb}$  have been recognised.

XVI. The existence of the compounds  $\text{LiSn}_2$ ,  $\text{LiSn}$  (m.p. 485°),  $\text{Li}_2\text{Sn}$ ,  $\text{Li}_3\text{Sn}_2$ ,  $\text{Li}_7\text{Sn}_2$  (m.p. 783°), and  $\text{Li}_4\text{Sn}$  (m.p. 765°) has been established. Li does not enter appreciably into solid solution in pure Sn.

E. S. H.

**System iron-nickel-molybdenum.** W. KÖSTER (Arch. Eisenhüttenw., 1934—1935, 8, 169—171).—The system has been investigated by dilatometric, magnetometric, hardness, and micrographic methods from the Fe corner to the line joining  $\text{FeMo}_2$  and  $\text{MoNi}$ , which form a continuous series of solid solutions ( $\delta$ ). The eutectic equilibria of the three component binary systems merge at 1350° into a 4-phase equilibrium in the ternary system: liquid +  $\alpha = \gamma + \delta$ , from which the 3-phase field  $\alpha + \gamma + \delta$  extends to room temp. The boundaries of the various fields in the solid state have been determined by observations on the occurrence of pptn.-hardening on tempering. The magnetic transformation ( $M$ ) of  $\alpha$ -alloys with 4% Ni occurs at 760—720° according to the Mo content, that of the irreversible Fe-Ni alloys falls with increasing Mo, and that of Ni-Mo alloys reaches room temp. at 9% Mo.  $M$  points for numerous other alloys have been determined in the heterogeneous and homogeneous states; they are generally lower in the latter than in the former. A. R. P.

**Influence of nickel on solubility and separation processes in the system silver-copper.** H. PRISTER and P. WIEST (Metallwirts., 1934, 13, 317—320; Chem. Zentr., 1934, ii, 503).—The solubility of Ag in Cu is reduced somewhat by 1% Ni. The influence on the separation processes has been studied by X-rays and by changes in the hardness. H. J. E.

**Carbon solubility of iron-chromium-silicon alloys.** O. LUCAS and H. WENTRUPP (Z. anorg. Chem., 1934, 220, 329—333).—Mixtures of Fe, Cr, and Si have been fused together under C at different temp. and the resulting alloys analysed. They contained approx. 40—80% Cr, 0—40% Si, 1—10% C. For the same alloy the C content falls by about 0.3% per 100° rise of temp. It increases with Cr content, but is strongly diminished by Si. M. S. B.

**Mechanism of eutectic crystallisation.** A. A. BOTSCHVAR (Z. anorg. Chem., 1934, 220, 334—336).—The progress of crystallisation at the eutectic has been followed microscopically using two differently coloured substances, azobenzene and piperonal (I). After supercooling, inoculation takes place only if both kinds of crystals are present. (I), however, actually begins to crystallise first. The character of the eutectic mixture varies with the degree of supercooling. M. S. B.

**Heterogeneity of a solid solution and its mechanical and chemical properties.** P. CHEVENARD (Compt. rend., 1934, 199, 861—863).—The mechanical properties and resistance to corrosion of samples of the austenitic Fe-Ni-Cr-C alloy, quenched



from 1200° in H<sub>2</sub>O and subsequently annealed, show analogous variation with the period of annealing.

J. W. S.

**Intermetallic solid solutions.** E. R. JETTE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Pub. 560, 1934, 16 pp.).—A discussion of the parallel between Raoult's law for solutions and the Vegard additive law for solid solutions.

CH. ABS. (e)

**Diffusion of elements in the solid state.** B. N. SEN (Compt. rend., 1934, 199, 1189—1190).—Diffusion phenomena (e.g., for Cu-Pt or Fe-C) are correlated with data for the min. distance of approach of the atoms.

H. J. E.

**Theory of supercooled solid solutions.** S. KONOBEJEVSKI (Z. physikal. Chem., 1934, 171, 25—35).—From consideration of the variation of solubility with particle size it is deduced that if in the separation of a second solid phase from a supersaturated solid solution a large no. of small nuclei are formed, the system will attain a comparatively stable state when supersaturation is still present. The primary process in separation is probably the concn. distribution of the components in the lattice of the solid solution, and by applying the theory of fluctuations to determine this distribution it becomes possible to calculate the conditions under which separation may occur, the results agreeing with experimental data. In the formation within a solid phase of a new cryst. species, the latter assumes such orientations as result in its surface energy being a min.; the formation of Widmanstätten structures is accounted for in this way.

R. C.

**Viscosity of mixtures of liquids at high pressures.** R. B. DOW (Physical Rev., 1933, [ii], 43, 502).—The effect of pressures up to 12,000 kg. per sq. cm. on the  $\eta$  of six mixtures has been investigated over the whole range of composition at 30° and at 75°. The isobaric  $\eta$ -composition graphs are linear for  $n$ -C<sub>6</sub>H<sub>14</sub>- $n$ -C<sub>10</sub>H<sub>22</sub> and  $n$ -C<sub>6</sub>H<sub>14</sub>-CS<sub>2</sub>, whilst those for  $n$ -C<sub>6</sub>H<sub>14</sub>-PhCl,  $n$ -C<sub>6</sub>H<sub>14</sub>-Et<sub>2</sub>O, and eugenol-CS<sub>2</sub> are complex; irregularities appear in certain regions of composition. The  $n$ -C<sub>5</sub>H<sub>12</sub>-C<sub>6</sub>H<sub>6</sub> isobaric curves show unusual sags which are functions of temp. Interlocking between mols. of different sizes and shapes is probably the cause of the large increase in  $\eta$  with an increase in pressure.

L. S. T.

**Viscosity of the binary systems Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-B<sub>2</sub>O<sub>3</sub> and NaBO<sub>2</sub>-NaPO<sub>3</sub> in the fused state.** M. P. VOLAROVICH and D. M. TOLSTOI (J. Soc. Glass Tech., 1934, 18, 209—221r).—The system Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-B<sub>2</sub>O<sub>3</sub> has been previously described (A., 1931, 676). For NaPO<sub>3</sub>  $\eta$  can be measured down to 450° and for NaBO<sub>2</sub> down to 844° only, but, in spite of supercooling,  $\eta$  remains comparatively low for both salts (cf. following abstract). The  $\eta$  isotherm at 650° for the binary system has a point of inflexion corresponding with the max. of the m.-p. curve at a composition which suggests the presence of an equimol. compound. The mixture containing 60% NaBO<sub>2</sub> has the anomalous  $\eta$  common to colloidal solutions and suspensions, the apparent  $\eta$  being a function of the velocity gradient and decreasing with increase of velocity. A two-phase system is apparently formed, owing to the

separation of cryst. particles. On coming to rest the mixture becomes plastic.  $\eta$  has been determined for K<sub>2</sub>SiO<sub>3</sub> at 875° and 906°.

M. S. B.

**Viscosity of the binary system Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-NaH<sub>2</sub>PO<sub>4</sub> in the fused state.** M. P. VOLAROVICH (J. Soc. Glass Tech., 1934, 18, 201—208r).— $\eta$  has been determined by the rotating-cylinder method in the temp. range 527—920°. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> alone readily supercools and the results confirm previous observations on the rapid rise in  $\eta$  for supercooled liquids as the temp. falls. At 590° (151° below the m.p.)  $\eta$  for Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> is 1000 times the val. at 741°. The  $\eta$ -composition isotherms for the binary system give no indication of the formation of complex compounds.

M. S. B.

**Refractivity of liquid mixtures.** G. NARASIMHAH (Proc. Indian Acad. Sci., 1934, A, 1, 34—38).—Mathematical. The Raman-Krishnan theory is extended to binary liquid mixtures. The formula obtained is verified for COMe<sub>2</sub>-H<sub>2</sub>O and MeOH-H<sub>2</sub>O mixtures.

N. M. B.

**Molecular polarisation and association.** K. L. WOLF and W. HEROLD (Z. physikal. Chem., 1934, B, 27, 58—70).—The form of the polarisation-composition curves for solutions of aliphatic alcohols in non-polar difficultly polarisable solvents may be accounted for by supposing the solutions to contain some double and triple alcohol mols., with dipole moments respectively < and > that of the single mol. The double mols. will have all forms between the two extremes in which the arrangement of the constituent mols. is parallel and anti-parallel. With increasing chain length and branching near the OH groups association occurs to a diminishing extent. In polarisable solvents the energy relations involved in association are considerably influenced by the polarisability of the solvent.

R. C.

**Thermodynamics of binary liquid mixtures: formic acid and water.** A. N. CAMPBELL and A. J. R. CAMPBELL (Trans. Faraday Soc., 1934, 30, 1109—1114).—The heat of mixing ( $H_m$ ) and of evaporation ( $H_e$ ), the v.p. and composition of the vapour of mixtures of H<sub>2</sub>O and HCO<sub>2</sub>H have been determined at 30° and 50°. The const.-boiling mixtures contain 63.5 and 66.0% HCO<sub>2</sub>H at 30° and 50°, respectively.  $H_e$  calc. from  $H_m$  and  $H_e$  for the pure components agrees approx. with the observed vals. The partial pressures of H<sub>2</sub>O and HCO<sub>2</sub>H at 50° have been calc. from the vals. at 30° by means of the Clausius-Clapeyron equation, and agree approx. with observed vals. for H<sub>2</sub>O, but for HCO<sub>2</sub>H large deviations occur owing to association in the vapour.

R. S. B.

**Measurement of vapour pressure of solutions by the dew-point method.** B. B. KUDRJAFTSEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 601—602).—Data are recorded for aq. H<sub>2</sub>SO<sub>4</sub>, the method depending on condensation of the vapour on a metallic junction cooled by the Peltier effect.

H. J. E.

**Thermal dissociation and vapour pressure of boric acid and its volatility in water vapour.** A. THIEL and H. SIEBENECK (Z. anorg. Chem., 1934, 220, 236—246).—The dissociation pressure of H<sub>3</sub>BO<sub>3</sub>



at 100° is 113±1 mm. and of H<sub>2</sub>O 4—5 mm. Pure H<sub>2</sub>BO<sub>3</sub> can therefore be prepared from H<sub>3</sub>BO<sub>3</sub> by drying at 100—111° in a current of gas in which the partial pressure of H<sub>2</sub>O vapour is between 5 and 113 mm. If it is < 4 mm. pure H<sub>2</sub>B<sub>2</sub>O<sub>7</sub> may be obtained. The volatility of H<sub>3</sub>BO<sub>3</sub> in H<sub>2</sub>O vapour depends on the partial pressure of H<sub>2</sub>O vapour ( $p_W$ ) in the transporting gas, since  $p_B$  (v.p. of H<sub>3</sub>BO<sub>3</sub> at 100°) =  $2.5 \times 10^{-6} \cdot p_W$ . For H<sub>2</sub>BO<sub>2</sub> at 105°  $p_B = 2.3 \times 10^{-3} \cdot p_W$ . The volatility of undecomposed H<sub>3</sub>BO<sub>3</sub> in boiling H<sub>2</sub>O increases with distillation velocity. The dependence of the volatility of H<sub>3</sub>BO<sub>3</sub> on the formation of complexes with H<sub>2</sub>O is discussed.

M. S. B.

**Droplet formation in vapours.** M. VOLMER and H. FLOOD (Z. physikal. Chem., 1934, 170, 273—285).—The relation between the crit. supersaturation,  $S$ , of H<sub>2</sub>O vapour and the temp. of cooling by adiabatic expansion agrees with Volmer and Farkas' theory of nucleus formation (A., 1926, 676; 1927, 524). For seven org. liquids the vals. of  $S$  agree with the theory, except for MeOH.

R. C.

**Formation of droplets in supersaturated mixtures of ethyl alcohol and water vapour.** H. FLOOD (Z. physikal. Chem., 1934, 170, 286—294; cf. preceding abstract).—Measurements of the min. adiabatic expansion required to cause formation of droplets in absence of air ions lead to a val. of the crit. saturation represented by  $S' = (p/p_0)^N (p'/p_0')^{N'}$ , where  $N$  and  $N'$  are mol. fractions in the nuclei,  $p$  and  $p'$  supersaturation pressures, and  $p_0$  and  $p_0'$  partial v.p. of EtOH and H<sub>2</sub>O over liquid of the composition of the nuclei. The vals. so obtained are throughout <, but run parallel with, the vals. obtained from the Volmer-Farkas equation  $\log S' = k(\gamma/T)^{2/3} V'$ , where  $\gamma$  is the interfacial tension between droplet and vapour and  $V'$  the mol. vol. of the liquid of the droplet.

R. C.

**Anomalous diffusion.** D. KRÜGER and H. GRUNSKY (Z. physikal. Chem., 1934, 170, 161—171; cf. A., 1930, 1358).—The possible reasons why the diffusion coeff.,  $D$ , determined by Oeholm's method, or methods fundamentally similar, varies in certain cases with the position in the diffusing system are critically reviewed. Solvation may cause an abnormally high rate of transport in those parts of the system which are remote from the stratum in which the diffusion started. In general, it may be anticipated that the presence together of several diffusible substances will cause deviations from Fick's law. The reason why the mol. wts. of cellulose derivatives cannot be deduced from data for diffusion in org. solvents is that such data do not permit the calculation of  $D$  (cf. A., 1934, 357).

R. C.

**Diffusion of heavy into light water.** W. J. C. ORR and D. W. THOMSON (Nature, 1934, 134, 776).—The preliminary val. obtained for the diffusion coeff. of H<sub>2</sub>O (0.5—3.0 mol.-%) in aq. solutions is approx.  $9 \times 10^{-4}$  cm.<sup>2</sup> per sec. at 15°. This unexpectedly high val. indicates than an at. interchange is involved.

L. S. T.

**Diffusion of gases through metals.** C. J. SMITHELLS and C. E. RANSLEY (Nature, 1934, 134, 814).—The rate of diffusion of H<sub>2</sub> through Cu, Ni, Fe,

and Mo, and of N<sub>2</sub> through Mo, has been measured. The results can be satisfactorily explained, when the influence of adsorption on diffusion is taken into account, by  $D = K[abP/(1+aP)]P^2$ , where  $abP/(1+aP)$  is the Langmuir isotherm representing the fraction of the surface covered by adsorbed mols. L. S. T.

**Solubility of hydrogen in liquid ammonia at 25°, 50°, 75°, and 100° and at pressures to 1000 atmospheres.** R. WIEBE and T. H. TREMEARNE (J. Amer. Chem. Soc., 1934, 56, 2347—2360).—The data recorded show that the solubility increases with rising temp. and increasing pressure. E. S. H.

**Solubility of sulphur dioxide at low partial pressures. Ionisation constant and heat of ionisation of sulphurous acid.** H. F. JOHNSTONE and P. W. LEPPLA (J. Amer. Chem. Soc., 1934, 56, 2233—2238).—The solubility of SO<sub>2</sub> in H<sub>2</sub>O has been measured between 0.2 and 10.3 mm. at 25°, 35°, and 50°. The ionisation const. (0.0130 at 25°) has been calc. from published conductance data. The free energy and heats of solution and ionisation (in g.-cal.) are: (1) for SO<sub>2</sub>(gas)  $\rightleftharpoons$  SO<sub>2</sub>(aq.)  $\Delta H = -6260$ ,  $\Delta F_{298} = -123$ , (2) for H<sub>2</sub>SO<sub>3</sub>  $\rightleftharpoons$  H<sup>+</sup> + HSO<sub>3</sub>'  $\Delta H = -3860$ ,  $\Delta F_{298} = 2725$ . The total heat of absorption of SO<sub>2</sub> in infinite dilution is -10,120 g.-cal.

E. S. H.

**Solubility of krypton and xenon in liquid oxygen.** M. VON STACKELBERG [with M. HEINRICH and W. SCHULTE] (Z. physikal. Chem., 1934, 170, 262—272).—The solubility at 70—90° abs. has been measured, saturation temp. being determined by v.-p. measurements. The solubilities are < the vals. calc. from the heats of fusion of the solutes assuming ideality of the systems, indicating that heat must be absorbed on mixing the liquid components. The O partial pressures are > those indicated by Raoult's law. Heats of mixing and, for the system O-Kr, the complete crystallisation curve have been calc.

R. C.

**Heterogeneous binary systems. I. System aniline-cyclohexane.** (MLLE.) H. SCHLEGEL (J. Chim. phys., 1934, 31, 517—529).—Previous work on partly miscible liquids is reviewed. The mutual solubility of NH<sub>2</sub>Ph and cyclohexane has been determined. Cryoscopic measurements indicate that neither substance is associated when dissolved in the other.

F. L. U.

**Solubility of magnesium sulphate heptahydrate.** H. H. TING and W. L. McCABE (Ind. Eng. Chem., 1934, 26, 1207—1208).—The results obtained suggest that previous vals. are too high. A. G.

**Solubility of sodium thiocyanate in ethyl alcohol.** J. R. PARTINGTON and R. J. WINTERTON (Trans. Faraday Soc., 1934, 30, 1104—1105).—The method of Hughes and Mead (A., 1929, 1375) is criticised; the solubility at 25° is 20.66 g. NaCNS per 100 g. of EtOH (cf. A., 1927, 1020). J. G. A. G.

**Solubility of ammonium thiocyanate in water, methyl alcohol, and ethyl alcohol.** L. SHNIDMAN (J. Physical Chem., 1934, 38, 901—906; cf. A., 1933, 897).—Vals. are given for the temp. interval 13—72° (H<sub>2</sub>O) and 20—70° (MeOH and EtOH). F. L. U.



**Solubility of chlorides and nitrates of alkali metals in ammonia-water mixtures.** A. GUYER, A. BIELER, and E. SCHMID (Helv. Chim. Acta, 1934, 17, 1530—1537).—The solubility of NaCl in mixtures of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  containing 0—100% of  $\text{H}_2\text{O}$  has been determined between  $-40^\circ$  and  $25^\circ$ . A diagram showing the region of stability of  $\text{NaCl}\cdot 5\text{NH}_3$  is given. Solubility curves of KCl at  $-15^\circ$  and  $25^\circ$ , and of  $\text{NaNO}_3$  and  $\text{KNO}_3$  at  $0^\circ$ , are also given. The three last-named form no ammoniate. F. L. U.

**Solubility isotherms for complex metal thiocyanates.** IV. The system  $\text{Ca}(\text{SCN})_2\text{—Co}(\text{SCN})_2\text{—H}_2\text{O}$ . A. DE SWEEMER (Natuurwetensch. Tijds., 1934, 16, 242—244).—The stable solid phases at  $25^\circ$  are  $\text{Co}(\text{SCN})_2\cdot 3\text{H}_2\text{O}$ ,  $\text{CaCo}(\text{SCN})_4\cdot 8\text{H}_2\text{O}$ , and  $\text{Ca}(\text{SCN})_2\cdot 4\text{H}_2\text{O}$ . D. R. D.

**Effect of one salt on the solubility of another.** VI. Solutions of cobaltammines in aqueous lanthanum thiocyanates. L. O'NEILL and J. R. PARTINGTON (Trans. Faraday Soc., 1934, 30, 1134—1144).—The solubilities of the isothiocyanato-salts  $[\text{Co}(\text{NH}_3)_5\text{CNS}](\text{NO}_3)_2$  (I) and  $[\text{Co}(\text{NH}_3)_5\text{CNS}]_2$  (II) in solutions of  $\text{La}(\text{CNS})_3$  (III), determined at  $25^\circ$ , do not agree with the simple Debye-Hückel theory, and the modified theory which allows for finite mean ionic diameter ( $a$ ) gives only the correct trend. The theory of La Mer *et al.* gives an adequate explanation up to an ionic strength 0.1. For (I) the assumption  $a_0 = 3.72 \text{ \AA}$ . ( $a_0 = a$  in pure solvent) gives an almost const. val. of  $a = 4.02 \text{ \AA}$ . (mean) for a range of concns. of (III); for (II) the constancy is not so good, the best agreement holding with  $a_0 = 5 \text{ \AA}$ . when  $a = 5.60 \text{ \AA}$ . (mean). R. S. B.

**Physical chemistry of amino-acids, peptides, and related substances.** II. Solubility of  $\alpha$ -amino-acids in water and in alcohol-water mixtures. E. J. COHN, T. L. McMEEKIN, J. T. EDSALL, and J. H. WEARE (J. Amer. Chem. Soc., 1934, 56, 2270—2282; cf. A., 1934, 595).—The solubilities of  $\alpha$ - $\text{NH}_2$ -acids in EtOH are very small and of the same order; the solubilities in  $\text{H}_2\text{O}$  are much greater, and increase as the hydrocarbon chain decreases. These properties are related to the high  $d$  in the solid state, which is characteristic of the close packing of charged mols. In dil. aq. EtOH the logarithm of the solubility of all  $\alpha$ - $\text{NH}_2$ -acids appears to diminish inversely as the dielectric const. The difference between the logarithm of the solubility in  $\text{H}_2\text{O}$  and in abs. EtOH decreases by the same amount for each  $\text{CH}_2$  group, rendering it possible to analyse the activity coeffs. in terms of electrical and non-electrical forces due to  $\text{NH}_3^+$  and  $\text{CO}_2^-$  groups.

**Solubility of cellobiose octa-acetate in binary organic liquids.** M. TANIGUCHI and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1934, 37, 682—685B).—For binary mixtures of two non-polar liquids, or of a non-polar liquid with a feebly associated polar liquid, the solubility-composition curves are approx. linear. When one (or both) is highly polar the curves may be markedly non-linear, the shape depending on the degree of association and on the tendency to complex formation. A. G.

**Dispersion relations in aqueous solutions of monocalcium aluminate.** H. KÜHL, F. THILO, and A. C. YÜ (Zement, 1934, 23, 249—256; Chem. Zentr., 1934, ii, 112).—On shaking  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  with aq.  $\text{Ca}(\text{OH})_2$  the solution became supersaturated with respect to  $\text{Al}_2\text{O}_3$ . This is attributed to colloidal dispersion. H. J. E.

**Supersaturation and crystal formation in seeded solutions.** H. H. TING and W. L. McCABE (Ing. Eng. Chem., 1934, 26, 1201—1207).—Seeded and stirred supersaturated solutions of  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  were cooled at a const. rate, and the degrees of supercooling corresponding with the first formation of new nuclei (I) and with the formation of a cloud of new crystals and a pronounced heat effect (II) were observed. (II) is  $>$  (I), but both are similarly affected by changing variables. They are diminished nearly linearly by increasing wt. of seed crystals, rise to a max. with seed crystals passing 28 mesh per in., increase with increasing rate of cooling, decrease with increasing concn., and decrease to a min. with increasing rate of stirring. A. G.

**Formation and properties of precipitates.** Theory of co-precipitation. IV—VI. I. M. KOLTHOFF (Chem. Weekblad, 1934, 31, 526—533, 550—558, 598—603; cf. A., 1934, 840).—IV—V. It is not certain that mixed crystal formation occurs in the adsorption of alkali perchlorates and permanganates by  $\text{BaSO}_4$ . The geochemical reactions described by O. Hahn and his school may be regarded as involving abnormal mixed crystal formation. The ageing of micro-cryst. ppts. is discussed; it may be due to recrystallisation, with consequent growth of the larger particles; to isolation of the internal active centres by adsorption at the surface, an effect which may be reversed by heating; or to complete change of structure as the result of transition to a more stable form. Heating a ppt. causes internal changes which in the case of amorphous and finely-divided materials may reduce the active surface and adsorptive power, whereas with cryst. materials the tendency is to the production of a more porous ppt.

VI. The hygroscopic properties of Ca oxalate are discussed; the decrease which occurs on ageing of the ppt. before filtration is due to recrystallisation and the growth of perfect crystals, which reduce the active surface. For analytical purposes the Ca solution, should be about 0.1N and have a  $p_{\text{H}}$  of 4—6, and should be treated with oxalate at room temp.; if the ppt. is digested at  $90^\circ$  for 20 hr. it contains, when air-dried, only 0.1—0.3% of  $\text{H}_2\text{O}$ . Co-pptn. of Na is  $>$  that of K or  $\text{NH}_4$ . Co-pptn. of alkalis is the greater when the  $\text{C}_2\text{O}_4^{2-}$  is in excess, but diminishes with rise of temp.; it varies exponentially with the concn. of the alkali salts. Pptn. by Willard's method, *i.e.*, in such a manner that large crystals are formed, results in greatly reduced co-pptn. Co-pptn. of one ion does not hinder that of a second. Excess of  $\text{Ca}^{++}$  favours co-pptn. of anions. From neutral solution  $\text{Ca}(\text{OH})_2$  is co-pptd., especially at  $100^\circ$ . It is shown that these results are in full accord with the author's theory of co-pptn. H. F. G.



**Mechanism of the Liesegang phenomenon.** E. C. BAUGHAN (*Nature*, 1934, 134, 778).—The migration of  $\text{Ag}^+$  ions under a fixed p.d. into gelatin gels containing  $\text{NaCl}$  (approx.  $0.01N$ ) gave sets of rings approx. equidistant along the direction of the current. The results support the theory that the phenomenon is due to the de Broglie wave-length of the diffusing mol. species. L. S. T.

**Liesegang phenomenon in silicic acid gel.** A. T. LINCOLN and J. C. HILLYER (*J. Physical Chem.*, 1934, 38, 907—917).—The formation of banded ppts. of  $\text{CuCrO}_4$ ,  $\text{HgI}_2$ ,  $\text{Hg}$ ,  $\text{PbCrO}_4$ ,  $\text{PbI}_2$ ,  $\text{PbSO}_4$ , and basic Bi dichromate in  $\text{SiO}_2$  gel has been studied by keeping the concn. of one of the reacting salts const. in the gel and in the superposed solution in alternate series of experiments, that of the other being varied. In the former case the no. of bands and the depth to which they extend increase with the concn. of salt in the solution. In general, the banding is best and deepest when the ratio of the concn. of salt in the solution to that in the gel is greatest. No bands were obtained with  $\text{PbBr}_2$ ,  $(\text{HCO}_2)_2\text{Pb}$ , Bi oxalate, citrate, or iodide. The results indicate the rate of diffusion as the controlling factor in the distribution of the ppt. F. L. U.

**Supersaturation theory of the intervals in space and time between Liesegang precipitates.** H. BAUER (*Z. physikal. Chem.*, 1934, B, 27, 145—160).—The theory previously developed (A., 1933, 898) has been reconstructed and improved. It now agrees excellently with Morse and Pierce's experimental data (A., 1904, ii, 14). R. C.

**Distribution of radioactive substances between crystalline and liquid phases. IX. Distribution of  $\text{U-X}_1$  between crystals and solution of  $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  at  $100^\circ$ .** A. E. POLESITZKI (*Trans. inst. étât radium (U.S.S.R.)*, 1933, 2, 82—86; cf. A., 1932, 1198).—The distribution follows the simple law. CH. ABS. (e)

**Adsorption. Silica gel and its applications.** A. TRAVERS (*Bull. Soc. chim.*, 1934, [v], 1, 1281—1304).—A lecture.

**Absorption and adsorption of hydrogen by nickel.** J. SMITTENBERG (*Rec. trav. chim.*, 1934, 53, 1065—1083; cf. A., 1934, 839).—The absorption ( $\alpha$ ) of  $\text{H}_2$  by Ni wire of diameter  $0.022$  mm., evacuated at  $900^\circ$ , has been measured isothermally at  $300^\circ$  and at  $600^\circ$ , at pressures ( $p$ )  $<$  approx.  $1.5 \times 10^{-2}$  cm., and isobarically from  $20^\circ$  to  $600^\circ$  at  $10^{-2}$  cm. For the isotherms  $\alpha \propto p$  and at const.  $p$  increases with rise of temp. in agreement with the results of Sieverts (cf. A., 1911, ii, 895). Equilibrium is established within 3 min. The heat of absorption is calc. from the isobar to be  $2.62$  kg.-cal. At  $90^\circ$  and  $193^\circ$  abs. a small adsorption occurs, the val. of which depends on the previous heat-treatment of the Ni. The amount of  $\text{H}_2$  adsorbed at successively smaller vals. of  $p$  is  $>$  that adsorbed at the same pressure at successively greater vals. of  $p$  (hysteresis), and the same result is obtained with A. The max. adsorption of  $\text{H}_2$  corresponds with only 4% of a monat. surface layer. It is inferred that the surface of the Ni is contaminated with impurities. R. S. B.

**Adsorption of light and heavy hydrogen on nickel.** R. KLAR (*Naturwiss.*, 1934, 22, 822; cf. Pace and Taylor, A., 1934, 1181).—There are considerable differences in the variation of the adsorption velocity ( $I$ ) of  $\text{H}_2^+$  and  $\text{H}_2^-$  on Ni powder with temp. between  $0^\circ$  and  $100^\circ$ . There is equality in ( $I$ ) only over a narrow temp. range. A. J. M.

**Adsorption of hydrogen and of carbon monoxide on a surface of zinc and molybdenum oxides.** H. S. TAYLOR and G. OGDEN (*Trans. Faraday Soc.*, 1934, 30, 1178—1190).—Adsorption isotherms and velocities have been determined for the low-temp. van der Waals and high-temp. activated adsorption of  $\text{H}_2$  and  $\text{CO}$  on a  $\text{ZnO-Mo}_2\text{O}_5$  catalyst prepared from  $\text{Zn NH}_4$  paramolybdate. The heats of activation and adsorption have been determined. The adsorption of  $\text{H}_2$  is  $<$  that of  $\text{CO}$  at low temp., but the reverse is true in the region of activated adsorption. The surface is stable, being only slightly affected by heat-treatment with  $\text{CO}$ . The addition of  $\text{Mo}_2\text{O}_5$  to  $\text{ZnO}$  lowers the catalytic efficiency because the amount of  $\text{H}_2$  adsorbed at high temp. is considerably reduced and the activation energy is increased. R. S. B.

**Chemistry of solid surfaces. II. Rate of adsorption of hydrogen and deuterium on chromic oxide.** H. W. KOHLSCHÜTTER (*Z. physikal. Chem.*, 1934, 170, 300—308; cf. A., 1934, 1168, 1181).—H and  $\text{H}^2$  are adsorbed at  $184^\circ/1$  atm. by hydrated  $\text{Cr}_2\text{O}_3$  acting as a hydrogenation catalyst at equal rates, and this is still the case if the adsorbent has previously taken up larger amounts of H or  $\text{H}^2$ . The  $\text{H}^2$  reversibly displaces H in the  $\text{H}_2\text{O}$  contained in the adsorbent. R. C.

**Clean-up of various gases by magnesium, calcium, and barium.** A. L. REIMANN (*Phil. Mag.*, 1934, [vii], 18, 1117—1132).—Pressure variation-time curves for the absorption or clean-up effect of dispersed Mg, Ca, and Ba on  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  in vac. vessels are given. Speed, capacity, temp. effect, mechanism, the re-liberation of gas, and the electric discharge-assisted clean-up of  $\text{CO}$  by Mg are discussed. N. M. B.

**Adsorption of alkali metals on metal surfaces. II. Dipole moment of adsorbed Cs ions; adsorption isotherm. III. Adsorption energy of the ions.** J. H. DE BOER and C. F. VEENEMANS (*Physica*, 1934, 1, 953—959, 960—965).—II. The lowering of the work function by  $\text{Cs}^+$  adsorbed on W (cf. A., 1934, 1066) has been calc. and the results are compared with Langmuir's theory (*Physical Rev.*, 1933, [ii], 44, 423). The energy of evaporation of Cs atoms, the adsorption isotherm, and the relation between the electron emission of a W filament covered by Cs and the v.p. of Cs have been deduced.

III. After the formation of a double layer on the surface of W by  $\text{Cs}^+$ , additional  $\text{Cs}^+$  will be attached more strongly on account of the electrical field formed. This increase in adsorption energy has been calc. and the expression for electron emission has been modified to conform with this increase. M. S. B.

**Chemisorption on charcoal. IV. Influence of activation on the sorption of water vapour.**



A. KING and C. G. LAWSON (Trans. Faraday Soc., 1934, 30, 1094—1103).—The increase in wt. in air of 31—85% R.H. of purified sugar C, outgassed at 1000° and activated at temp. between 17° and 900° in a stream of O<sub>2</sub>, has been determined. At low humidities the total adsorption by C activated at 385° is > that by C activated at 880°, but this relation is reversed at high humidities. Higher rates of flow of O<sub>2</sub> during activation and exposure of the C to air (I) increase the rate and amount of adsorption. The effect of (I) is attributed to chemisorption of O<sub>2</sub> and the formation of a low-temp. oxide. As the temp. of activation,  $T_a$ , is raised, the rate of adsorption rises to a max. which probably corresponds with the highest temp. at which the acidic oxide of C oxidised at 200—500° is stable. The adsorption of I, AcOH, and NH<sub>3</sub> increases with rise of  $T_a$ , but that of NH<sub>3</sub> is almost const. with  $T_a$  > 450°, showing that there is less adsorption per unit area at the higher temp. The initial rate of adsorption of AcOH and NH<sub>3</sub> is max. with  $T_a$  approx. 450°. The data are interpreted in terms of the acidic surface oxide formed at  $T_a$  200—600°, and another oxide existing at higher temp. J. G. A. G.

**Adsorption of oxygen by platinum, ferric oxide, and chromium oxide.** B. NEUMANN and E. GOEBEL (Z. Elektrochem., 1934, 40, 754—764).—Adsorption is normal with Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> so long as chemical reaction does not occur; with Cr<sub>2</sub>O<sub>3</sub> reaction begins at 65°. With Pt, dissolution of at. O occurs in addition to adsorption. Measurements between 20° and 400° at different pressures are in fair agreement with Langmuir's equation. On the basis of these results and those for the adsorption of SO<sub>2</sub> (cf. following abstract) a mechanism for the catalytic combination of SO<sub>2</sub> and O<sub>2</sub> is proposed. E. S. H.

**Adsorption of sulphurous acid by vanadium pentoxide.** B. NEUMANN and E. GOEBEL (Z. Elektrochem., 1934, 40, 764—765).—The form of the adsorption isotherms indicates that the reaction  $V_2O_5 + SO_2 = V_2O_4 + SO_3$  occurs. E. S. H.

**Activated adsorption of hydrocarbons.** J. TURKEVICH and H. S. TAYLOR (J. Amer. Chem. Soc., 1934, 56, 2254—2259).—The changes which occur in the adsorption of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> on MnO—Cr<sub>2</sub>O<sub>3</sub> and of C<sub>2</sub>H<sub>4</sub> on active Cu have been examined at —78.5° to 444°. The results are interpreted in terms of activated adsorption and C<sub>2</sub>H<sub>4</sub> decomp. The adsorption measurements define the conditions for exchange reactions between H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>. E. S. H.

**Adsorption from solution. II. Adsorption of styphnic acid by activated sugar charcoal.** L. T'SAI and H. YÜ (J. Chinese Chem. Soc., 1934, 2, 193—197).—The adsorption isotherm consists of five sections, each of which satisfies the Langmuir equation. A. G.

**Adsorption by precipitated barium sulphate.** E. G. R. ARDAGH, R. E. RICHARDSON, L. A. RICHARDSON, and C. M. HUMBER (Chem. and Ind., 1934, 1035—1041).—The influence of temp., acidity, and presence of NH<sub>4</sub>Cl on the shape of pptd. BaSO<sub>4</sub> crystals has been investigated. Conditions for the production of perfect, orthorhombic crystals have been worked out;

such crystals remain colourless when formed in presence of a dye, whilst irregular crystals are always stained uniformly throughout. Adsorption probably occurs during brief periods in which a change in the manner of crystal growth occurs. The error in the gravimetric determination of Ba<sup>++</sup> and SO<sub>4</sub><sup>--</sup> is probably reduced under conditions such that the bulk of the ppt. consists of orthorhombic crystals. E. S. H.

**Adsorbing power of manganese for ionium.** A. N. PULKOV (Trans. inst. métrol. stand. U.R.S.S., 1934, No. 6, 13—20).—MnO<sub>2</sub> is pptd. from the solution by treating with H<sub>2</sub>SO<sub>4</sub> (*d* 1.84) and then with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The MnO<sub>2</sub> carries down with it the Io and its isotope U-X<sub>1</sub>. MnO<sub>2</sub> is superior to Ce(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> as an adsorbent. CH. ABS. (e)

**Sorption of vapours by ferric oxide gel. I. Aliphatic alcohols.** A. G. FOSTER (Proc. Roy. Soc., 1934, A, 147, 128—140).—Isothermals of MeOH, EtOH, Pr<sup>n</sup>OH, Pr<sup>i</sup>OH, and Bu<sup>n</sup>OH on Fe<sub>2</sub>O<sub>3</sub> gel have been determined at 25°. All show a large hysteresis loop extending over nearly half the entire range. The relative pressures at which hysteresis occurs decrease from MeOH to BuOH, but the capillary radius remains const. at about 22 Å. The amounts of the different alcohols adsorbed at corresponding pressures below about 0.01 of the saturation val. or their mol. wts. The evidence suggests that the surface is covered by an adsorbed unimol. layer. With BuOH this process is followed immediately by capillary condensation, but with the lower alcohols there is a tendency to form a second layer. L. L. B.

**Adsorption of water by silica gel and an examination of Patrick's adsorption formula.** R. C. RAY and P. B. GANGULY (Trans. Faraday Soc., 1934, 30, 997—1007).—The adsorption isotherms for H<sub>2</sub>O vapour on SiO<sub>2</sub> gel in an air-free system at 32° and 40° conform to the Freundlich equation except at pressures approaching saturation. The utility of Patrick's formula is limited, since the consts. vary with factors other than the structure of the gel. The heat of wetting, *W*, decreases linearly with increasing H<sub>2</sub>O content of the gel. Since *W* is almost identical with the heat of adsorption and is zero at the saturation point, which corresponds with the composition 2H<sub>2</sub>O : SiO<sub>2</sub>, the formation of an unstable adsorption compound is inferred. J. G. A. G.

**Adsorption of gases by chromium oxide gel.** J. HOWARD and H. S. TAYLOR (J. Amer. Chem. Soc., 1934, 56, 2259—2264).—Isotherms have been obtained for van der Waals adsorption of N<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> over a wide temp. range, for H<sub>2</sub> and He at 85° and 194.5° abs., and for C<sub>2</sub>H<sub>4</sub> at 194.5° abs. on Cr<sub>2</sub>O<sub>3</sub> gel. The corresponding heats of adsorption have been calc. The rates of activated adsorption of H<sub>2</sub> (373—457° abs.) and C<sub>2</sub>H<sub>4</sub> (353° and 388° abs.) by Cr<sub>2</sub>O<sub>3</sub> gel have been measured and the activation energies calc. The decomp. of C<sub>2</sub>H<sub>4</sub> associated with activated adsorption at high temp. has been studied analytically. On surfaces similar in area, as deduced from van der Waals adsorption, there is a variable proportionality factor between velocity of activated adsorption and the activation energy term in the kinetic expression for velocity of adsorption. The rate of



activated adsorption is the rate-determining stage in the hydrogenation of ethylene; variations in this rate account for differences in the observed activities of various oxides. E. S. H.

Adsorption of methylamine on silica gel, alumina gel, and charcoal. Heats of adsorption of ammonia and the methylamines on silica gel. W. A. FELSING and C. T. ASHBY (J. Amer. Chem. Soc., 1934, 56, 2226—2229).—Adsorption isotherms have been determined at 0°, 30°, and 40°. The heats of adsorption by SiO<sub>2</sub> gel at 25° are: NH<sub>3</sub> 14.8, NH<sub>2</sub>Me 18.7, NMe<sub>3</sub> 19.0, NHMe<sub>2</sub> 20.1 kg.-cal. E. S. H.

Reaction metal hydroxide solution-cellulose fibre; comparison of X-ray results with equilibrium measurements of the metal hydroxide distribution in the system fibre-solution. W. SCHRAMMEK [with H. VELTEN, C. SCHUBERT, H. NEUMANN, and O. VIERTTEL] (Kolloid-Beih., 1934, 40, 87—157).—The adsorption of NaOH in aq. solution at different concns. by cellulose (I) has been measured under various conditions, and the X-ray diagram of the product investigated. In < 8% NaOH native (I) and (I) hydrate behave in accordance with Langmuir's adsorption isotherm; raw (I) adsorbs NaOH more strongly than does the pure material; in this region of concn. none of the forms of (I) gives a changed X-ray pattern. In > 8% NaOH, pure and raw native (I), (I) hydrate, and ramie show a change in the X-ray diagram, which is traced to the formation of Na-(I). The various equilibria and reactions involved are discussed. E. S. H.

Swelling of charcoal. III. Experiments with lower alcohols. D. H. BANGHAM, N. FAKHOURY, and A. F. MOHAMED. IV. Stoichiometric relations for the films of the alcohols. D. H. BANGHAM (Proc. Roy. Soc., 1934, A, 147, 152—175, 175—188; cf. A., 1932, 1199).—III. Adsorption-expansion measurements carried out with MeOH, EtOH, PrOH, BuOH, and pinewood charcoal, using the apparatus and technique previously described (*loc. cit.*), confirm the view that the expansion  $\propto$  the surface pressure of the adsorbed phase. The Gibbs equation holds for EtOH and MeOH, except at low pressures. The straight-chain alcohols form two types of film, "primary" and "annealed"; transition from the former to the latter occurs more rapidly at high temp. than at low. A comparison of the expansion data with those for the lowering of the surface tension of Hg by the vapours of the same alcohols reveals so much resemblance as to indicate a similarity of mechanism in the two cases. The branched-chain alcohols give rise to larger expansions than their straight-chain isomerides and have also a much slower rate of adsorption.

IV. A study of the "annealed" films of MeOH, EtOH, PrOH, and BuOH on charcoal shows that the amounts of each alcohol causing equal expansions of the charcoal are equal. Comparison of the expansion data with the data of Cassel and Salditt (A., 1931, 1120) for the films on Hg indicates that on Hg also there occurs, with rise of concn., a transition from the primary to the annealed type of film. The primary films are probably unimol., whilst the thick-

ness of the annealed films  $\approx$  about 2 C chains. Coeffs. of thermal dilatation and compressibility are calc. for the annealed films of the *n*-alcohols. L. L. B.

Influence of surface tension on the rate of rise of aqueous solutions in porous bodies. P. BERTHIER (Compt. rend., 1934, 199, 1221—1223).—Data are recorded for the wetting of filter-paper by aq. camphor, *iso*amyl alcohol, menthol, and saponin. Comparison with vals. for H<sub>2</sub>O shows that the rate is independent of the surface tension of the solution and is the same as for H<sub>2</sub>O. H. J. E.

Surface tension and tangential pressure in the capillary film in connexion with the osmotic pressure in the film theory of Pockels, Langmuir, and Adam. G. BAKKER (Z. physikal. Chem., 1934, 171, 49—69).—It is shown from purely mechanical considerations that in the surface film of a liquid there is a tangential pressure,  $p_T$ , connected with the normal pressure,  $p_N$ , surface tension,  $\gamma$ , and thickness of the film,  $\zeta$ , by  $\gamma = (p_N - p_T)\zeta$ .  $p_T < p_N$  and for low temp. is negative and may be numerically very large. For a pure liquid in equilibrium with its vapour  $p_N$  is the v.p. and  $p_T$  can be calc. from the equation of state. It is calc. that at low temp.  $\zeta \sim 2-3$ , and at a reduced temp. of 0.9  $\sim 4-5$  mol. diameters. The thermodynamic potential is the same in the surface film and in the two extended phases. In Langmuir's trough apparatus for studying insol. films on H<sub>2</sub>O the force experienced by the movable barrier is equal to the difference between the vals. of  $p_T\zeta$  for the two sides. For a gaseous film this leads to Adam and Jessop's osmotic pressure formula. R. C.

Applications of a method of capillary analysis. R. DUBRISAY (Compt. rend., 1934, 199, 1304—1305; cf. A., 1934, 728).—Data are recorded for changes in the interfacial tension between a C<sub>6</sub>H<sub>6</sub> solution of sapamine and H<sub>2</sub>O due to the solubility of MgO in H<sub>2</sub>O, to the acids formed in the photo-oxidation of alcohols, and to the solubility of glass in H<sub>2</sub>O. H. J. E.

Why does water wet glass? M. HOLDERER (Compt. rend., 1934, 199, 1046).—The wetting of glass by H<sub>2</sub>O is attributed to the affinity between O atoms combined in the glass and the O atoms of unassociated H<sub>2</sub>O mols. Similar affinity explains why Hg adheres at certain points to glass in presence of a trace of HgO. J. W. S.

Structure of monolayers of myristic acid. Erratum. N. W. H. ADDINK (J. Chem. Physics, 1934, 2, 822; cf. A., 1934, 1169). F. L. U.

Quantitative correlation of interfacial free surface energies. F. E. BARTELL and L. S. BARTELL (J. Amer. Chem. Soc., 1934, 56, 2205—2210).—Theoretical. A linear relation between the cosine of the interfacial angle and the adhesion tension of any given liquid for a series of solids has been established. Equations are developed by which the adhesion tension of a solid for any liquid can be calc. from a single measurement of adhesion tension or of contact angle for the solid and a given liquid. E. S. H.

Properties of albumin in unimolecular layers. E. GORTER [with G. M. PHILIPPI] (Chem. Weekblad,



1934, 31, 586—589).—When albumin solution (5 mg. per c.c.) is allowed to flow on to the surface of 0.1*N*-HCl, a film about 7.5 Å. thick is formed. With casein the max. spreading is obtained at the isoelectric  $p_H$  and below  $p_H$  2, and the min. at  $p_H$  3.6, whilst with pepsin the min. is at  $p_H$  6. The influence of electrolytes on the spreading shows that at the max. the  $\cdot\text{CO}\cdot\text{NH}\cdot$  groups lie on the surface, and that at the min. ionisation occurs. These views are confirmed by measurements with a long-chain tripeptide (from  $\alpha$ -amino-octioic acid), which spreads to the extent of 1.2 m.<sup>2</sup> per mg.; the area is increased in acid solution by cations, and at  $p_H$  8 by anions.

H. F. G.

**Validity of Antonov's rule.** E. G. CARTER and D. C. JONES (Trans. Faraday Soc., 1934, 30, 1027—1038).—With very carefully purified materials and with special precautions for keeping the liquid phases saturated, it is found that Antonov's rule is followed by the systems of H<sub>2</sub>O with C<sub>6</sub>H<sub>6</sub>, PhNO<sub>2</sub>, COEt<sub>2</sub>, and *o*-C<sub>6</sub>H<sub>4</sub>Me·OMe. Systems which do not conform involve either (1) org. substances which have a negative initial spreading coeff., *S*, on H<sub>2</sub>O, e.g., CH<sub>2</sub>I<sub>2</sub>, CS<sub>2</sub>, or (2) org. substances which have high initial *S* on H<sub>2</sub>O and for which the final *S* is not zero but negative, e.g., C<sub>7</sub>H<sub>15</sub>·OH, isoamyl alcohol, Bu<sup>o</sup>OH, and *m*-cresol. The non-conformity with the "rule" is attributed to an oriented adsorption film on the saturated aq. phase.

J. G. A. G.

**Streaming potentials using paraffin capillaries.** H. R. KRUYT and R. RUYSSSEN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 498—505).—The electrokinetic  $\zeta$ -potentials are calc. from the p.d. between the ends of a paraffin wax capillary through which 0—1*M*-KCl, -BaCl<sub>2</sub>, -AlCl<sub>3</sub>, and -Th(NO<sub>3</sub>)<sub>4</sub> is forced under pressure. With KCl,  $\zeta$  has a max. at 0.1*M*; BaCl<sub>2</sub> affords a sharp max. at 0.005*M* and a min. at 0.2*M*. Paraffin wax is charged positively by AlCl<sub>3</sub> and Th(NO<sub>3</sub>)<sub>4</sub> except at very low concn. The differences observed in earlier work (A., 1928, 1091) are attributed to the chemical properties of glass.

J. G. A. G.

**Electric potential and charge of dissolved and adsorbed proteins.** H. A. ABRAMSON (Cold Spring Harbor Symposium Quant. Biol., 1933, 1, 39—50).—A study of the electric potential of ovalbumin, serum-albumin, caseinogen, and insulin, and of the effects thereon of various ions and alcohols.

CH. ABS.

**Dielectric potentials of physiologically-active substances.** B. KAMIENSKI (Nature, 1934, 134, 776).—The potential (*I*) at the interface solution-air is large at low concns. compared with that for other substances. Vals. for quinine, cinchonine, cinchonidine, and morphine are given. (*I*) changes with [H<sup>+</sup>]. The *d*- and *l*-isomerides of the same substance have different vals.

L. S. T.

**Electrical potential of amorphous and crystalline amphoteric surfaces in liquids.** O. WINTERSTEINER and H. A. ABRAMSON (Physical Rev., 1933, [ii], 43, 372—373).—The electric mobility of crystals of insulin (*I*) has been compared with that of amorphous (*I*), adsorbed or in particle form.

L. S. T.

**Influence of the dielectric constant of the medium on the potential and charge of a protein surface in a liquid.** H. A. ABRAMSON and J. DANIEL (Physical Rev., 1933, [ii], 43, 773).—Correlation of the surface potential and surface charge calc. from the observed electric mobilities of microscopic quartz particles covered with a film of adsorbed protein in different concns. of EtOH, with the charge obtained by the thermodynamic method indicates that the characterisation by the two parameters  $\eta$  and  $\epsilon$  of the solvent in the Helmholtz-Debye theory is correct. The data are considered in relation to their biological importance, particularly in connexion with cell permeability.

L. S. T.

**Cataphoresis of gliadin. I. Adsorption of gliadin on quartz. II. Effect of strong electrolytes on the mobility.** I. KEMP and E. K. RIDEAL (Proc. Roy. Soc., 1934, A, 147, 1—10, 11—24).—I. The velocity of adsorption of gliadin mols. at the surface of suspended quartz particles is unimol. Preferential adsorption of gliadin occurs at the gliadin-liquid interface. The electrical work function at the quartz-liquid interface is of the order of the measured electrokinetic potential.

II. The acid and basic dissociation consts. of gliadin are calc. from mobility- $p_H$  curves and titration data. The isoelectric point is dependent on the ionic strength of the medium, and the no. of OAc' adsorbed per mol. of gliadin are computed from the shifts of the isoelectric point. The Debye-Hückel expression for cataphoretic velocity is applicable to the systems investigated over a limited range of concns. The application of a correction for ionic adsorption gives good agreement with theory for conc. solutions, but with more dil. solutions the decrease of the effective surface charge on the protein owing to the existence of a Donnan ionic equilibrium between ions inside and outside the double layer must be considered.

L. L. B.

**Electro-osmosis.** V. S. IMAI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1351—1362).—The electrokinetic potentials of liquid org. compounds have been determined by measuring the electro-osmotic velocity through sintered SiO<sub>2</sub> diaphragms, and are < the vals. obtained using a diaphragm of hard glass powder.

R. S. B.

**F.p. of aqueous solutions. VIII. Mixtures of sodium chloride with glycine and ethyl alcohol. IX. Mixtures of the reciprocal salt pair potassium nitrate-lithium chloride.** G. SCATCHARD and S. S. PRENTISS (J. Amer. Chem. Soc., 1934, 56, 2314—2319, 2320—2326; cf. A., 1934, 963).—VIII. The analytical expression of the thermodynamic functions of dil. solutions has been extended to solutions containing ions. Measurements of f.p. depressions of mixed aq. solutions of NaCl with glycine and EtOH are treated by this method and the results compared with other properties of the solutions.

IX. F.p. measurements have been made for aq. solutions of all the possible mixtures of the reciprocal salt pair KNO<sub>3</sub>-KCl. The derivation of the coeffs. for the sp. interaction of ions is extended to the coeffs. of the higher powers of the concn. The parameters necessary to determine the thermodynamic functions



of any mixture of this reciprocal salt pair agree with the extended theory of Brönsted. E. S. H.

**Apparent volume of salts in solution and their compressibilities.** A. F. SCOTT and R. W. WILSON (J. Physical Chem., 1934, 38, 951—977).—Masson's empirical equation (A., 1930, 31) connecting apparent mol. vol. of a solute with its concn. is shown to be valid for solutions under high pressures. A relationship between apparent mol. compressibility ( $B$ ) and concn. derived from this equation is employed to determine  $B$  of a solute at infinite dilution, using experimental data for alkali metal halides (cf. following abstract). The results are discussed from the point of view of contraction of the solvent caused by the solute.

F. L. U.

**Compressibility coefficients of solutions of alkali halides.** A. F. SCOTT, V. M. OBENHAUS, and R. W. WILSON (J. Physical Chem., 1934, 38, 931—940; cf. A., 1933, 556).—Compressibility coeffs. ( $B$ ) of aq. solutions of LiCl, LiBr, NaCl, NaBr, NaI, KCl, KBr, and KI have been determined at different concns. The  $B$ -concn. curves of the Li salts show discontinuities.

F. L. U.

**Viscosity and fluidity of lithium chloride in acetone solution.** G. R. HOOD and L. P. HOHLFELDER (J. Physical Chem., 1934, 38, 979—986).—Measurements have been made over the range 0.004—0.274*M* at 18° and 0.008—0.271*M* at 25°. The results are discussed from the point of view of interionic forces and of solvation.

F. L. U.

**Effect of magnetic field on Brownian movement.** J. MÉTADIER (Compt. rend., 1934, 199, 1196—1198).—With fields  $\gt 20,000$  gauss no effect on the Brownian movement was observed for emulsions of Prussian-blue, Fe(OH)<sub>3</sub>, chrome-yellow, or gamboge.

H. J. E.

**Derivation of distribution functions in problems of Brownian motion.** L. S. ORNSTEIN and W. R. VAN WIJK (Physica, 1934, 1, 966).—Corrections (cf. A., 1934, 486).

M. S. B.

**Dynamic investigations of colloidal systems.** I. Basis and method of investigation of mechanical properties of solutions of organic compounds of high mol. wt. II. Determination of the dynamic viscosity of Cellite solutions and derivation of a dispersion formula. W. PHILIPPOFF (Physikal. Z., 1934, 35, 884—900, 900—905).—I. From streaming and relaxation experiments, and the dependence of the dynamic viscosity (I) and of the deformation resistance on frequency, a complete picture of the mechanical behaviour of a system may be obtained. A method for the determination of the abs. viscosity of viscous liquids (10—1000 c.g.s.) under the influence of a high-frequency field is described. (I) of honey, gum-arabic (44% solution in H<sub>2</sub>O), glycerol (II), and aq. solutions of (II) is independent of frequency and agrees with the static viscosity. (I) of an 8% solution of Cellite in dioxan, however, decreases considerably with frequency.

II. The variation of (I) with frequency, of solutions of Cellite in dioxan is given by  $\eta = \eta_0 [1 + (\omega\tau)^{3/4}]^{-1}$ , where  $\omega$  is frequency and  $\tau$  the relaxation time. The Maxwell relationship,  $\tau = \eta_{\text{stat}}/\gamma$ , where  $\gamma$  is the modulus

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of elasticity, holds.  $\gamma$  calc. from this formula agrees with the vals. obtained by Rabinovitsch (A., 1933, 1115) by a capillary method.

A. J. M.

**Measurement of the viscosity of hydrophilic sols.** H. G. B. DE JONG (Chem. Weekblad, 1934, 31, 584—586).—Limitations of the simple Einstein expression, the influence on viscosity of solvation and desolvation, and the electroviscous effect are discussed.

H. F. G.

**Lowering the viscosity of cellulose nitrate. I. Action of strong and weak bases.** S. N. DANILOV and L. I. MIRLAS (J. Gen. Chem. Russ., 1934, 4, 817—829).—For COMe<sub>2</sub> solutions of cellulose nitrate (I)  $\eta$  is lowered to a greater degree by weak (aq. NH<sub>3</sub>, C<sub>5</sub>H<sub>5</sub>N) than by equiv. concns. of strong bases (NaOH). The action of bases consists in partial denitration, with oxidation of cellulose by NO<sub>3</sub>' with production of NO<sub>2</sub>'. At the same time, the micellar structure of unchanged (I) is loosened, owing to formation of labile complexes of (I) with weak bases. 90% of (I) becomes EtOH-sol. after treatment with 0.2% aq. NH<sub>3</sub>, the product being a heterogeneous mixture of (I) of different N contents and degrees of dispersion.

R. T.

**Theory of lyosorption phenomena.** E. LANDT (Z. physikal. Chem., 1934, 171, 119—120).—Comments are made on recent papers (cf. A., 1934, 960), and the part played by attractive forces between the particles in determining the settled vol. of a powder suspended in a liquid is emphasised.

R. C.

**Physico-chemical transformation of gum-arabic sols on heating.** A. BOUTARIC and (MILLE.) M. ROY (Compt. rend., 1934, 199, 1219—1221).—Vals. are recorded for the change in viscosity, optical  $d$ , and surface tension after varied periods of boiling. The sols should be classed as micelles (I) and not as mol. colloids. Boiling causes hydrolysis and a growth of (I).

H. J. E.

**Physico-chemical studies on gum-arabic solutions.** D. R. BRIGGS (J. Physical Chem., 1934, 38, 867—881).—The equiv. conductivity of electro-dialysed arabic acid (I) solutions shows a max. at very high dilution, whilst the Li, Na, K, and Ca salts show min. at about 0.0025 equiv. per litre. This behaviour, which bears a superficial resemblance to that of soaps, is explained by the varying mobility of the cations as the solution is diluted, since the current is carried chiefly by these, and with the strychnine salt no min. is observed. The ionisation "const." of (I) decreases with dilution from 10<sup>-3</sup> to 2 × 10<sup>-7</sup>. The titration curve shows only one buffer range. (I) does not, however, act as a monobasic acid, but as one having several acid groups of rather uniformly graded strengths.

F. L. U.

**Soya lecithin. IV. Emulsifying action for oil-water mixtures. V. Properties of lecithin soap solutions.** T. INABA, K. KITIGAWA, and M. SATO (J. Soc. Chem. Ind. Japan, 1934, 37, 595B).—With increasing concn.,  $\eta$  of lecithin (I) solution increases and drop vol. against soya-bean oil (II) falls. (II) also falls with rising temp. (I) added to Na soap solution increases surface tension, foam no., stability, and Au no.; it lowers the turbidity and clearing temp.



by 3–5°. The drop no. against kerosene passes through a max. at 0.25% (I). G. H. C.

**Variation in the capacity for [ionic] exchange of colloidal clay.** A. L. S. BAR and H. J. C. TENDELOO (Rec. trav. chim., 1934, 53, 1128–1132).—Theoretical. The theory of Verwy and Kruyt (cf. A., 1934, 143) affords a quant. explanation of the increase in the capacity for ionic exchange ( $E$ ) of colloidal clay after treatment with alkali in terms of changes in the electrical double layer; increase in  $E \propto$  increase in the concn. of the potential-determining electrolyte on the clay surface. R. S. B.

**Surface studies on ferric oxide by the emanation method.** O. HAHN and V. SENFTNER (Z. physikal. Chem., 1934, 170, 191–211).—The changes in structure and surface of  $\text{Fe}_2\text{O}_3$  gels when the temp.,  $T$ , is progressively raised have been followed. With rise in  $T$  the surface,  $S$ , gradually decreases due to shrinkage caused by loss of adsorbed  $\text{H}_2\text{O}$ , but at about 400°, corresponding with the "glow temp." of  $\text{Fe}_2\text{O}_3$ , there is a sudden rapid fall in  $S$ . There is then a slower decrease up to about 850°, when there is a further abrupt fall in  $S$  due to expulsion from the lattice of the last traces of  $\text{H}_2\text{O}$  followed by rapid recrystallisation to the pure hæmatite lattice. The amount of  $\text{H}_2\text{O}$  eliminated at this point is very small and varies with the history of the specimen; with an alcogel there is none, or very little compared with a gel aged under  $\text{H}_2\text{O}$ . Above about 1000° the increasing vigour of mol. motions causes a loosening of the lattice. The behaviour of co-pptd. mixtures of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  is similar to that of  $\text{Fe}_2\text{O}_3$  if the proportion of  $\text{Al}_2\text{O}_3$  is  $>$  the solubility in  $\text{Fe}_2\text{O}_3$ ; an excess of  $\text{Al}_2\text{O}_3$  acts as a foreign substance. Artificial admixture of  $\text{Al}_2\text{O}_3$  with  $\text{Fe}_2\text{O}_3$  markedly hinders recrystallisation of the latter.  $\text{ThO}_2$  gel behaves on heating like  $\text{Fe}_2\text{O}_3$  gel, whilst  $\text{Th}(\text{C}_2\text{O}_4)_2$  behaves quite differently. R. C.

**Lyophilic colloids. XXIII. Heats of wetting and gelation of gelatin.** L. W. J. HOLLEMAN, H. G. B. DE JONG, and R. S. T. MODDERMAN (Kolloid-Beih., 1934, 40, 211–240; cf. A., 1934, 842).—Determinations of heat changes in the system gelatin– $\text{H}_2\text{O}$  as a function of  $\text{H}_2\text{O}$  content and temp. show that two effects can be distinguished. By progressively adding  $\text{H}_2\text{O}$  to gelatin, heat is evolved independently of temp.; this is regarded as heat of hydration. At const.  $\text{H}_2\text{O}$  content ( $>$  a crit. val.) lowering of temp. causes evolution of heat over a certain temp. range. This quantity is traced to a transformation in the system and is regarded as heat of gelation. E. S. H.

**Diffusion of electrolytes in silica gel.** F. H. MACDOUGALL (J. Physical Chem., 1934, 38, 945–949).—A discussion of a paper by Patrick and Allan (A., 1934, 842), whose experiments on diffusion in  $\text{SiO}_2$  gel are shown to be in quant. agreement with Nernst's theory. F. L. U.

**Properties and structure of solutions of gum gels.** L. AMY (Ann. Chim., 1934, [xi], 2, 287–414).—The sol. gum arabic and the insol. cherry-tree gum have been examined and compared. By electro-dialysing gum arabic the mineral constituents are removed and there remains a gel which readily breaks

up into a sol. portion, arabin, and an insol. gel. Arabin is very unstable and is readily hydrolysed, especially when heated, forming a reducing solution; it is a true acid and may be called arabic acid (I). It has not, however, a definite composition, since variations in equiv. wt., rotatory power, viscosity ( $\eta$ ), conductivity ( $\Lambda$ ), etc., with variation in origin, are observed, or even exist between different samples of the same origin. E.m.f. measurements give a dissociation const. of  $2 \times 10^{-4}$  at 19°, but  $[\text{H}^+]$  in partly neutralised solutions of (I) varies much more rapidly on dilution than is accounted for by the ordinary dissociation theory. This effect is inhibited by neutral salts.  $\eta$  increases as neutralisation proceeds and is a linear function of the no. of real or apparent positive ions in the solution. Addition of excess of base or of neutral salts diminishes  $\eta$ .  $\Lambda$  in a partly neutralised solution is of the same order as in solutions of dialysable salts. It also varies with time. The diffusion of aq. Na arabate conforms to Fick's law at concn. below 1%. There is a sudden change above this concn. and a surface of separation is formed. Dehydration of (I) forms an acid gel, metagummic acid, of the same degree of acidity. Addition of alkali causes swelling, the slightest excess resulting in peptisation and re-formation of the arabate. The gel extracted from the natural gum behaves similarly. The insol. org. part of cherry-tree gum forms a gel with acid properties, cerasic acid (II), behaving towards bases in the same way as (I). It has two dissociation consts.,  $3.0 \times 10^{-4}$  and  $10^{-5}$ – $10^{-6}$ , at 25°, determined by e.m.f. measurements with and without the addition of an auxiliary salt. The second dissociation const. may be due to an impurity, since there is no simple relation between the amounts of base necessary for neutralisation of the separate stages. The gel swells as neutralisation proceeds. Addition of a neutral electrolyte produces contraction. By fine grinding, a suspension of (II), with properties very similar to those of (I), may be obtained. The resemblance is especially remarkable in the variation of  $\Lambda$  with dilution, and of  $\eta$  on the addition of an electrolyte. The colorimetric determination of  $[\text{H}^+]$  by indicators, in a suspension of (II), results in considerable differences, according as the whole suspension or the intergranular liquid is taken into account. The similarity of the behaviour of (II) and (I) may be interpreted by assuming that arabates exist in solution, to a large extent, in the form of microscopic particles of swollen gel, filling the whole vol. available when the concn. is above 1%.

M. S. B.

**Pectin. III. General theory of pectin jelly formation.** A. G. OLSEN (J. Physical Chem., 1934, 38, 919–930; cf. B., 1933, 650).—The influence of sugar concn. ( $S$ ),  $p_{\text{H}}$ , length of interval between mixing and pouring, and temp. on the strength of apple pectin jellies has been determined. As with citrus pectin, the effect of low acidity can be compensated by increasing  $S$ . Adopting Kruyt's theory of stability factors, the sugar is regarded as a dehydrating agent, and the acid as a discharging electrolyte. With low  $S$ , low temp., or short interval between mixing and pouring, an optimum  $p_{\text{H}}$  is no longer observed. The greater strength of jellies rapidly prepared at 55°, compared with that obtained by the boiling method, is not due



to hydrolysis of pectin at the higher temp., but to structural differences in the pectin network.

F. L. U.

**Colloidal behaviour of sericin. VI. Colloidal behaviour of sericin-A and -B.** H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 461—474; cf. A., 1934, 1306).—When pptd. sericins are added to acid or alkaline solutions they combine stoichiometrically with the acid or alkali. The solubility is least at  $pH$  4.5, which corresponds with the isoelectric point of natural sericin. The electric cataphoresis and the effect of salts on the cataphoretic velocity of the sericins have been studied. Sericin-A has greater protective action than sericin-B, and is more sensitive to heat, being converted gradually into sericin-B by heating. Apparent sp. gr. at 15°, colour reactions, biuret reaction, fluorescence in ultra-violet light, and swelling phenomena with changes of medium and temp. are discussed.

W. R. A.

**Physical chemistry of starch and bread making. XXII. Comparative study of retrogression of starch pastes from various native starches by means of X-ray diagrams.** J. R. KATZ [with T. B. VAN ITALLIE]. **XXIII. Effect of alcohol concentration on X-ray diagram retrogression of starch pastes containing alcohol.** (Preparation of starch for X-ray examination by dehydration with alcohol.) J. R. KATZ [with T. B. VAN ITALLIE and A. WEIDINGER] (Z. physikal. Chem., 1934, 170, 421—429, 430—439; cf. A., 1930, 1126; 1934, 1069).—XXII. Starch paste from the most diverse native starches retrogresses at room temp. to a state with a *B* diagram, observed with preps. dehydrated by means of EtOH, but the rate of appearance of the *B* diagram varies considerably with the variety of starch. Wheat starch paste, and *Gramineæ* starch pastes generally, retrogress much more slowly than paste of native starches with a *B* or *C* diagram.

XXIII. Addition of ~15 vol.-% EtOH markedly accelerates retrogression, as revealed by the X-ray diagram, whilst with >50% EtOH retrogression is delayed or suppressed. This is to be correlated with the observation that with increase in the amount of H<sub>2</sub>O in starch paste free from EtOH the rate of retrogression passes through a max.; the action of the EtOH depends primarily on dehydration, but EtOH is also adsorbed. The technique of EtOH dehydration of starch pastes is described.

R. C.

**Equilibrium constant of  $HH^2O + H_2 = H_2O + HH^2$ .** T. FÖRSTER (Z. physikal. Chem., 1934, B, 27, 1—5).—The equilibrium const. has been calc. from spectroscopic data (cf. A., 1934, 1070). The calc. and observed vals. agree better if the zero point energy of HH<sup>2</sup>O is derived from the fundamental frequencies of H<sub>2</sub>O, allowing for the difference in mass, than if it is deduced from the observed frequencies for HH<sup>2</sup>O.

R. C.

**"Isotopic equilibria" in the hydrogen-hydrogen oxide system.** R. H. CRIST and G. A. DALIN (J. Chem. Physics, 1934, 2, 735—738; cf. A., 1934, 1070).—The distribution of H<sub>2</sub> between H<sub>2</sub> and H<sub>2</sub>O has been determined at the temp. of boiling S and in presence of Pt. The amounts found agree with those

given by the equilibrium consts. which have been calc. for the reactions involved.

F. L. U.

**Equilibrium  $H_2O + HH^2 = HH^2O + H_2$ .** L. FARKAS and A. FARKAS (Trans. Faraday Soc., 1934, 30, 1071—1079).—The establishment of the equilibrium of H<sub>2</sub> with heavy H<sub>2</sub>O and heavy steam of known H<sup>2</sup> content has been investigated in the presence of Pt catalysts. The vapour-phase equilibrium const.,  $K = [HH^2O][H_2]/[H_2O][HH^2]$  in the range 3—450° is given by  $\log_{10} K = -0.1335 + 750/2.3RT$ . The difference between the zero point energies of H<sub>2</sub>O and HH<sup>2</sup>O is 1567 g.-cal., compared with the val. 1704 derived from spectroscopic data.

J. G. A. G.

**Esterification constant in the gas phase co-existing with the liquid phase.** W. SWIENIOWSKI and J. SALCEWICZ (Compt. rend., 1934, 199, 1308—1310).—Vals. of the const. for EtOAc (70—300°) are recorded.

H. J. E.

**Theory of strong electrolyte solutions.** J. G. KIRKWOOD (J. Chem. Physics, 1934, 2, 767—781).—Mathematical. A detailed investigation of the quant. importance of the approximations involved in the derivation of the Debye-Hückel equations confirms the validity of the theory within the limitations originally imposed.

F. L. U.

**Two theorems concerning electrolytes.** R. M. FUOSS (J. Chem. Physics, 1934, 2, 818—821).—(1) Fluctuations in the total electrostatic energy of the free ions of an electrolytic solution as calc. by the theory of Debye and Hückel are negligibly small at concns. at which the thermodynamic properties of the solution are measurably different from those of the solvent. (2) A new proof of the theorem that the free energy = 2/3 of the average electrostatic energy is given.

F. L. U.

**Strength of acids.** E. DARMOIS and Y. K. HENG (Compt. rend., 1934, 199, 1123—1125).—A method of measuring the strength of acids in terms of the lowering (I) of the rotatory power of NH<sub>4</sub> tetramolybdomalate is developed. (I)  $\propto$  the strength of the acid. Data for HCl, HClO<sub>4</sub>, and PhSO<sub>3</sub>H are recorded.

H. J. E.

**Thermodynamic primary dissociation constants of some normal dibasic acids at 25°.** A. I. VOGEL and G. H. JEFFERY (Chem. and Ind., 1934, 964).—A preliminary note on the primary dissociation consts.,  $K_1$ , of the dibasic acids (CH<sub>2</sub>)<sub>*n*</sub>(CO<sub>2</sub>H)<sub>2</sub> for *n* = 1—6. The vals. of  $K_1 \times 10^5$  are: 139.7, 6.626, 4.535, 3.715, 3.097, and 2.994, respectively.

O. J. W.

**Dissociation constants of dicarboxylic acids. Strain relations in dicyclic systems.** H. BODE (Z. physikal. Chem., 1934, 170, 231—252).—The first and second dissociation consts. of various dicyclic dicarboxylic acids have been determined and used to calculate the effect of the CO<sub>2</sub>H groups on each other through the mol., and thus the amount of strain. The results indicate that strain present in the mol. is operative only in the direction of the plane containing the C atoms which cause the strain. In cyclopoly-methylenedicarboxylic acids the interaction of the CO<sub>2</sub>H groups increases with increasing strain for the



*cis*-acids, and falls for the *trans*-acids, and is apparently transmitted wholly through the solvent.

R. C.

Ionisation constants of the tartaric acids and the nature of borotartaric acids. I. JONES and F. G. SOPER (J.C.S., 1934, 1836—1842).—The first and second ionisation consts. of *d*- and meso-tartaric acids have been determined for ionic strengths 0.016—0.0016, and at temp. 25°, 50°, and 74°, electrometrically. The use of the liquid-liquid junction has been avoided by employing, as reference electrode, Ag-AgCl immersed in the acid mixture containing const. [Cl<sup>-</sup>].  $K_1$  and  $K_2$  for the *d*-acid are > for the meso-acid, but the ratio of the two consts. for the meso- is > for *d*-acid. With rise of temp.  $K_2$  decreases and  $K_1$  increases to a max. and then decreases, for both acids. The difference in  $K_1$  for the two acids indicates the absence of free rotation, and may be explained on the basis of a difference of internal co-ordination as a result of the spatial configuration. Electrometric titrations of the two acids have also been carried out in the presence of different amounts of H<sub>3</sub>BO<sub>3</sub>. The secondary ionisation of both acids is increased. The configuration of the complex borotartaric acids is discussed.

M. S. B.

Dissociation constants of weak and moderately strong electrolytes. I. Dissociation constant of 2:4-dinitrophenol, and range of validity of Debye-Hückel limiting formula. H. VON HALBAN and G. KORTUM (Z. physikal. Chem., 1934, 170, 351—379).—The methods of determining dissociation consts. are critically reviewed. The optical methods, as distinguished from electrometric and conductometric methods, are practically independent of hypotheses, e.g., concerning the behaviour and mutual interaction of ions and mols., and optical absorption is const., independent of electrostatic forces, at far higher concns. than is, say, the conductivity. The classical dissociation const.,  $K_c$ , of 2:4-dinitrophenol has been determined at 25° with a precision of 0.1% in pure aq. solution and in solutions of KClO<sub>4</sub>, KCl, NaCl, and HCl at ionic concns. of  $5 \times 10^{-5}$  to 2.28M by photo-electric determination of the concn. of the absorbing anion. The results permit very precise extrapolation to zero concn. to obtain the thermodynamic dissociation const.,  $8.13 \pm 0.01 \times 10^{-5}$ . Using this val., the Debye-Hückel limiting formula agrees excellently with the experimental data up to an ionic concn. of  $\sim 3 \times 10^{-3}M$ ; at higher concns. systematic deviations appear. In presence of univalent neutral salts  $K_c$  increases uniformly up to an ionic concn. of  $\sim 0.01M$  and passes through a max. at  $\sim 0.5M$ .

R. C.

Erroneous conception with regard to carbonate solutions. Y. KAUKO (Maataloustiet. Aikakausk., 1934, 6, No. 2; Suomen Kem., 1934, 7, 96B).—Free CO<sub>2</sub> is practically non-existent in these solutions, and the usual conception of the relation between free and bound CO<sub>2</sub> is false. H carbonate solutions are not buffer solutions. It is shown that Henry's law does not hold for dil. H carbonate solutions, but that the solubility of CO<sub>2</sub> obeys the same laws as the surface adsorption of the vapour.

J. W. S.

Graphical representation of the equilibrium relations in the system base-carbon dioxide-water in dilute solutions from the viewpoint of the classical dissociation theory. Y. KAUKO (Ann. Acad. Scient. Fenn., 1934, A, 39, 1; Suomen Kem., 1934, 7, 96B; cf. A., 1934, 732).—The graphical representation of the mathematical relations developed previously has been applied to the hardness of H<sub>2</sub>O. The usual methods of determining the free and combined CO<sub>2</sub> can lead to misleading results. The method recommended is the determination of basicity and [H<sup>+</sup>].

J. W. S.

Activities of ethylene and ethyl alcohol in sulphuric acid. M. GALLAGHER and D. B. KEYES (J. Amer. Chem. Soc., 1934, 56, 2221—2224).—The activities have been calc. from measurements of the partial pressures of C<sub>2</sub>H<sub>4</sub> (from dil. solutions to mol. fraction 0.3122) in conc. H<sub>2</sub>SO<sub>4</sub>, and of EtOH (from dil. solutions to mol. fraction 0.2400) in dil. H<sub>2</sub>SO<sub>4</sub>.

E. S. H.

Activity coefficient of sulphuric acid at temperatures from 0° to 50°. J. SHRAWDER, jun., and I. A. COWPERTHWAIT (J. Amer. Chem. Soc., 1934, 56, 2340—2345).—The data have been calc. from e.m.f. measurements of the cells Pb-Hg (2-phase), PbSO<sub>4</sub>(s), H<sub>2</sub>SO<sub>4</sub>(m), H<sub>2</sub> at different concns.

E. S. H.

Apparent and real activity coefficients in solutions of electrolytes. II. L. BRÜLL (Gazzetta, 1934, 64, 734—742; cf. A., 1934, 1307).—The activities of CdCl<sub>2</sub> in aq. solutions of alkali and alkaline-earth chlorides have been calc. from e.m.f. measurements of the cell CdHg|CdCl<sub>2</sub>-MCl<sub>n</sub>|Hg<sub>2</sub>Cl<sub>2</sub>|Hg, where MCl<sub>n</sub> represents the chlorides of Li, Na, K, Ca, Sr, and Ba, respectively.

O. J. W.

Activity of the hydrogen ions in Veibel's solution at different temperatures. Y. KAUKO (Maataloustiet. Aikakausk., 1933, 5, 149; Suomen Kem., 1934, 7, 96B).—The activity of H<sup>+</sup> has been determined from the conductivity and  $p_H$  of these solutions.

J. W. S.

Raman spectrum, structure, and hydrolysis of solutions of stannic chloride. J. GUÉRON (Compt. rend., 1934, 199, 945—948).—Previous results (cf. A., 1934, 254, 960) are discussed in detail.

N. M. B.

Substitution equilibrium between different halogens in  $\alpha$ -halogeno-fatty acids. E. HANNERZ (Svensk Kem. Tidskr., 1934, 46, 233—250).—Equilibrium consts. in the reaction R·CHX·CO<sub>2</sub>H + KX' = R·CHX'·CO<sub>2</sub>H + KX (R=H or Me) have been determined in aq. solution at 50°. The equilibria were approached from both sides.

F. L. U.

Influence of  $p_H$  on the dissociation of hexamethylenetetramine and the hydriodide of hexamethylenetetramine-ethanol. G. TOUSSAINT, J. DÉTRIE, and M. VÉRAIN (Compt. rend. Soc. Biol., 1934, 171, 191—193).—The dissociation of the hydriodide of hexamethylenetetramine-ethanol to give CH<sub>2</sub>O is > that of (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> (I) at  $p_H$  1—9. (I) is dissociated only below  $p_H$  5.

A. L.

Physico-chemical studies of complex acids. XIII. Constitution of quinquevalent and quadri-



valent vanadium solutions with a note on their respective reduction and oxidation. H. T. S. BRITTON (J.C.S., 1934, 1842—1846).—Electrometric titrations of aq. alkali vanadate with  $\text{H}_2\text{SO}_4$ , and of  $\text{V}_2\text{O}_5$  solutions in  $\text{H}_2\text{SO}_4$  with  $\text{NaOH}$ , have been made, using the glass electrode. At  $85^\circ$  well-defined inflexions are observed in the titration curves, indicating the formation of metavanadate,  $\text{Na}_2\text{O}\cdot\text{V}_2\text{O}_5$ . At lower temp. the inflexions are indefinite and depend on time and temp. Glass electrode electrometric titration with  $\text{NaOH}$  of the blue solution obtained by reducing  $\text{V}_2\text{O}_5$  in  $\text{H}_2\text{SO}_4$  with  $\text{SO}_2$ , confirms the view that  $\text{VOSO}_4$  is formed, and shows also that  $\text{V}_2\text{O}_4$  cannot react with any greater amount of  $\text{H}_2\text{SO}_4$ . Contrary to the usual view,  $\text{V}_2\text{O}_4$  is not amphoteric. The re-dissolution observed in alkaline solutions is caused by the oxidation in air to vanadic acid. Electrometric titrations of  $\text{VOSO}_4$  solutions have been made, at  $22^\circ$ ,  $50^\circ$ , and  $75^\circ$ , with  $0.1N\text{-KMnO}_4$ , using a bright Pt electrode, and  $45^\circ$  was selected as a suitable temp. at which to investigate the oxidation of  $\text{V}^{\text{IV}}$ . Back titrations have also been made with  $0.1N\text{-FeSO}_4$ . M. S. B.

Complex formation due to polarisation. J. H. HILDEBRAND and S. E. WOOD (J. Chem. Physics, 1934, 2, 822—823).—The conclusions of Glockler and co-workers (A., 1934, 21) on compound formation between Kr and HCl are criticised. F. L. U.

Complex formation due to polarisation. Definition of a molecule. G. GLOCKLER (J. Chem. Physics, 1934, 2, 823—824; cf. preceding abstract).—Reply to Hildebrand and Wood. A mol. is defined as any configuration of atoms, simple mols., or radicals which shows a potential min. F. L. U.

Amphoteric behaviour of metal hydroxides. VIII. Chromites. R. SCHOLDER and R. PARSCH (Z. anorg. Chem., 1934, 220, 411—424).—The dependence of the solubility of  $\text{Cr}_2\text{O}_3$  in aq.  $\text{NaOH}$  on temp. varies with the concn. of the latter. The behaviour is due both to colloidal solutions and to the formation of complexes. A study of the system  $\text{Cr}_2\text{O}_3\text{-Na}_2\text{O-H}_2\text{O}$  indicates the existence of the following *hydroxo-salts*:  $[\text{Cr}(\text{OH})_6]\text{Na}_3$ ,  $[\text{Cr}(\text{OH})_7(\text{H}_2\text{O})]\text{Na}_4\cdot 2\text{-}3\text{H}_2\text{O}$  (I), and  $[\text{Cr}(\text{OH})_8]\text{Na}_5\cdot 4\text{H}_2\text{O}$  (II). (I) and (II) also form mixed crystals. By pptn. of aq. Na chromite with  $\text{Ba}(\text{OH})_2$  or  $\text{Sr}(\text{OH})_2$  the *compounds*  $[\text{Cr}(\text{OH})_6]_2\text{M}_3$  (M=Ba or Sr) are obtained. Aq. Na chromite deposits  $\text{Cr}(\text{OH})_3$  on long keeping, but Ba and Sr chromite are more stable. It is probable that  $\text{Na}_1$  chromite exists, and possibly the  $\text{Na}_2$  compound also. The constitution of chromites is discussed. M. S. B.

Equilibrium in the system vanadium tetroxide-carbon monoxide-vanadium trioxide-carbon dioxide. H. M. SPENCER and J. C. JUSTICE (J. Amer. Chem. Soc., 1934, 56, 2306—2311).—The equilibrium const. has been determined at temp. between  $750^\circ$  and  $896^\circ$ . Free energies and heats of formation have been calc. E. S. H.

Vapour pressures of saturated solutions. Lithium chloride and lithium sulphate. M. P. APPLEBY, F. H. CRAWFORD, and K. GORDON (J.C.S., 1934, 1665—1671).—Solubilities of  $\text{LiCl}$  and  $\text{Li}_2\text{SO}_4$  have been determined, and also  $d$  and v.p. of the

saturated solutions, at temp. up to and including the b.p. at atm. pressure. The transition temp. for  $\text{LiCl}\cdot 2\text{H}_2\text{O}$  to  $\text{LiCl}\cdot \text{H}_2\text{O}$  is  $19.1 \pm 0.25^\circ$  and for  $\text{LiCl}\cdot \text{H}_2\text{O}$  to  $\text{LiCl}$   $93.5 \pm 0.5^\circ$ . Osmotic pressures have been calc. by the Porter equation and compared with the data for other alkali salts.  $\text{Li}^+$  has a very high osmotic activity. M. S. B.

Position of the separation quadruple point in the system ether-water. F. DE BOER (Z. physikal. Chem., 1934, 170, 253—255).—The equilibrium pressures corresponding with the two conjugate solutions + vapour and solution + ice + vapour have been determined at  $-19^\circ$  to  $34^\circ$ . The quadruple point lies in the  $p$ - $T$  diagram above the v.-p. curve of pure  $\text{Et}_2\text{O}$ . R. C.

System mercuric chloride-mercuric bromide. A. J. VAN PELT, jun., and F. DE BOER (Z. physikal. Chem., 1934, 170, 256—261).—From solubility measurements in the system  $\text{EtOH-HgCl}_2\text{-HgBr}_2$  at  $25^\circ$  and measurements of heat of dissolution in  $\text{CMe}_2$  it is probable that  $\text{HgCl}_2$  and  $\text{HgBr}_2$  form mixed crystals. R. C.

M.-p. diagram of the system  $p$ -cresol-benzoic acid. D. J. DA SILVA (Rec. trav. chim., 1934, 53, 1097—1100).—The system has a eutectic at  $27.5^\circ$  and 10.8 mol.-%  $\text{BzOH}$ . The  $\text{BzOH}$  curve is very nearly the same as for the system  $\text{PhOH-BzOH}$  (cf. A., 1933, 906), and  $(1/T + \text{const.}) \propto \log \text{mol.-% BzOH}$ . Extrapolation gives 5.59 kg.-cal. for the heat of fusion of  $\text{BzOH}$ . It is inferred that the dipole moment of non-associated  $\text{BzOH}$  is  $1.64\text{--}1.7 \times 10^{-18}$  e.s.u. R. S. B.

Behaviour of the hydronitrogens and their derivatives in liquid ammonia. IX. Equilibria in the system ammonium trinitride-ammonia. D. H. HOWARD, jun., F. FRIEDRICH, and A. W. BROWNE. X. Equilibria in the system hydrazine trinitride-ammonia. D. H. HOWARD, jun., and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 2332—2340, 2348—2357).—IX. The system has been examined over the ranges 0—4000 mm.,  $-90^\circ$  to  $30^\circ$ , and 0—100%  $\text{NH}_3$ . Two *cryst. compounds*,  $\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$  and  $\text{NH}_4\text{N}_3\cdot 5\text{NH}_3$ , have been obtained. The eutectic is at  $-87^\circ$  and 76%  $\text{NH}_3$ .

X. The system has been investigated over the ranges 0—3200 mm.,  $-15^\circ$  to  $80^\circ$ , and 0—100%  $\text{NH}_3$ . A deliquescent, stable, white, *cryst. solvate*,  $2\text{N}_2\text{H}_5\text{N}_3\cdot \text{NH}_3$ , with an inversion point at about  $50^\circ$ , has been obtained. Ammonolysis occurs in liquid  $\text{NH}_3$ , depending on the temp. and concn. E. S. H.

Phases formed by the reduction of mixtures of iron oxide with other oxides. E. JENCKEL (Z. anorg. Chem., 1934, 220, 377—388).—From the experimental data of Schenck *et al.* (A., 1930, 43; 1932, 811) phase diagrams have been constructed for the ternary systems above  $800^\circ$  consisting of Fe and  $\text{Fe}_2\text{O}_3$  with one of the following oxides:  $\text{BeO}$ ,  $\text{SiO}_2$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{ZnO}$ . M. S. B.

Slag systems. R. HAY, D. D. HOWAT, and J. WHITE (J. West Scot. Iron Steel Inst., 1934, 41, 97—105).—Diagrams are given for the systems  $\text{FeO-MnO}$ ,  $\text{MnO-SiO}_2$ ,  $\text{FeO-SiO}_2$ .  $\text{FeO}$  has not a definite m.p. At  $1370^\circ$  it undergoes a peritectic reaction giving a small amount of saturated solution of O in Fe (m.p.



1480°). At 1430° 37% of MnO is sol. in FeO and 44% FeO in MnO. CH. ABS. (e)

**System sulphuric acid-ammonium sulphate-water.** P. LOOUTY and P. LAFFITTE (Compt. rend., 1934, 199, 950—952; cf. A., 1933, 570).—Investigations previously reported are extended to 10° and 90°. The salts which separate at 10° are:  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 \cdot 3(\text{NH}_4)_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ , and  $3\text{H}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ ; at 90° the last-named is absent, but a small zone of mixed crystals appears. A three-dimensional diagram indicates the most favourable conditions for the deposition of a given salt.

N. M. B.

**Ternary systems cerous sulphate-alkali sulphate-water. I. Cerous sulphate-potassium sulphate-water.** W. SCHRÖDER and H. SCHACKMANN (Z. anorg. Chem., 1934, 220, 389—410).—Data and diagrams are given for the system  $\text{Ce}_2(\text{SO}_4)_3$ - $\text{K}_2\text{SO}_4$ - $\text{H}_2\text{O}$  at 0°, 25°, 50°, and 75°. The presence of the following compounds is indicated:  $\text{Ce}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,  $2\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{Ce}_2(\text{SO}_4)_3 \cdot 4-5\text{K}_2\text{SO}_4$ .

M. S. B.

**System bismuth iodide-potassium iodide-water.** (MLLE.) M. L. DELWAULLE (Compt. rend., 1934, 199, 948—950).—At 15°, 35°, and 55°, the compounds  $\text{BiI}_3 \cdot \text{KI} \cdot \text{H}_2\text{O}$  and  $\text{BiI}_3 \cdot 2\text{KI} \cdot \text{H}_2\text{O}$  are formed. By slow evaporation these were obtained in the form of bright red monoclinic prisms and deep red pyramids, respectively.

N. M. B.

**System cadmium sulphate-acetic acid-water at 25°.** W. C. CAGLE, G. TARBUTTON, and W. C. VOSBURGH (J. Amer. Chem. Soc., 1934, 56, 2331—2332).—The solubility of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  decreases rapidly as AcOH is added and is very small in aq. solutions containing > 55% AcOH.  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  is the stable phase when [AcOH] is < 85%. The composition of  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  has been confirmed.

E. S. H.

**Ternary system potassium perchlorate-potassium borofluoride-water at 25°.** R. C. RAY and H. C. MITRA (Trans. Faraday Soc., 1934, 30, 1161—1163).— $\text{KClO}_4 \cdot 2\text{KBF}_4$  and  $\text{KClO}_4 \cdot 8\text{KBF}_4$  are formed, but cannot be isolated, as they are decomposed by  $\text{H}_2\text{O}$  with separation of solid  $\text{KBF}_4$ , and are stable only in solutions containing more  $\text{KClO}_4$  in proportion to  $\text{KBF}_4$  than the salts themselves.

R. S. B.

**Equilibrium diagrams of salts for salt baths. I. System  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{NaCl}$ - $\text{KCl}$ .** T. SATŌ and J. SUNAMI. **II. System  $\text{Na}_2\text{CO}_3$ - $\text{NaCl}$ - $\text{KCl}$ .** T. SATŌ (Tech. Rep. Tôhoku, 1934, 31, 383—402, 403—416).—Numerical data and diagrams are given for the binary and ternary systems concerned. F. L. U.

**Technique of thermal analysis in systems of three organic components, and summary of systems examined.** K. HRYNAKOWSKI (Z. physikal. Chem., 1934, 171, 99—118).—A method of thermal analysis is described, and the results obtained for 22 ternary systems with components only partly miscible in the molten state are recorded. A scheme of classification of ternary systems is outlined.

R. C.

**Dilatometer study of ternary silica-soda-alumina glasses.** E. RENCKER (Compt. rend., 1934, 199, 1114—1116).—The transformation temp. and linear expansion of glasses of varying composition are represented in diagrams. Replacement of  $\text{Na}_2\text{O}$  or  $\text{SiO}_2$  by  $\text{Al}_2\text{O}_3$  lowers the expansion coeff. except in a limited region at > 20%  $\text{Al}_2\text{O}_3$ .

H. J. E.

**Heats of formation and dissolution of hydrogen sulphide.** H. ZEUMER and W. A. ROTH (Z. Elektrochem., 1934, 40, 777—783).—The heat of formation, determined by combustion in  $\text{O}_2$ , is  $+4.80 \pm 0.15$  kg.-cal. per mol. The heat of dissolution is  $4.52 \pm 0.03$  kg.-cal. per mol. The calc. heat of ionisation ( $\text{H}^+ + \text{SH}^-$ ) is 3.8 kg.-cal.

E. S. H.

**Thermal decomposition and heat of formation of sodium carbamate.** S. ABE and R. HARA (J. Soc. Chem. Ind. Japan, 1934, 37, 699—700B).—When heated,  $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{Na}$  decomposes as follows:  $3\text{NH}_2 \cdot \text{CO}_2 \cdot \text{Na} \rightarrow \text{Na}_2\text{CO}_3 + \text{NaCNO} + \text{CO}_2 + 2\text{NH}_3$ ,  $\text{NaHCO}_3$  being an intermediate product. In  $\text{O}_2$ :  $2\text{NH}_2 \cdot \text{CO}_2 \cdot \text{Na} + 3\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2$ . From the heat of this reaction (bomb calorimeter) the following data for const. vol. and const. pressure at 18° are calc.: heat of combustion 74.11, 73.97, heat of decomp. 15.04, 15.62, heat of formation 175.45, 176.89 kg.-cal. (all  $\pm 0.036$ ).

A. G.

**Thermochemistry of compounds occurring in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .** V. Heats of formation of tricalcium silicate and dicalcium silicate. O. K. JOHANSSON and T. THORVALDSON (J. Amer. Chem. Soc., 1934, 56, 2327—2330; cf. A., 1930, 1524).—The prep. of  $\beta$ - $2\text{CaO}, \text{SiO}_2$  is described. The isothermal heats of decomp. of  $\beta$ - and  $\gamma$ - $2\text{CaO}, \text{SiO}_2$  and of  $3\text{CaO}, \text{SiO}_2$  in dil. HCl have been determined, and the following quantities calc.: (a) the isothermal heats of formation at 20° of  $\beta$ - $2\text{CaO}, \text{SiO}_2$ ,  $\gamma$ - $2\text{CaO}, \text{SiO}_2$ , and  $3\text{CaO}, \text{SiO}_2$  from CaO and  $\text{SiO}_2$  gel, (b) the isothermal heats of formation at 20° of  $3\text{CaO}, \text{SiO}_2$  from CaO and the above two forms of  $2\text{CaO}, \text{SiO}_2$ , (c) the heat of transition at 20° of  $\beta$ - into  $\gamma$ - $2\text{CaO}, \text{SiO}_2$ . At 20°,  $\beta$ - $2\text{CaO}, \text{SiO}_2$  is metastable with respect to  $\gamma$ - $2\text{CaO}, \text{SiO}_2$ , and  $3\text{CaO}, \text{SiO}_2$  is metastable with respect to CaO and  $\beta$ - and  $\gamma$ - $2\text{CaO}, \text{SiO}_2$ .

E. S. H.

**Keten. III. Heat of formation and heat of reaction with alcohols.** F. O. RICE and J. GREENBERG (J. Amer. Chem. Soc., 1934, 56, 2268—2270; cf. A., 1934, 1091).—From measurements of the heat of reaction of  $\text{CH}_2\text{CO}$  with dil. aq. NaOH the calc. heat of formation of gaseous  $\text{CH}_2\text{CO}$  from graphite and gaseous  $\text{H}_2$  and  $\text{O}_2$  is  $+14.78$  kg.-cal. The following heats of reaction of  $\text{CH}_2\text{CO}$  with aliphatic alcohols have been determined: MeOH 36.93, EtOH 36.44, Pr<sup>n</sup>-OH 35.32, Bu<sup>n</sup>-OH 35.11, Bu<sup>s</sup>-OH 34.37, Pr<sup>s</sup>-OH 35.91, sec.-BuOH 34.53, Bu<sup>t</sup>-OH 23.49 kg.-cal. per mol.

E. S. H.

**Heats of dilution of strong electrolytes.** A. L. ROBINSON and H. S. FRANK (J. Amer. Chem. Soc., 1934, 56, 2312—2313).—Examination of published data suggests that Åkerlöf's rule (A., 1934, 1173) is not equally valid at all temp.

E. S. H.

**Partial molal heat of dilution of sulphuric acid from electromotive force measurements.** I. A. COWPERTHWAIT and J. SHRAWDER, jun. (J.



Amer. Chem. Soc., 1934, 56, 2345—2347).—The data are derived from e.m.f. measurements of the cells Pb—Hg,  $\text{PbSO}_4(s)$ ,  $\text{H}_2\text{SO}_4(m)$ ,  $\text{H}_2$  at intervals of 12.5° between 0° and 50° and at different concns.

E. S. H.

Water as a weak electrolyte in the heats of dilution of strong electrolytes. E. DOEHLEMANN and E. LANGE (Z. physikal. Chem., 1934, 170, 391—406).—The observed heat of dilution,  $V_m$ , of aq. solutions of salts and acids includes heat effects,  $Q$ , due to changes in the ionisation of the  $\text{H}_2\text{O}$ : (1) with neutral salts,  $Q$  is due to shift in the equilibrium  $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$  owing to change in activity coeff. of  $\text{H}_2\text{O}$  with salt concn.; (2) with acids,  $Q$  is due to repression of ionisation of  $\text{H}_2\text{O}$  by  $\text{H}^+$  of acid; (3) with hydrolysing salts,  $Q$  is due to variation of hydrolysis with concn. Examples of the calculation of these vals. are reproduced, and the correction required for deviation of the  $\text{H}_2\text{O}$  used for dilution from  $p_H$  7 is calc. After application of these corrections to the  $V_m$  curve of  $\text{NH}_4\text{Cl}$  it fits in with the curves of the other Me-substituted  $\text{NH}_4$  salts.  $V_m$  also probably includes a  $Q$  due to variation with concn. of the degree of association of the  $\text{H}_2\text{O}$ .

R. C.

Heats of dissolution and reaction in liquid ammonia. III. C. A. KRAUS and F. C. SCHMIDT (J. Amer. Chem. Soc., 1934, 56, 2297—2300; cf. A., 1934, 256).—Modifications in apparatus and technique are described. Data are recorded for heats of dissolution of Na, K,  $\text{NH}_2\text{Ac}$ , Li, NaBr, ice, phthalimide, Na in presence of KBr, and K in presence of NaBr, and for the heat of reduction of  $\text{SnMe}_2\text{Br}$  to  $\text{SnMe}_3\text{Na}$ .

E. S. H.

Thermochemical study of *d*-gluconic acid and its modifications. R. H. LE ROY and B. C. HENDRICKS (J. Amer. Chem. Soc., 1934, 56, 2243—2245).—The heats of dissolution to a dilution of 0.0003 mol. of solute per mol. of  $\text{H}_2\text{O}$  at 25° for *d*-glucono acid (I), *d*-glucono- $\delta$ -lactone (II), *d*-glucono- $\gamma$ -lactone (III), and Na *d*-gluconate have been determined, as well as the heats of neutralisation of (I), (II), and (III) with 0.0102*N*-NaOH. The transformation of (II) into (III) is an endothermic change.

E. S. H.

Thermometric study of the precipitation of insoluble ferrocyanides. R. PARIS (Compt. rend., 1934, 199, 863—865; cf. A., 1934, 491).—The curves obtained by plotting the temp. rise against the amount of  $\text{K}_4\text{Fe}(\text{CN})_6$  added to solutions of  $\text{Pb}(\text{OAc})_2$ ,  $\text{AgNO}_3$ ,  $\text{ZnSO}_4$ , and  $\text{FeCl}_3$  show sharp breaks corresponding with the complete pptn. of  $\text{Pb}_2\text{Fe}(\text{CN})_6$ ,  $\text{Ag}_3\text{KFe}(\text{CN})_6$ ,  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ , and  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ . With Ni,  $\text{Cu}^{\text{II}}$ , Co, and Cd salts the breaks do not correspond with simple formulæ, and differ according as the  $\text{K}_4\text{Fe}(\text{CN})_6$  is added to the salt or *vice versa*.

J. W. S.

Effect of ammonia and pyridine on mobility of cupric ion. J. WILLE (Z. physikal. Chem., 1934, 171, 93—98).—From the effect of the addition of  $\text{NH}_3$  and  $\text{C}_5\text{H}_5\text{N}$  on the transport no. of  $\text{Cu}^{\text{II}}$  in aq.  $\text{CuSO}_4$  it is concluded that  $\text{NH}_3$  forms  $[\text{Cu}_4\text{NH}_3]^{\text{II}}$  and  $[\text{Cu}_5\text{NH}_3]^{\text{II}}$ , that 2—4  $\text{C}_5\text{H}_5\text{N}$  mols. may be added to  $\text{Cu}^{\text{II}}$ , and that in pure Cu salt solutions there is equilibrium between  $\text{Cu}^{\text{II}}$  and  $[\text{Cu}_x\text{H}_2\text{O}]^{\text{II}}$ , where  $x=1-5$ .

R. C.

Electrical conductivity of strong electrolytes and its variation with temperature. C. J. B. CLEWS (Proc. Physical Soc., 1934, 46, 764—771).—Precision data are given for  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ , and  $\text{Na}_2\text{SO}_4$ , in the temp. range 18—85°, using a bridge method with a.c. supplied by a vac.-tube oscillatory circuit and amplified detector; temp. control was accurate to 0.02°.

N. M. B.

High-frequency conductivity of the solution of magnesium sulphate in a mixture of glycerol and water. M. HARADA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1340—1350).—Data for  $\text{MgSO}_4$  solutions at 25° and -20° are recorded. At 25° the results agree qualitatively with the theory of Debye and Falkenhagen, but at -20° inexplicable deviations occur.

R. S. B.

Wien effect of a long-chain salt in aqueous solution, and an appropriate modification of the method of measurement for brief current pulses. J. MALSCH and G. S. HARTLEY (Z. physikal. Chem., 1934, 170, 321—336).—The Wien effect with aq. solutions of cetylpyridinium chloride at concns. < 0.001*N* is very small and of the same order as for normal electrolytes, but at higher concns. increases and at about 0.002*N* becomes very large, the conductivity for high field strength being > the conductivity at infinite dilution. The explanation is that with increasing concn. large multivalent ions are formed and part of the counter-ions contained in them are released, so that there are present more ions of high mobility and the charge of the large ions is increased. Examination of the effect of varying the duration of the current pulses gives no indication that strong fields break up the multivalent ion aggregates. A source of error in the Malsch-Wien apparatus has been eliminated (Ann. Physik, 1927, [iv], 83, 305).

R. C.

Revision of normal electrode potentials. J. SHRAWDER, jun., I. A. COWPERTHWAITTE, and V. K. LA MER (J. Amer. Chem. Soc., 1934, 56, 2348).—The following data for  $E_{298}^\circ$  are recorded: Pb—Hg(2-phase),  $\text{PbSO}_4(s), \text{SO}_4^{\text{II}}$  + 0.3505; Hg,  $\text{Hg}_2\text{SO}_4(s), \text{SO}_4^{\text{II}}$  - 0.6141; Zn—Hg(2-phase),  $\text{Zn}^{\text{II}}$  + 0.7614; Zn,  $\text{Zn}^{\text{II}}$  + 0.7620; Cd—Hg(2-phase),  $\text{Cd}^{\text{II}}$  + 0.3519; Cd,  $\text{Cd}^{\text{II}}$  + 0.4024.

E. S. H.

Polarographic studies with the dropping mercury electrode. I. Anodic polarisation and the influence of anions. J. REVENDA (Coll. Czech. Chem. Comm., 1934, 6, 453—467).—Anions at concns. < 10<sup>-3</sup>*M* give rise to characteristic limiting currents  $\propto$  the concn. on the current-voltage curves of the dropping Hg anode. The magnitudes of these currents are of the same order as those obtained with cations at the dropping Hg cathode, and have not been previously observed owing to the large concns. of anion used. The depolarising effect of large concns. of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{OH}^-$ , and  $\text{S}^{\text{II}}$  is due to ppts. formed with  $\text{Hg}^{\text{II}}$ , whilst that of  $\text{CN}^-$ ,  $\text{CNS}^-$ ,  $\text{SO}_3^{\text{II}}$ , and  $\text{S}_2\text{O}_3^{\text{II}}$  is due to complex formation. The technique is detailed, and with traces of  $\text{S}^{\text{II}}$  or  $\text{CN}^-$  the range of anodic polarisation extends from -0.7 to +0.3 volt with respect to the *N*- $\text{Hg}_2\text{Cl}_2$  electrode.

J. G. A. G.



**Application of the glass electrode to a study of chromic acid.** J. D. NEUSS and W. RIEMAN (J. Amer. Chem. Soc., 1934, 56, 2238—2243).—Measurements of  $H^+$  activity of  $H_2CrO_4$  and its salts at 25° by the glass electrode give  $3.20 \times 10^{-7}$  (error  $\pm 3\%$ ) as the second ionisation const. The first ionisation is not quite complete; at an ionic strength 0.16, the const. is  $0.18 \pm 0.04$ . The equilibrium const. of the reaction  $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$  is  $0.023$  ( $\pm 9\%$ ).  
E. S. H.

**Benzaldehyde electrode.** T. C. HERNDON and H. A. WEBB (J. Amer. Chem. Soc., 1934, 56, 2500—2501).—Reproducible determinations between  $p_H$  7 and 13.64 have been made, substituting PhCHO for quinhydrone. The PhCHO system is irreversible.  
E. S. H.

**Comparison of activity of alcohols and carboxylic acids under various conditions.** B. V. TRONOV and L. P. KULEV (J. Gen. Chem. Russ., 1934, 4, 783—789).—The activity (I) of the H atom of  $CO_2H$  and OH groups, as measured by the e.m.f. of a Na electrode, diminishes with increase in the no. of C atoms in the chain. In  $C_5H_5N$  certain concns. exist at which max. (I) is found; these correspond with formation of 1:2 compounds of  $C_5H_5N$  and acid. The (I) of acids and of PhOH in  $C_5H_5N$  is considerably  $>$  in the absence of solvent.  
R. T.

**Potential series of acids and bases.** (Acidity potential as a quantitative measure of acidity and basicity.) E. WIBERG (Z. physikal. Chem., 1934, 171, 1—24).—Accepting Brönsted's definition of acids and bases, the relation between an acid and the corresponding base is comparable with that between an oxidation-reduction pair. For an acid-base pair, there thus exists a "normal acidity potential," analogous to normal oxidation-reduction potential, and a potential series of acids and bases may be drawn up. Illustrations of the application of these principles are discussed.  
R. C.

**Oxidation-reduction potentials in non-aqueous solutions. I. Systems cuprous-cupric chlorides and ferrous-ferric chlorides in pyridine.** J. R. PARTINGTON and J. W. SKEEN (Trans. Faraday Soc., 1934, 30, 1062—1071).—The e.m.f. of the cells  $Cu|0.00228M-CuCl_2|0.0049-0.02M-CuCl_2 + 0.0038-0.032M-CuCl|Pt$ ,  $Ag|0.0265M-AgCl|0.001-0.02M-CuCl_2 + 0.001-0.026M-CuCl|Pt$  and  $Ag|0.027M-AgCl|0.001-0.02M-FeCl_2 + 0.001-0.028M-FeCl_3|Pt$  at 25° is recorded for anhyd.  $C_5H_5N$  solutions. The development of potential is explained on the basis of electron transfer between ions of different valency without the intervention of the solvent.  
J. G. A. G.

**Changes in the oxidation-reduction potential of a glucose solution under the influence of light and a photosensitiser.** P. DUBOULOZ (Compt. rend. Soc. Biol., 1934, 116, 435—437).—The potential (I) is reduced on illuminating an O-free solution of glucose (0.05 mol.) in a phosphate buffer ( $p_H$  7.7) containing eosin (1:5,000). For reductions with (I)  $<$  350 mv. the phenomenon is reversible. A connexion with biological photosensitisation is suggested.  
CH. ABS. (e)

**Buffer mechanism of sea-water.** E. G. MÖBERG, D. M. GREENBERG, R. REVELLE, and E. C. ALLEN (Bull. Scripps Inst. Oceanog. Univ. Calif. Tech. Ser., 1934, 3, 231—278).—The buffering of sea- $H_2O$  (I) is discussed in terms of  $p_H$ , titratable base, and total  $CO_2$ . The difference between the solubility product of  $CaCO_3$  in (I) and in pure  $H_2O$  is due in part to the low activity coeff. of  $CO_3^{2-}$  in (I).  
CH. ABS. (e)

**Indicators. XXIV. Protein error of indicators.** A THIEL and G. SCHULZ (Z. anorg. Chem., 1934, 220, 225—235).—Measurements of the protein error of Me-orange give results in accordance with Hartley's observations (A., 1934, 618). The distribution of the indicator between disperse phase and homogeneous solution has been determined and shows that the degree of dispersion of the protein changes with dilution. For small protein concn. the systems of isobaths for Me-orange are normal, but optical anomalies appear at higher concns. and indicate a qual. change in the character of the colour.  
M. S. B.

**Effect of pressure on overvoltage of electrolysis of water.** H. M. CASSEL and E. KRUMBEIN (Z. physikal. Chem., 1934, 171, 70—82).—Examination of the effect of pressure,  $p$ , on the overvoltage,  $E$ , of H in  $N-H_2SO_4$  and  $N-KNO_3$  at Pt, Ni, and Ag electrodes has given results similar to those previously reported (A., 1933, 677). With increase in  $p$  the  $E$  of O on Pt and  $PbO_2$  in  $N-H_2SO_4$  and on Cr-Ni steel in  $N-Cd(NO_3)_2$  falls, the effect being smallest with  $PbO_2$ . The variation of  $E$  with  $p$  agrees, in direction, with Butler's theory (cf. A., 1924, ii, 598), but is  $\gg$  the theoretical val. The fall in conductivity of aq. solutions of H and O with increasing gas pressure has been determined.  
R. C.

**Optical investigation of passivity of metals. II. Natural oxide film on polished iron surfaces.** L. TRONSTAD and T. HÖVERSTAD (Z. physikal. Chem., 1934, 170, 172—190).—The film can be removed, apparently completely, by anodically polarising in  $N-Na_2SO_4$  and at the same time making contact with a Zn rod and brushing, or by intermittently polarising cathodically in a solution containing 0.2 g.-equiv.  $Na_2C_2O_4$  and 0.02 g.-equiv.  $H_2C_2O_4$  per litre. The resulting optical change in the surface corresponds with the removal of a film of average thickness 15—30 Å. and average  $n \sim 3.5$ . Even assuming that, due to roughness, the actual surface area is twice the measured val., this film cannot be regarded as a unimol. O film; it is rather a three-dimensional system of partly hydrated oxide. The passivity film produced by anodic passivation in  $N-Na_2SO_4$  has an average thickness of 50—70 Å. and mean  $n \sim 3.5$ . The discrepancy between Müller and Machu's observations on initial c.d. and time of passivation and the results of the optical method of detecting thin films (A., 1932, 993) is explained.  
R. C.

**Electric penetration of thin layers of aluminium oxide in an electrolyte.** W. C. VAN GEEL (Physica, 1934, 1, 989—995).—Penetration voltages for a thin layer of  $Al_2O_3$  on Al in saturated aq.  $H_3BO_3$ , containing varying concns. of  $Na_2B_4O_7$ , have been



determined at different temp.  $V=A+BT \log C/N-DT^2$ , where  $A$ ,  $B$ ,  $C$ , and  $D$  are consts. and  $N$  is the no. of ions per c.c. The penetration of the oxide layer is brought about by cold electron emission (A., 1934, 240). Two penetration voltages are found, the difference between them depending on the concn. of the electrolyte. This is explained by von Hippel's theory (A., 1933, 999) according to which penetration may take place in the different directions of the cryst. lattice. M. S. B.

**Anodic passivation of gold in chloride solutions.** G. ARMSTRONG and J. A. V. BUTLER (Trans. Faraday Soc., 1934, 30, 1173—1177).—The time of passivation of Au immersed in unstirred solutions containing Cl<sup>-</sup> is given by  $(i-i_0)t=\alpha$  ( $i$ =current,  $t$ =time,  $i_0$  and  $\alpha$  are consts.), and is unaffected when HCl is replaced by KCl, in agreement with the results of Shutt and Walton for stirred solutions (cf. A., 1934, 1178). A diffusion mechanism is suggested,  $\alpha$  representing the amount of electrolysis required to form a uniform diffusion layer, and  $i_0$  the const. rate of diffusion in the steady state. The thickness of the diffusion layer is calc. to be  $4 \times 10^{-4}$  cm. (Shutt and Walton's data), and  $3-4 \times 10^{-2}$  cm. and  $1.5 \times 10^{-2}$  cm. from the authors' vals. of  $i_0$  and  $\alpha$ , respectively. R. S. B.

**Electrolysis of copper into rock-salt.** S. A. ARZIBISCHEV and U. A. PARFIANOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 25—30).—The mobility of Cu ions through rock-salt varies exponentially with temp., and has 1/50 the val. of that for electrons. A. B. D. C.

**Unstable intermediate products and the classical chemical mechanics.** A. SKRABAL (Monatsh., 1934, 64, 289—332).—Mathematical. A complete reaction scheme, including a determination of unstable intermediate reaction products, has been developed for systems of simultaneous reactions which lead to one final reaction by a single reaction path. The scheme is illustrated by reference to the combination of H<sub>2</sub> with Br. M. S. B.

**Rôle of charged particles in the propagation of flames.** Propagation of flames in transverse electric fields. A. SOKOLIK and B. SLATOV (Physikal. Z. Sovietunion, 1934, 5, 676—686).—A 25% CO mixture was extinguished by 14 kv. Positively-charged diaphragms prevented passage of flames. A photographic method was used. CH. ABS. (e)

**Thermal decomposition of ozone.** M. RITCHIE (Proc. Roy. Soc., 1934, A, 146, 848—866).—The thermal decomp. of O<sub>3</sub> has been studied between 80° and 100° for pressures between 10 and 100 mm. The first stage is O<sub>3</sub>=O<sub>2</sub>+O, followed by O+O<sub>3</sub>=2O<sub>2</sub>. The addition of inert gases, in the absence of appreciable amounts of O<sub>2</sub>, increases the rate by preventing the diffusion of O to the wall. In the presence of O<sub>2</sub> the rate is retarded by the triple collision effect O+O<sub>2</sub>+M=O<sub>3</sub>+M, where M is a mol. of O<sub>2</sub> or of other added gas. At the higher pressures of O<sub>3</sub> the first reaction is predominantly unimol.;  $k_1$  is approx.  $4 \times 10^{-4}$  sec.<sup>-1</sup> at 90°, agreeing with the val. of  $k_1$  obtained for the decomp. of O<sub>3</sub> in CCl<sub>4</sub> solution. At the lower pressures the reaction becomes increasingly

bimol. The heat of activation of the first reaction is 19,000 g.-cal. (18 mm. pressure of O<sub>3</sub>), that of the second is 14,000 g.-cal., and that of the triple collision O+O<sub>2</sub>+O<sub>2</sub>=O<sub>3</sub>+O<sub>2</sub> is 5000 g.-cal. L. L. B.

**Decomposition of ozone.** A. W. EWELL (Physical Rev., 1933, [ii], 43, 779).—The decomp. of O<sub>3</sub> has been investigated under the various conditions of its use in purifying air. The reaction is unimol., O<sub>3</sub>=O<sub>2</sub>+O, following  $dc/dt=-kc$ , where  $k$  varies from 0.01 to 0.1 corresponding with half-disappearance in from 69 to 6.9 min. The equations  $c=C(1-e^{-kt})$  and  $c=Ce^{-kt'}$ , where  $C$  is the final equilibrium concn.,  $t$  the time after the supply  $m=kC$  per min. starts, and  $t'$  the time after the supply of O<sub>3</sub> is cut off, are confirmed. L. S. T.

**Kinetics of the thermal hydrogen-chlorine reaction.** R. N. PEASE (J. Amer. Chem. Soc., 1934, 56, 2388—2391).—The thermal reaction is inhibited strongly by O<sub>2</sub>. A packing of broken Pyrex does not affect the rate in absence of O<sub>2</sub>, but accelerates the reaction in presence of O<sub>2</sub>. In absence of O<sub>2</sub> the reaction is approx. of the second order. HCl is not an inhibitor. No appreciable amount of O<sub>2</sub> is consumed in the inhibition process. E. S. H.

**Reaction of heavy hydrogen with bromine vapour.** F. BACH, K. F. BONHOEFFER, and E. A. MOELWYN-HUGHES (Z. physikal. Chem., 1934, B, 27, 71—78).—Results for the reaction with ordinary H<sub>2</sub> confirm those of Bodenstein and Lind (A., 1907, ii, 76) and supplement them at higher temp. The reaction with H<sub>2</sub><sup>2</sup> is materially slower, Br+H<sub>2</sub>=HBr+H and Br+H<sub>2</sub><sup>2</sup>=H<sup>2</sup>Br+H<sup>2</sup> having heats of activation,  $q$ , of  $17.2 \pm 0.5$  and  $19.33 \pm 0.5$  kg.-cal., respectively. This difference in  $q$  may be explained by the difference in zero point energies of H<sub>2</sub> and H<sub>2</sub><sup>2</sup>. R. C.

**Reaction between oxygen and the heavier isotope of hydrogen.** C. N. HINSHELWOOD, A. T. WILLIAMSON, and J. H. WOLFENDEN (Proc. Roy. Soc., 1934, A, 147, 48—57; cf. A., 1934, 736).—For the chain reaction in the gas at 550—560°, the ratio of the rates with H<sub>2</sub><sup>2</sup> and with H<sub>2</sub> is 0.6 in the early stages, but decreases to 0.4 as steam is formed. The smaller diffusion coeff. of the chain carriers in H<sub>2</sub><sup>2</sup> partly compensates for the lower reactivity in the early stages of the reaction, but as the latter proceeds the steam minimises the compensation, and the difference in reactivity appears. L. L. B.

**Recombination of hydrogen atoms, and their reaction with oxygen and carbon monoxide.** L. FARKAS and H. SACHSSE (Z. physikal. Chem., 1934, B, 27, 111—129).—By means of the reaction  $H+p-H_2 \rightleftharpoons o-H_2+H$  the stationary concn. of H atoms, produced by collisions of the second kind with photochemically excited Hg atoms, has been determined in H<sub>2</sub> and mixtures of this with N<sub>2</sub>, A, O<sub>2</sub>, and CO. The results indicate that the velocity coeff. of  $H+H+M=H_2+M$  is of the same order whether M is H<sub>2</sub>, A, or N<sub>2</sub>.  $H+O_2=HO_2$  occurs by a triple collision process and the ratio  $k_{H+O_2}:k_{H+H}$  is  $\sim 1:500$ . In presence of CO a decomp. reaction of HCO (1) occurs at the same time as the addition CO+H (2), the ratio of the velocity of (2) to that of (1) being  $\sim 1:370$ . R. C.



**Thermal and electrical theories of spark ignition.** J. D. MORGAN (Phil. Mag., 1934, [vii], 18, 827—832; cf. B., 1933, 134).—Combustion of a mixture of 5% of coal gas with air brought about by an electrically heated Pt wire occurs with a slightly smaller heating current when a point discharge at 4 kv. takes place near the wire, provided that the point is electrified in a discontinuous or fluctuating manner. The effect is due to radiation and not to the simple movement of ionised mols. in the field near the point. F. L. U.

**Reaction between sulphur trioxide and water vapours and a new periodic phenomenon.** C. F. GOODEVE, A. S. EASTMAN, and A. DOOLEY (Trans. Faraday Soc., 1934, 30, 1127—1133).—The reaction between  $H_2O$  and  $SO_3$  vapours has been studied at room temp. by allowing air streams carrying the vapours to interdiffuse. At low partial pressures of the reactants a ring of liquid  $H_2SO_4$  is formed on the wall; at higher concns. a flame-shaped mist is produced. The latter could not be used for determining the velocity, but from measurements on the ring it is inferred that, within a factor of approx. 10, 1 collision in 100 between reactants produces  $H_2SO_4$ . Probably ternary collisions involving the carrier gas are necessary for reaction. Under certain conditions a periodic pptn. of mist occurs, which is explained by a modification of Ostwald's theory for Liesegang rings. R. S. B.

**Kinetics of the reaction between hydrogen and nitrous oxide. II. III. Effect of oxygen.** H. W. MELVILLE (Proc. Roy. Soc., 1934, A, 146, 737—759, 760—775).—II. The kinetics of the  $H_2-N_2O$  reaction have been studied at 500—750°/1—30 mm. The reaction rate  $\propto [N_2O]^2$ , is nearly independent of  $[H_2]$ , is retarded by packing the reaction vessel, and is not affected by  $N_2$  or A. The energy of activation is 49 kg.-cal. The kinetics differ from those of the high-pressure reaction, but complete correlation is obtained by assuming that the chains now end by the combination of H atoms on the walls. Chains may be initiated by H atoms produced by optically excited Hg atoms. At low pressures the photo-reaction rate  $\propto [N_2O]$ , and the intensity of the light ( $I$ ), but is independent of  $[H_2]$ ,  $[N_2]$ , and  $[A]$ . The activation energy is 17 kg.-cal. At high pressures the rate varies as  $\sqrt{I}$ .

III. The effect of the addition of  $O_2$  on the  $H_2-N_2O$  reaction has been investigated. The thermal and Hg-photosensitised reactions have been studied between 1 and 300 mm. At high pressures the kinetics change entirely; small quantities of  $O_2$  increase the velocity, and the energy of activation decreases. Photochemical methods show that  $O_2$  participates in the initiation and propagation of the chains. Packing experiments show that the initiation is homogeneous. At low pressures in the thermal reaction a transition point is observed, above which the reaction is rapid and below which it is slow, if wide bulbs are used. This point depends on the  $O_2$  content and the temp., and is displaced to higher temp. on packing the reaction bulb. Photo-experiments confirm these measurements; as the temp.

rises the val. of  $n$  in rate = const.  $\times I^n$  decreases from 1 to nearly 0. L. L. B.

**Oxidation of ethane.** W. A. BONE (Chem. and Ind., 1934, 962—963).—A criticism of the work of Steacie and Plewes (A., 1934, 1311), whose chain-reaction mechanism for the oxidation of  $C_2H_6$  is considered to be unproven, mainly because their experimental procedure was not suitable for the identification of the primary reaction or the nature of the initial oxidation product. O. J. W.

**Oxidation of ethane.** H. H. GRAY (Chem. and Ind., 1934, 1007).—A reply to criticism (cf. preceding abstract). E. S. H.

**Mechanism of the formation of methane and condensation products by the pyrolysis of ethane, ethylene, etc.** M. W. TRAVERS and T. J. P. PEARCE (J.S.C.I., 1934, 53, 321—336r).—The pyrolysis of equilibrium mixtures of  $C_2H_6$ ,  $C_2H_4$ , and  $H_2$  was investigated between 550° and 620°, and at pressures up to 6 atm., by heating measured quantities of the mixtures in sealed  $SiO_2$  tubes, and analysing the contents after definite periods.  $CH_4$  and condensate (aromatic compounds) are formed by processes which are quite distinct, although in both cases the rate of reaction depends on  $[C_2H_4]$ . The rate of formation of condensate  $\propto [C_2H_4]^2$ , the parent reaction resulting in the formation of a four-C complex which has a very short life. The rate of formation of  $CH_4 \propto [C_2H_4] \times ([H_2] + [C_2H_6] + [CH_4])$ . The mechanism of the process is discussed. The pyrolysis of pure  $C_2H_6$  results first in the primary decomp. into  $H_2$  and  $C_2H_4$ , with secondary formation of condensate and  $CH_4$  at rates which are more rapid than in the case of the equilibrium mixtures. It is suggested that there is here an energy chain mechanism superimposed on the mechanism by which these products are formed from equilibrium mixtures. The rate of the processes taking place in the equilibrium mixtures appears to be independent of the surface, but dependent on the surface to a marked extent in the case of pure  $C_2H_6$ .

**Thermal decomposition of methyl alcohol.** C. J. M. FLETCHER (Proc. Roy. Soc., 1934, A, 147, 119—128).—The influence of surface and initial pressure on this reaction has been investigated at 669°, and the temp. coeff. determined for initial pressures of 200 mm. over the temp. range 626—730°. The results can be expressed by  $\log_e 1/t^{1/2} = 30.8 - 68,000/RT$ . The reaction takes place in two stages,  $MeOH \rightarrow H_2 + CH_2O \rightarrow 2H_2 + CO$ , and is largely homogeneous. The first stage is mainly unimol. over the pressure range 10—400 mm., and determines the rate of reaction. The min. no. of energy terms which must be involved to account for the rate of reaction is 12. L. L. B.

**Thermal decomposition of methyl alcohol.** W. A. BONE (Chem. and Ind., 1934, 1006—1007).—A criticism (cf. preceding abstract). E. S. H.

**Thermal decomposition and oxidation of nickel carbonyl.** A. P. GARRATT and H. W. THOMPSON (J.C.S., 1934, 1822—1825).—The initial rate of decomp. of 16—65 mm. of  $Ni(CO)_4$  at 60—100°  $\propto [Ni(CO)_4]$ . CO retards the reaction, which has an activation energy of approx. 12,000 g.-cal. A mechanism similar to that of the photodecomp. is proposed



(A., 1934, 582). There exists for  $\text{Ni}(\text{CO})_4\text{-O}_2$  mixtures a crit. pressure limit,  $P$ , below which there is no pressure change and above which explosions occurs.  $P$  decreases markedly with rise of temp. from  $40^\circ$  to  $60^\circ$ . The data indicate a chain mechanism and deactivation at the walls.

J. G. A. G.

**Auto-ignition temperatures of aromatic ortho-compounds.** O. KRUBER and W. SCHADE (Brennstoff-Chem., 1934, 15, 404; cf. A., 1932, 1093).—The ignition temp. ( $T$ ) of aromatic compounds having substituents in the *o*-position are considerably < those of the corresponding *m*- and *p*-compounds; cf., e.g., *o*-xylene  $550^\circ$ , *m*- or *p*-xylene  $640^\circ$ ; *o*-cresol  $540^\circ$ , *m*- or *p*-cresol  $620^\circ$ ; 1:2- $\text{C}_{10}\text{H}_6\text{Me}_2$   $510^\circ$ , 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$   $525^\circ$ , 1:4-, 1:6-, 2:6-, or 2:7- $\text{C}_{10}\text{H}_6\text{Me}_2$   $600^\circ$ .  $T$  vals. were determined in Jentsch's apparatus.

A. B. M.

**Third-order ionic reaction without appreciable salt effect.** H. A. LIEBHAFSKY and A. MOHAMMAD (J. Physical Chem., 1934, 38, 857—866; cf. A., 1933, 1250).—Of two rate-determining steps in the reduction of  $\text{H}_2\text{O}_2$  by  $\text{I}^-$  in acid solution, one exhibits a normal salt effect, whilst another,  $\text{H}_2\text{O}_2 + \text{I}^- + \text{H}^+ = \text{H}_2\text{O} + \text{HOI}$ , is without any appreciable salt effect. The salts used were  $\text{NaClO}_4$  and  $\text{Ba}(\text{ClO}_4)_2$ , and the ionic strength was varied between 0.05 and 3.7.

F. L. U.

**Mechanism of the oxidation of hydrazo-compounds by iodine.** M. GONZE (Bull. Acad. roy. Belg., 1934, [v], 20, 789—808).—The reaction between *mm*-trifluorohydrazotoluene and  $\text{I}$  in 65 vol.-%  $\text{EtOH}$  is unimol. with respect to both the reactants and is practically independent of  $p_{\text{H}}$  between 2 and 5. Salts of strong acids do not influence the velocity of the reaction, but citrates and, more especially, acetates produce considerable acceleration. The mechanism involves a reaction between free  $\text{I}$  and  $\text{I}_3^-$ . The equilibrium const. of the system  $\text{KI-KI}_3\text{-I}_2$  is of the order of  $10^{-4}$ . It is not known whether the "free"  $\text{I}$  is at. or mol.

H. F. G.

**Esterification of the four isomeric 3-benzoyl-2-phenylcyclopropane-1-carboxylic acids in methyl, ethyl, and isopropyl alcohol in presence of hydrochloric acid.** Effect of structure on rate of esterification. F. SCHENCK (Z. physikal. Chem., 1934, 170, 309—316).—A relation has been observed between the velocity coeffs.,  $k$ , for a given alcohol, indicating that if the configuration of one of the acids is changed by rotating two of the substituents from one side of the plane of the ring to the other the net result on  $k$  is the product of the results produced by either rotation singly. For each isomeride ( $k$  in  $\text{MeOH}$ )/( $k$  in  $\text{Pr}^n\text{OH}$ ) = [ $k$  in  $\text{MeOH}$ ]/( $k$  in  $\text{EtOH}$ ) $^{n-2}$ .

R. C.

**Molecular structure and rate of reaction.** W. HÜCKEL (Ber., 1934, 67, [A], 129—138).—A lecture.

H. W.

**Rate of absorption of carbon dioxide. Effect of concentration and viscosity of caustic solutions.** L. B. HITCHCOCK (Ind. Eng. Chem., 1934, 26, 1158—1167).—On the two-film theory of absorption of a gas by a liquid the initial rate of absorption ( $dV/d\theta$ ) =  $k'(C_i + C_s)/f(z)$ , where  $C_i$  and  $C_s$  are concns. at the interface and in the main body of the liquid and

$f(z)$  is some function of the viscosity, in a given apparatus with given liquid velocity.  $C_i$  may be taken as approx. const. Steady initial rates of absorption of  $\text{CO}_2$  into solutions of  $\text{NaOH}$  and  $\text{KOH}$  at  $30^\circ$  were determined and viscosities (up to 7*N* for  $\text{NaOH}$  and to 14*N* for  $\text{KOH}$ ) measured by an Ostwald viscosimeter. Good agreement with the above equation was obtained by writing  $f(z)$  as  $e^{az}$ , where  $a=0.4164$  for  $\text{NaOH}$  and 0.3846 for  $\text{KOH}$ . These consts. apply only to the apparatus used. If absorption is continued the rate falls more rapidly than can be accounted for by decrease in  $[\text{NaOH}]$ , perhaps owing to rising viscosity.

C. I.

**Velocity of absorption of gases by liquids.**

**IV. [Determination of] absorption of carbon dioxide by potassium carbonate solutions by a bubbling method.** S. HATTA and A. BABA (Tech. Rep. Tôhoku, 1934, 11, 99—116).—See A., 1933, 233.

F. L. U.

**Rate of decomposition of strontium peroxide.** M. BLUMENTHAL (J. Chim. phys., 1934, 31, 489—497; cf. A., 1933, 351).—Curves representing the rate of decomp. of  $\text{SrO}_2$  at 1 atm. and at 1 mm. are similar, and above  $232^\circ$  and  $205^\circ$ , respectively, present a sharp max. This effect is due to an exothermic change, probably the formation of a second modification of  $\text{SrO}_2$  stable at the higher temp. The curves for specimens containing > 90% of  $\text{SrO}_2$ , and for pure  $\text{SrO}_2$  below the temp. named, do not exhibit a max. A formula is given to represent the velocity of decomp. under the last-named conditions.

F. L. U.

**Optical observations on the effect of ozone and air on metals.** L. TRONSTAD and T. HÖVERSTAD (Trans. Faraday Soc., 1934, 30, 1114—1127).—The phase retardation and ratio of absorption coeffs. have been measured, and the thickness has been calc., for films formed on  $\text{Ag}$ ,  $\text{Cu}$ ,  $\text{Zn}$ ,  $\text{Fe}$ , eutectoid steel, and austenitic stainless steel, in moist and dry 1.2% ozonised  $\text{O}_2$ , mainly at  $18\text{--}20^\circ$ . The rate of oxidation in moist is much > in dry  $\text{O}_2$ , and in the former no protective films are formed. With  $\text{Ag}$ ,  $\text{Fe}$ , and the steels in dry  $\text{O}_2$  a film of limiting thickness is formed, but with  $\text{Cu}$  and  $\text{Zn}$  the film allows diffusion of  $\text{O}_2$ , and no stationary state is reached. On heating  $\text{Ag}$  mirrors in air a sharp change in optical properties occurs at  $180^\circ$ , above which the decomp. of the oxide is more rapid than the oxidation, and at  $280^\circ$  a stationary state is reached (complete decomp.); on cooling, the film returns to the val. at room temp. by a different path. With  $\text{Zn}$  in dry and moist  $\text{O}_2$ , and in pure air, the film thickness increases linearly with the time; in pure air at the slow rate of  $5\text{--}6 \text{ \AA}$ . in 500 hr. It is suggested that the layer of protective pseudomorphic  $\text{ZnO}$  in contact with the metal is of const. thickness, and that the overlying layer of natural  $\text{ZnO}$  offers practically no resistance to diffusion.  $\text{Cu}$  and  $\text{Fe}$  in  $\text{I}$  vapour rapidly form thick films which are porous and cracked.

R. S. B.

**Corrosion phenomena. XVIII. Localisation of inhibiting action of surface-active substances in dissolution of metals in acids.** A. THIEL and C. KAYSER (Z. physikal. Chem., 1934, 170, 407—420; cf. A., 1931, 46).—Experiments on the reaction with acids of  $\text{Cd}$  and  $\text{Zn}$  electrodes connected to a  $\text{Pt}$  or  $\text{Cu}$



electrode in the same solution have shown that, contrary to Schunkert's findings (A., 1934, 37), the retarding action of adsorbed foreign substances on the dissolution in acids of metals reacting spontaneously with acids is due primarily to their hindering the evolution of gas by blocking the necessary local-element cathodes, and only in a minor degree to retardation of dissolution of the metal itself. R. C.

**Kinetics of acetylation of cellulose fibres.** IV. Acetylation of ramie swollen with acetic acid and the X-ray diagram of cellulose triacetate. I. SAKURADA and M. SHOJINO (J. Soc. Chem. Ind. Japan, 1934, 37, 599—603B).—The following vals. were found for the consts.  $k$  and  $m$  in the equation  $x=kt^m$  ( $x$ =mols. AcOH per 100 mols.  $C_6H_{10}O_5$ ) for the acetylation of ramie after various pretreatments: untreated 0.0576, 0.780; dried at 105°, 0.0129, 0.810; stored 12 days at room temp. in closed vessel with 30%  $H_2O$  (I), 8.318, 0.495; boiled with AcOH for 2 hr. (II), 12.59, 0.400; boiled with AcOH for 8 hr., 14.12, 0.391; boiled with  $C_6H_6$  for 8 hr., 0.1122, 0.693. The X-ray diagrams of the cellulose acetates (I) and (II) are nearly identical. A. G.

**Kinetics of penetration.** IX. Models of mature cells. S. E. KAMERLING and W. J. V. OSTERHOUT (J. Gen. Physiol., 1934, 18, 229—234; cf. A., 1934, 486).—A model consists of two aq. solutions  $A$  and  $C$  separated by a mixture of guaiacol and  $p$ -cresol shaken with KOH.  $C$  contains  $KHCO_3$  and  $CO_2$  is bubbled in. The  $[K^*]$  and vol. of  $C$  increase to const. vals. On decreasing the  $CO_2$  supply by 0.75 the  $[K^*]$  and vol. of  $C$  fell and rose subsequently. Replacing  $CO_2$  by air causes an abrupt fall in  $[K^*]$  and increased vol. The increase in vol. of  $C$  was prevented by addition of sucrose to  $A$ . By this means the vol. remained const. for > 2 weeks with a  $[K^*]$  in  $C$  of 3.6 times that in  $A$ . H. D.

**Influence of lead tetraethyl on the combination of hydrogen and oxygen.** H. G. TANNER (J. Amer. Chem. Soc., 1934, 56, 2250—2252).—Addition of  $PbEt_4$  increases the yield of  $H_2O_2$ . A reaction mechanism which is consistent with the anti-knock effect is proposed. E. S. H.

**Oxidation of sulphurous acid.** III. Catalysis by manganous sulphate. IV. Catalysis by a glass powder containing manganese and iron. R. C. HOATHER and C. F. GOODEVE (Trans. Faraday Soc., 1934, 30, 1149—1156, 1156—1161; cf. A., 1934, 1157).—III. 0.001—0.01N aq.  $SO_2$  is oxidised by aq.  $O_2$  in presence of  $0.3 \times 10^{-5}$  to  $8 \times 10^{-5}$ N- $MnSO_4$  at a const. rate until near completion of the reaction, which is of order 0 with respect to reactants, but of order 1.7 with respect to catalyst in spherical 150-c.c. vessels; temp. for most observations was 35°. In cylindrical vessels the order changes, owing probably to the influence of surface/vol. ratio on reaction chains. The reaction is mainly homogeneous, and is retarded by  $H_2SO_4$  (0—0.004N), the influence of which is correlated with  $[SO_3^{''}]$ , but the  $H_2SO_4$  produced in the reaction does not appear to exert a retarding influence. The dependence on  $[SO_3^{''}]$  was confirmed by the addition of NaOH. The heat of activation is 27,300 g.-cal.  $\pm 4\%$ .  $FeSO_4$  is 12 times as effective as

$MnSO_4$ , but  $10^{-4}$ M- $CuSO_4$  does not change the uncatalysed rate.

IV. Glass powder containing approx. 3% Fe and 5% Mn catalyses the oxidation in 150-c.c. spherical vessels with an approx. const. velocity, of order 0, cc the amount of glass, whereas glass free from Fe and Mn has no influence. In cylindrical vessels the order is 1 with respect to  $O_2$ . On addition of  $H_2SO_4$  and NaOH results similar to those in III are obtained. The heat of activation is < for  $MnSO_4$  catalysis. The reaction does not proceed by dissolution of Mn and Fe from the glass, except that for Fe glass dissolved Fe may have an effect towards the end of the reaction, and does not proceed at the surface of the glass, as the rate is independent of stirring, and continues the same if the solution is transferred to another vessel, leaving the glass. It is suggested that a rapid reaction between  $H_2SO_4$  and  $O_2$  occurs on the glass, producing a compound which acts as a homogeneous catalyst by a chain mechanism.

R. S. B.

**Kinetics and catalysis of the decomposition of calcium hydrogen carbonate in aqueous solution.** R. STUMPER (Chim. et Ind., 1934, 32, 1023—1037).—The effects of temp., pressure, and concn. of  $Ca(HCO_3)_2$  and  $CO_2$  on the equilibria involved are considered. The rate-controlling step in the decomp. of  $Ca(HCO_3)_2$  is  $2HCO_3' \rightleftharpoons CO_3^{''} + H_2CO_3$ , and by the decomp. of 0.005—0.02N- $Ca(HCO_3)_2$  with a current of air at 20°, the induction period,  $T$ , before pptn. commences is given by  $T[Ca(HCO_3)_2]^2 = \text{const.}$ , from which the reaction is of third order.  $T$  decreases with rise of temp. and is zero at 90°; the temp. coeff. of the velocity coeff.,  $k$ , is < 2 between 30° and 80° and a change of mechanism at > 80° is inferred.  $T$  is eliminated by the initial addition of sufficiently fine  $CaCO_3$ , and  $k$  is increased by increasing the wt. of added  $CaCO_3$ . Similar but less marked effects are produced by C and shavings of Fe, Cu, and Al, but Zn and Zn<sup>++</sup> diminish  $k$  and increase  $T$ . J. G. A. G.

**Effect of hydrogen-ion concentration on the decomposition of hypohalites.** R. M. CHAPIN (J. Amer. Chem. Soc., 1934, 56, 2211—2215).—OCI' is most stable at  $p_H$  13.1 (except in strongly acid solutions) and least at  $p_H$  6.7; OBr' is most stable at  $p_H$  13.4 and least at  $p_H$  7.3. The stability of OI' increases with increasing  $[OH']$  between  $p_H$  12.5 and 5N-KOH.

E. S. H.

**Catalytic decomposition of hydrogen peroxide by the iodine-iodide couple.** IV. Approach to the steady state. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1934, 56, 2369—2372; cf. A., 1932, 818, 1212).—The mechanism postulated by Abel (A., 1928, 1194) is capable of explaining the results obtained.

E. S. H.

**Effect of electrolytes in ionic reactions.** M. KILPATRICK (J. Amer. Chem. Soc., 1934, 56, 2326—2327).—The disagreement of the measurements of La Mer and Greenspan (A., 1934, 971) with the Brönsted theory is due to the fact that the results are not in the range of concn. to which this theory applies.

E. S. H.

**Catalysis of an interface reaction by adsorbed molecules.** B. TOPLEY and M. L. SMITH (J.C.S.,



1934, 1754—1755; cf. A., 1932, 26).—The rate (I) of the reaction  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$  is increased by the presence in the reaction interface of adsorbed HCl. Small partial pressures of  $\text{NH}_3$  and MeOH diminished (I), but  $\text{SO}_2$  had no effect.

J. G. A. G.

Heats of activation of the acetone-iodine reaction. G. F. SMITH (J.C.S., 1934, 1744—1750).—From velocity measurements at  $0^\circ$  and  $25^\circ$ , the energy of activation of the  $\text{COMe}_2$ -I reaction has been evaluated with respect to the following catalysts:  $\text{H}^+$  20,680, AcOH 20,010,  $\text{EtCO}_2\text{H}$  19,370,  $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$  and  $\text{CHCl}_2 \cdot \text{CO}_2\text{H}$  19,230, AcO' 22,800, and  $\text{EtCO}_2'$  22,910 g.-cal. Vals. of the probability factor,  $P$ , in the bimol. velocity equation  $k = Pze^{-E/RT}$  (cf. A., 1934, 971) range from 0.15 for  $\text{H}^+$  to  $4 \times 10^{-5}$  for  $\text{EtCO}_2\text{H}$ , and for acid catalysts (dissociation const.  $K_a$ ),  $P \sim K_a^{0.5}$  approx. This result is interpreted on the view that in a collision involving mols. of catalyst and reactant, in which the necessary energy conditions are satisfied, an essential condition for reaction is the simultaneous ionisation of the catalyst mol.

J. G. A. G.

Enzymic sucrose inversion in heavy water. E. W. R. STEACIE (Z. physikal. Chem., 1934, B, 27, 6—10; cf. A., 1934, 607).—The rate of inversion by  $\beta$ -*h*-fructosidase is a little < in ordinary  $\text{H}_2\text{O}$ .

R. C.

Kinetics of esterification. Reaction between acetic acid and methyl alcohol catalysed by hydrions. A. T. WILLIAMSON and C. N. HINSHLEWOOD (Trans. Faraday Soc., 1934, 30, 1145—1149).—The reaction between MeOH and AcOH in presence of HCl has been studied at  $0$ — $45^\circ$ , with results in agreement with Goldschmidt (cf. A., 1912, ii, 1154). The heat of activation is 10,200 g.-cal. Assuming binary collisions between AcOH and  $\text{MeOH}_2^+$  the efficiency of activating collisions is  $1.17 \times 10^{-5}$ , but if ternary collisions involving in addition the solvent MeOH mols. are necessary for reaction the efficiency is calc. to be  $0.78 \times 10^{-3}$ , allowing for the temp. coeff. of  $\eta_{\text{MeOH}}$ . The latter result may be contrasted with the efficiency  $1.5 \times 10^{-7}$  for catalysis by undissociated AcOH.

R. S. B.

Application of quantum mechanics to certain cases of homogeneous catalysis. I. A. E. STEARN (J. Gen. Physiol., 1934, 18, 171—191).—The configurative energies of the groups in the reaction  $:\text{C}:\text{N}^+ + \text{HOH} \rightarrow :\text{C}:\text{OH} + :\text{NH}$  are plotted for different configurations corresponding with degrees of reaction and the energies of activation deduced for catalysis with  $\text{OH}^-$  and  $\text{H}^+$  on the assumption that these ions alter the proportions of coulombic to vibrational energy; the vals. obtained are 14.5 and 18.6 kg.-cal. This would correspond with relative speeds of hydrolysis of 700:1; correcting this val. for the greater effective  $[\text{H}^+]$  than indicated by  $p_{\text{H}}$  a val. of 13:1 is deduced.

H. D.

Vegetable lecithin as an antioxidant. E. W. KOCHENDERFER and H. G. SMITH (Proc. Iowa Acad. Sci., 1932, 39, 169—170).—Two samples of soya-bean lecithin acted as weak antioxidants. CH. ABS. (e)

Catalysis by palladium the union of hydrogen and oxygen. New phenomenon of contact

catalysis. D. L. CHAPMAN and G. GREGORY (Proc. Roy. Soc., 1934, A, 147, 68—75).—Adsorbed  $\text{H}_2$  does not react with  $\text{O}_2$  at room temp., and can thus render the surface inoperative as a catalyst for the reaction. Kinetic measurements show that  $\text{H}_2$  is an inhibitor and  $\text{O}_2$  an accelerator of the reaction, in agreement with the above conclusion. The mechanism of the catalysis by Pd is mainly one of alternate oxidation of metal and reduction of the oxide.

L. L. B.

Activation of gases by metals. L. KAHLBERG, N. J. JOHNSON, and A. W. DOWNES (J. Amer. Chem. Soc., 1934, 56, 2218—2221).—A disagreeable odour observed when most metals are heated in  $\text{H}_2$ ,  $\text{N}_2$ , He, A,  $\text{CO}_2$ , or  $\text{O}_2$  has been traced to impurities acquired by contamination of the metal surfaces. The apparent ability of  $\text{H}_2$ , after having passed over heated metals, to unite with S at room temp. and to reduce  $\text{Fe}^{+++}$ ,  $\text{KMnO}_4$ , etc. is due to the formation of  $\text{H}_2\text{S}$  by reaction with S compounds adsorbed by the metals from the air. These reactions are not obtained after the  $\text{H}_2$  has passed for some time, but momentary exposure of the metal to the air at once produced the apparent "activation." A small fraction of the  $\text{H}_2$  released from cathodically hydrogenated Pd, Ni, Si, or C reduced S above  $65^\circ$ .

E. S. H.

Catalysts for the production of nitric acid by the oxidation of ammonia. L. MARMIER (Compt. rend., 1934, 199, 868—869).—By passing a mixture of  $\text{NH}_3$  and air over platinised porcelain at suitable temp., yields of 3.2—7 kg. of  $\text{HNO}_3$  can be obtained per g. of Pt present per 24 hr. Other metals catalyse the reaction in the following order of activity:  $\text{Fe} < \text{Sr} < \text{U} < \text{Mn} < \text{Ce} < \text{Mo} < \text{W} < \text{Cr}$ . Cr is almost as active as Pt. Ozonisation of the air leads to increased yields, but these do not warrant the energy consumption in the ozoniser.

J. W. S.

Effect of ferrous iron in solutions of citric acid of different hydrogen-ion concentration on the corrosion of iron in presence of a limited supply of air. J. M. BRYAN (Trans. Faraday Soc., 1934, 30, 1059—1062; cf. A., 1933, 1251).—At  $p_{\text{H}} < 5$ , added  $\text{Fe}^{II}$  facilitates the corrosion of steel in the presence of a limited supply of air. The vol. of  $\text{H}_2$  evolved is parallel with the corrosion, and  $\text{Fe}^{II}$  increases the vol. of  $\text{O}_2$  absorbed, particularly at  $p_{\text{H}} 4$ — $6$ , and of  $\text{H}_2$  depolarised.

J. G. A. G.

Catalytic oxidation of organic compounds in the vapour state. G. CHARLOT (Ann. Chim., 1934, [xi], 2, 415—490; cf. A., 1933, 680, 1019).—Each catalyst may have two sp. activities, one for complete oxidation to  $\text{CO}_2$  and one for partial oxidation to aldehydes, acids, etc. The influence of surface area, amount, concn., and method of prep. of the catalyst has been studied for the particular case of the oxidation of PhMe. 35 oxide catalysts have been examined, and also metallic Pd, several reduced metals, and mixed catalysts in the form of salts, such as Sn vanadate or tungstate, both of which are often particularly active, or of simple mixtures of oxides of which the activity obeys approx. the mixture rule. Partial oxidation is obtained with the oxide catalysts only, not with metallic catalysts. The activity of a catalyst varies with time, three



periods being noticeable. For 10—20 min. there is a high activity, then a long period from a few hr. to 4 or 5 days of a const. lower activity, and finally a period during which there is a gradual diminution to zero activity. The catalytic oxidation of CO, SO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub> has been studied and compared with that of org. vapours, but there is no simple relation between them. An apparatus for the separation of the products of partial oxidation is described.

M. S. B.

**Exchange reactions of hydrogen on metallic catalysts.** I. HORIUTI and M. POLANYI (Trans. Faraday Soc., 1934, 30, 1164—1172).—H<sup>1</sup> in C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> is not replaced by H<sup>2</sup> from H<sub>2</sub>O containing 2.7% H<sub>2</sub>O in presence of Pt-black or Ni catalysts at room temp., but exchange reactions are observable at 80°, the rate for C<sub>6</sub>H<sub>6</sub> being < that for C<sub>2</sub>H<sub>4</sub>. Exchange of H<sup>2</sup> between C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> containing H<sup>2</sup> is slower than exchange between H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub>, and the latter is 10<sup>5</sup> slower than the exchange between H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> on Ni; a similar ratio is probable for C<sub>2</sub>H<sub>4</sub>. It is inferred that exchange does not proceed by the mechanism C<sub>6</sub>H<sub>6</sub> ↔ PhK + HK, where K is the catalyst, and that hydrogenation or exchange proceeds by the chemisorption of H<sub>2</sub> and ethylenoid compound producing adsorbed H atoms and an opening of the double linking, the two halves of which unite with the catalyst, followed by union of adsorbed H and C. This gives replacement by elimination of H, or hydrogenation by the subsequent union of another adsorbed H with a second C. Hydrogenation is then bimol., whereas replacement is unimol., with respect to H, and hence the latter predominates at low pressures.

R. S. B.

**Reaction of carbon monoxide on molybdenum oxides.** H. M. SPENCER and J. L. JUSTICE (J. Amer. Chem. Soc., 1934, 56, 2301—2306).—MoO<sub>3</sub> is reduced very slowly by CO at 400°, probably to MoO<sub>2</sub>. At 560° the reduction of Mo by CO yields Mo<sub>2</sub>C, which catalyses the decomp. of CO. At 810° MoO<sub>2</sub> reacts with CO to form Mo<sub>2</sub>C according to the reversible equation 2MoO<sub>2</sub> + 6CO ⇌ Mo<sub>2</sub>C + 5CO<sub>2</sub>. The equilibrium const. of this reaction is 1.46.

E. S. H.

**Hydrogenation of benzene with nickel oxide [catalyst].**—See B., 1934, 1049.

**Catalytic action of soda in the reduction of carbon dioxide with charcoal.** H. EDENHOLM and T. WIDELL (IVA, 1934, 26—39; Chem. Zentr., 1934, ii, 1257).—0.7% of Na<sub>2</sub>CO<sub>3</sub> had no appreciable effect, whilst 2—3% lowered the reaction temp. by 150—200°. The dependence of the rate of CO<sub>2</sub> + C = 2CO on the CO<sub>2</sub> pressure and extent of C surface has been studied. The Na<sub>2</sub>CO<sub>3</sub> has no effect on diffusion processes.

H. J. E.

**Catalytic action of Japanese acid earth.** VI. Action on *cyclohexylamine* and its derivatives. VII. Relation between the constituents of the earth and its catalytic action. H. INOUE and K. ISHIMURA (Bull. Chem. Soc. Japan, 1934, 9, 423—430, 431—439).—VI. On heating *cyclohexylamine* (I) and its Me derivatives with Japanese acid earth at 350° and atm. pressure NH<sub>3</sub> is first eliminated and then *cyclohexene* (II) or the appropriate Me deriv-

ative. (II) undergoes isomeric change yielding methyl-*cyclopentane* (III). The earth promotes dehydrogenation; methyl-*cyclohexylamine* yields NH<sub>2</sub>Ph and carbazole, whilst Me derivatives of (II) give PhMe. 15—20% of the reaction products are polymerisation or condensation products. The yields of (III) and of polymerides are greatest from (I).

VII. When C<sub>10</sub>H<sub>8</sub> is heated with powdered Japanese earth in a sealed tube at 300° a quantity of a resinous substance, mainly ββ'-dinaphthyl (IV), is produced. The yield of (IV) was studied with earth which had been pretreated before use as the catalyst, and with essential constituents of the earth separately or in groups. Other similar catalysts were used and results are discussed. (IV) is produced when SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> coexist in the catalyst, the yield being uninfluenced by Fe(OH)<sub>3</sub> and Mg(OH)<sub>2</sub>, but considerably diminished by hydroxides of alkali or alkaline-earth metals.

W. R. A.

**Active oxides.** LXXX. Characterisation of active states of system magnesium oxide-ferric oxide by their activity in catalysing the decomposition of nitrous oxide. G. F. HÜTTIG, W. NOVÁK-SCHREIBER, and H. KITTEL (Z. physikal. Chem., 1934, 171, 83—92).—The magnetic susceptibility and catalytic activity, *A*, of equimol. mixtures of MgO and Fe<sub>2</sub>O<sub>3</sub> which have been heated at various temp., *T*, have been measured. With rise in *T*, *A* passes through a max. The high *A* of forms intermediate between the mixture MgO + Fe<sub>2</sub>O<sub>3</sub> and cryst. MgFe<sub>2</sub>O<sub>4</sub> depends on the presence in great no. of only a single species of active mol., the heat of activation of which for the N<sub>2</sub>O decomp. is 37,960 g.-cal. Variation in *A* is caused by variations, not in the quality, but in the no. of active points. The corners and edges of the cryst. phases have a higher *A* than the "active" amorphous intermediate stages.

R. C.

**Oxidising action of colloids.** III. Oxidising action of colloidal metals. Y. SHIBATA and K. YAMASAKI (J. Chem. Soc. Japan, 1934, 55, 693—698).—The oxidation rate of pyrogallol is accelerated by colloidal Pt, but not by colloidal Au or Ag.

CH. ABS. (e)

**Concentration of heavy water.** A. I. BRODSKI, V. A. ALEXANDROVITSCH, M. M. SLUTZKAJA, and M. K. SCHELUKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 615—619).—A process of electrolysis using Fe electrodes with 3—4% KOH or Pb or Pt electrodes with 2—4% H<sub>2</sub>SO<sub>4</sub> gave approx. a 5—6-fold concn. of H<sub>2</sub>O for a 10-fold vol. reduction.

H. J. E.

**Concentration of deuterium in some industrial waters.** M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1934, 9, 457—459).—Samples of H<sub>2</sub>O from a commercial electrolytic cell (I) (1 year), Cr-plating bath (II) (4 years), Pb accumulators (III) (9 years), and Edison batteries (IV) (6—9 months) were purified and their *d* determined by the buoyancy balance method. The increases in *d*, due to H<sup>2</sup> enrichment occurring throughout the period given in parentheses, are (p.p.m.) (I), 28; (II), 7; (III), 0—3; (IV), 27—28. It is uncertain whether the increase for (IV) arises from increased H<sup>2</sup> content or from impurities retained in H<sub>2</sub>O.

W. R. A.



**Potentiometric and conductometric studies.**  
**I. Potentiometric.** J. PIEPER (Z. Elektrochem., 1934, 40, 793—805).—A study of the Sb electrode in acid-alkali, oxidation-reduction, and pptn. titrations has been made. The val. of Sb deposited on Pt depends on the conditions of prep.; such electrodes are not easily reproducible, but a correction may be applied. The use of the triodometer for potentiometric titrations has been studied; the influence of temp. and other variables is considered. E. S. H.

**Electrometallurgy of aluminium.** W. D. TREADWELL and L. TEREBESI (Z. Elektrochem., 1934, 40, 744).—A reply to criticism (cf. A., 1934, 1078). E. S. H.

**Cathodic behaviour of organic copper salts. Study of the electrolysis as a function of time.** G. KRAVTSOFF (Compt. rend., 1934, 199, 1029—1031; cf. A., 1933, 913).—From the change in  $p_H$  and the Cu deposited during the electrolysis of  $(\text{HCO}_2)_2\text{Cu}$ ,  $\text{Cu}(\text{OAc})_2$ , and  $\text{CuSO}_4$  for periods of 15 min. to 24 hr. and at c.d. of 10—500 milliamp. per sq. dm., it is shown that the  $\text{Cu}_2\text{O}$  content is the greater the shorter is the period of electrolysis, and the longer the electrolysis the lower is the  $p_H$ . It is suggested that  $\text{Cu}^{++}$  is initially reduced to  $\text{Cu}_2^{+}$ , but that the latter hydrolyses to  $\text{Cu}_2\text{O}$ , which deposits at the cathode, and the acid, the increase in acidity favouring the discharge of  $\text{Cu}^{++}$ . J. W. S.

**Evolution of  $\text{CO}_2$  in the a.-c. electrolysis of sodium carbonate and hydrogen carbonate solutions and the discharge potentials of carbonate and hydrogen carbonate ions.** J. W. SHIPLEY (Canad. J. Res., 1934, 11, 539—546).—No  $\text{CO}_2$  is evolved in the a.-c. electrolysis of aq.  $\text{Na}_2\text{CO}_3$  at voltages up to 110, even when arcing occurs. With aq.  $\text{NaHCO}_3$  and Pt electrodes  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{CO}_2$  are evolved freely until  $\text{Na}_2\text{CO}_3$  only is left, when evolution of  $\text{CO}_2$  ceases. In the a.-c. electrolysis of aq.  $\text{NaHCO}_3$  and aq. Na salts of aliphatic acids, finely-divided Pt is deposited on the electrodes and inhibits the evolution of gases, probably due to recombination, but does not affect current flow. The decomp. potential of aq.  $\text{NaHCO}_3$  for evolution of  $\text{CO}_2$  on smooth Pt with d.c. is 2.2 volts, and of aq.  $\text{Na}_2\text{CO}_3$  3.5 volts. The anodic discharge potential of  $\text{HCO}_3^-$  is -1.45 to -1.50 volt and of  $\text{CO}_2^{--}$  -1.90 to -1.95 volt. Evolution of  $\text{CO}_2$  does not cause polarisation. M. S. B.

**Electro-deposition of zinc-cadmium alloys from alkaline cyanide solutions.**—See B., 1934, 1107.

**Effect of oxidising agents on nickel solutions.**  
**I. Hydrogen peroxide and nickel nitrate.** A. W. HOTHERSALL and R. A. F. HAMMOND (Trans. Faraday Soc., 1934, 30, 1079—1094).—With solutions buffered with  $\text{H}_3\text{BO}_3$  or  $(\text{NH}_4)_2\text{SO}_4$ , the cathode efficiency decreased linearly with increasing concn. of added  $\text{Ni}(\text{NO}_3)_2$  and  $\text{H}_2\text{O}_2$ ; the effect increased slightly as the  $p_H$  was raised from 2.7 to 5.9. The primary process is depolarisation of H;  $\text{NO}_3^-$  is reduced to  $\text{NH}_3$ , and the effects produced are dependent on the oxidising powers of  $\text{NO}_3^-$  and  $\text{H}_2\text{O}_2$ . With increasing  $[\text{NO}_3^-]$  and  $[\text{H}_2\text{O}_2]$ , the quantity of gaseous  $\text{H}_2$  evolved at the cathode gradually fell to

zero and no gas was discharged over a concn. range. At still higher  $[\text{NO}_3^-]$  and  $[\text{H}_2\text{O}_2]$ , coincident with a sharp rise of cathode potential, evolution of gas recommenced, except with  $(\text{NH}_4)_2\text{SO}_4$  solutions containing  $\text{NO}_3^-$ . Addition of  $\text{NO}_3^-$  and  $\text{H}_2\text{O}_2$  increased the hardness, stress, and brightness of the Ni deposits, which tended to crack and become exfoliated. This is attributed to increased pptn. of colloidal basic matter with rising rate of  $\text{H}^+$  discharge, i.e., diminishing cathode efficiency. The prevention of pitting by  $\text{H}_2\text{O}_2$  and  $\text{NO}_3^-$  is parallel with their effects in inhibiting  $\text{H}_2$  evolution from pure solutions;  $\text{H}_2\text{O}_2$  also prevents pitting in solutions containing impurities (II) responsible for pitting by oxidising and pptng. Fe compounds on which (II) are adsorbed. J. G. A. G.

**Influence of temperature on the products of electrolysis of acetate solutions.** J. ROBERTSON (Trans. Faraday Soc., 1934, 30, 1007—1017).—In the electrolysis of KOAc in anhyd. AcOH, the ratio  $\text{C}_2\text{H}_6 : \text{H}_2$  is approx. 0.95 : 1 and is little affected by electrode material or change of temp., but small quantities of  $\text{H}_2\text{O}$  decrease the yield of  $\text{C}_2\text{H}_6$  and increase the oxidation, whilst the products are affected by the anode material. Electrolysis of aq. KOAc leads to  $\text{C}_2\text{H}_6$  formation (I),  $\text{O}_2$  formation (II), and complete oxidation (III). (I) predominates at low temp., but diminishes with rise of temp. as (III) increases to a max., after which (II) increases as (III) decreases and (I) tends to zero. (I) with a Au anode is < with bright Pt, but in all cases (I) increases with rise of c.d. and increasing [KOAc]. The results are consistent with the discharge theory of the reaction. J. G. A. G.

**Mechanism of Kolbe's reaction. I. Electrolysis of free acetic acid.** M. MATSUI and K. KIZAKI (Mem. Coll. Sci. Kyoto, 1933, A, 16, 297—307).—The reaction has been investigated with 5—60% aq. AcOH at 15—45°. At 15° and c.d. 0.071 amp. per sq. cm. the proportion of  $\text{C}_2\text{H}_6$  in the evolved gas is max. with 30% AcOH and the  $\text{C}_2\text{H}_6 : \text{H}_2$  vol. ratio is 0.75 : 1, but the proportion of  $\text{C}_2\text{H}_6$  decreases with rise of temp. and increases with rise of c.d. Evolution of  $\text{C}_2\text{H}_6$  is greatly diminished by small quantities of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , and  $\text{HCO}_2\text{H}$ , but is not affected by  $\text{H}_3\text{BO}_3$ , which does not change the dissociation of AcOH. Strong electrolytes also diminish  $\text{C}_2\text{H}_6$  evolution owing to decreased concn. of discharged  $\text{AcO}^-$ . The results discriminate against the "simple oxidation theory" in favour of the "discharge theory." J. G. A. G.

**Mechanism of the electrochemical chlorination of benzene.** W. JEUNEHOMME (Compt. rend., 1934, 199, 1027—1029).—On electrolysis of a MeOH solution of HCl, containing  $\text{C}_6\text{H}_6$ , the latter is chlorinated by two simultaneous processes, a surface reaction with Cl atoms at the electrode, and a homogeneous reaction with  $\text{Cl}_2$  in solution. The efficiency of the current in producing PhCl can reach 85%. Traces of  $\text{C}_6\text{H}_4\text{Cl}_2$ ,  $\text{C}_6\text{H}_6\text{Cl}_6$ , and chlorinated phenols are also produced. J. W. S.

**Chemical action in the glow discharge. XIII. Chain reactions in the oxidation of hydrogen in the positive column.** A. K. BREWER and P. D.



KUECK (J. Physical Chem., 1934, **38**, 889—900; cf. A., 1930, 1533).—The rate of oxidation of  $H_2$  in the positive column increases with both current and voltage, with rise of temp., and linearly with the addition of A up to 50%, whilst the proximity of glass surfaces retards it. The results are explained by the presence in the positive column of reaction chains of the cluster type. F. L. U.

**Electrolytic oxidation. V. Formation of hydrogen peroxide by electrolysis with a glow-discharge anode.** S. GLASSTONE and A. HICKLING (J.C.S., 1934, 1772—1773).—With 0.05—0.1N acid and salt solutions, and a glow-discharge anode, yields of  $H_2O_2$  50—100% of those calc. from Faraday's laws were obtained.  $H_2O_2$  persists in the solution only if formed out of contact with the solid electrode. With a glow-discharge cathode,  $H_2O_2$  was not detected. The results accord with the view that  $H_2O_2$  is formed by the union of discharged OH ions (cf. A., 1934, 258). J. G. A. G.

**Decomposition of sulphur dioxide by electric discharge.** S. S. JOSHI and K. K. SHARMA (J. Chim. phys., 1934, **31**, 511—516).—The decomp. of  $SO_2$  by a silent electric discharge has been followed by measuring the change of pressure occurring. The reaction becomes slower with time and tends towards an equilibrium. Under the conditions used (a.c. 6000—12,000 volts, 50 cycles) no decomp. is observed at pressures  $> 200$  mm. The final mixture contains  $SO_3$ ,  $O_2$ , about 10% of  $SO_2$ , and two solid products not identified. F. L. U.

**Dissociation products of carbon monoxide formed by primary electron impact.** W. W. LOZIER (Physical Rev., 1933, [ii], **43**, 776; cf. A., 1934, 1159).— $O^-$  and  $C^+$  ions both appear as primary products of electron impact.  $O^-$  ions first appear at  $9.5 \pm 0.1$  volts electron energy, and again at  $20.9 \pm 0.1$  volts electron energy accompanied by an equal no. of  $C^+$  ions. At  $22.8 \pm 0.1$  volts electron energy the production of  $C^+$  ions markedly increases. L. S. T.

**Chemical change of carbon disulphide under electrodeless discharge.** M. EMI (Bull. Chem. Soc. Japan, 1934, **9**, 442—446).—Experimental details are given. When  $CS_2$  at 0.08 mm. was subjected to electrodeless discharge the pressure fell to 0.075 mm. and dark solid deposits sol. in  $CS_2$  were formed on the condenser. These are polymerised forms of CS and  $C_3S_2$ . W. R. A.

**Heterogeneous chemical reactions under the silent electric discharge. X. Preparation of colloidal solutions by silent electric discharge.** S. MIYAMOTO (J. Chem. Soc. Japan, 1934, **55**, 611—617; cf. A., 1934, 739).—The prep. of Au sols from aq.  $HAuCl_4$  and aq. Au hydroxide suspensions, Ag sols from aq.  $AgNO_3$ , or aq. suspensions of  $Ag_2O$ ,  $AgCO_3$ , or  $AgCN$ , Pt sols from  $H_2PtCl_6$ , and Pd sols from  $PdCl_2$  dissolved in dil. HCl is described. Ag sols in  $Bu^iOH$  or amyl alcohol are prepared similarly. CH. ABS. (e)

**Dissociation of nitrous oxide in the high-frequency glow discharge.** E. A. STEWARDSON (Trans. Faraday Soc., 1934, **30**, 1018—1027).—By means of the diaphragm gauge described, the rate of

decomp. at const. vol. of  $< 3$  mm. of  $N_2O$  is shown to be unimol. with respect to  $N_2O$  in sufficiently intense fields, but in weak fields the initial rate is approx. independent of the initial pressure (cf. A., 1926, 619), although the decomp. as a whole approximates to a first-order law of which the coeff. depends on the initial pressure. J. G. A. G.

**Photolysis of water and the action of light in electrodes.** R. AUDUBERT (J. Phys. Radium, 1934, [vii], **5**, 567).—Errata (see A., 1934, 1315).

**Inability of X-rays to decompose water.** H. FRICKE and E. R. BROWNSCOMBE (Physical Rev., 1933, [ii], **44**, 240).—Irradiation with dosages up to 150 kiloroentgen showed that pure air-free  $H_2O$  is not decomposed by X-rays. L. S. T.

**Photochemical reaction of oxygen with hydrogen in the Schumann region.** H. NEUJMIN and B. POPOV (Z. physikal. Chem., 1934, **B**, **27**, 15—27).—The reaction with  $H_2$  of  $O_2$  optically dissociated by light of  $\lambda$  1350—1750 Å. into O atoms in the normal state and a metastable state ( $^1D$ ) has been examined. The reaction is homogeneous and the quantum yield  $\sim 0.1$ , and the metastable O atoms are much more reactive than the normal O atoms. Probably the processes involved are  $O^+ + H_2 \rightarrow OH + H$ ,  $OH + H_2 \rightarrow H_2O + H$ , and  $OH + OH + M \rightarrow H_2O_2 + M$  ( $M =$  wall). Preliminary measurements have been made on the reaction of O atoms with CO. R. C.

**Comparison of the photosensitised reaction of hydrogen and oxygen, and deuterium and oxygen.** M. G. EVANS (J. Chem. Physics, 1934, **2**, 726—732).—There is very little difference between the rates of reaction of  $H_2$  and of  $D_2$  with  $O_2$  when illuminated by ultra-violet light in presence of Hg vapour. The temp. coeffs. between  $30^\circ$  and  $50^\circ$  are also equal within the experimental error. Possible mechanisms are discussed. F. L. U.

**Induction period of the photochemical reaction between hydrogen and chlorine.** J. G. A. GRIFFITHS and R. G. W. NORRISH (Proc. Roy. Soc., 1934, **A**, **147**, 140—151).—In the induction period of the photochemical  $H_2-Cl_2$  reaction, due to  $NCl_3$  produced by interaction of dry  $NH_3$  and  $Cl_2$ ,  $NCl_3$  is decomposed photosensitively by the  $Cl_2$  in a zero-order reaction. If  $H_2O$  is absent,  $NH_4Cl$  does not cause an induction period, as it does not react with  $Cl_2$ . The quantum efficiency of the decomp. is given by  $\gamma = 2.5 + 1/(0.0038P_{Cl_2} + 0.0009P_{H_2})$ . Hence  $H_2$  behaves like an inert gas in shortening the chain length of the photosensitised decomp. of  $NCl_3$ . In the inhibition period, which lasts until all the  $NCl_3$  is decomposed, the yield of HCl is  $< 0.2$  mol. per quantum absorbed. L. L. B.

**Inert gas effects in the photosynthesis of hydrogen bromide.** M. RITCHIE (Proc. Roy. Soc., 1934, **A**, **146**, 828—848).—The rate of photochemical formation of HBr at  $200^\circ$  in presence of various foreign gases has been investigated from two points of view: (a) the removal of Br atoms from the gas phase by diffusion to the wall of the reaction vessel, and (b) the removal of Br atoms by a recombination process involving a third atom as stabiliser. In (a) the addition of foreign gas increases the rate of reaction in the order



$\text{CCl}_4 > \text{CO}_2 > \text{N}_2 > \text{A} > \text{H}_2$  and He. In (b) the rate of reaction is decreased by facilitating the recombination of Br atoms. The series is given by  $\text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{A} > \text{He} > \text{H}_2$ . L. L. B.

**Photolysis of dry ozone at  $\lambda$  208, 254, and 280 m $\mu$ .** I. Quantum yields. L. J. HEIDT and G. S. FORBES (J. Amer. Chem. Soc., 1934, 56, 2365—2368).—The quantum yield,  $\phi$ , is as high as 6.7, indicating an energy chain mechanism. The temp. coeff. of  $\phi$  is 1.2 per 10°. No direct dependence of  $\phi$  on wave-length was observed. E. S. H.

**Photochemistry of mixtures of chlorine and ozone.** A. C. BYRNS and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 2245—2250; cf. A., 1934, 369).—When mixtures of  $\text{Cl}_2$  and  $\text{O}_3$  are illuminated with blue light,  $\text{ClO}_2$  and  $\text{Cl}_2\text{O}_7$  are formed in appreciable quantities. The  $\text{Cl}_2\text{O}_7$  is relatively inert, but the  $\text{ClO}_2$  undergoes a thermal decomp., a  $\text{Cl}_2$ -sensitised photo-decomp., and a reaction with  $\text{O}_3$ . One product of the last reaction is  $\text{Cl}_2\text{O}_7$ . One of the primary products of the thermal decomp. is  $\text{ClO}_2$ . E. S. H.

**Kinetic expression for rate of the photosensitised decomposition of ammonia and deutero-ammonia.** M. G. EVANS and H. S. TAYLOR (J. Chem. Physics, 1934, 2, 732—734; cf. A., 1934, 1078).—The cause of the deviation of the experimental data from the kinetic expression used by Melville (A., 1933, 35) is considered to be due partly to the assumption, made in deriving the expression, that every quenching collision leads to decomp. Further, in addition to a difference between  $\text{NH}_3$  and  $\text{ND}_3$  in quenching excited Hg, there is a difference in the probabilities of decomp. of the  $\text{NH}_3$  and  $\text{ND}_3$  mols. which have received energy from the Hg. An empirical expression in harmony with the data is given. F. L. U.

**Photochemical oxidation of phosphine above the upper explosion limit.** H. W. MELVILLE (J. Chem. Physics, 1934, 2, 739—752; cf. A., 1933, 678).—Speeds of the direct and of the Hg-sensitised photo-reaction have been measured. The former is given by  $-d[\text{PH}_3]/dt = k_1[\text{PH}_3]^2/[\text{O}_2]^2$ , and the latter by  $-d[\text{PH}_3]/dt = k_2[\text{PH}_3]/[\text{O}_2]^2I$ . The reactions are of the chain type, and the results are consistent only with the destruction of the chain-carrier in a ternary collision either with  $2\text{O}_2$  or with  $\text{O}_2 + \text{N}_2$  (or A). The carrier is probably an O atom. The observed displacement of the upper limit to higher pressures by illumination is not predicted by theory. F. L. U.

**Combined action of radiation and a catalyst.** I. Influence of ultra-violet light on the activity of the catalyst in the catalysis of hydrogen peroxide in aqueous solution. L. V. PISAR-SHEVSKI, R. K. KORABELNIK, and E. S. RINSKAJA (Bull. Acad. Sci. U.R.S.S., 1934, 7, 931—951).—The activity (I) of  $\text{PbO}_2$  and Pt is increased by previous exposure to ultra-violet light. Irradiation during the  $\text{H}_2\text{O}_2$  catalysis increases the (I) of graphite, charcoal,  $\text{PbO}_2$ , and Pt, but may produce a decrease in the latter case. The results are in agreement with the theory that electrons are transferred from  $\text{H}_2\text{O}_2$  to mols. adsorbed on inactive regions to those at the active centres. R. S.

**Spectra and photochemical decomposition of metallic carbonyls. II. Photochemical data.** A. P. GARRATT and H. W. THOMPSON (J.C.S., 1934, 1817—1822).—The absence of both pressure change and deposition of Ni when  $\text{Ni}(\text{CO})_4$  vapour is irradiated with  $\lambda$  366—301 m $\mu$  is attributed to the rapid recombination  $\text{CO} + \text{Ni}(\text{CO})_3 \rightarrow \text{Ni}(\text{CO})_4$  (cf. A., 1934, 582) and the inferred relation between the energy levels of  $\text{Ni}(\text{CO})_4$ . Consistent with the absorption spectrum, photo-decomp. occurs in solution only with  $\lambda < 400$  m $\mu$ . In  $\text{CCl}_4$ , the quantum efficiency,  $\gamma$ , is 2.2 and increases as  $\lambda$  decreases. Smaller vals. of  $\gamma$  are found in  $\text{C}_6\text{H}_{14}$  and cyclohexane. The deviation of  $\gamma$  from the val. 4 required by the mechanism previously advanced (*ibid.*) is discussed. J. G. A. G.

**Optimum composition of uranyl oxalate solutions for actinometry.** G. S. FORBES and L. J. HEIDT (J. Amer. Chem. Soc., 1934, 56, 2363—2365).—When a solution containing 0.01M- $\text{UO}_2\text{SO}_4$  and 0.05M- $\text{H}_2\text{C}_2\text{O}_4$  is diluted 10-fold, the quantum yields,  $\phi$ , at  $\lambda$  313, 280, 254, and 208 m $\mu$  are unchanged (within 3%). Advantages of the more dil. solution at the shorter wave-lengths are indicated. By substituting  $\text{UO}_2\text{C}_2\text{O}_4$  for  $\text{UO}_2\text{SO}_4$  purification is simplified and  $\phi$  remains unchanged.  $\phi$  also remains unchanged (except at 208 m $\mu$ ) in a solution containing 0.005M- $\text{UO}_2\text{C}_2\text{O}_4$  and 0.0025M- $\text{H}_2\text{C}_2\text{O}_4$ . E. S. H.

**Higher order reversals in the solarisation region.** L. T. DEVORE and W. J. SAYLOR (J. Opt. Soc. Amer., 1934, 24, 303—304).—Experiments have been made to determine the characteristics of higher order reversals in a photographic emulsion on prolonged exposure. The H. and D. curves show a second max. and the commencement of a second downward slope. The slopes of the original and second upward straight-line portions are identical, but the second max. is much  $<$  the first. Colour changes are also observed in the images. J. L.

**Action of various elements and compounds on photographic plate.** A. AOYAMA, T. FUKUROI, and I. TAKAHASHI (Sci. Rep. Tôhoku, 1934, 23, 384—404).—The effect of metals and other substances on photographic plates in the dark is attributed to the formation of activated gases in the vicinity of the specimen, due to desorption or to reflexion from active centres, and the action of these activated mols. on the plate. J. W. S.

**Ultra-short-time effect and its interpretation.** A. NARATH (Z. wiss. Phot., 1934, 33, 145—150, 153—166).—The failure of the reciprocity law with ultra-short exposures is explained as a surface effect, dependent on the predominant colour-sensitivity of the surface layers of an emulsion. Using known double-layer emulsions, one having a yellow- and the other a blue-sensitive top layer, the results are in agreement with theoretical expectations. For the usual homogeneous emulsions the effect is found to be dependent on development time; the dispersion effects of development are examined by means of the Kerr electro-optical effect. Four different emulsions show the different types of effect obtainable. (Cf. Küster and Schmidt, Wiss. Veröff. Agfa, 2, 94.)

J. L.



**Photo-bromination of acetylene.** J. E. BOOHER and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 2288—2294).—The reaction, forming  $C_2H_2Br_2$ , has been studied kinetically at  $150^\circ$ . Measurements of the quantum yield indicate a chain reaction with a chain length of approx. 500 at  $15^\circ$ , increasing to about 3000 at  $20^\circ$ , independently of wave-length. Equations representing the rate laws at high and low concns. of  $C_2H_2$  have been derived and are supported by a mechanism involving  $Br$ ,  $Br_3$ ,  $C_2H_2Br_3$ , and  $C_2H_2Br$  as intermediates. The influence of temp. is very small. The calc. heat of activation is about  $-1500$  g.-cal.

E. S. H.

**Chemical action of light on di-iodo-derivatives of hydrocarbons: di-iodoethanes, di-iodomethane.** G. EMSCHWILLER (Compt. rend., 1934, 199, 854—856).—In its mode of photochemical decomp.,  $CHMeI_2$  resembles  $CH_2I_2$  in the affinity shown between the H and I atoms, instead of between the I atoms, as in  $(CH_2I)_2$ .  $CHI_3$  is only very slowly decomposed in solution in the absence of  $O_2$ , and this with liberation of HI, again showing affinity between the H and I atoms.

J. W. S.

**Reactions involving free alkyl groups. I. Photo-reaction of methane, chlorine, and oxygen. II. Photo-oxidation of gaseous ethyl iodide.** L. T. JONES and J. R. BATES (J. Amer. Chem. Soc., 1934, 56, 2282—2284, 2285—2287).—I. The photochemical reaction between  $CH_4$  and  $Cl_2$  accords with Thon's equation for the inhibiting effect of  $O_2$  and takes place through a Nernst chain mechanism. The chain carrier is probably the Me group.

II. After illumination for a long period,  $EtI$  decomposes to an uncondensable gas, probably  $C_2H_4$  and  $C_2H_6$ . Oxidation is rapid, giving  $MeCHO$  and  $EtOH$ , at a rate which increases to a max. with increasing  $O_2$  content and then falls asymptotically. A mechanism involving the intermediate formation of  $Et_2O_2$  is proposed.

E. S. H.

**Quantum yield in the photo-decomposition of liquid ethyl iodide at 3130, 2654, and 2537 Å.** B. M. NORTON (J. Amer. Chem. Soc., 1934, 56, 2294—2297).—Using a modified technique the quantum yield at  $20^\circ$  is 0.315 at 3130 Å., 0.38 at 2654 Å., and 0.41 at 2537 Å.

E. S. H.

**Free radicals and atoms in primary photochemical processes. Photo-dissociation of aliphatic ketones and aldehydes.** T. G. PEARSON (J.C.S., 1934, 1718—1722).—Free alkyl radicals have been detected, by the action on Sb, Te, and Pb mirrors, in the primary products of the photolysis of the vapours of  $COMe_2$ ,  $COMeEt$ , and  $COEt_2$ , but not in the case of  $COMeBu$ ,  $MeCHO$ , and  $EtCHO$ . These results are in complete accord with the mechanism proposed by Norrish, Kirkbride, and Appleyard (A., 1931, 1138; 1934, 852) for the photolysis of aliphatic aldehydes and ketones. Under the conditions described, the half-life period of the Me radicals from  $COMe_2$  was  $5.3 \times 10^{-3}$  sec., whilst the radicals from  $COEt_2$  had a shorter period.

J. G. A. G.

**Transformation of formic acid by irradiation of its aqueous solution with X-rays.** H. FRICKE and E. J. HART (J. Chem. Physics, 1934, 2, 824; cf.

A., 1933, 793).—The mode of decomp. of aq.  $HCO_2H$  by X-rays depends on the concn. and on the  $pH$ . Results so far obtained indicate that the neutral mol. gives  $H_2 + CO_2$ , and the ionised form  $H_2 + H_2C_2O_4$ .

F. L. U.

**Photo-isomerisation of o-nitrobenzaldehydes. I. Photochemical results. II. Mathematical treatment.** P. A. LEIGHTON and F. A. LUCY (J. Chem. Physics, 1934, 2, 756—759, 760—766).—I. The quantum yield in the photochemical conversion of  $o\text{-NO}_2 \cdot C_6H_4 \cdot CHO$  and of  $2:4\text{-C}_6H_3(NO_2)_2 \cdot CHO$  into the corresponding NO-acids either in the solid state or dissolved in  $COMe_2$  or ligroin is 0.5. For the  $2:4:6$ -trinitroaldehyde it is higher on account of the effects of a  $NO_2$ -group on both sides of the aldehyde.

II. The probable course of the reaction is discussed mathematically.

F. L. U.

**Possibility of separating  $D_2O$  from  $H_2O$  by fractional freezing.** G. BRUNI (Atti R. Accad. Lincei, 1934, [vi], 20, 73—75).—After 9 fractionations, in which 4000 litres of ordinary purified  $H_2O$  were reduced to 280 c.c., no separation of  $H_2^2O$  from  $H_2O$  was obtained.

O. J. W.

**Content of deuterium in water of crystallisation.** K. OKABE, M. HARADA, and T. TITANI (Bull. Chem. Soc. Japan, 1934, 9, 460—461).—20 litres of tap- $H_2O$  were saturated with anhyd.  $Na_2SO_4$  and the solution was quickly cooled.  $Na_2SO_4 \cdot 10H_2O$  crystallised and was separated from the mother-liquor ( $R_1$ ), and converted by heating into  $Na_2SO_4$  and the remaining clear solution ( $C_1$ ) was filtered off. The process was repeated with  $R_1$  and  $C_1$  eight times, each time retaining only the fractions corresponding with  $R_1$  and  $C_1$ . The final fractions  $R_8$  and  $C_8$  were purified and their densities compared with normal  $H_2O$  were 2 p.p.m. greater. Similar work has been done on  $Na_2CO_3$ . With such salts at low  $[H^2]$  no isotopic fractionation occurs.

W. R. A.

**Production of large single crystals of ice.** J. M. ADAMS and W. LEWIS (Rev. Sci. Instr., 1934, [ii], 5, 400—402).—One face of a columnar fragment of commercial ice is frozen to the bottom of a metal can kept at  $-10^\circ$ , and the opposite face allowed to dip into previously boiled distilled  $H_2O$ .

C. W. G.

**Additive compounds of alkali halides and organic bases.** M. RAGNO and S. FRASTI (Gazzetta, 1934, 64, 746—748).—By mixing saturated solutions of  $(CH_2)_6N_4$  and alkali halide the compounds  $MX \cdot 4H_2O \cdot (CH_2)_6N_4$  have been obtained, where  $MX = LiBr$ ,  $NaI$ , and  $NaBr$ , respectively. No compounds were obtained with  $NaCl$ ,  $LiCl$ ,  $KBr$ ,  $KCl$ , and  $KI$ .

O. J. W.

**Decomposition of sodium carbonate.** E. PRESTON and W. E. S. TURNER (J. Soc. Glass Tech., 1934, 18, 182—193r).—On heating in air  $Na_2CO_3$  shows appreciable decomp. with formation of  $NaOH$  at  $800^\circ$ , which is lower than the temp., viz.,  $980^\circ$ , at which a dissociation pressure can be observed in vac. (A., 1931, 800). A slight decomp. may even be detected on heating for 1 day in air at  $400^\circ$ . The reaction appears to be due to atm.  $H_2O$  and, by heating in a current of  $N_2$  containing  $H_2O$  vapour, it has been shown to



depend on the partial pressure of the latter. In the prep. of pure  $\text{Na}_2\text{CO}_3$  for analytical purposes it is not advisable to heat above  $400^\circ$ . M. S. B.

**Reactivity of sodium amide.** A. PERRET and R. PERRON (Compt. rend., 1934, 199, 955—957).—The following reactions were observed:  $3\text{NaNH}_2 + \text{NaN}(\text{CN})_2 \rightarrow 2\text{Na}_2\text{CN}_2 + 2\text{NH}_3$ , above  $150\text{--}160^\circ$ ;  $\text{COCl}_2 + 3\text{NaNH}_2 \rightarrow \text{NaNCN} + 2\text{NaCl} + 2\text{NH}_3$ , in the cold;  $\text{COCl}_2 + 5\text{NaNH}_2 \rightarrow \text{Na}_2\text{CN}_2 + 2\text{NaCl} + \text{NaOH} + 3\text{NH}_3$ , at approx.  $250^\circ$ ;  $\text{S}_2\text{Cl}_2$  in PhMe, after about 60 hr. gives  $\text{N}_4\text{S}_4$ ; at  $120^\circ$  in absence of air the reaction is  $3\text{S}_2\text{Cl}_2 + 12\text{NaNH}_2 \rightarrow 3\text{Na}_2\text{S}_2 + 8\text{NH}_3 + 6\text{NaCl} + 2\text{N}_2$ . N. M. B.

**Potassium oxides.** C. A. KRAUS and E. F. PARMENTER (J. Amer. Chem. Soc., 1934, 56, 2384—2388).—The prep. of  $\text{K}_2\text{O}_2$  and  $\text{K}_2\text{O}_4$  by oxidation of K in liquid  $\text{NH}_3$  is described. The existence of  $\text{K}_2\text{O}_3$ ,  $\text{K}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,  $\text{K}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{K}_2\text{O}_3 \cdot \text{H}_2\text{O}$  has been established and their properties and reactions are described. E. S. H.

**Basic copper carbonate and green patina.** W. H. J. VERNON (J.C.S., 1934, 1853—1859).—Cu immersed in aq.  $\text{CO}_2$  affords green basic Cu carbonate (I), the rate of conversion of arsenical Cu being  $>$  of pure Cu. In air containing  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , (I) is formed only in the presence of another reactant, e.g., traces of carboxylic acid vapours (II); chlorides and traces of  $\text{SO}_2$  behave similarly but less effectively. Probably a normal Cu salt is formed initially and (I) is formed when this is hydrolysed in presence of  $\text{CO}_2$ . Thus, in an atm. containing  $\text{CO}_2 \gg \text{SO}_2$ , the green deposit contained 31.5%  $\text{SO}_4^{2-}$  and 0.76%  $\text{CO}_3^{2-}$ . Fourcroy's statement (1786) that open-air patina consists of (I) is incorrect, since the (I) in patina formed near the sea is secondary to basic chloride and inland is secondary to basic sulphate, but in certain urban districts the proportion of (I) rises to 25% probably owing to the action of (II). J. G. A. G.

**So-called diaquobisethylenediaminocupric ion. Reinvestigation of its simple salts and alleged optical isomerism.** C. H. JOHNSON and S. A. BRYANT (J.C.S., 1934, 1783—1786).—The ion hitherto believed to be  $[\text{Cu}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2(\text{H}_2\text{O})_2]^{2+}$  affords a nitrate which, however it is prepared, is completely anhyd., a chloride and bromide having only  $1\text{H}_2\text{O}$  per mol., an efflorescent iodide with  $2\text{H}_2\text{O}$  per mol., efflorescent sulphates with 4.5 and  $2\text{H}_2\text{O}$  per mol., and a tartrate (I). In all cases,  $\text{H}_2\text{O}$  is quickly and completely removed over  $\text{P}_2\text{O}_5$  in vac. (I) could not be resolved (cf. A., 1928, 395, 1077), and from electrode potential determinations the complex ion is unstable. The ion is  $[\text{Cu}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]$ , the Cu<sup>2+</sup> having a co-ordination valency of 4, and therefore optical isomerism is excluded. J. G. A. G.

**Addition of hydrogen phosphide to cuprous and silver halides.** R. SCHOLDER and K. PATOCK (Z. anorg. Chem., 1934, 220, 250—256).—By the action of  $\text{PH}_3$  on EtOH solutions of  $\text{Cu}^1$  and Ag halides, containing the corresponding acids, the following compounds have been obtained:  $\text{CuCl} \cdot \text{PH}_3$  (I),  $\text{CuBr} \cdot \text{PH}_3$  (II),  $\text{CuI} \cdot 2\text{PH}_3$  (III),  $2\text{AgI} \cdot \text{PH}_3$ . The stability of the  $\text{Cu}^1$  compounds decreases in the order

(I)  $>$  (II)  $>$  (III). No  $\text{PH}_3$  additive compounds could be obtained with AgCl and AgBr. The results indicate that an ionic lattice, and not a mol. lattice only (cf. Holtje, A., 1933, 127), can take up  $\text{PH}_3$ . M. S. B.

**Preparation and properties of aurothiosulphates of ammonium, calcium, and quinine.** PRON (Compt. rend., 1934, 199, 952—954).—From aq. quinine hydrochloride, quinine aurothiosulphate can be obtained by double decomp. and crystallisation; by the action of excess of  $\text{NH}_3$  and evaporation in vac. the  $\text{NH}_4$  salt is obtained. The Ca salt is prepared by the action of  $\text{Ca}(\text{S}_2\text{O}_3)_2$  on  $\text{AuCl}_3$  neutralised by  $\text{CaCO}_3$  in presence of excess of  $\text{Ca}(\text{OH})_2$ , and isolated by the elimination of  $\text{CaCl}_2$  with EtOH. The three salts are sol., and in most reactions the Au is eliminated as a higher sulphide, or as  $\text{Au}_2\text{S}$  in neutral solution. Reducing agents give Au. Evidence points to the structure  $\text{O}_2\text{S}(\text{ONa})\text{SAu} \cdot \text{Na}_2\text{S}_2\text{O}_3$ . N. M. B.

**Hydrothermal synthesis of some carbonates.** W. BILTZ and A. LEMKE (Z. anorg. Chem., 1934, 220, 312—316).—By heating the corresponding chlorides in HCl solution with  $\text{CO}(\text{NH}_2)_2$  in a bomb for 18—24 hr. at  $200^\circ$ , carbonates of Cd, Sr, Ba, Mn,  $\text{Fe}^{\text{II}}$ , Co, and Pb have been synthesised.  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  has also been obtained. Analytical and density data are given. M. S. B.

**Additive compounds of halides of bivalent metals with organic bases.** VIII. G. SCAGLIARINI and G. C. CESARI (Gazzetta, 1934, 64, 742—745; cf. A., 1930, 328).—By mixing cold conc. solutions of  $(\text{CH}_2)_6\text{N}_4$  (X) and the metallic halide in the solvents given in parentheses the following compounds have been obtained:  $(\text{H}_2\text{O}) \text{ZnCl}_2 \cdot 4\text{H}_2\text{O} \cdot \text{X}$ ;  $2\text{ZnBr}_2 \cdot 8\text{H}_2\text{O} \cdot 3\text{X}$ ;  $2\text{ZnI}_2 \cdot 8\text{H}_2\text{O} \cdot 3\text{X}$ ;  $\text{ZnI}_2 \cdot 3\text{H}_2\text{O} \cdot 2\text{X}$ ; (95% EtOH)  $3\text{ZnCl}_2 \cdot 2\text{X}$ ;  $\text{ZnBr}_2 \cdot \text{X}$ ;  $2\text{ZnI}_2 \cdot 3\text{X}$ ;  $(\text{COMe}_2) \text{ZnCl}_2 \cdot \text{X}$ . O. J. W.

**Hydrates of dicalcium aluminate.** R. SALMONI (Gazzetta, 1934, 64, 719—734).—The hydrates  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , where  $n=1, 3, 6, 10$ , and 11, have been prepared. Heats of dissolution and X-ray structures of the hydrates with  $n=1, 3, 5, 7$ , and 9 are given. The higher hydrates all have the same lattice structure as the pentahydrate; this differs from that of the monohydrate. O. J. W.

**Effects of fluorides on thermal synthesis of calcium aluminates.** I. S. NAGAI and T. YOSHURA (J. Soc. Chem. Ind. Japan, 1934, 37, 693—695B).—The interaction of a mixture of  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$  (3:1) at  $900\text{--}1400^\circ$  for 1 hr. is accelerated by the presence of 1% of  $\text{CaF}_2$  and the product at the lower temp. is richer in CaO. The amount of  $\text{CaF}_2$  volatilised increases with the temp. and the amount originally present. J. A. S.

**Effect of fluorides on thermal synthesis of calcium silicates.** III. S. NAGAI and M. MIYASAKA (J. Soc. Chem. Ind. Japan, 1934, 37, 549—552B).—In presence of  $\text{CaF}_2$ ,  $3\text{CaO} \cdot \text{SiO}_2$  is formed when  $\text{CaCO}_3$  is heated with  $\text{SiO}_2$  at  $< 1300^\circ$ ; in its absence  $2\text{CaO} \cdot \text{SiO}_2$  is formed up to  $1400^\circ$ . More  $\text{CaF}_2$  remains in the product when heated dry than when the heating gas contains  $\text{H}_2\text{O}$ . A. G.



**Hydrothermal synthesis of calcium hydro-silicates.** V. A. VIGFUSSON, G. N. BATES, and T. THORVALDSON (Canad. J. Res., 1934, 11, 520—529).—A *Ca hydrosilicate*,  $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ , identical with a cryst. substance observed in steam-cured Portland cement mortar (B., 1930, 146), can be prepared by hydrothermal synthesis from mixtures of  $\text{SiO}_2$  sand with  $\text{Ca}(\text{OH})_2$ ,  $\text{Ca}_2$  with  $\text{Ca}_3$  silicate, or  $\text{SiO}_2$  gel with  $\text{Ca}(\text{OH})_2$ , after preliminary steam treatment and ignition, or, finally, by the action of saturated aq.  $\text{Ca}(\text{OH})_2$  on quartz crystals or fused  $\text{SiO}_2$  plates. The compound is slowly decomposed by aq.  $\text{MgSO}_4$  and alkali carbonates and rapidly by dil. acids and  $\text{NH}_4$  salts. Aq.  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ , or alkali hydroxides have no action. The crystals are thin prisms showing parallel extinction, positive elongation, and moderate birefringence. A second cryst. *Ca hydrosilicate* was obtained, as very small needles, by hydrothermal synthesis from excess  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  gel.  $\text{CaO}:\text{SiO}_2$  is 2:1 with an uncertain amount of  $\text{H}_2\text{O}$  of at least 1 mol. The birefringence is very low. Optical and X-ray data for both compounds are given; they differ from the data for hillebrandite, which has the same composition. M. S. B.

**Preparation of boron hydride. II. Action of phosphoric acid on magnesium and beryllium boride.** E. WIBERG and K. SCHUSTER (Ber., 1934, 67, [B], 1805—1808; cf. A., 1930, 720).—The yield of B hydrides (essentially  $\text{B}_4\text{H}_{10}$ ) from  $\text{Mg}_3\text{B}_2$  is increased from 4.6% to 11.4% if 4*N*-HCl is replaced by 8*N*- $\text{H}_3\text{PO}_4$ . Increase of  $[\text{H}_3\text{PO}_4]$  depresses the yield. Similar replacement in the case of  $\text{Be}_3\text{B}_2$  doubles the yield. H. W.

**Composition and constitution of the alkali aluminates. (Are the aluminates hydroxocompounds?)** P. JUCAITIS (Z. anorg. Chem., 1934, 220, 257—267).—The composition of the aluminates,  $\text{Al}_2\text{O}_3\cdot\text{K}_2\text{O}\cdot 3\text{H}_2\text{O}$  (I),  $\text{Al}_2\text{O}_3\cdot\text{Na}_2\text{O}\cdot 2.5\text{H}_2\text{O}$  (II), and  $\text{Al}_2\text{O}_3\cdot 3\text{Na}_2\text{O}\cdot 6\text{H}_2\text{O}$  (III), has been determined by Schreinemaker's residue method and confirmed by drying experiments. By dehydration at different temp. in a current of air it is shown that (I) and (II) are true salts. (I) becomes anhyd. at 370° and (II) at 100°. (III) is probably an oxo-hydroxo-aluminate,  $\text{Na}[\text{OAl}(\text{OH})_4]\text{Na}_2\cdot\text{H}_2\text{O}$ . M. S. B.

**Substitution and decomposition of alkalis in blue ultramarine.** K. LESCHEWSKI, H. MÖLLER, and E. PODSCHUS (Z. anorg. Chem., 1934, 220, 317—328).—By fusing Na ultramarine (I) with alkali nitrates at temp. below 500° an alkali exchange takes place. The extent depends on the ionic vol. of the metal. A yellowish-brown Ag Na ultramarine may be similarly formed. By treating (I) with boiling aq.  $\text{NH}_4\text{Cl}$  a Na  $\text{NH}_4$  ultramarine (II) is obtained and is specially suitable for the prep. of other ultramarines by decomp. with aq. metallic nitrites, when  $\text{NH}_4\text{NO}_2$  is completely removed. By heating (II) with aq.  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  a blue  $\text{N}_2\text{H}_5$  Na ultramarine containing 6.8%  $\text{N}_2\text{H}_5$  is obtained. By heating an incompletely dehydrated blue ultramarine in a current of  $\text{Cl}_2$  at 400°, the colour gradually disappears, giving a yellow product from which three different substances have been obtained: a white, alkali-free, cryst. Cl-compound, a white, alkali-free, amorphous

compound similar to that obtained by treating ultramarine with  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$  (A., 1932, 351), and a greenish-yellow amorphous compound with full alkali content. All the compounds contain S. For the appearance of the blue colour it seems necessary for  $\text{S}''$  and  $\text{Na}'$  to form part of the recognised ultramarine crystal lattice. M. S. B.

**[Primary processes in the oxidation of graphite.]** V. SIHVONEN (Z. Elektrochem., 1934, 40, 743—744; cf. A., 1934, 1082).—A reply to criticism. E. S. H.

**Volatility of silica.** E. PRESTON and W. E. S. TURNER (J. Soc. Glass Tech., 1934, 18, 222—224T).— $\text{SiO}_2$  discs do not change in wt. when heated in air for 20 hr. at 1400°, but if subjected to the action of  $\text{H}_2\text{O}$  vapour under the same conditions of time and temp., or for 4 hr. at 1500°, there is a small but definite loss in wt. The surface becomes slightly pitted and glossy, suggesting that the loss is due to chemical action rather than true volatility. At 1300° the loss in wt. after 20 hr. is negligible. M. S. B.

**Stannic and stannous thiocyanates.** I. V. KROTOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 603—608).—The compounds  $\text{Sn}(\text{CNS})_2\cdot 2\text{EtOH}$  and  $\text{Sn}(\text{CNS})_4\cdot 9\text{EtOH}$  were prepared by the interaction of  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  and  $\text{SnCl}_4$ , respectively, with KCNS in EtOH solution. H. J. E.

**Lead acetato-chloride.** E. GRILLOT (Compt. rend., 1934, 199, 1049—1051).—The solubility of  $\text{PbCl}_2$  is increased in presence of  $\text{Pb}(\text{OAc})_2$ . When a warm 70%  $\text{Pb}(\text{OAc})_2$  solution, saturated with  $\text{PbCl}_2$ , is cooled, crystals of the lead acetato-chloride,  $\text{Pb}_2(\text{OAc})_3\text{Cl}\cdot 1.5\text{H}_2\text{O}$  (I), are deposited. In  $\text{H}_2\text{O}$  (I) is hydrolysed giving  $\text{Pb}(\text{OH})\text{Cl}$ , showing it to be a complex and not a double salt. (I) is also formed by interaction of  $[\text{Pb}_2(\text{OAc})_3]\text{ClO}_4$  and KCl, and of  $\text{Pb}_2(\text{OAc})\text{OH}$  and HCl. J. W. S.

**Preparation of standard solutions of thorium chloride and its disintegration products.** A. N. PULKOV (Trans. inst. métrol. stand. U.R.S.S., 1934, No. 6, 3—12).—Allanite  $[(\text{SiO}_4)_6\text{Ce}_5\text{Ca}_4(\text{OH})_2]$  (I) contains no U, and is therefore suitable for preparing standard  $\text{ThCl}_4$  solutions. 100 g. of (I) are treated with 250 c.c. of aqua regia,  $\text{SiO}_2$ , Fe, Ca, Mg, and the rare earths are removed, and the  $\text{ThCl}_4$  solutions standardised by the emanation method.

CH. ABS. (e)

**Spontaneous decomposition of ammonium nitrate melts.** H. TRAMM and H. VELDE (Angew. Chem., 1934, 47, 782—783).— $\text{NH}_4\text{NO}_3$  is stable at 175° when pure or in presence of chloride or acid, but when both these are present an accelerating decomp. occurs at 145° with evolution of gas (30%  $\text{N}_2\text{O}$ , 70%  $\text{N}_2$ ) and rise of temp. The decomp. can be stopped by neutralisation with  $\text{NH}_3$ . A. G.

**Preparation of ammonium azide from dry mixtures of sodium azide and an ammonium salt.** W. J. FRIERSON and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 2384).—Equimol. mixtures of  $\text{NaN}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  are heated in a sealed tube in vac. or in a sublimation apparatus through which a current of dry air is passed. The yield of  $\text{NH}_4\text{N}_3$  is 87%. E. S. H.



**Nitrogen compounds of germanium. V. Germanous nitride.** W. C. JOHNSON and G. H. RIDGELY (J. Amer. Chem. Soc., 1934, 56, 2395—2397; cf. A., 1933, 38, 683).— $Ge_2N_2$  has been prepared by thermal decomp. of  $GeNH_3$ . Its properties have been determined. At  $> 500^\circ$   $Ge_2N_2$  decomposes into Ge and  $N_2$ . E. S. H.

**Action of potassium and sodium hydroxides on germanoformic acid.** A. TCHAKIRIAN (Compt. rend., 1934, 199, 866—868; cf. A., 1932, 901).—Treatment of  $Ge(OH)_2$  with 50% NaOH or KOH yields  $Na_2GeO_3$  or  $K_2GeO_3$  with liberation of  $H_2$ , and small quantities of  $GeH_4$  and Ge. The mechanism of the reaction is discussed. J. W. S.

**Oxygen preparation from sodium peroxide: a dangerous experiment.** J. N. FRIEND and S. MARKS (Nature, 1934, 134, 778).—Owing probably to the presence of unoxidised Na, the gas obtained by the action of  $H_2O$  on  $Na_2O_2$  exploded violently on ignition. L. S. T.

**Sulphur monoxide. IV. Oxidation of sulphur.** P. W. SCHENK (Z. anorg. Chem., 1934, 220, 268—272).—An apparatus for the prep. of SO by burning S in  $O_2$  at reduced pressure is described. The yield improves as the pressure is diminished down to 5 mm. and for each pressure there is an optimum temp. M. S. B.

**Processes in the reaction between hydrogen sulphide and sulphurous acid in aqueous and alkaline solutions and their efficiency for purposes of preparation.** O. VON DEINES and H. GRASSMANN (Z. anorg. Chem., 1934, 220, 337—369).—Mixtures of  $H_2S$  and  $SO_2$  in proportions varying from 2:1 to 1:2 have been passed slowly, at different temp., through  $H_2O$  and aq. NaOH and the solutions obtained have been analysed. At  $20-40^\circ$   $H_2S_5O_6$  alone is formed in pure  $H_2O$ . At higher temp. a little  $H_2S_4O_6$  appears. In aq. NaOH  $Na_2S_2O_3$  is obtained, and the yield is quant. and unaccompanied by the separation of S if  $H_2S:SO_2=2:1$  and the passage of gas is interrupted at the neutral point. On passing excess of gas  $Na_2S_2O_3$  disappears and  $S_5O_6^{2-}$  is formed and partly decomposed to  $S_4O_6^{2-}$ . A large excess of  $SO_2$  favours the production of polythionates. The following salts have been prepared:  $CaS_4O_6 \cdot 2H_2O$ , white, stable; a mixture of  $Fe^{II}$  pentathionate and dipentathionate, white;  $ZnS_5O_6$  containing 7% of the acid salt. By stabilisation with  $CH_2O$  the existence of a labile intermediate product in the reaction is demonstrated. It is probably thiosulphurous acid,  $H_2S_2O_2$ . The most favourable ratio of  $H_2S:SO_2$  for its production is 1:1. The mechanism of the reactions in Wackenroder's liquid is discussed. M. S. B.

**Active chromic oxide.** H. W. KOHLSCHÜTTER (Z. anorg. Chem., 1934, 220, 370—376).— $Cr_2O_3$  prepared by pptg. gelatinous  $Cr(OH)_3$  from dil. aq.  $Cr^{III}$  and drying, readily adsorbs  $H_2$  above  $100^\circ$ . Its behaviour varies according to whether pptn. takes place slowly and in stages (I) or rapidly and continuously (II). (II) takes up  $H_2$  at a higher temp. than (I), but constituents adversely affecting adsorption, such as residual  $H_2O$ , are more difficult to remove from (II) than from (I). M. S. B.

**Fluorine. II. Reactions of oxygen fluoride with water and solutions of sodium hydroxide.** F. ISHIKAWA, T. MUROOKA, and H. HAGISAWA (Sci. Rep. Tôhoku, 1934, 23, 431—448; cf. A., 1934, 1187).—Dissolution of  $OF_2$  in  $H_2O$  obeys Henry's law. The velocity of reaction between gaseous  $OF_2$  and  $H_2O \propto [OF_2]$ . The temp. coeff. is 2.7 per  $10^\circ$ .  $OF_2$  reacts instantaneously with very dil. alkali solution, dissolution occurring slowly relative to the velocity of reaction in the liquid phase. The velocity of decomp. of  $OF_2$  in contact with undisturbed aq. NaOH  $\propto$  the concn. of gaseous  $OF_2$ , but the temp. coeff. is 1.5 per  $10^\circ$ . J. W. S.

**Iodine monochloride.** J. CORNOG, R. A. KARGES, and H. W. HORRABIN (Proc. Iowa Acad. Sci., 1932, 39, 159).—ICl is prepared from I and liquid Cl at  $-78^\circ$ .  $NH_4Cl$  or  $KCl$  dissolved in liquid ICl yields conducting solutions. V.-p. measurements ( $30-60^\circ$ ) indicate that ICl is polar. CH. Abs. (e)

**Periodic acid and periodates. IV. Reactions of disodium paraperiodate with soluble salts of zinc and metals of the alkaline earths.** J. R. PARTINGTON and R. K. BAHL (J.C.S., 1934, 1771—1772).—The substances pptd. by boiling  $Na_2H_3IO_6$  with conc. solutions of Zn, Ca, and Ba salts have the following const. compositions when dried at  $85^\circ$ :  $4ZnO \cdot I_2O_7 \cdot 5H_2O$ ,  $2CaO \cdot I_2O_7 \cdot 4H_2O$ , and  $2 \cdot 3BaO \cdot I_2O_7 \cdot 3H_2O$ . The existence of salts described in the lit. was not confirmed. The composition of the ppt. from Sr salts is variable. J. G. A. G.

**Physico-chemical investigation of a new basic ferric ammonium sulphate.** R. JIRKOVSKÝ (Coll. Czech. Chem. Comm., 1934, 6, 445—452).—The salt  $(NH_4)_2O \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$  crystallises slowly from Mohr's salt solution in a closed bottle exposed to diffuse light.  $2H_2O$  are evolved at  $220-280^\circ$ ,  $1H_2O$  and all the  $NH_3$  at  $280-320^\circ$ , and  $4H_2O$  at  $320-325^\circ$ . The dehydration and thermal decomp. of the analogous  $Fe^{III}$  Na salt, natrojarosite, follows a similar course. It is inferred that the salt crystallising from a  $Fe^{III}$  sulphate solution is always more basic than corresponds with the composition of the original solution. J. G. A. G.

**Mechanism of the oxidation of iron. Reactions and equilibria involving iron in wines.** J. RIBEREAU-GAYON (Bull. Soc. chim., 1934, [v], 1, 1269—1280; cf. A., 1931, 575).—The data for oxygenated liquids are consistent with the existence of an equilibrium (I) between the  $Fe^{II}$  and  $Fe^{III}$  ions, respectively, in equilibrium with undissociated  $Fe^{II}$  and  $Fe^{III}$  compounds. In the solutions considered,  $Fe^{III}$  was present chiefly as complex ions and (I) was shifted by salts which formed  $Fe^{III}$  so that the total  $Fe^{III}$  was rapidly increased by oxidation, whilst  $[Fe^{II}]$  and  $[Fe^{III}]$  were diminished. As the  $p_H$  val. of a white wine was raised, the concn. of  $Fe^{III}$  complexes increased parallel with an increased rate of oxidation of  $Fe^{II}$ , and the pptn. of  $FeSO_4$  diminished at  $> a$  sp.  $p_H$  val. The reaction of  $K_4Fe(CN)_6$  with the Fe in wines is discussed. J. G. A. G.

**Configuration of bisdimethylglyoximediamine cobaltic salts.** Y. NAKATSUKA and H. IINUMA



(J. Chem. Soc. Japan, 1934, 55, 630—643).—Compounds of the type

$[\text{Co}(\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2(\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{NO})_2]\text{X}$  are obtained in which the  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$  acts as a monobase. In  $[\text{Co}(\text{NH}_2\text{Ph})_2(\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{NO})_2]\text{X}$ , 2 dimethylglyoximes are in a plane in a very firm combination and the 2  $\text{NH}_2\text{Ph}$  groups are always *trans*. New compounds are derived by replacing  $\text{NH}_2\text{Ph}$  by other bases and with  $\text{X}=\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{CNS}$ , or  $0\cdot5\text{SO}_4$ .

CH. ABS. (e)

Action of magnesium on solutions of nickel sulphate and cobalt sulphate. G. GIRE (Bull. Soc. chim., 1934, [v], 1, 1241—1247).—Mg powder added to excess of aq.  $\text{NiSO}_4$  evolves  $\text{H}_2$  and ppts. a salt which effloresces to  $\text{NiSO}_4\cdot4\text{NiO}\cdot17\text{H}_2\text{O}$  at room temp. and affords  $\text{NiSO}_4\cdot4\text{NiO}\cdot10\text{H}_2\text{O}$  at  $100^\circ$ . The salt dissolves in warm aq. acids only. From aq.  $\text{CoSO}_4$  Mg evolves  $\text{H}_2$  and deposits a mixture of  $\text{CoSO}_4\cdot5\text{CoO}$  and  $\text{Co}$ .

J. G. A. G.

Platinum-black. G. VON HEVESY and T. SOMIYA (Z. physikal. Chem., 1934, 171, 41—48).—Pt-black (I) obtained by electrolysis of aq.  $\text{H}_2\text{PtCl}_6$  containing  $\text{Pb}(\text{OAc})_2$  (II) contains an appreciable amount of Pb, which increases rapidly with  $[\text{Pb}(\text{OAc})_2]$ , and most of it is apparently not present in solid solution. The best (I), judged by its resistance to cathodic polarisation, is given by an electrolyte made up according to Lummer and Kurlbaum's formula, and has the largest particles. Pure Pt solutions do not give (I), but Au, Tl, or Cd may be used instead of Pb.

R. C.

Complex platinum compounds with ter- and quinque-valent platinum. VII. P. C. RAY and N. N. GHOSH (Z. anorg. Chem., 1934, 220, 247—249; cf. A., 1934, 44).—By the action of  $\text{C}_5\text{H}_5\text{N}$  on  $\text{PtCl}_2\text{Et}_2\text{S}_2$  under different conditions the compounds  $\text{Pt}_2\text{Cl}_2(\text{Et}_2\text{S}_2)_2\cdot2\text{C}_5\text{H}_5\text{N}$  (I), m.p.  $190^\circ$ ,  $\text{Pt}_3\text{Cl}_2(\text{Et}_2\text{S}_2)_2\cdot2\text{C}_5\text{H}_5\text{N}$  (II),  $\text{Pt}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$ , m.p.  $288^\circ$ , and  $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$ , m.p.  $285^\circ$ , are obtained. (I) is insol. in ordinary org. solvents. Determinations of the electrical conductivity of (II) is  $\text{COMe}_2$  have been made. By the action of  $\text{C}_5\text{H}_5\text{N}$  on  $\text{PtBrEt}_2\text{S}_2$  the compound  $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Br}_2$ , m.p.  $297^\circ$ , is obtained.

M. S. B.

Spectrographic analysis. II. Spectrum analysis of solutions. Y. UZUMASA and H. OKUNO (J. Chem. Soc. Japan, 1934, 55, 622—626).—The min. concn. for the spectrographic detection of the characteristic lines of 16 common elements has been determined. The lines are weakened by the presence of HCl.

CH. ABS. (e)

Extraction and analysis of gases in rocks and minerals. A. A. CHEREPENNIKOV (Trav. inst. étât radium (U.S.S.R.), 1933, 2, 136—139).—The specimen is either dissolved in HCl or  $\text{HNO}_3$  or heated at  $380^\circ$ .

CH. ABS. (e)

Potentiometric titration in non-aqueous solutions. II. Source of error in acidimetry. I. E. WOOTEN and A. E. RUEHLE (Ind. Eng. Chem. [Anal.], 1934, 6, 449—451; cf. B., 1931, 849).—In titrating a moderately strong acid in  $\text{Bu}^\circ\text{OH}$  with alkali a weak acid may be introduced as the alkali salt, due to oxidation of the alcohol. A quant. test

for the presence of such impurities may be made by titrating portions of standard picric acid solution.

E. S. H.

Electrometric determination of total acidity of intensely coloured solutions by the Bucharov-Evstigneev method. B. A. MINAEV (Zavod. Lab., 1934, 3, 863—864).—A potentiometric procedure is described.

R. T.

New indicators for acidimetry. E. S. VASSERMAN (Zavod. Lab., 1934, 3, 863—869).—Wenker's nitrazine-yellow, and its 8-Cl-, -Br-, and -I-derivatives, give sharp transition points, from yellow to blue or grey at  $p_H$  6.5—6.8. Directions for preparing the indicators are given.

R. T.

Determination of  $p_H$  of natural waters. J. I. USATENKO (Zavod. Lab., 1934, 3, 946—948).—For natural  $\text{H}_2\text{O}$   $p_H=7\cdot719+\log k/a$ , where  $k$  is the temporary hardness in  $^\circ$  German, and  $a$  the  $\text{CO}_3$  content in mg. per litre.

R. T.

Micro-determination of base by electrodiagnosis. G. S. ADAIR and A. B. KEYS (J. Physiol., 1934, 81, 162—166).—Stoddard's method is modified for samples containing 0.2 mg.-equiv. of base.

CH. ABS. (p)

Drop reaction for hydrogen peroxide. E. PLANK (Z. anal. Chem., 1934, 99, 105—106).—Fresh aq.  $\text{K Ce}^{\text{III}}$  carbonate [*i.e.*,  $\text{Ce}_2(\text{SO}_4)_3$ +excess  $\text{K}_2\text{CO}_3$ ] gives a yellow coloration with  $< 10^{-7}$  g. of  $\text{H}_2\text{O}_2$ .

J. S. A.

Determination of active chlorine by a combined reagent. A. V. JAKOVLEV (Zavod. Lab., 1934, 3, 900—903).—The solution, containing  $\text{OCl}'$  or  $\text{MnO}_4'$ , is added to 3—10 ml. of reagent (0.5 g. of starch in 20 ml. of  $\text{H}_2\text{O}$  are added to 100 ml. of 20% aq.  $\text{NaCl}$  at  $100^\circ$ , the solution is filtered, 2.5 g. of  $\text{KI}$  are added 2.5 hr. later, followed by 40 ml. of 7%  $\text{KOH}$ , 20 ml. of 40%  $\text{AcOH}$ , and 10 ml. of 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$ ; the reagent has  $p_H$  4.4, and is stable for  $< 6$  months) to the appearance of a blue coloration. The method is rapid (4—6 min.) but not very accurate.

R. T.

Electrometric determination of chlorides in the ash and sap of plants and in ground waters. J. R. NELLER (Ind. Eng. Chem. [Anal.], 1934, 6, 426—428).—Comparison of the electrometric and volumetric titrations gives good agreement, but the electrometric method is preferred.  $\text{Cl}'$  can be titrated directly in some plant saps, but the ashing step must be included in juices containing appreciable amounts of the salts of weak acids (*e.g.*, citrus fruits). The electrometric method gives a more sensitive end-point than the volumetric method in determining  $\text{Cl}'$  in ground  $\text{H}_2\text{O}$  containing  $\text{SO}_4''$  and  $\text{S}''$ .

E. S. H.

Volatilisation of iodine from dilute iodine-potassium iodide solutions. W. A. HOUGH and J. B. FICKLEN (Ind. Eng. Chem. [Anal.], 1934, 6, 460).—No significant loss of I occurs at room temp. by the passage of air under the usual conditions of sampling gas or vapour. The loss is minimised by reducing the temp., rate of air flow, and [I].

E. S. H.

Detection of traces of iodides in the presence of chlorates, bromates, and iodates. A. VASSILOV (Praktika, 1933, 8, 324—326).—10 c.c. of the



neutralised test solution are shaken with 2 c.c. of a 0.05% solution of I in  $\text{CHCl}_3$ . After addition of 3 drops of 1% starch solution the mixture is again shaken. A blue coloration in the aq. layer indicates I'. Other salts, notably  $\text{BrO}_3'$ , may yield a violet coloration. A. G. P.

Rapid detection and determination of iodates in presence of bromates and chlorates. A. VASSILIOU (Praktika, 1933, 8, 252—254; Chem. Zentr., 1934, ii, 287).—To 10 c.c. of a (5%) solution of the salt mixture are added 2 c.c. of  $\text{CHCl}_3$ , 1 c.c. of  $N\text{-H}_2\text{SO}_4$ , and 1 c.c. of 0.001N- $\text{Na}_2\text{S}_2\text{O}_3$ . After 1 min. the mixture is well shaken. With solutions containing 1 in 100,000 of  $\text{IO}_3'$  the  $\text{CHCl}_3$  is coloured reddish-violet. On a quant. scale the I in  $\text{CHCl}_3$  solution may be determined colorimetrically or by titration. A. G. P.

Greiff's method for the determination of small quantities of fluorine. M. GIORDANI (Annali Chim. Appl., 1934, 24, 496—503).—Visintin's procedure (A., 1934, 980) leads to inaccurate results. T. H. P.

Determination of fluorine in fluorspar.—See B., 1934, 1098.

Determination of sulphide-sulphur in alkaline solutions containing other sulphur compounds. E. L. BALDESCHWIELER (Ind. Eng. Chem. [Anal.], 1934, 6, 402—403).— $S''$  can be determined in alkaline solutions containing  $\text{SO}_4''$ ,  $\text{SO}_3''$ ,  $\text{S}_2\text{O}_3''$ , mercaptide, and sulphonate by making use of the solubility of Pb salts of the above in aq.  $\text{NH}_4\text{OAc}$ . With the procedure described an accuracy of  $\pm 0.3\%$  is claimed. E. S. H.

Use of ultra-violet light for detection of traces of sulphides. J. GRANT and H. PROCTER-SMITH (Analyst, 1934, 59, 749).—The method of detection of  $\text{SO}_3''$  (A., 1932, 1009) is modified for the detection of  $S''$  by the use of aq. quinine (Q) in place of the solid. The max. sensitiveness is 0.1 mg. of  $S''$ . A method is described by means of which the fluorescence of 1 part of Q in  $0.5 \times 10^8$  of  $\text{H}_2\text{O}$  may be detected. E. C. S.

Determination of sulphuric acid in aerosols by electro-filtration methods. N. S. ARTAMONOV (Zavod. Lab., 1934, 3, 818—820).—The mist is passed through a high-tension electric field, and the condensed  $\text{H}_2\text{SO}_4$  is determined by the ordinary methods. R. T.

Volumetric determination of sulphates. D. POLUSHIN (Iskuss. Volokno, 1934, 5, No. 2, 33—34).—The determination of sulphates by pptn. with  $\text{Pb}(\text{NO}_3)_2$  and back-titration of excess  $\text{Pb}(\text{NO}_3)_2$  with  $\text{Na}_2\text{CO}_3$  gives low vals. in presence of  $(\text{NH}_4)_2\text{SO}_4$  owing to decomp. of  $\text{NH}_4\text{NO}_3$  by  $\text{Na}_2\text{CO}_3$ . Accurate results are obtained by first converting the  $(\text{NH}_4)_2\text{SO}_4$  into  $(\text{CH}_2)_6\text{N}_4$ . CH. ABS. (e)

Titration of adsorption indicators. IV. *o*-Cresolphthalein as an indicator in the argentometric titration of thiocyanates and halides. Y. UZUMASA and Y. MIYAKE (J. Chem. Soc. Japan, 1934, 55, 627—629).—A 1% solution of *o*-cresolphthalein in an  $\text{EtOH-H}_2\text{O}$  mixture is suitable. CH. ABS. (e)

Conductometric titration of selenocyanates with silver nitrate. R. RIPAN-TILICI (Z. anal. Chem., 1934, 99, 110—112).— $\text{SeCN}'$  may be rapidly and accurately titrated conductometrically with  $\text{AgNO}_3$ . J. S. A.

Determination of tellurium in [copper anode] sludges.—See B., 1934, 1064.

Rapid determination of nitrogen by a Kjeldahl-Nessler process. W. H. KITTO (Analyst, 1934, 59, 733—735).—The material is digested with Chiles' mixture (A., 1928, 312) containing in addition 1.15 g. of  $\text{NaSeO}_4$  per 100 ml. The solution after digestion is suitable for Nesslerisation. E. C. S.

Stability of aqueous solutions of boric acid used in the Kjeldahl method. A. EISNER and E. C. WAGNER (Ind. Eng. Chem. [Anal.], 1934, 6, 473).—The solutions are stable when pure  $\text{H}_2\text{O}$  is used (cf. A., 1934, 46). E. S. H.

Determination of ammonia in aqueous hydrogen cyanide solutions. R. CUTHILL and J. JACKSON (J.S.C.I., 1934, 53, 354—356r).—Various methods of determination have been examined, the most satisfactory consisting in vac. distillation of the  $\text{NH}_3$  from alkaline solution into standard acid.  $\text{NH}_3$  may be removed completely from alkaline cyanide solutions by prolonged aeration. R. C.

Apparatus for the detection and determination of arsenic by the Gutzeit and Beck-Merres methods. J. D. GNESSIN (Pharm. Zentr., 1934, 75, 719—722).—Simplified forms of apparatus are described. J. S. A.

Reducing action of mercurous chloride. Separation, detection, and determination of arsenic, gold, platinum, palladium, selenium, tellurium, and iodine. G. G. PIERSON (Ind. Eng. Chem. [Anal.], 1934, 6, 437—439).—By reducing  $\text{HCl}$  solutions of the compounds to the element by means of  $\text{Hg}_2\text{Cl}_2$  and comparing the colours produced with a series of standards, it is possible to detect and approx. determine Au (0.00005 mg.), Pd (0.00005 mg.), Pt (0.0002 mg.), Se (0.0002 mg.), Te (0.0005 mg.), As (0.00002 mg.), and I (0.003 mg.). Methods of separation are indicated. E. S. H.

Determination of carbon in rocks and minerals. B. E. DIXON (Analyst, 1934, 59, 739—743).—A wet combustion method, based on Morgan's  $\text{H}_3\text{PO}_4\text{-H}_2\text{CrO}_4$  method (J.C.S., 1904, 85, 1004), is described.  $\text{CO}_3''$  and non- $\text{CO}_3''$  C are determined consecutively on the same sample in the same apparatus. All the typical C minerals tested were completely oxidised. The method is especially suited to the determination of C in rocks containing a considerable amount of  $\text{CO}_3''$ . E. C. S.

Determination of carbon monoxide by Nicloux's method. (MME.) S. KAGAN (Bull. Soc. chim., 1934, [v], 1, 1201—1206).—With air containing 0.02—0.05 mg. of CO per litre, Nicloux's method (A., 1925, ii, 834) affords data in error by 50%. J. G. A. G.

Iodometric determination of phosgene. M. P. MATUSZAK (Ind. Eng. Chem. [Anal.], 1934, 6, 457—459).—The low results obtained by the usual method



are traced to side reactions. Modified procedure is recommended. E. S. H.

**Micro-chemical detection of hydrogen cyanide.** M. T. KOSLOVSKI and A. J. PENNER (Arch. Pharm., 1934, 272, 792—794).—Directions are given for detection of HCN by its catalysis of the alloxan-NH<sub>3</sub> reaction observed by the microscope. NH<sub>3</sub> cannot be replaced by pure C<sub>5</sub>H<sub>5</sub>N (cf. lit.). R. S. C.

**Spectroscopic detection of argon in argon-nitrogen mixtures.** J. A. M. VAN LIEMPT and S. H. R. VISSER (Rec. trav. chim., 1934, 53, 1084—1086).—A can be detected in A-N<sub>2</sub> mixtures by observation on the line 4159 Å., excited in a discharge tube at 2 cm. pressure; the glow around the upper electrode is the best source of light. R. S. B.

**Determination of radium emanation in the atmosphere.** A. B. VERIGO (Trav. inst. état radium (U.S.S.R.), 1933, 2, 126—130).—A modification of Elster and Geitel's method of exposing a negatively charged wire to the atm. was employed. CH. ABS. (e)

**Determination of the common and rare alkalis in mineral analysis.** R. C. WELLS and R. E. STEVENS (Ind. Eng. Chem. [Anal.], 1934, 6, 439—442).—The chlorides are separated into two groups, (a) Li and Na, (b) K, Rb, Cs, by means of H<sub>2</sub>PtCl<sub>6</sub>. Li and Na are determined by the usual methods. A modified method of separation of Rb and Cs from K is described and suitable procedure for their determination indicated. E. S. H.

**Determination of potassium by the cobaltinitrite method.** S. D. SUNAWALA and K. R. KRISHNASWAMI (J. Indian Inst. Sci., 1934, 17A, 105—112).—K<sub>2</sub>NaCo(NO<sub>2</sub>)<sub>6</sub>·H<sub>2</sub>O is pptd. by boiling 0.1 g. of KNO<sub>3</sub> in 5 c.c. H<sub>2</sub>O and 1—2 c.c. AcOH with 2—3 c.c. each of 50% NaNO<sub>2</sub> (I) and 25% CoSO<sub>4</sub> (II). 1 g. of KNO<sub>3</sub> required 25—27 ml. each of (I) and (II). If the ratio of (I) to KNO<sub>3</sub> was diminished, the ppt. was contaminated with K<sub>2</sub>Na(NO<sub>2</sub>)<sub>6</sub>·0.5H<sub>2</sub>O, and with excess of (I) the ppt. contained K<sub>2</sub>NaCo(NO<sub>2</sub>)<sub>6</sub>·2H<sub>2</sub>O. Variation of [CoSO<sub>4</sub>] had no effect on the composition of the ppt., which, in all cases, was stable at 100—110°. J. G. A. G.

**Colorimetric determination of small quantities of sodium.** K. L. MALJAROV and T. JUDENITSCH (Zavod. Lab., 1934, 3, 904—906).—An equal vol. of 95% EtOH and excess of reagent (I) are added to the solution, and the ppt. is collected after 1 hr. in an unglazed porcelain filter, washed once with 4 c.c. of EtOH, and repeatedly with 2:5 EtOH-Et<sub>2</sub>O, and the dry residue dissolved in 2% AcOH, H<sub>2</sub>O added to 100 c.c., 1 c.c. of 20% K<sub>4</sub>Fe(CN)<sub>6</sub> added, and the brown coloration compared with that given by standard aq. UO<sub>2</sub>(OAc)<sub>2</sub> (II). (I) consists of equal vols. of a solution of 10 g. of (II) in 50 c.c. of 12% AcOH, and of 3 g. of Zn(OAc)<sub>2</sub> in 50 c.c. of 6% AcOH; 1.2 c.c. of (I) ppts. 1 mg. of Na. The experimental error is > 2% for 0.1—70 mg. Na. In presence of K the pptn. should be repeated, whilst MgCl<sub>2</sub> and CaCl<sub>2</sub>, and Fe, Al, SiO<sub>2</sub>, Cl', SO<sub>4</sub>'', and CO<sub>3</sub>'' in the concns. present in soil-H<sub>2</sub>O do not interfere. R. T.

**Metallic silver as an ultimate standard in volumetric analysis.** C. W. FOULK and L. A.

PAPPENHAGEN (Ind. Eng. Chem. [Anal.], 1934, 6, 430—433).—A scheme for standardising HCl against Ag is put forward. The Ag is dissolved in HNO<sub>3</sub>, and the equiv. vol. of HCl is determined by the point at which two portions of the supernatant liquid above the AgCl ppt. give equal opalescence on treating one with excess Ag' and the other with excess Cl'.

E. S. H.

**Photometric determination of calcium and oxalic acid.** L. JENDRASSIK and F. TAKÁCS (Biochem. Z., 1934, 274, 200—204).—Ca (e.g., in 2 c.c. of blood-serum) is pptd. in presence of aq. NaCl and NH<sub>4</sub>Cl with (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, left for 10—24 hr., and centrifuged. The ppt. is dissolved, in the absence of daylight, in dil. HCl+FeCl<sub>3</sub>, 2 drops of aq. KH(IO<sub>3</sub>)<sub>2</sub> are added to prevent autoxidation, and the colour (I) produced on immediate addition of 2% aq. sulphosalicylic acid is measured with a step photometer. (I) inversely  $\propto$  the amount of CaC<sub>2</sub>O<sub>4</sub>. The average error is  $\pm 3\%$ . H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (e.g., in gallstones) is determined in almost the same way, but a correction must be applied if H<sub>3</sub>PO<sub>4</sub> is present. W. Mc.C.

**Detection of calcium in presence of strontium and barium.** E. R. CALEY (Ind. Eng. Chem. [Anal.], 1934, 6, 445—447).—The conc. chloride solution is acidified with HCl, boiled to expel CO<sub>2</sub>, and KI is added. The presence of Ca is indicated by the appearance of a white, cloudy ppt. on adding HgO to the boiling solution. The reaction involved is represented by CaCl<sub>2</sub>+HgO+4KI+H<sub>2</sub>O→Ca(OH)<sub>2</sub>+2KCl+K<sub>2</sub>HgI<sub>4</sub>. Other metals forming insol. hydroxides, NH<sub>4</sub>', and oxidising anions (other than NO<sub>3</sub>') must be removed. E. S. H.

**Precipitation of barium in the copper-tin group of qualitative analysis.** W. T. HALL and R. B. WOODWARD (Ind. Eng. Chem. [Anal.], 1934, 6, 478).—If the pptn. is carried out in presence of HNO<sub>3</sub> there is risk of BaSO<sub>4</sub> being pptd. E. S. H.

**Determination of radium in rocks and minerals by the emanation method.** I. E. STARIK and A. S. SMAGINA (Trav. inst. état radium (U.S.S.R.), 1933, 2, 104—116).—The sample is dissolved, Ra being pptd. with BaSO<sub>4</sub>, and converted into RaCl<sub>2</sub> with HCl. Fe or porcelain dishes may be used instead of Pt. Vals. are recorded for a series of minerals. CH. ABS. (e)

**Colour reaction of the magnesium cation.** S. AUGUSTI (Annali Chim. Appl., 1934, 24, 531—534; cf. A., 1933, 1024).—A drop of the solution is evaporated to dryness on a clock-glass at a moderate temp., the cold residue being treated with a drop of the alkali hypoidite reagent: a reddish-brown ppt. indicates Mg''; sensitivity 3×10<sup>-7</sup> g. of Mg. Evaporation is unnecessary with amounts < 6×10<sup>-6</sup> g. The reaction is disturbed by NH<sub>4</sub>', Co'', Mn'', or Al''', but not by alkali or alkaline-earth cations. T. H. P.

**Micro-determination of zinc.** P. L. HIBBARD (Ind. Eng. Chem. [Anal.], 1934, 6, 423—425).—Zn (0.5—0.1 mg.) in plant material (5 g.) may be determined by igniting to remove org. material, extracting with HCl, and separating Zn by H<sub>2</sub>S or H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and K<sub>4</sub>Fe(CN)<sub>6</sub>. Details of the subsequent determin-



ation by (a) nephelometry, (b) iodometric titration, or (c) micro-titration with  $K_4Fe(CN)_6$  are given.

E. S. H.

**Fused beads on platinum wire as solvents for small particles of insoluble material.** A. P. LAURIE (Analyst, 1934, 59, 746—747).—The particle is dissolved in a bead of  $Na_2B_4O_7$ , or microcosmic salt, or a mixture of the two. Sp. reactions for the metallic elements are given when the bead is immersed in the appropriate reagents. The metals can be electro-deposited from the bead on Pt wire.

E. C. S.

**Determination of lead as periodate.** H. H. WILLARD and J. J. THOMPSON (Ind. Eng. Chem. [Anal.], 1934, 6, 425—426).—Pb can be separated from Ni, Cu, Zn, Cd, Al, Ca, and Mg by pptn. as  $Pb_3H_4(IO_6)_2$  from 0.025*N*-HNO<sub>3</sub> by adding NaIO<sub>3</sub>. The ppt. can be weighed or determined volumetrically by dissolving in conc. HCl containing excess of standard  $Na_3AsO_3$ , and titrating the excess with standard NaIO<sub>3</sub>, using CHCl<sub>3</sub> as indicator.

E. S. H.

**Gravimetric determination of lead dioxide in red lead.**—See B., 1934, 1056.

**Flame determination of copper by carbon tetrachloride.** P. GABRIEL (Ind. Eng. Chem. [Anal.], 1934, 6, 420).—The green flame produced by Cu turns blue when CCl<sub>4</sub> vapour is passed through the draught of the Bunsen burner. Other substances giving a green flame do not show this effect.

E. S. H.

**Detection of mercury.** E. STATHIS (Z. anal. Chem., 1934, 99, 106—108).—To the solution of Hg, KI and KOH are added, forming  $K_2HgI_4$ , then 5 c.c. of 0.01% AuCl<sub>3</sub>. In presence of Hg, reduction occurs, forming a violet colloidal solution of Au.

J. S. A.

**Determination of mercury in medicinal preparations.**—See B., 1934, 1083.

**Apparatus for volumetric determination of aluminium.** P. J. IVANNIKOV (Zavod. Lab., 1934, 3, 865).—The Al content is determined from the vol. of H<sub>2</sub> evolved with aq. NaOH.

R. T.

**Spectrographic analysis of aluminium alloys.**—See B., 1934, 1107.

**Micro-colour reaction of the manganese cation.** S. AUGUSTI (Annali Chim. Appl., 1934, 24, 535—538).—A drop of the Mn<sup>2+</sup> salt solution is treated with 1 drop of Na(or K)OH on a watch-glass, which is left in the air for a few min. and then heated gently. The cold, dry residue is treated with 1—2 drops of a 1% solution of strychnine in H<sub>2</sub>SO<sub>4</sub>; a violet-blue colour, changing to red, indicates Mn<sup>2+</sup>, 1.8×10<sup>-7</sup> g. of which is detectable. Co<sup>2+</sup> interferes and may be removed either (1) by addition to the original solution of a few drops of 10% KCN, followed by heating, treatment with a few drops of HCl, and pptn. of Mn(OH)<sub>2</sub>, or (2) by pptn. with 1:2-NO·C<sub>10</sub>H<sub>6</sub>·OH. CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Fe(CN)<sub>6</sub><sup>3-</sup>, and Fe(CN)<sub>6</sub><sup>4-</sup> give colorations similar to Co<sup>2+</sup>, but are usually destroyed before the test is applied.

T. H. P.

**Determination of manganate and permanganate present together.** L. N. SOKOLOVA (Zavod. Lab., 1934, 3, 805—809).—2.5 g. of KHSO<sub>4</sub> are added

to 50 c.c. of solution, the washed ppt. of MnO<sub>2</sub> is dissolved in 25 c.c. of 0.1*N*-Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (I) and 10 c.c. of 10% H<sub>2</sub>SO<sub>4</sub>, and excess of (I) is determined by KMnO<sub>4</sub> titration. The filtrate + washings are made up to 250 c.c., and KMnO<sub>4</sub> is determined in 100 c.c. The MnO<sub>4</sub><sup>2-</sup> and MnO<sub>4</sub><sup>1-</sup> contents are calc. from the equation  $3K_2MnO_4 + 4KHSO_4 \rightarrow 2KMnO_4 + MnO_2 + 4K_2SO_4 + 2H_2O$ .

R. T.

**Titration with alkaline permanganate.** H. STAMM (Angew. Chem., 1934, 47, 791—795).—The rapid reduction of MnO<sub>4</sub><sup>2-</sup> to MnO<sub>4</sub><sup>1-</sup> in alkaline solution is utilised, further reduction being checked by pptg. MnO<sub>4</sub><sup>1-</sup> as BaMnO<sub>4</sub>. Near the end-point, the action is catalysed by addition of Ni<sup>2+</sup>, Cu<sup>2+</sup>, or Co<sup>2+</sup> as O<sub>2</sub> carriers. HCO<sub>2</sub><sup>1-</sup> may be so determined by direct titration against KMnO<sub>4</sub> at room temp. H<sub>2</sub>PO<sub>2</sub><sup>1-</sup>, PO<sub>3</sub><sup>3-</sup>, and CNS<sup>1-</sup> (oxidised to CNO<sup>1-</sup>+SO<sub>4</sub><sup>2-</sup>) are determined by treating with excess of alkaline KMnO<sub>4</sub>, then adding BaCl<sub>2</sub> and titrating back the excess of KMnO<sub>4</sub> with HCO<sub>2</sub>Na. I<sup>1-</sup> and IO<sub>3</sub><sup>1-</sup> are determined similarly, being oxidised to IO<sub>4</sub><sup>1-</sup>. CN<sup>1-</sup> (oxidised to CNO<sup>1-</sup>) can be titrated directly or indirectly. MeOH and CH<sub>2</sub>O are titrated directly. COMe<sub>2</sub>, fumaric acid, and erythritol are completely oxidised with alkaline KMnO<sub>4</sub>, and the solution is acidified. Excess of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is then added, and titrated back with KMnO<sub>4</sub> in acid solution.

**Systematic procedure for potentiometric analysis. I. General principles.** W. HILTNER and W. GITTEL (Z. anal. Chem., 1934, 99, 97—105).—Potentiometric reduction-titrations of the following ions in presence of one another may be carried out with the appropriate reagents (given in parentheses), which will reduce all ions following in the series, but not those preceding. MnO<sub>4</sub><sup>1-</sup> (with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>); CrO<sub>4</sub><sup>2-</sup> (with As<sub>2</sub>O<sub>3</sub>); Hg<sup>2+</sup>, Fe<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup> (with Sn<sup>2+</sup>); Bi<sup>3+</sup>, Cu<sup>2+</sup>, Sb<sup>v</sup> (with Ti<sup>3+</sup>); Sn<sup>iv</sup>, Ti<sup>iv</sup> (with Cr<sup>3+</sup>).

J. S. A.

**Permanganometric investigations. II.** J. H. VAN DER MEULEN (Chem. Weekblad, 1934, 31, 633—634; cf. A., 1931, 927).—For the determination of Mn<sup>2+</sup>, 50 c.c. of the solution are treated with 5 c.c. of conc. H<sub>3</sub>PO<sub>4</sub> (*d* 1.5), 2 g. of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 5 g. of Na<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O, 10 c.c. of 5*N*-H<sub>2</sub>SO<sub>4</sub>, and 10 c.c. of 0.1*N*-AgNO<sub>3</sub>. After gentle warming, the whole is refluxed for 5 min., cooled and diluted, treated with 10 c.c. of *N*-KI, and titrated with 0.1*N*-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The error is about 0.1%.

H. F. G.

**Colorimetric determination of manganese in phosphorites and apatites.**—See B., 1934, 1056.

**Application of an old method for the removal of iron.** E. WAINER (J. Chem. Educ., 1934, 11, 526—527).—Fe is converted into ferrocyanide by reducing the acid sulphate solution with SO<sub>2</sub>, removing excess of SO<sub>2</sub>, adding NaOH until most of the Fe is pptd., and quickly adding excess of powdered KCN. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is added, and the solution is diluted and made just alkaline to phenolphthalein. On adding aq. NH<sub>3</sub> no Fe is pptd., but other elements (*e.g.*, Be, Al, In, rare earths, Cr, or Bi) are pptd as hydrated oxides. Some Fe is adsorbed in the ppt.

CH. ABS. (e)



**Volumetric determination of cobalt and nickel.** J. T. DOBBINS and J. P. SANDERS (Ind. Eng. Chem. [Anal.], 1934, 6, 459—460).—The solution containing  $C_5H_5N$  is treated with excess of standard  $NH_4CNS$ ;  $Co(C_5H_5N)_4(CNS)_2$  is pptd., and the excess of  $CNS$  determined by titration with  $AgNO_3$ . The results for Co and Ni compare favourably with those obtained by other methods.

E. S. H.

**Oxidation-reduction indicators for use with dichromate.** L. E. STRAKA and R. E. OESPER (Ind. Eng. Chem. [Anal.], 1934, 6, 465—466).—Among numerous org. compounds examined, phenyl-*p*- and -*m*-toluidine are satisfactory in absence of Hg salts, whilst naphthidine and an unidentified product, derived from the action of  $Et_2SO_4$  on acetyldiphenylamine, are satisfactory even in presence of Hg salts.

E. S. H.

**cycloHexanol in the colorimetric determination of molybdenum.** L. C. HURD and F. REYNOLDS (Ind. Eng. Chem. [Anal.], 1934, 6, 477—478).—*cycloHexanol* is preferred to  $Et_2O$  as an extractor in the determination by the usual method.

E. S. H.

**Separation and determination of metallic and phosphate ions in presence of one another.** I. S. ISHIMARU (J. Chem. Soc. Japan, 1934, 55, 732—740).—Mo can be pptd. in presence of  $OAc'$  buffer as the 8-hydroxyquinoline derivative,  $MoO_2(C_9H_6ON)_2$  (I), without disturbance due to presence of a phosphate. After collection the ppt. is decomposed by adding  $KMnO_4$  acidified with  $HNO_3$ . The phosphate is determined with  $NH_4$  molybdate. The P in a steel can be separated as  $NH_4$  phosphomolybdate, which is transformed into (I) and weighed. The P is thus determined indirectly.

CH. ABS. (e)

**Volumetric determination of tungsten.** Do-treppe's method. M. L. HOLT (Ind. Eng. Chem. [Anal.], 1934, 6, 476—477).—The method (Chim. et Ind., 1931, Spec. no., 173) gives low results, mainly because of the difficulty of reducing  $WO_3$ .

E. S. H.

**Analytical applications of the inhibition, under the influence of certain ions, of the fluorescence of the uranyl ion.** VOLMAR and MATHIS (Bull. Soc. chim., 1934, [v], 1, 1266—1269; cf. A., 1933, 924).—Impurities containing ions active in suppressing the fluorescence (I) of  $UO_2^{II}$  are detected in substances which do not inhibit (I). The concn. of known active ions is determined in terms of the vol. necessary to suppress (I).

J. G. A. G.

**Pure titanium oxide as a standard in the volumetric determination of titanium.** W. W. PLECHNER and J. M. JARMUS (Ind. Eng. Chem. [Anal.], 1934, 6, 447—448).—The prep. of pure  $TiO_2$  from  $TiCl_4$  and its use in standardising  $Fe^{III}NH_4$  sulphate are described.

E. S. H.

**Inclusion of rarer metals in elementary qualitative analysis.** II. Inclusion of titanium and vanadium in group III. L. E. PORTER (Ind. Eng. Chem., 1934, 6, 448—449; cf. A., 1934, 502).—Suitable methods are indicated.

E. S. H.

**Application of Schott glass filters for the determination of thorium by the emanation method.** P. L. BOBIN (Trav. inst. état radium (U.S.S.R.), 1933, 2, 54—61).—Emanation (I) is extracted from  $H_2O$  by placing the  $H_2O$  in a vertical glass tube constricted at both ends and fitted with a Schott glass filter above the lower constriction, and passing an air stream up the column. Addition of  $NaCl$  or  $EtOH$  to the  $H_2O$  facilitates the removal of (I).

CH. ABS. (e)

**Detection of small quantities of germanium in presence of arsenic.** S. A. COASE (Analyst, 1934, 59, 747—749; cf. A., 1934, 983).—0.05 mg. of  $GeO_2$  can be detected in presence of  $AsO_4^{III}$  when Na amalgam is used as a reducing agent, or 0.16 mg. when Al and KOH are used. Devarda's alloy,  $NH_2OH$ ,  $HCl$ , and  $2N_2H_4.H_2SO_4$  are less sensitive.

E. C. S.

**Determination of vanadium with potassium iodate, with notes on chloramine-T as an oxidising agent.** A. J. BERRY (Analyst, 1934, 59, 736—739).—V is determined volumetrically by oxidation from  $V^{II}$  to  $V^{III}$  by the ICN method (I). Chloramine-T (II) can replace  $KIO_3$  for the direct titration of various oxidisable substances in conjunction with KI. In particular,  $Ti^{II}$  salts, for which (I) is unsuitable, can be determined by the ICl method, or by titration with (II) in presence of  $HCl$  and  $KBr$ .

E. C. S.

**Determination of gold by photometric titration with potassium iodide.** S. HIRANO (J. Soc. Chem. Ind. Japan, 1934, 37, 561—562b).— $AuCl_3$  may be titrated photometrically with KI in  $> 0.05N$ -acid. Excess of  $Cl_2$  is added and breaks in the curve correspond with reduction of this and of  $AuCl_3$ , respectively. Small amounts of Pb, Cu, and Fe do not interfere.

A. G.

**Micro-determination of platinum and iridium, and of associated chlorine and potassium.** H. D. K. DREW, H. J. TRESS, and G. H. WYATT (J.C.S., 1934, 1787—1790).—5—20 mg. of the Pt compound are fused with 2 : 1  $Na_2CO_3-NaNO_3$  mixture in a Pt or porcelain crucible. The product is mixed with  $H_2O$  and  $HNO_3$  and is passed through a micro-Neubauer filter or a Pregl filter just previously washed with conc.  $HNO_3$  and weighed. The Pt is washed with hot conc.  $HNO_3$  and dried at  $130^\circ$ . Cl is determined in the filtrate from the above by pptn. with  $AgNO_3$  in conc.  $HNO_3$  (I) or on 5—12 mg. of substance by a micro-Carius method, the products of which are evaporated, and the halide extracted from the reddish insol. Pt compound by conc. aq.  $NH_3$  and subsequently pptd. as  $AgCl$ . Since Ir is partly oxidised when heated in air, the product of the ignition with conc.  $H_2SO_4$  of a K-Ir compound is cooled in  $CO_2$  and weighed, and the loss in wt. after extracting with  $H_2O$  gives the  $K_2SO_4$ . The partly oxidised Ir is then ignited in  $H_2$  and weighed as the metal. Cl in the presence of Ir is determined as in method (I).

J. G. A. G.

**M.-p. apparatus with rapid mechanical stirring.** K. S. MARKLEY (Ind. Eng. Chem. [Anal.], 1934, 6, 475).—A modified Thiele tube is described.

E. S. H.



**M.-p. determination. II. Evaluation of stem correction and the principle of simultaneous determination of m.p. by the capillary tube method.** C. TSENG (Sci. Quart. Nat. Univ. Peking, 1934, 4, 283—324).—Stem corrections when using the capillary-tube method are best determined by comparison with results by the Dennis apparatus (A., 1930, 1265). CH. ABS. (e)

**Apparatus for m.p. and micro-b.p. [determinations].** W. L. WALSH (Ind. Eng. Chem. [Anal.], 1934, 6, 468—469).—The substance, contained in a capillary tube, is observed through a low-power microscope. E. S. H.

**Apparatus for b.p. and boiling range measurements.** D. QUIGGLE, C. O. TONGBERG, and M. R. FENSKE (Ind. Eng. Chem. [Anal.], 1934, 6, 466—468).—A modification of the Cottrell apparatus is described. A side tube permits any quantity of material to be distilled off, so that mixtures may be examined. E. S. H.

**Cryoscopy in concentrated solution at a low temperature. Method of successive equilibria.** A. LALANDE (J. Chim. phys., 1934, 31, 498—510; cf. A., 1934, 1086).—The chief disadvantage of existing methods of determining the f.p. of two-component liquids is the difficulty of maintaining the system sufficiently close to the equilibrium point. A method is described in which, starting with the partly frozen liquid, the rises of temp. ( $\Delta t$ ) produced, after attainment of the corresponding equilibria, by the development within the system of successive equal quantities of heat are measured. The val. of  $\Delta t$  for the interval in which the last trace of solid disappears is intermediate between the approx. equal smaller vals. which precede and the larger vals. which follow it, and a simple graphical construction permits the time, and hence the temp., at which the disappearance occurs to be determined with a high degree of accuracy. A full description of apparatus and procedure suitable for work at a low temp. (e.g., for a mixture of EtOH and Et<sub>2</sub>O) is given. F. L. U.

**Micro-calorimetry.** B. WHIPP (Phil. Mag., 1934, [vii], 18, 745—759).—The max. sensitivity of a series of thermo-couples used with a galvanometer is discussed. The most favourable conditions are given by a low resistance in the galvanometer and the couples. The construction of a calorimeter with 5 couples of 1 ohm total resistance is described. The sensitivity is 1 mm. deflexion for  $3 \times 10^{-6}$  g.-cal. F. L. U.

**Isothermal diphenylmethane calorimeter.** A. N. SCHUKAREV, I. P. KRIVOBABKO, and L. A. SOBUKAREVA (Phys. Z. Sovietunion, 1934, 5, 722—724).—CH<sub>2</sub>Ph<sub>2</sub> is substituted for H<sub>2</sub>O in a Bunsen ice calorimeter. At the m.p. of CH<sub>2</sub>Ph<sub>2</sub> (24.68°) the sensitivity was 0.140 g.-cal. per mm. of capillary. CH. ABS. (e)

**Liquefaction of helium by an adiabatic method.** P. KAPITZA (Proc. Roy. Soc., 1934, A, 147, 189—211).—An account is given of the liquefaction of He by means of an expansion engine which works without lubrication at low temp. The liquefier is pre-cooled by liquid N<sub>2</sub>, further cooling of the He being effected down to 10° abs. by means of the expansion

engine, and finally down to liquefaction point by using the Joule-Thomson effect. It seems probable that the Joule-Thomson effect has a pressure inversion point at low temp., appearing at about 17 atm. The liquefier uses 1.5 litres of liquid N<sub>2</sub> to produce 1 litre of liquid He. L. L. B.

**Sensitivity of thermopiles, micro-radiometers, radiometers, and bolometers.** C. H. CARTWRIGHT (Z. Physik, 1934, 92, 153—171).—The vac. thermopile can be made most sensitive. Thermodynamics predicts that ideal thermo-electric metals would increase sensitivity at room temp. fivefold. A. B. D. C.

**Application of Newton's law of cooling to the measurement of weak thermal effects.** W. SWIENTOSLAWSKI and J. SALCOWICZ (Compt. rend., 1934, 199, 935—937).—Using a special type of calorimeter, the law was applied to the measurement of the heat emitted by a sample of pitchblende over varying periods. N. M. B.

**Aluminium coating of gratings.** C. P. BUTLER and F. J. M. STRATTON (Nature, 1934, 134, 810).—A speculum metal grating coated with Al showed an improvement in the shorter wave-lengths and an average increase in reflectivity of approx. 50%. L. S. T.

**Two-crystal moving-film spectrometer.** J. M. ROBERTSON (Phil. Mag., 1934, [vii], 18, 729—745).—Apparatus recording reflexions from any two crystal specimens on one film in one operation is described. Examples of results are given. F. L. U.

**Light intensity for spectral apparatus, spectrographs, and monochromators.** C. LEISS (Z. Physik, 1934, 91, 816—817).—Precautions for using apparatus of large focal aperture are given. A. B. D. C.

**Practicality of etched quartz crystals for X-ray spectrometers.** L. G. PARRATT (Rev. Sci. Instr., 1934, [ii], 5, 395—400).—The widths of the (1, -1) curves at half max. intensity, % reflexion, and coeff. of reflexion have been measured for quartz and etched calcite. The resolving power of X-ray spectrometers is increased 2—4 times by using quartz instead of calcite, but at the expense of considerable loss of intensity. C. W. G.

**High-potential porcelain X-ray tube.** R. CRANE and C. C. LAURITSEN (Physical Rev., 1933, [ii], 43, 212).—A tube operating up to 560,000 volts at 10<sup>-5</sup> mm. is described. L. S. T.

**Projection instrument for analysis of spectrographic plates.** C. H. EDLIN (J. Sci. Instr., 1934, 11, 357—359).—Photographed spectra are projected side by side on a white screen. Wave-lengths can be read at  $\pm 1$  Å. between 2100 and 3000 Å. C. W. G.

**Use of lithium for an X-ray window.** R. E. CLAY (J. Sci. Instr., 1934, 11, 371—372).—The outer surface is covered with a thin layer of tap grease to prevent oxidation. The absorption is very small. C. W. G.

**Equalisation of the temperatures of interferometer tubes.** J. J. MANLEY (Proc. Physical Soc., 1934, 46, 745—746).—In one method the twin tubes



of the Jamin interferometer are wound with spirals of soft Cu wire; in the other they are enclosed in an Al chamber with removable ends. N. M. B.

**Spectro-polariscopic method of Oumov applied to the microscopic examination of minerals.** N. VEDENCEVA and S. GRUM-GRSHIMAILO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 583—588).—Applications of the method are described (cf. Umoff, A., 1912, ii, 1019). H. J. E.

**Trichromatic colorimeter.** H. P. J. VERBEEK (Physica, 1934, 1, 1082—1084).—Improvements have been made in a colorimeter previously described (*ibid.*, 1933, 13, 77). M. S. B.

**Photometric method for optical spectral analysis.** S. PIÑA DE RUBIES (Z. Physik, 1934, 92, 228—231).—The spectrum is projected on to a layer of several films, and the intensity is given by the logarithmic sum of the blackening of the different films. A. B. D. C.

**Apparatus for photo-electric titration.** W. W. RUSSELL and D. S. LATHAM (Ind. Eng. Chem. [Anal.], 1934, 6, 463—464).—Apparatus for the photo-electric determination of the end-point, using bromothymol-blue as indicator, is described. The error is about 0.05 c.c. of 0.01N-alkali. E. S. H.

**Salt bridge for use in electrometric measurements.** G. W. IRVING, jun., and N. R. SMITH (Ind. Eng. Chem. [Anal.], 1934, 6, 480).—Plugs are ground into the tapered ends of the bridge; electrical contact is maintained through the film of KCl solution in the ground-glass joints. E. S. H.

**Simple pointer instrument for  $p_H$  measurements.** W. HILTNER (Chem. Fabr., 1934, 7, 429—430).—A convenient form of potentiometer is described, the balancing current being read directly in terms of  $p_H$ . J. S. A.

**Measurement of the current generated by a rectifier photo-electric cell.** H. H. POOLE and W. R. G. ATKINS (Nature, 1934, 134, 810—811).—A modification of the Campbell-Freeth method (J. Sci. Instr., 1934, 11, No. 4) suitable for measuring illuminations ranging from full sunlight to a fraction of a metre candle is described. L. S. T.

**Crystal spectroscopy with  $\gamma$ -rays.** H. HULUBEI and (MLLE.) Y. CAUCHOIS (Compt. rend., 1934, 199, 857—859).—A new form of crystal spectroscope has been devised for studies with X-rays or  $\gamma$ -rays; it gives sharp definition and requires comparatively short exposures. J. W. S.

**Electrostatic generation of high voltages for nuclear investigations.** R. J. VAN DE GRAAFF, K. T. COMPTON, and L. C. VAN ATTA (Physical Rev., 1933, [ii], 43, 382). L. S. T.

**Dielectric methods of investigation in the chemical laboratory. The dielkometer.** R. BULL and J. H. MOC (Oesterr. Chem.-Ztg., 1934, 37, 183—185; cf. A., 1934, 749).—The principle and use of the instrument are described. The val. of determinations of dielectric const. in analysis is indicated, particularly in connexion with the determination of H<sub>2</sub>O content by Exluan (dioxan) desiccating agents. R. S.

**Electronography—a new method of examination of substances.** M. M. UMANSKI (Zavod. Lab., 1934, 3, 810—818).—Known methods and apparatus are described. R. T.

**Amplifier systems for the measurement of ionisation by single particles.** J. R. DUNNING (Rev. Sci. Instr., 1934, [ii], 5, 387—394).—Detailed descriptions of circuits to measure the no. of ions suddenly produced by high-speed particles are given. C. W. G.

**Electric manometer for pressures up to 3000 atmospheres.** A. MICHELS and M. LENSSEN (J. Sci. Instr., 1934, 11, 345—347).—The variation of resistance of manganin with pressure is utilised. After annealing at 140°, when further change of resistance with time is negligible, the manometer is calibrated against a pressure balance. Results are reproducible to 0.05 atm. up to 1000 atm., to 0.1 atm. up to 1500 atm., and to 0.2 atm. up to 2500 atm. C. W. G.

**Chemically fixed trace of electric waves.** V. ARKADIEV (Z. Physik, 1934, 92, 194—203).—Coherers and paper sensitive to electric current can be used to trace the path of an electric wave. A. B. D. C.

**Simple arrangement for the magnetic cooling method.** N. KÜRTI and F. SIMON (Physica, 1934, 1, 1107—1108).—The paramagnetic substance to be cooled is loosely packed as a powder in a thin-walled glass capsule filled with He at 1 cm. pressure, cooled in liquid He, magnetised, and demagnetised. In this way Mn NH<sub>4</sub> sulphate was cooled from 1.2° to 0.1° abs. Some other substance might be cooled with it. M. S. B.

**Apparatus for the production of small pressure differences.** L. M. PARR (J. Sci. Instr., 1934, 11, 371).—Air escapes slowly through a capillary tube. C. W. G.

**Microvolumenometer.** H. HAUPTMANN and G. E. R. SCHULZE (Z. physikal. Chem., 1934, 171, 36—40).—An apparatus permitting determination of  $d$  on 0.01 c.c. of a substance with a precision of 1% is described. R. C.

**Converted air-pump shaker.** A. A. MORTON (Ind. Eng. Chem. [Anal.], 1934, 6, 469—470). E. S. H.

**Sintered Pyrex glass aeration tubes.** R. D. COOL and J. D. GRAHAM (Ind. Eng. Chem. [Anal.], 1934, 6, 479).—The prep. of a sintered Pyrex glass thimble is described. E. S. H.

**Gas-absorption bulb for use with small amounts of reagent.** J. A. SHAW (Ind. Eng. Chem. [Anal.], 1934, 6, 479—480).—The apparatus is designed to use < 5 c.c. of scrubbing solution. E. S. H.

**Apparatus for observation of reactions at liquid interfaces.** A. CLEMENTI (Biochem. Z., 1934, 274, 205—207).—By using test-tubes to which smaller tubes or dropping funnels (with or without stop-cock) are attached near the lower end, or by employing long-stemmed funnels with lateral opening or capillary at the jet, layers of miscible liquids of different  $d$  may be brought together without mixing when it is desired to observe reactions at the interface. W. McC.



**Separation of isotopic mixtures by diffusion in streaming mercury vapour.** G. HERTZ (Z. Physik, 1934, 91, 810—815). A. B. D. C.

**Bunsen burner.** ANON. (Chem. and Ind., 1934, 975—976).—The gas is controlled by a needle valve operated by an external screw and burns at a large perforated head; a handle is provided. A. G.

**Application of the aërometer in investigating very small density changes of metals.** A. E. BRÜCHANOV (Metallwirts., 1934, 13, 206—208; Chem. Zentr., 1934, i, 3391).—Changes in  $d$  are observed by measuring changes in the depth at which a glass vessel (I) floats, the metal object to be examined being hung from the lower end of (I). H. J. E.

**Apparatus and method for metallographic work at low temperatures.** O. A. KNIGHT (Met. and Alloys, 1934, 5, 256—258).—The upper, unpolished face of the specimen forms the base of a chamber, the vertical walls of which are metal tubes screwed one within the other. Small specimens are mounted in Wood's metal. The chamber is supported above the microscope objective and connected to it by a short length of rubber tubing. A branch tube connects the air space so confined to a  $P_2O_5$  bulb. When the air has been dried,  $Et_2O$  and solid  $CO_2$  or liquid air is admitted to the upper chamber. Formation of martensite from austenite has been traced. E. H. B.

**Micro-determination of vapour density.** D. A. PEAK and R. A. ROBINSON (J. Physical Chem., 1934, 38, 941—943).—A method requiring only a few mg. of substance, which is vaporised under reduced pressure in an apparatus of the V. Meyer type, is described. Results are within 3—5% of calc. vals. F. L. U.

**High-voltage vacuum tube.** D. H. SLOAN (Physical Rev., 1933, [ii], 43, 213).—Absorption curves indicated  $6 \times 10^5$  volts radiation with 5 milliamp. emission from the apparatus described. L. S. T.

**Attainment of high vacua in large metal chambers.** M. S. LIVINGSTON (Physical Rev., 1933, [ii], 43, 214).—Pressures  $< 5 \times 10^{-7}$  mm. can be maintained. L. S. T.

**Rapid filtration of viscous liquids.** E. B. MOSS (J. Sci. Instr., 1934, 11, 372).—A tight wad of

cotton-wool is pushed down through the liquid contained in a test-tube. C. W. G.

**Ultra-centrifuge and its region of applicability.** T. SVEDBERG (Ber., 1934, 67, [A], 117—129).—A lecture. H. W.

**Efficient small-scale fractionating equipment.** C. O. TONGBERG, D. QUIGGLE, and M. R. FENSKE (Ind. Eng. Chem., 1934, 26, 1213—1217).—Details are given of an all-glass still (I) of 50—100 c.c. capacity, and of a steel and Ni still (II) of 11 litres capacity. In (I) the column is lagged with a vapour jacket and packed with single-turn glass helices; the rate of reflux is measured with a small siphon cup. (II) is packed with Ni wire helices or staples and the rate of reflux is measured by the rate of flow of condenser  $H_2O$  and its temp. rise. A. G.

**Packing materials for [laboratory] fractionating columns.** M. R. FENSKE, C. O. TONGBERG, and D. QUIGGLE (Ind. Eng. Chem., 1934, 26, 1169—1177).—A no. of columns of varying diam. up to 2 in. and having varying types of packing were worked with suitable liquid pairs under total reflux until equilibrium was established. The height of a theoretical plate equiv. to the packing (I) was then determined. Such pairs as  $CCl_4-C_6H_6$  which could be readily analysed by determination of  $n$  were chiefly used. The best results were given by one- and two-turn helices of wire or glass and carding teeth  $\frac{1}{8}$  in. wide. Increase of height and of diam. tended to reduce efficiencies, partly owing to increase of channelling. Different hydrocarbon mixtures gave approx. the same results. The product of the no. of sq. in. of surface area per cu. in. and the % of free space, divided by 100, gives a no. parallel to the efficiency as determined by (I). Even slight corrosion greatly alters the behaviour of a packing, generally unfavourably. C. I.

**Apparatus for vacuum distillation.** A. W. STOUT and H. A. SCHUETTE (Ind. Eng. Chem. [Anal.], 1934, 6, 476—477).—A multiple receiver for collecting successive fractions of a condensate from a vac. distillation without interruption is described. E. S. H.

**Determination of tie lines in ternary systems without analyses for the components.** T. W. EVANS (Ind. Eng. Chem. [Anal.], 1934, 6, 408—409).—Mathematical. E. S. H.

## Geochemistry.

**Ozone and the sunspot cycle.** F. E. FOWLE (Trans. Amer. Geophys. Union, 1933, 110—111).—The dependence of the amount of  $O_3$  in the atm. on solar conditions, as indicated by sunspots, is not confirmed. CH. ABS. (e)

**Luminescence of the upper atmosphere.** J. CABANNES (Compt. rend., 1934, 199, 909—911).—An explanation is proposed for the presence in the least refrangible light emitted by the night sky of groups of radiations of atm. origin: bands of the first positive system of  $N_2$ , and  $O_2$  and  $H_2O$  bands. N. M. B.

**Atmospheric ozone in the neighbourhood of Shanghai.** P. LEJAY (Compt. rend., 1934, 199, 879—881).—Atm.  $[O_3]$  near Shanghai, as measured by the ratio of the intensities of solar radiation within and outside the  $O_3$  absorption band, shows an annual variation, being greatest in February and March and a min. in about November. J. W. S.

**Determination of arsenic content of the air.** O. M. FABER (Zentr. Gewerbehyg. Unfallverh., 19, 214—216; Chem. Zentr., 1934, i, 3888).—Counts of the no. of particles are made on photographs of a dust



sample before and after heating at 250°. At 250°,  $As_2O_3$  is removed, but other constituents are unaltered.

H. J. E.

**Mineral waters of Venice. Bromo-lithia water of Scorzè.** G. BRAGAGNOLO (*Annali Chim. Appl.*, 1934, 24, 493—495).—Composition and physico-chemical constns. are given. The  $H_2O$  contains mainly  $CaHCO_3$ , with 0.0003 g. Li and 0.0005 g. Br per litre.

T. H. P.

**Analysis of the water of the Zomaro (Calabria) spring.** B. RICCA and P. MEDURI (*Annali Chim. Appl.*, 1934, 24, 519—530).—This contains chiefly  $Cl^-$ ,  $HCO_3^-$ ,  $NO_3^-$ ,  $Na^+$ ,  $Ca^{++}$ , and  $SiO_2$ , and shows slight radioactivity. Composition, physico-chemical data, and results of bacteriological tests are given.

T. H. P.

**Waters of L. Boza.** V. CARCAMO (*Bol. Soc. Quím. Peru*, 1934, 1, 44—48).—A detailed analysis of the saline  $H_2O$  is given; the principal components are  $NaCl$ ,  $Na_2CO_3$ ,  $NaHCO_3$ ,  $Na_2SO_4$ ,  $KCl$ , and  $LiCl$ .  $H_3BO_3$ , I, and Br are also present.

E. L.

**Radioactive content of water and its sedimentations in pit-hole No. 1 of Oukhta region.** V. I. BARANOV and I. D. KUBBATOV (*Trans. inst. état radium*, U.S.S.R., 1933, 2, 139—156).—The average content was  $7.48 \times 10^{-9}$  g. Ra and  $2.1 \times 10^{-11}$  g. Ms-Th I per litre.

CH. ABS. (e)

**Relation between the temperature and the  $p_H$  of the bottom deposits from Takasukanuma pond.** K. SUGAWARA (*Bull. Chem. Soc. Japan*, 1934, 9, 446—448).—The  $p_H$  remains const. for temp. below 18.7°, which is  $>$  the highest temp. (17.5°) of the bottom of the pond during the year. At higher temp. the  $p_H$  is lowered. The effect on benthic fauna and flora is mentioned.

W. R. A.

**Radon content of mineral springs of Korea.** S. IMORI, J. YOSHIMURA, and S. HATA (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, 13, 1363—1372).—Rn contents of 8 mineral springs of Korea have been determined.

R. S. B.

**Origin of balthashite.** L. D. SHTURM (*Khim. Tver. Topl.*, 1934, 5, 16—32).—Balthashite ( $H_2O$  1.40—1.8, ash 4.3—8.4, and material extractable with  $C_6H_6 + EtOH$  9.65—33.0%) develops from seaweeds. The ash contains  $SiO_2$  28.61,  $Al_2O_3$  3.11,  $TiO_2$  0.35,  $Fe_2O_3$  7.30,  $CaO$  20.00,  $MgO$  16.22,  $K_2O$  1.56,  $Na_2O$  5.62,  $MnO$  0.03,  $SO_3$  15.98, and  $P_2O_5$  0.34%. Analyses for sapropel are also given.

CH. ABS. (e)

**Gold-bearing stony meteorite from Melrose, New Mexico.** H. H. NININGER (*Amer. Mineral.*, 1934, 19, 370—374).—Analyses are given. The material (1 large, 4 small, stones) contained 0.24 oz. Pt metals and 0.02—0.32 oz. Au per ton.

CH. ABS. (e)

**Processes of the formation of the earth, and periods of world drought.** W. MATHESIUS (*Naturwiss.*, 1934, 22, 787—792).—The variations in the composition of the earth and its atm. during the cooling process are described. The problem of periods of drought, and methods for preventing and alleviating them, are discussed.

A. J. M.

**Petrological study of Malka river granodiorite laccolith (in Northern Caucasus) in connexion with its radium content.** S. P. SOLOVIEV

(*Trans. inst. état radium*, U.S.S.R., 1933, 2, 223—245).

—Data for the Ra content of various rock samples are recorded.

CH. ABS. (e)

**Nature and deposition relations of the quartzite schist of Kupferberg, Silesia.** G. BERG (*Tsch. Min. Mitt.*, 1934, 46, 1—19).—The quartzites are related chemically and structurally to the Scandinavian leptites.

H. J. E.

**Sanidinites of the Laacher lake region.** G. KALB (*Tsch. Min. Mitt.*, 1934, 46, 20—55).—Two groups of sanidinites are described.

H. J. E.

**Pseudoleucitic and epileucitic rocks.** A. N. ZAVARITSKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 3, 645—651).—Two specimens pseudomorphic with leucite, occurring with the alkaline rocks of the Ishim river (West Siberia), are described and discussed.

H. J. E.

**Albite from Druzhnaya Gorka works with a small angle of optical axes.** D. S. BELLANKIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 3, 651—655).

—Albite was found in the crusts from the arch of a regenerative chamber in a glass works. Optical properties are recorded. The angle of optical axes is small and negative, the abnormality being due to the high temp. of formation.

H. J. E.

**Thermally metamorphosed diorite near Brookfield, Connecticut.** W. M. AGAR (*Amer. J. Sci.*, 1934, [v], 28, 401—411).—The local rocks (granodioritic gneiss and gneissoid diorite) are described. Their formation is discussed.

H. J. E.

**Limonite deposits at the Orient mine, Colorado.** J. B. STONE (*Econ. Geol.*, 1934, 29, 317—329).—The limonite is formed by near-surface oxidation of replacement bodies of Fe-bearing carbonate in limestone. Analyses are given.

CH. ABS. (e)

**Chloritoid from Dutchess County, New York.** T. F. W. BARTH and R. BALK (*Amer. Mineral.*, 1934, 19, 345—350).—The mineral ( $H_2FeAl_2SiO_7$ ) occurs as dark-green flakes scattered through a lens of sericite and quartz in a dark biotite-sericite schist.

CH. ABS. (e)

**Unusual occurrence of asbestos.** E. E. WAHLSTROM (*Amer. Mineral.*, 1934, 19, 178—180).—Fibrous and sheet-like masses of asbestos were found in a banded fissure-vein (Snowy Range mine, Boulder Co., Colorado), associated with Cu-bearing pyrite, galena, sphalerite, calcite, feldspar, quartz, and pyroxene.

CH. ABS. (e)

**Oligonite, a manganosiderite from Leadville, Colorado.** E. B. MAYO and W. J. O'LEARY (*Amer. Mineral.*, 1934, 19, 304—308).—Pale "taffy-coloured" crystals ( $MnO$  35.28,  $FeO$  26.18,  $CO_2$  37.98%) in radiating bundles of small columns were found associated with galena, chalcopyrite, and sphalerite.

CH. ABS. (e)

**Vanadium, molybdenum, tungsten, and chromium in oxidised lead deposits.** W. H. NEWHOUSE (*Amer. Mineral.*, 1934, 19, 209—220).—Analyses of sulphides found in Pb and Pb-Zn-Cu deposits indicate that they may contain small amounts of V, Mo, Cr, and W, and hence be the source of these elements in the oxidised Pb deposits.

CH. ABS. (e)



**Selective incrustation of crystal forms.** C. FRONDEL (Amer. Mineral., 1934, 19, 316—329).—Specimens of quartz, calcite, and galena are described and discussed. CH. ABS. (e)

**Paragenesis of the Traföss serpentine reaction aureole.** F. WEINZEDL (Tsch. Min. Mitt., 1934, 46, 73—84).—The paragenesis is discussed. Analyses of the following minerals are recorded: andradite, diopside, epidote, hornblende, antigorite serpentine, and orthoamphibolite. H. J. E.

**Classification of deformed shales by optical and X-ray means.** B. SANDER (Z. Krist., 1934, 89, 97—124).—A general survey from the mineralogical viewpoint, with particular reference to those rocks in which owing to included fossils the deformation process can be followed. B. W. R.

**Relation between phosphoric acid and fluorine contents of the Chibin apatite-nepheline deposits.** E. N. ISAKOV (Zavod. Lab., 1934, 3, 796—799).—For Chibin apatite containing  $> 38\%$   $P_2O_5$ , % F is given by  $y/12.7062$ , where  $y$  is the %  $P_2O_5$  content; the results differ from experimental by  $\pm 0.06\%$ . R. T.

**Is the colour of the natural ruby due to iron?** W. J. O'LEARY, G. L. ROYER, and J. PAPISH (Science, 1934, 80, 412—414).—Fe and Cr determinations of natural rubies show that (i) the total amount of pigmentsing oxides (I) varies between 0.83 and 3.5%, (ii) apparently the depth of colour  $\propto$  the total amount of (I), irrespective of the  $Cr_2O_3$  present, (iii) there is no fixed ratio of Fe : Cr, and (iv) the amount of (I) in the more deeply coloured natural rubies coincides with the amount which must be added to synthetic preps. in order to produce the same colour. L. S. T.

**Distribution of arsenic in relation to rock structure in the Eastern Alps.** R. SCHWINNER (Tsch. Min. Mitt., 1934, 46, 56—72).—A discussion. H. J. E.

**Arsenic content of soils.** J. E. GREAVES (Soil Sci., 1934, 38, 355—362).—The total and  $H_2O$ -sol. As of orchard soils varied widely. Vals. were unrelated to sol. salt or org. N contents. A. G. P.

**Subdivision of the Upper Peninsula experimental forest on the basis of soils and vegetation.** S. A. WILDE and H. F. SCHOLZ (Soil Sci., 1934, 38, 383—399).—An ecological study on 5 soil profiles. A. G. P.

**Functional relationships between soil properties and rainfall.** H. JENNY and C. D. LEONARD (Soil Sci., 1934, 38, 363—381).—In soils situate

along the  $11^\circ$  isotherm the  $CO_3$  content decreases and the N content increases with rainfall. High rainfall favours colloidal clay formation.  $p_H$  vals. decline with increasing rainfall, neutrality being associated with an annual pptn. of 25 in. Exchangeable  $H^+$  appears in areas having  $< 26$  in. of rain and increases with rainfall, max. exchangeable bases being found in soils having 26 in. A. G. P.

**Formation and stability of soil structure.** P. I. ADRIANOV (Z. Pflanz. Düng., 1934, A, 36, 26—37).—The structure of soils is examined in relation to vol.-temp. changes and variations in internal cohesive forces. A. G. P.

**Origin of brilliant coal (vitrain).** M. LEGRAYE (Rev. Univ. Mines, 1934, [viii], 10, 352—354; Fuel, 1934, 13, 345—347).—Bright coal may consist of thin deposits of accumulated ulmic matter, which form the rarely-occurring structureless vitrain, or of lenticles of tissues ulmified *in situ*, forming structure vitrain. Dull coal is formed by accumulation of undecomposed vegetable debris, generally cuticles, spores, etc., which may be cemented together by a little ulmic matter. A. B. M.

**Microscopical structure of vitrain. I. Band of vitrain occurring in bright coal.** R. G. H. B. BODDY (Fuel, 1934, 13, 326—332).—A vitrain band occurring in a specimen of clarain from the Top Hard seam exhibited when examined microscopically a well-preserved structure which showed that it had once been a piece of coniferous-like wood. The structure is illustrated by photomicrographs. A. B. M.

**Petrographic characteristic of Irkutsk sapropel coals.** Y. A. ZHEMCHUZHNIKOV (Khim. Tver. Topl., 1934, 5, 97—107).—The coals are described and their formations discussed. CH. ABS. (e)

**Origin of Barzass coals.** Z. ERGOLSKAYA (Khim. Tver. Topl., 1934, 5, 32—39).—A discussion. CH. ABS. (e)

**Petrographical investigation of the coal deposits of the Borovichi district.** E. S. KORZHENEVSKAYA (Khim. Tver. Topl., 1933, 4, 198—204).—The composition and formation of the deposits are discussed. CH. ABS. (e)

**Occurrence of sal ammoniac at Tamaki, Auckland.** J. A. BARTRUM (New Zealand J. Sci. Tech., 1934, 16, 80).—Formation of  $NH_4Cl$  results from the natural combustion of a thick bed of lignite. The salt is deposited on overlying clay strata. A. G. P.

## Organic Chemistry.

[Pseudo-atoms.] H. ERLIENMEYER (Helv. Chim. Acta, 1934, 17, 1558—1559; cf. A., 1933, 557).—Comments on papers by Perret and Perrot and by von Platz (A., 1933, 815; 1934, 1209). F. L. U.

**Specific refractive dispersion as a method for distinguishing between different series of hydro-**

carbons. A. L. WARD and W. H. FULWEILER (Ind. Eng. Chem. [Anal.], 1934, 6, 396—400).—The  $d$  and  $n$  (for 6563, 5893, 5461, 4861, and 4358 Å.) have been determined for several hydrocarbons and their mixtures. In general, the effect of substitution on dispersion is related to its effect in decreasing the benzenoid and increasing the paraffinoid character of the hydro-



carbon. Individual effects in paraffins, olefines, and aromatic hydrocarbons are described. The possibilities of the use of sp. dispersion data are discussed.

E. S. H.

**Thermal decomposition of organic compounds from the viewpoint of free radicals. X. Identification of methyl groups as dimethyl ditelluride.** F. O. RICE and A. L. GLASEBROOK (J. Amer. Chem. Soc., 1934, 56, 2472).—The fragments obtained by thermal decomp. of  $C_4H_{10}$ ,  $COMe_2$ , or  $Et_2O$  at 800–900° combine with Te to give *dimethyl ditelluride* (I), b.p. 196° (decomp.), m.p. –19.5°, as the sole product; radicals other than Me are not produced. (I) is comparatively stable in air and has a low v.p. at room temp.

H. B.

**Thermal decomposition of organic compounds from the viewpoint of free radicals. XI. Methylene radical.** F. O. RICE and A. L. GLASEBROOK (J. Amer. Chem. Soc., 1934, 56, 2381–2383; cf. A., 1933, 930).— $CH_2$  is formed when  $CH_2N_2$  is decomposed at < 500° in a current of  $Et_2O$  or  $C_4H_{10}$ . At > 650° and < the decomp. temp. of  $Et_2O$  Me is formed.  $CH_2$  reacts with Te, Se, As, and Sb, but not with Zn, Cd, Hg, Tl, Pb, and Bi. Me reacts with all these elements. The reaction of  $CH_2$  with Te yields a red solid,  $(CH_2Te)_n$ , whilst Me yields  $Te_2Me_2$ .

E. S. H.

**Mechanism of the formation of methane and condensation products by the pyrolysis of ethane, ethylene, etc.**—See this vol., 40.

**Isomerisation of allene hydrocarbons by silicates. I. Isomerisation of asymmetric dimethylallene in presence of floridin.** J. M. SLOBODIN (J. Gen. Chem. Russ., 1934, 4, 778–782).— $CP^{\beta}:CH$  yields a mixture of isoprene (I) and  $CH_2:CMc:CH:CH_2$  (II) when heated with floridin; the yields of (I) rise from 3.2% at 215° to 20% at 280°, above which they remain const., owing to polymerisation to the dimeride. The yields of (II) rise continuously from 25% at 215° to 60% at 334°.

R. T.

**Preparation and cationoid reactivity of dichlorodinitromethane.** E. DOWNING and W. B. ORR (J.C.S., 1934, 1671–1672).— $CCl_2(NO_2)_2$  [from  $s-C_6H_2Cl_3 \cdot NH_2$  and warm  $HNO_3$  ( $d$  1.42) followed by distillation] and  $N_2H_4 \cdot H_2O$  in aq.  $EtOH-NaOH$  react thus:  $2CCl_2(NO_2)_2 + N_2H_4 \rightarrow 2CHCl(NO_2)_2 + N_2 + 2HCl$ . In the absence of alkali, reduction continues slowly beyond this stage. In accordance with expectation, similar reductions of  $CBr_2(NO_2)_2$  occur more rapidly (cf. Macbeth and Pratt, *ibid.*, 1921, 119, 1356).

H. B.

**Halogenation inhibition by oxygen.** R. M. DEANESLY (J. Amer. Chem. Soc., 1934, 56, 2501–2502; cf. Bauer and Daniels, A., 1934, 1216).—Chlorination of  $C_3H_8$ ,  $C_4H_{10}$ , and pentanes is inhibited by  $O_2$  even in presence of light or olefines (cf. B., 1933, 1046). Addition of  $Cl_2$  to, e.g.,  $\Delta^{\beta}$ -butene is not inhibited by  $O_2$  even in the dark or absence of catalysts; reaction is very fast (accordingly, any retardation is not easy to detect).

H. B.

**Catalysis in hydrogen bromide-olefine additions.** V. N. IPATIEV, H. PINES, and R. C. WACKER (J. Amer. Chem. Soc., 1934, 56, 2398—

2400).—When  $C_3H_6$  is passed through  $AcOH-HBr$ , some of the  $C_3H_6$  dissolves, but no reaction occurs. Addition of  $C_6H_{14}$ , *cyclohexane*,  $C_6H_6$ ,  $Bu^{\gamma}Br$ ,  $EtBr$ , or  $PhBr$  to the  $AcOH-HBr$  promotes reaction;  $H_2O$  and  $EtOH$  have no effect. Reaction also occurs when an equimol. mixture of  $C_3H_6$  and  $HBr$  is passed through  $C_6H_{14}$ . When an equimol. mixture of  $C_3H_6$  and *isobutene* is passed through  $AcOH-HBr$ , the  $C_3H_6$  reacts (slowly at first and then more rapidly) owing to the catalytic effect of the  $Bu^{\beta}Br$  produced. Reaction between  $C_4H_8$  and  $AcOH-HBr$  is similarly autocatalytic. All experiments are carried out at 5°.

H. B.

**Rule relating to the formation of a double linking in aliphatic halogeno-compounds.** S. C. J. OLIVIER (Rec. trav. chim., 1934, 53, 1093–1096).—The elimination of  $HHal$  from aliphatic halogeno-compounds (saturated) involves the removal of the H attached to the C bearing the largest no. of negative atoms or groups. Various examples (lit.) are given. In  $CHMeBr_2$ , where the elimination of such a H cannot occur, reaction with  $KOH$  must be much slower than with  $CH_2Br-CH_2Br$  (cf. following abstract).

H. B.

**Action of acids and bases on  $\alpha$ - and  $\alpha\beta$ -dibromoethanes.** S. C. J. OLIVIER and A. P. WEBER (Rec. trav. chim., 1934, 53, 1087–1092).—Hydrolysis (method: A., 1934, 971) of  $CHMeBr_2$  (I) and  $CH_2Br-CH_2Br$  (II) by aq.  $COMe_2$  at 60° is not accelerated by  $H^+$ . (I) and (II) are not hydrolysed (cf. Burkhardt and Cocker, A., 1931, 1031) by aq.  $KOH$  in various org. solvents, but are converted into  $CH_2:CHBr$  (and to some extent into  $C_2H_2$ ); in aq.  $COMe_2$  at 30° the velocity coeffs. for (I) and (II) are 0.000023 and 0.0047, respectively.

H. B.

**Chlorobutene  $C_4H_7Cl$  obtained in the action of phosphorus pentachloride on methyl ethyl ketone.** P. CHARPENTIER (Bull. Soc. chim., 1934, [v], 1, 1407–1411).—The chlorobutene obtained, together with  $CMeEtCl_2$ , by the action of  $PCl_5$  on  $COMeEt$  (Dupont, A., 1909, i, 545) is a mixture of  $\beta$ -chloro- $\Delta^{\alpha}$  (I) and  $\Delta^{\beta}$  (II) *n*-butene, since, after careful fractionation, oxidation of the low fraction, b.p. 58.5–59°, with 2 mols. of alkaline  $KMnO_4$  affords a mixture of  $EtCO_2H$  and  $AcOH$ , and  $CO_2$  (from  $HCO_2H$ ), and is thus a mixture of (I) and (II); the fraction, b.p. 64–66°, gives only  $AcOH$  and is thus almost pure (II). The composition of the mixed acids is determined by analysis of their Ba salts.

J. W. B.

**Preparation of  $\psi$ -butylene chlorohydrin.** V. S. BATALIN and P. G. UGRIMOV (J. Gen. Chem. Russ., 1934, 4, 871–874).—The chlorohydrin is obtained in 50–60% yield by Gomberg's method (A., 1919, i, 567), and in 60–65% yield by McElroy's method (U.S.P. 1,253,616; B., 1918, 167).

R. T.

**Splitting of ditertiary alkylcarbinols by dehydration. Dehydration of *tert*-butyl*tert*-amyl- and *tert*-butyl*tert*-hexyl-carbinols.** I. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 612–615; cf. A., 1934, 753).—Pinacolin with  $NaNH_2$  and  $MeI$  or  $EtI$  gives, respectively, *tert*-butyl *tert*-amyl, b.p. 172–177°, and *tert*-hexyl ketone, b.p. 193–198°, which are reduced ( $Na-EtOH$ ) to *carbinols*, b.p. 186–190° (I) and 206–211° (II), respectively. (I)



with 1:4-C<sub>10</sub>H<sub>6</sub>Br·SO<sub>3</sub>H (III) at 150° affords a mixture of CHMe:CHEt, CMe<sub>2</sub>:CHMe (IV), and δ-methyl-Δ<sup>β</sup>-pentene (V). With H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at 150–160°, (I) affords some (IV) and a mixture of decenes, which with (III) gives products similar to the above. Similarly, (II) gives (IV), (V), γ-ethyl-Δ<sup>β</sup>-pentene, and higher-boiling hydrocarbons. J. L. D.

**Synthesis of allostulcitol and dulcitol.** R. LESPIEAU (Bull. Soc. chim., 1934, [v], 1, 1374–1376).

—When heated with H<sub>2</sub>O the oxide  $\left[ \text{O} \begin{array}{l} \text{CH}_2 \\ \text{CH:C} \end{array} \right]_2$  (not a mixture of stereoisomerides) affords the crude acetylenic (OH)<sub>4</sub>-derivative (I) from which by repeated extraction with MeOH is isolated only a small amount of one stereoisomeride, m.p. 116–117.5°, reduced by Pd–H<sub>2</sub> to *cis*-Δ<sup>γ</sup>-*n*-hexene-αβεζ-tetraol (II), m.p. 80–82°. Similar reduction of (I) and subsequent acetylation gives an Ac<sub>4</sub> derivative (III), b.p. 170°/12 mm. Oxidation of (II) with AgClO<sub>3</sub>–OsO<sub>4</sub> gives almost exclusively allostulcitol, sinters 142°, m.p. 148°, but a trace not melting until 160°, most probably dulcitol (IV). Similar oxidation of (III) and acetylation of the product gives the Ac<sub>8</sub> derivative of (IV), and a *substance*, m.p. 50–59°. J. W. B.

**Dry ether as a solvent for anhydrous aluminium chloride in organic synthesis.** R. C. SHAH (Current Sci., 1934, 3, 157).—A solution (I) of anhyd. AlCl<sub>3</sub> in dry Et<sub>2</sub>O may be used with advantage in Friedel–Crafts syntheses which occur under mild conditions, or in place of ZnCl<sub>2</sub>–Et<sub>2</sub>O suspension in the Hoesch synthesis, examples being cited. In some cases Et<sub>2</sub>O reacts to give ethers; e.g., BzCl → EtOBz, CPh<sub>2</sub>Cl → CPh<sub>3</sub>·OEt → CHPh<sub>3</sub>+MeCHO.

J. W. B.

**Hydration of ethylene oxide.** C. MATIGNON, H. MOUREU, and M. DODÉ (Bull. Soc. chim., 1934, [v], 1, 1308–1317).—By the action of (CH<sub>2</sub>)<sub>2</sub>O (I) on (CH<sub>2</sub>:OH)<sub>2</sub> (II) in presence of 0.5% H<sub>2</sub>SO<sub>4</sub> at 90°, pure specimens of tri- (III) and tetra- (IV) -ethylene glycol HO·CH<sub>2</sub>·[CH<sub>2</sub>·O·CH<sub>2</sub>]<sub>n</sub>·CH<sub>2</sub>·OH, are prepared, and the *n<sub>v</sub>*-composition curves for synthetic mixtures of (II)–diethylene glycol (V), (III)–(V), and (IV)–(V) are determined. The compositions of the mixtures of glycols obtained when (I) is hydrolysed with varying amounts of H<sub>2</sub>O (0.5% H<sub>2</sub>SO<sub>4</sub> at 90–95°) are thus determined by measurement of *n<sub>p</sub>* for the binary mixtures obtained by fractional distillation. Temp. and [H<sup>+</sup>] have little effect on the composition of the product, which is determined mainly by the mol. ratio (R) H<sub>2</sub>O/(I). As R is decreased successively from 10.5 to 0.61 the % of (II) decreases continuously from 82.3 to 15.7%; that of (V) increases from 12.7 to a max. of 34.5% at R=2.1 and then decreases to 26%. No (III) is formed until R=4.2 (2.3%), and it then increases to 19.8%; no (IV) is formed until R=2.1 (0.3%), increasing to 19%. Higher glycols are not formed until R=1.40. Thus to obtain pure (II), R must be < 2.0. J. W. B.

**Complex platinum compounds with ter- and quinque-valent platinum.** VII.—See this vol., 52.

**Decomposition of neutral alkyl sulphites by heat.** P. CARRÉ and D. LIBERMANN (Bull. Soc. chim., 1934, [v], 1, 1248–1250).—Alkyl sulphites (2

mols.) are decomposed by heat to give the olefine (1 mol.) and alcohol (1 mol.), if the alkyl group has a high mol. wt. The temp. of decomp. is lowered by approach of a substituent Ph nearer to S, by unsaturation in the alkyl, or addition of C<sub>5</sub>H<sub>5</sub>N. In the first case, the decomp. may take an alternative course. Thus, SO(OBu<sup>α</sup>)<sub>2</sub> is stable at the b.p. (228°). *Decyl sulphite* (from SOCl<sub>2</sub> and the alcohol in C<sub>5</sub>H<sub>5</sub>N), b.p. about 250°/15 mm., decomposes to decene and C<sub>10</sub>H<sub>21</sub>·OH at 310°. SO(OPr<sup>β</sup>)<sub>2</sub> gives C<sub>3</sub>H<sub>6</sub> and Pr<sup>β</sup>OH at 310° alone or 210° in C<sub>5</sub>H<sub>5</sub>N. *β-Phenyl-ethyl sulphite*, b.p. 238–240°/15 mm., at 290° gives (CH<sub>2</sub>Ph·CH<sub>2</sub>)<sub>2</sub>O, b.p. 194–195°/20 mm., and SO(O·CH<sub>2</sub>Ph)<sub>2</sub> (lit. b.p. 193–199°/15 mm.) decomposes at 130° to (CH<sub>2</sub>Ph)<sub>2</sub>O, b.p. 166–168°/13 mm., 295–298°/760 mm. *Allyl sulphite*, b.p. about 110°/45 mm., gives 45% of CH<sub>2</sub>:CH·CH<sub>2</sub>·OH and only a trace of olefine (most of that formed resinifies) at 190° alone or 110–120° in C<sub>5</sub>H<sub>5</sub>N. *Cinnamyl sulphite* decomposes at 100° (even in vac.) to form resins and cannot be distilled. R. S. C.

**Cleavage of lecithin by heat.** M. SATO and N. WADA (J. Soc. Chem. Ind. Japan, 1934, 37, 717–718B).—In agreement with Page and Schmidt (A., 1931, 1082) and contrary to Paal (A., 1929, 1337), lecithin (from soya-bean oil) is comparatively stable to heat in EtOH solution, only 3–4% hydrolysis occurring after 3 hr. at 120°. H. N. R.

**Fermentation of mannose by dried yeast.**—See A., 1934, 1405.

**Intramolecular transpositions. I. Influence of carboxyl, ester, and nitrile groups on allylic intramolecular transpositions.** R. RAMBAUD (Bull. Soc. chim., 1934, [v], 1, 1206–1232).—A summary of experiments not yet described in detail. Formation during a reaction of CH<sub>2</sub>:CH·CHYR (I) from CH<sub>2</sub>X·CH:CHR (II) is prevented if R=CO<sub>2</sub>H, CO<sub>2</sub>R' (R'=H, Me, Et, or Pr), or CN, and that of (II) from (I) is similarly rendered more difficult, but the formation of CHMe:CYR from (I) is facilitated; these rules apply only if X and Y ≠ H. Replacement is termed "normal" if such changes are not involved. The following are exclusively "normal": acetylation in presence of H<sub>2</sub>SO<sub>4</sub> or NaOAc of (I) (Y=OH; R=CO<sub>2</sub>H, CO<sub>2</sub>Me, CO<sub>2</sub>Et, or CN) and of *trans*-γ-hydroxycrotonic acid (the resulting Ac derivatives resist isomerisation); reaction of (II) (X=Br; R=CO<sub>2</sub>R') with NaOAc; alkaline hydrolysis of the Ac derivatives resulting from the above reactions; hydrolysis of (II) (X=Br; R=CO<sub>2</sub>R') by AgOH in the cold (giving OH-esters) or KOH or Ba(OH)<sub>2</sub> cold (giving the Br-acid) or hot (giving the OH-acid) [(CO<sub>2</sub>H·CH:CH·CH<sub>2</sub>)<sub>2</sub>O is also formed under certain conditions]; replacement of X=Br by NET<sub>3</sub>, and of X or Y=OH (R=CN or an ester) by Cl (SO<sub>2</sub>Cl–C<sub>5</sub>H<sub>5</sub>N). Anionotropic isomerism occurs in the following cases: α-hydroxy-Δ<sup>β</sup>-butenoic acid and its esters with PBr<sub>3</sub> give mixtures of α- and γ-Br-compounds with more or less decomp.; reaction of Et α-bromo-Δ<sup>β</sup>-butenoate with NaOAc or AgOH (cold) gives Et γ-acetoxy- or γ-bromo-crotonate; α-chloro-Δ<sup>β</sup>-butenoates with CaBr<sub>2</sub> give α-bromocrotonates (the nitrile reacts similarly, but more slowly); CH<sub>2</sub>:CH·CHCl·CO<sub>2</sub>Me and HCl give a little



$\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , which is the only case observed of anionotropy involving Cl. The following "abnormal" reactions involving prototropy are recorded. (a) Substances of type (I) in which  $\text{Y}=\text{Cl}$ : if  $\text{R}=\text{CO}_2\text{R}'$  or  $\text{CN}$ ,  $\text{NaOH}$  gives rapidly  $\text{CHMe}\cdot\text{CCl}\cdot\text{CO}_2\text{H}$  (III); if  $\text{R}=\text{CO}_2\text{R}'$ , aq.  $\text{NH}_3$  gives (III) or its amide, and anhyd.  $\text{NH}_4\text{Et}_2$  gives its esters (with a 10% yield of  $\alpha\text{-NEt}_2$ -ester), also formed (exclusively) by  $\text{NaOAc}$  in  $\text{AcOH}$ ; if  $\text{R}=\text{CN}$  or an ester group, conc.  $\text{HCl}$  gives slowly (III) and oily by-products, but in this case the migration may have occurred after hydrolysis. (b) Substances of type (I) in which  $\text{Y}=\text{OH}$ ; here migration of H gives  $\text{CHMe}\cdot\text{CR}\cdot\text{OH}$ , which ketonises to  $\text{EtCOR}$ ;  $\alpha$ -hydroxy- $\Delta^{\beta}$ -butenoic acid gives  $\text{COEt}\cdot\text{CO}_2\text{H}$  more readily in aq.  $\text{K}_2\text{CO}_3$  than in  $\text{HCl}$ ; the  $\text{OH}$ - and  $\text{OAc}$ -esters are similarly isomerised and hydrolysed (hydrolysis of  $\text{CO}_2\text{R}'$  must precede that of  $\text{OAc}$ ) by alkali, but not by acid; if  $\text{R}=\text{CN}$ ,  $\text{PBr}_3$  alone gives a complex mixture of Br-compounds, but in  $\text{Et}_2\text{O}$  acts catalytically to yield  $\text{EtCO}\cdot\text{CN}$ , which in presence of aq. acid forms  $\text{EtCO}_2\text{H}$ ;  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CN}$  and  $\text{PBr}_3$  in  $\text{Et}_2\text{O}$  give, however, much Br-nitrile and little  $\text{PrCO}_2\text{H}$ . These and other results recorded in the lit. are interpreted as due to reaction of the unsaturated substance as a "tripolar ion,"  $\bar{\text{C}}\text{H}_2\cdot\bar{\text{C}}\text{H}\cdot\bar{\text{C}}\text{HR}$ , if  $\text{R}=\text{H}$  or alkyl, but as a "pentapolar ion,"  $\bar{\text{C}}\text{H}_2\cdot\bar{\text{C}}\text{H}\cdot\bar{\text{C}}\text{X}\cdot\bar{\text{C}}(\text{OR}')\cdot\bar{\text{O}}$  or  $\bar{\text{C}}\text{H}_2\cdot\bar{\text{C}}\text{H}\cdot\bar{\text{C}}\text{X}\cdot\bar{\text{C}}\cdot\bar{\text{N}}$ , if  $\text{R}=\text{CO}_2\text{R}'$  or  $\text{CN}$ ; in the latter case prototropic ionisation is favoured and anionotropic ionisation is hindered by the electrical nature of R. Similar considerations apply to substances of type (II). The relative ease of fission as ion is  $\text{Cl}^-$ ,  $\text{OH}^- < \text{H}^+ < \text{Br}^-$ .

R. S. C.

Reaction between esters of organic acids and mixed organomagnesium compounds, especially with magnesium isopropyl chloride. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1934, [v], 1, 1419—1424).—The vol. of hydrocarbon evolved (tabulated) in the interaction of  $\text{MgRX}$  with esters depends on the mol. ratio ( $r=\text{MgRX}/\text{ester}$ ), and is greatest with  $\text{MgPr}^{\beta}\text{Cl}$  (I). By determination of the vol. of  $\text{C}_3\text{H}_8$  (accompanied by a little  $\text{C}_3\text{H}_6$ ) evolved in such interaction of (I) and various esters at  $35^\circ$  the following four types of reaction are recognised, examples being given in parentheses: (a) simple enolisation (max.  $r=2:1$ ),  $\text{CH}_2\text{R}\cdot\text{CO}_2\text{Et} \rightarrow \text{CHR}\cdot\text{C}(\text{OEt})\cdot\text{OMgX}$  [ $\text{CH}_2(\text{CO}_2\text{Et})_2$ ,  $\text{CH}_2\text{Et}(\text{CO}_2\text{Et})_2$ ,  $\text{CHPh}_2\cdot\text{CO}_2\text{Et}$ , and  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Pr}^{\alpha}$ ]; (b) condensation and enolisation of the product ( $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ ); (c)  $\text{EtOAc}$  affords  $\text{COMePr}^{\beta}$ , which enolises (max.  $r=3:1$ ) [similarly with  $\text{Et}\cdot\text{CO}_2\text{Et}$  and  $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ ]; and (d) a combination of (a), (b), and (c) ( $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ ,  $\text{CHCl}_2\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CO}_2\text{Et}$ ,  $\text{Pr}^{\alpha}\text{CO}_2\text{Et}$ , and  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ ). Similar types of results are obtained with other  $\text{MgRX}$  compounds.

J. W. B.

Mechanism of Kolbe's reaction. I. Electrolysis of free acetic acid.—See this vol., 45.

Lead acetato-chloride.—See this vol., 50.

Electrolysis of acetate solutions.—See this vol., 45.

Intramolecular transformations. II. Preparation and study of  $\alpha$ -hydroxyvinylacetic acid and its derivatives. Experimental study of their normal reactions and the normal reactions of the isomeric  $\gamma$ -substituted crotonic acids. III. Abnormal reactions of  $\alpha$ -substituted derivatives of vinylacetic acid. R. RAMBAUD (Bull. Soc. chim., 1934, [v], 1, 1317—1341, 1342—1355).—Experimental details of results previously summarised (A., 1933, 489, 1275, 1281) are given. The following appears to be new: the lactide,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}\langle\text{CO}\cdot\text{O}\rangle\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ,

m.p.  $151\text{--}152^\circ$  ( $\text{Br}_4$  additive compound, m.p.  $225^\circ$ ); hydrolysis of esters of the *trans*- $\gamma$ -Br-acid with  $\text{NaOH}$  at room temp. affords the ether ( $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ) $_2\text{O}$ , m.p.  $195^\circ$  (*Ag* and *Ba* salts), of *trans*- $\gamma$ -hydroxy- $\Delta^{\alpha}$ -butenoic acid, and interaction with  $\text{NH}_4\text{Et}_2$  in dry  $\text{Et}_2\text{O}$  gives *Et*  $\gamma$ -diethylamino- $\Delta^{\alpha}$ -butenoate, b.p.  $111\text{--}111.5^\circ/15$  mm. (*picrate*, m.p.  $97\text{--}98^\circ$ );  $\alpha\beta$ -dichlorobutyronitrile, b.p.  $74\text{--}78^\circ/17.5$  mm. (*amide*, m.p.  $121^\circ$ ). *Me*, b.p.  $87^\circ/15$  mm., and *Pr}^{\alpha}*, b.p.  $108\text{--}109^\circ$ ,  $\gamma$ -bromo- $\Delta^{\alpha}$ -butenoate are described. J. W. B.

Toxic principle of croton oil. I. Acids of croton oil. B. FLASCHENTRÄGER and R. VON WOLFFERSDORFF (Helv. Chim. Acta, 1934, 17, 1444—1452).—Analysis of croton oil gives the following results: toxic substances, 3.4%; unsaponifiable matter, 0.25%; oleic, 37.0%, linoleic, 19.1%, arachidic, 1.52%, stearic, 0.31%, palmitic, 0.89%, myristic, 7.45%, lauric, 0.05%, valeric, trace, tiglic acid, 0.03%;  $\text{PrCO}_2\text{H}$ , trace;  $\text{AcOH}$ , 0.6%;  $\text{HCO}_2\text{H}$ , 0.8%; acids insol. in light petroleum, 6.93%; undetermined acids, 0.64%; glycerol, 7.20%; loss, 13.83%. H. W.

Composition of cacao butter. Partial hydrolysis of mixed azelaic glycerides. J. BOUGAULT and G. SCHUSTER (Bull. Soc. chim., 1934, [v], 1, 1416—1419).—Contrary to the criticism of Hilditch *et al.* (A., 1933, 592), analytical data (C, 74.14; H, 11.95%) and mol. wt. (595) determinations for the product obtained by partial hydrolysis [cold aq.  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$ , or in  $\text{Et}_2\text{O}$ - $\text{EtOH}$ - $\text{KOH}$  (I)] of the triglyceride (II), m.p.  $59^\circ$ , from cacao butter confirm the original conclusion (A., 1931, 820) that it is glyceryl  $\alpha$ -palmitate  $\gamma$ -stearate, m.p.  $45\text{--}46^\circ$  (*loc. cit.*, m.p.  $34^\circ$ ), and not *Et* stearate, although the latter is also formed in (I). (II) is therefore  $\alpha$ -palmito- $\beta$ -oleo- $\alpha$ -stearin (A., 1931, 1199). J. W. B.

Heneicosoic acid. S. SHIINA (J. Soc. Chem. Ind. Japan, 1934, 37, 721B).—*Et* nonadecoate is converted successively into *n*-nonadecanol, m.p.  $61.8\text{--}62.0^\circ$ , the iodide, m.p.  $42.0\text{--}42.2^\circ$ , *n*-nonadecylmalonic acid, and *n*-heneicosoic acid, m.p.  $73.9\text{--}74.2^\circ$  (*Et*, m.p.  $44.2\text{--}44.4^\circ$ , and *Me*, m.p.  $46.8\text{--}47.2^\circ$ , ester). H. N. R.

Alkylation of acetoacetic, malonic, and succinic esters. B. WOJCIK and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 2424—2425).— $\text{CH}_2\text{R}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , where  $\text{R}=\text{H}$ , *Me*, *Pr*, hexyl, *Ph*, and furyl, are prepared by reduction ( $\text{H}_2$ , Raney Ni at room temp.) of  $\text{CHR}\cdot\text{C}(\text{CO}_2\text{Et})_2$  [from  $\text{RCHO}$ ,  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , and piperidine]. *Et* heptylidenemalonate has b.p.  $143\text{--}145^\circ/5$  mm. *Et* itaconate is simi-



larly reduced to Et  $\alpha$ -methylsuccinate; Et  $\alpha$ -isopropylidenesuccinate [from  $(\text{CH}_2\text{CO}_2\text{Et})_2$ ,  $\text{COMe}_2$ , and EtOH-NaOEt] gives Et  $\alpha$ -isopropylsuccinate; Et  $\alpha$ -methylbenzylidenesuccinate affords Et  $\alpha$ -methylbenzylsuccinate; Et  $\alpha$ -heptylidene- and  $\alpha$ -cinnamylidene-acetoacetates yield Et  $\alpha$ -heptylacetate and  $\alpha$ -acetyl- $\delta$ -phenylvalerate, respectively. H. B.

**Derivatives of glyoxylic acid and their use in the Hopkins-Cole reaction.** P. P. T. SAH, C. H. KAO, and T. Y. CHANG (J. Chinese Chem. Soc., 1934, 2, 234—239).—The following compounds of glyoxylic acid (I) are described: *o*-nitrophenyl-, m.p. 213—214° (decomp.), and  *$\beta$* -naphthyl-, m.p. 208°; 3-nitro-, m.p. 206—207°, 3:5-dinitro-, m.p. 223—224° (decomp.), *o*-, m.p. 199° (decomp.), and *p*-chloro-benzoyl-hydrazone, m.p. 210° (decomp.); phenyl-, m.p. 183—184°, *o*-, m.p. 194—195° (decomp.), and *p*-tolyl-, m.p. 217—218°, and  $\alpha$ -naphthyl-semicarbazone, m.p. 190—191° (decomp.). These compounds in conc.  $\text{H}_2\text{SO}_4$  give a violet coloration with tryptophan and are recommended as substitutes for (I) in the Hopkins-Cole reaction. J. L. D.

**Acetolic condensations of ethyl acetoacetate with acetaldehyde.** H. GAULT and T. WENDLING (Compt. rend., 1934, 99, 1052—1054; cf. A., 1934, 1332).— $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  is added gradually to a mixture of 33% MeCHO and  $\text{K}_2\text{CO}_3$  at 0°. When the solution no longer gives a colour with  $\text{FeCl}_3$ , the temp. is lowered to  $-15^\circ$  and  $\text{K}_2\text{CO}_3$  and a large excess of MeCHO are added, whereby Et di- $\alpha'$ -hydroxyethylacetoacetate (I), m.p. 33°, is prepared. (I) is too unstable to permit the isolation of derivatives and passes when kept in vac. over  $\text{H}_2\text{SO}_4$  at  $> 20^\circ$  into the unstable, non-cryst. Et  $\alpha'$ -hydroxyethylacetoacetate (II) (phenyl-hydrazone, m.p. 92°; corresponding pyrazolone, m.p. 275°), also obtained directly from  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ , MeCHO, and  $\text{K}_2\text{CO}_3$ . In presence of  $\text{NH}_4\text{Et}_2$  at  $-10^\circ$  (II) passes into non-cryst. Et<sub>2</sub>  $\delta$ -hydroxy- $\alpha$ -diacetyl- $\beta$ -methylpentane- $\alpha$ -dicarboxylate (corresponding dipyrazolone, m.p. 267—268°), which slowly loses MeCHO on exposure to air, thereby passing into Et<sub>2</sub> ethylenediacetoacetate, which isomerises spontaneously to Et<sub>2</sub> hydroxydimethylcyclohexanedicarboxylate, m.p. 80°. H. W.

**Polymembered heterocyclic compounds. VI. Preparation of pure ambrettolide.** Preparation of the lactones of  $\lambda$ -hydroxystearic acid and  $\nu$ -hydroxypentadecic acid. M. STOLL and R. E. GARDNER (Helv. Chim. Acta, 1934, 17, 1609—1612; cf. A., 1934, 1201).—Oxidation of civetone with Caro's acid yields only traces of a lactone,  $\text{C}_{17}\text{H}_{30}\text{O}_2$ , b.p. 135—145°/0.3 mm., the greater part of the material being either unattacked or resinified. Similarly, a homogeneous lactone is not obtained from  $\alpha$ -methyl-exaltone. Ambrettolic acid (isolation from musk-kernel oil described) is slowly added to a solution of  $\text{PhSO}_2\text{H}$  in much  $\text{C}_6\text{H}_6$ , thus giving homogeneous ambrettolide,  $\text{C}_{16}\text{H}_{28}\text{O}_2$ , b.p. 154—156°/0.9—1.1 mm. (cf. Kerschbaum, A., 1927, 541). Similarly,  $\lambda$ -hydroxystearolactone, b.p. 140—145°/0.11 mm., and  $\nu$ -hydroxypentadecolactone, b.p. 105—105.5°/0.1 mm., are obtained from the respective OH-acids. H. W.

**Photometric determination of calcium and oxalic acid.**—See this vol., 54.

**Formation of active racemates as a method of resolving racemates and a means of determining relative configurations.** M. DELÉPINE (Bull. Soc. chim., 1934, [v], 1, 1256—1265).—If two racemates, *dl*-A and *dl*-B, and the active components are isomorphous, and if "active racemates," *l*-A, *d*-B and *d*-A, *l*-B, are formed, then crystallisation of mixtures of, e.g., *l*-A (1 mol.) and *dl*-B (2 mols.) may lead to a less sol. fraction which is partly or entirely the active racemate, *l*-A, *d*-B. Thus, *dl*-B will have been resolved without a chemical reaction. Presence or absence of resolution is decided by the  $\alpha$  of the successive fractions. Resolutions were obtained with *dl*-(Rh en)<sub>3</sub>Br<sub>3</sub> by *l*-(Co en)<sub>3</sub>Br<sub>3</sub> and the following K<sub>3</sub> trioxalates,  $[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]\text{K}_3$ : *dl*-Ir by *d*-Rh, *dl*-Co<sup>III</sup> by *d*- or *l*-Ir, and *dl*-Cr<sup>III</sup> by *d*-Ir; no resolution occurred with the K<sub>3</sub> trioxalates of *dl*-Al or *dl*-Fe<sup>III</sup> and *d*-Ir. The active and ordinary racemates of the K<sub>3</sub> trioxalates contain 4.5H<sub>2</sub>O. Substances forming active racemates are enantiomorphous. It is thus proved that the various M<sup>III</sup> trioxalates giving the less sol. strychnine salts are homeomorphous; homeomorphism in this series is not related to the sign of  $\alpha$ , which changes with  $\lambda$ . R. S. C.

**Norcaperatic acid and agaricic acid.** M. ASANO and Z. OHTA (Ber., 1934, 67, [B], 1842—1845; cf. A., 1933, 823).—Condensation of Et<sub>3</sub> propane- $\alpha\beta$ -tricarboxylate (I) with *n*-tetradecyl iodide in presence of NaOEt-EtOH at 130°, followed by hydrolysis and heating of the product at 130—140°, leads to an anhydride (II), transformed by boiling KOH and EtOH with subsequent acidification into  $\alpha$ -methyl- $\beta$ -*n*-tetradecylsuccinic acid, m.p. 134—136°. (II) is transformed by  $\text{NH}_2\text{Ph}$  at 160—170° into  $\alpha$ -methyl- $\beta$ -*n*-tetradecylsuccinyl anil, m.p. 63.5—64.5°, identical with the anil from norcaperatic acid (*loc. cit.*). Agaricic acid is heated at 155—160° and the product is treated successively with HI (*d* 1.7) at 170—180° and Zn-HCl, thus giving methylhexadecylsuccinic acid (III), m.p. 133.5—135°, whence methylhexadecylsuccinyl anil (IV), m.p. 67.5—69.5°. The synthesis of (III) and (IV) from (I) and cetyl iodide is described. H. W.

**Physical properties and chemical constitution. II. Esters of  $\beta\beta$ -substituted glutaric acids.** A. I. VOGEL (J.C.S., 1934, 1758—1765; cf. A., 1934, 475).—By comparison of substituted malonic esters with the corresponding  $\beta\beta$ -substituted glutaric esters the parachor and mol. refraction coeff. differences for  $2\text{CH}_2$  are found to vary from 70.8 to 78.4 and 41.30 to 43.32, respectively, thus showing that these consts. are not purely additive (and often not identical for isomeric substances), but are affected by valency deflexion. Small, but irregular, divergences are shown by  $[\text{R}]_D$  and sp. dispersions. Valency angles are in the order Pr, Pr < Et, Pr < Et, Et < Me, Pr < Me, Et < Me, Me < Me, H < H, H. Directions are given for the prep. (Guareschi) of 14 dicyano-imides and their hydrolysis. The following data are new or have been disputed. (a)  $\beta\beta$ -Disubstituted glutaric acids: Me<sub>2</sub>-, m.p. 101°; MeEt-, m.p. 85° (Me ester, b.p. 124°/21 mm.); Et<sub>2</sub>-, m.p. 106°; MePr<sup>-</sup>-, m.p. 92—93° (Me ester, b.p. 130°/17 mm.); EtPr<sup>-</sup>-, m.p. 69° (Me ester, b.p. 142°/20 mm.); Pr<sub>2</sub><sup>-</sup> (Me ester, b.p. 151°/



20 mm.). (b) 3-, m.p. 142°, and 4-Methylcyclohexane-1:1-diacetic acid, m.p. 158—159° ( $Me_2$  ester, b.p. 164°/20 mm.). (c)  $Me_2$  (and in parentheses  $Et_2$ ) cycloparaffin-1:1-diacetates: cyclopentane-, b.p. 141°/17 mm. (b.p. 177°/21 mm.); 3-methylcyclopentane-, b.p. 148°/19 mm.; 3-, b.p. 155°/15 mm. (b.p. 177°/21 mm.), and 4-methylcyclohexane-, b.p. 164°/20 mm. (b.p. 178°/21 mm.); trans-decahydronaphthalene-, b.p. 193°/14 mm. (b.p. 208°/17 mm.); trans-hexahydrohydrindene-, b.p. 179°/12 mm. (b.p. 196°/14 mm.); and cyclohexane- (b.p. 165°/14 mm.).  $Me \beta$ -methylglutarate has b.p. 110°/19 mm. R. S. C.

**Glutaconic acids. XXIV. Catalytic effect of alkalis on the rate of racemisation of *l*-trans- $\alpha$ -dimethylglutaconic acid.** (Miss) J. E. BULL, J. S. FITZGERALD, J. PACKER, and F. J. THORPE (J.C.S., 1934, 1653—1657; cf. A., 1933, 789).—The velocity of racemisation of this acid (I) (0.125*M*) by aq. KOH or  $NH_3$  at 100° rises to a max. at 0.075*M* [half-neutralisation of (I)] and falls to a min. at 0.25*M* (full neutralisation); thereafter it rises rapidly with KOH, but remains nearly const. with  $NH_3$ . The conns. of fully (*A*) and half-dissociated (*B*) and non-ionised (I) are calc. from  $k_1$  and  $k_2$ . An equation is derived, which is accurate for HCl, KOH, and dil. aq.  $NH_3$  solutions. The undissociated acid has prototropic mobility  $10^3$  times that of (*A*) and  $10^5$  times that of (*B*). R. S. C.

**Constitution of antimony emetics and the hydroxy-acids from which they are derived.** P. DUQUENOIS (Bull. Soc. chim., 1934, [v], 1, 1387—1396).—Whereas the complexes of polyhydroxylic compounds with  $B(OH)_3$  and  $As_2O_3$  are acidic ( $B > As$ ), those with  $V_2O_5$ ,  $Sb_2O_3$ , or  $Bi_2O_3$  are not. The fixation of  $Sb_2O_3$  (determined iodometrically; Volmar *et al.*, A., 1933, 376, 948) by various polyhydric alcohols [which show large conductivity increases with  $B(OH)_3$  in 0.1*N* solution at 100° is small, and is but slightly increased in *N* solution, indicating the different nature of the B and Sb complexes. Much greater fixation occurs with  $\alpha$ -OH-acids (I). On the basis of these results and others previously summarised (A., 1933, 1142; 1934, 187) it is concluded that in (I) when the OH is *tert.* the  $CO_2H$  is hydrated, e.g., oxalic  $HO \cdot CO \cdot C(OH)_3$  and citric acid  $(CO_2H \cdot CH_2)_2C(OH) \cdot C(OH)_3$ , and, in agreement with experimental data, the max. fixation of  $Sb_2O_3$  occurs when the fraction of acid H neutralised is that given by the ratio total no. of  $>C(OH) \cdot CO_2H$  groups/total no. OH groups, e.g., oxalic 1/4; citric 1/6; tartaric  $[ \cdot CH(OH) \cdot CO_2H ]_2$  2/4. J. W. B.

**Determination of citric acid as pentabromoacetone in aqueous citric acid solutions, citrates, fruit juices, and fruit-juice preparations.** O. REICHARD (Z. anal. Chem., 1934, 99, 81—96).—A considerable excess of both Br and  $KMnO_4$  in the determination of citric acid (I) as pentabromoacetone (II) is not harmful. Aq. solutions of (I) or its salts (dissolved in HCl if necessary) are acidified strongly with  $H_2SO_4$ , 50% aq. KBr is added, and the solution oxidised to (II) by addition of saturated aq.  $KMnO_4$  at  $\approx 5^\circ$ . Pptd.  $MnO_2$  is removed by adding KBr. Small amounts of sugar (< 0.5 g. in sample), as in fruit juices, do not interfere. When larger amounts

are present (e.g., in syrups), sugar may be first removed by fermentation with yeast or, better, (I) may be separated as the Ba salt and then determined. J. S. A.

**Experimental verification of Sah's proposed synthesis of vitamin-C (*l*-ascorbic acid).** P. P. T. SAH (J. Chinese Chem. Soc., 1934, 2, 288—290).—The work of Reichstein *et al.* (cf. A., 1934, 511) verifies Sah's prediction in a very large measure. J. L. D.

**Colour reaction of isoascorbic acid (iso-vitamin-C).**—See A., 1934, 1417.

**Optical rotatory dispersion in the carbohydrate group. IV. Tetramethyl- $\gamma$ -mannonolactone.** T. L. HARRIS, E. L. HIRST, and C. E. WOOD (J.C.S., 1934, 1825—1829; cf. A., 1934, 1092).—The rotatory dispersion of tetramethyl- $\gamma$ -mannonolactone (I) is simple in  $H_2O$ , but anomalous in  $Et_2O$ ,  $COMe_2$ ,  $EtOH$ ,  $CHCl_3$ ,  $C_6H_6$ , and dioxan. In the last 5 solvents it can be expressed by a two-term Drude equation with terms of opposite sign, the rotation depending on centres of absorption at about  $\lambda$  1500 and 2500 (II). The former centre is identified with the aliphatic ether, the latter with the lactonic CO. (I) thus diverges from Hudson's rule in non-aq. solvents owing to the pronounced effect due to C2 in these solvents. The effect of solvent is further shown by variation of  $[\alpha]$  with concn. in  $C_6H_6$ . (I) does not show absorption bands in  $H_2O$ ,  $EtOH$ , or  $CHCl_3$ , but in  $H_2O$  and  $EtOH$  a step-up occurs at  $\lambda$  2200, possibly correlated with (II). R. S. C.

**Derivatives of *l*- $\alpha$ -rhamnohexonic acid. Synthesis of *l*- $\alpha$ -rhamnohexonolactone.** E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2455—2456).—*l*-Rhamnose is treated with NaCN and  $Ba(OAc)_2$  in  $H_2O$  at about 0° for 70 hr.; subsequent hydrolysis [ $Ba(OH)_2$ ] gives 55% of  $\alpha$ -rhamnohexonolactone (I), m.p. 171—171.5° (all m.p. are corr.),  $[\alpha]_D^{20}$  (in  $H_2O$ ) +87.3°  $\rightarrow$  +74.4° (after 67 days).  $\alpha$ -Rhamnohexonic acid, m.p. 171° (lit. 174—175°),  $[\alpha]_D^{20}$  (in  $H_2O$ ) +21.5°  $\rightarrow$  +74° [calc. as (I)], its *Et* ester, m.p. 165—166° (decomp.),  $[\alpha]_D^{20}$  (in  $H_2O$ ) +12.9°  $\rightarrow$  +74° [calc. as (I)], amide, m.p. 177.5—178° (decomp.) (lit. 194°),  $[\alpha]_D^{20}$  (in  $H_2O$ ) -19.9° (lit. -47.3°), and phenylhydrazide, m.p. 205—206° (decomp.),  $[\alpha]_D^{20}$  -5.2° in  $H_2O$ , are described. H. B.

**Pharmacology of rare earths.**—See A., 1934, 1400.

**[Aldehyde of violet leaves.]** H. WALBAUM and A. ROSENTHAL (Ber., 1934, 67, [B], 1804; cf. B., 1929, 1049).—A question of priority (cf. Späth *et al.*, A., 1934, 1204). H. W.

**Substances with the odour of violets. IV. Oil of violet leaves. Constitution of the aldehyde of violet leaves.  $\Delta^{\alpha}$ -Nonadienal. V. Synthesis of the aldehyde of violet leaves.  $\Delta^{\alpha}$ -Nonadienal or a stereoisomeride thereof.** L. RÜZICKA and H. SCHINZ (Helv. Chim. Acta, 1934, 17, 1592—1601, 1602—1608).—IV. The treatment of the oil by distillation with steam and by fractionation in vac. is described, the crude aldehyde being transformed into its semicarbazone (I), m.p. 157—158°, from which it is regenerated with difficulty. In presence of Pt-black (I) absorbs  $2H_2$  giving *n*-nonaldehyde-



semicarbazone (II), m.p. 97—98°, whereas in presence of PtO<sub>2</sub> it absorbs 3H<sub>2</sub> yielding *n-nonylsemicarbazide*, m.p. 104—106°, also obtained from (II). Ozonisation of (I) yields EtCHO (*p*-nitrophenylhydrazone, m.p. 120°), two substances, C<sub>14</sub>H<sub>14</sub>O<sub>6</sub>N<sub>6</sub>, red needles, m.p. 177—179°, and yellow crystals, m.p. 178—179°, apparently compounds of *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub> and glyoxylic acid *p*-nitrophenylhydrazone, *succinaldehydic acid p-nitrophenylhydrazone*, incipient decomp. about 300°, and (?) glyoxaldisemicarbazone. The work of Späth *et al.* (A., 1934, 1204) is thus confirmed.

V. Energetic reduction of Et Δ<sup>β</sup>-hexenoate with Na and EtOH at 100—110° gives a mixture of little hexenol and much hexyl alcohol and a substance, C<sub>8</sub>H<sub>18</sub>O<sub>2</sub>, b.p. 88—89°/12 mm., whilst the regenerated acid is mainly hexoic acid. Similar treatment of Et sorbate at > 80° smoothly yields a hexenol, b.p. 62—63°/13 mm., proved by ozonisation to be essentially Δ<sup>γ</sup>-hexenol (I). Treatment of (I) with SOCl<sub>2</sub> in CHCl<sub>3</sub>-C<sub>5</sub>H<sub>5</sub>N gives Δ<sup>γ</sup>-hexenyl chloride (II), b.p. 59—61°/60 mm. (the corresponding bromide cannot be prepared analogously), converted by anhyd. NaI in COMe<sub>2</sub> into Δ<sup>γ</sup>-hexenyl iodide (III), b.p. 62—63°/12 mm. The Grignard compound, best prepared from a mixture of (II) and (III), is converted by acraldehyde into the corresponding (impure) carbinol, b.p. 80—90°/12 mm., transformed by the successive action of PBr<sub>3</sub> and C<sub>5</sub>H<sub>5</sub>N in light petroleum and of AgOBz in abs. Et<sub>2</sub>O into *nonadienyl benzoate* (IV), b.p. 137°/0.3 mm. (IV) is hydrolysed to Δ<sup>β</sup>-*nonadienol*, b.p. 100°/13 mm. [ozonisation product, (-CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>], oxidised by CrO<sub>3</sub> to Δ<sup>αα</sup>-*nonadienal* (semicarbazone, m.p. 156—157°, does not depress the m.p. of the similar product from oil of violet leaves). The synthetic and natural aldehydes may be *cis-trans*-isomerides. H. W.

Resolution of *r*-glyceraldehyde. M. BETTI and P. PRATESI (Biochem. Z., 1934, 274, 1—3).—A certain amount of resolution can be effected by means of β-hydroxynaphthylbenzylamine. P. W. C.

*d*-isoPropylidenedioxysuccindialdehyde (*l*-isopropylidenetartardialdehyde). H. O. L. FISCHER and H. APPEL (Helv. Chim. Acta, 1934, 17, 1574—1582).—Triisopropylidenemannitol is converted by HCl in H<sub>2</sub>O-EtOH at 40° into γδ-*isopropylidene-mannitol* (I), m.p. 85°, [α]<sub>D</sub><sup>20</sup> +29.5°, which is oxidised by Pb(OAc)<sub>4</sub> in anhyd. C<sub>6</sub>H<sub>6</sub> at 100° to *d*-isopropylidenedioxysuccindialdehyde (II), [α]<sub>D</sub><sup>18</sup> +26.6° to +5.2° in abs. EtOH. Distillation of (II) under diminished pressure appears to be accompanied by polymerisation in varying degree, but by repeatedly interrupting the process, dissolving the residue in abs. CHCl<sub>3</sub> or COMe<sub>2</sub>, evaporating the solution, and immediately resuming the distillation, it is possible to volatilise all at > 100°/2 mm. Within > 24 hr. (II) passes from a mobile liquid to a colourless glass. With CH<sub>2</sub>N<sub>2</sub> (II) affords a liquid, b.p. 50—51°/0.025 mm., which is not the expected diketone. (I) is converted by Pb(OAc)<sub>4</sub> and treatment of the product with CH(OEt)<sub>3</sub> into *d*-isopropylidenedioxysuccindialdehyde Et<sub>3</sub> acetal, b.p. 88—89°/0.08 mm., [α]<sub>D</sub><sup>19</sup> +16.1° in abs. EtOH. (II) yields a *diphenylhydrazone* (+1H<sub>2</sub>O), m.p. 145°, [α]<sub>D</sub><sup>20</sup> -239.0° in EtOH or (anhyd.), [α]<sub>D</sub><sup>22</sup> -250° in EtOH. *d*-Dihydroxysuccindialdehydediphenylhydrazone has m.p. 181° (decomp.), [α]<sub>D</sub><sup>20</sup> -114.3° in C<sub>6</sub>H<sub>5</sub>N.

Hydrolysis of (II) with 0.1*N*-HCl followed by oxidation of the product with Br leads to *l*-tartaric acid. Treatment of Me<sub>2</sub> *d*-tartrate with ZnCl<sub>2</sub> and much PhCHO and of the product with NaHSO<sub>3</sub> leads to Me<sub>2</sub> *d*-benzylidenetartrate, m.p. 74°, [α]<sub>D</sub><sup>20</sup> -44.2° in EtOH (corresponding dihydrazide, m.p. 179—180.5°).

H. W.

Polymerisation and thermal decomposition of keten. A. T. WILLIAMSON (J. Amer. Chem. Soc., 1934, 56, 2216—2218).—Keten polymerises to diketene at 400—500°. Above 530° it decomposes, giving CO, CH<sub>4</sub>, and a C-like deposit. E. S. H.

Thermal decomposition of acetone. F. O. RICE, E. L. RODOWSKAS, and W. R. LEWIS (J. Amer. Chem. Soc., 1934, 56, 2497—2498).—Keten is not formed from COMe<sub>2</sub> containing approx. 1% of HgMe<sub>2</sub> (I) at 350—400°; (-CH<sub>2</sub>·COMe)<sub>2</sub> (II) [amount = (I) used] is produced: COMe<sub>2</sub> + Me → CH<sub>4</sub> + COMe·CH<sub>2</sub>·; 2COMe·CH<sub>2</sub>· → (II). At lower temp. the Me groups do not attack COMe<sub>2</sub>. Decomp. of COMe<sub>2</sub> or MeCHO in presence of small amounts of (II), diallyl, and dibenzyl does not give COMeEt, Δ<sup>β</sup>-butene, and PhEt, respectively. The production of Me from COMe<sub>2</sub> at 700°/200 mm. could not be detected by Te. H. B.

Formation of methylglyoxal from trioses at neutral *p*<sub>H</sub> and body temperature under the influence of phosphate and arsenate. Z. DISCHE and S. S. ROBINS (Biochem. Z., 1934, 274, 42—44).—When a solution of glyceraldehyde or CO(CH<sub>2</sub>·OH)<sub>2</sub> in physiological saline is kept at body temp. for 24 hr. at *p*<sub>H</sub> 7.2, a small amount of AcCHO is formed, the process being greatly accelerated by the presence of PO<sub>4</sub><sup>'''</sup> or AsO<sub>4</sub><sup>'''</sup> at *p*<sub>H</sub> 7—7.2. Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> has only a slight effect. P. W. C.

Auto-condensations of methylglyoxal. I. Humic acids from three-carbon systems. G. HAHN and O. SCHALES (Ber., 1934, 67, [B], 1816—1826).—Oxidation of boiling COMe<sub>2</sub> with SeO<sub>2</sub> followed by distillation of the product in vac. gives a mixture of dimeric (I) and trimeric (II) AcCHO (the re-conversion of Se into SeO<sub>2</sub> is described). Particularly at low temp., (I) passes rapidly into a solid modification, 8AcCHO, 4H<sub>2</sub>O, which is not hygroscopic, and hence is not identical with Harries' product. It can be kept unchanged for a long period, whereas (II) slowly passes into AcCO<sub>2</sub>H when kept in a glass vessel. It is readily depolymerised when heated with H<sub>2</sub>O or distilled in vac. Treatment of AcCHO with acid gives solutions which slowly when cold, but rapidly when heated, become yellow and then red and from which a dark brown, amorphous humic acid (III), m.p. 220° (decomp.), separates which is sol. in EtOH, COMe<sub>2</sub>, CHCl<sub>3</sub>, and dioxan and differs from the glucose-humic acid. The mother-liquors yield very small amounts of an acid, C<sub>14</sub>H<sub>14</sub>O<sub>8</sub>, decomp. 248° (*dinitrophenylhydrazone*, m.p. 320°). Optimum yields of (III) are obtained in solutions of *p*<sub>H</sub> 5.9, these being far in excess of those achieved with carbohydrates, excepting xylose. Even after very protracted action, humic acids are not obtained from natural hexoses at *p*<sub>H</sub> 6, but fructose gives a 2.4% yield. CO(CH<sub>2</sub>·OH)<sub>2</sub> reacts at about the same rate as AcCHO. It appears, therefore, that carbohydrates are first transformed by



bacteria into trioses, which then pass, most readily in the physiological  $p_H$  region, into humic acids.

H. W.

**Determination of reducing sugars.** C. GIORGIO (Ind. ital. conserv. aliment., 1934, 9, 100—103; Chem. Zentr., 1934, ii, 156).—The Cu solution contains  $\text{CuSO}_4$ , NaOH, and glycerol. Following the customary reduction (hot) by the sugar solution, the liquid is filtered and the filtrate titrated with  $\text{H}_2\text{SO}_4$  (contored). Formation of  $\text{Cu}_2\text{O}$  utilises an equiv. wt. of NaOH.

A. G. P.

**Reactions of carbohydrates in liquid ammonia.**

**II. Apparatus and methods. Alkyl, acyl, and metallic and non-metallic derivatives of diisopropylidene-glucose.** I. E. MUSKAT (J. Amer. Chem. Soc., 1934, 56, 2449—2454).—Details are given (cf. A., 1934, 512) for the prep. of alkali metal salts of carbohydrates. The K derivative (I) of diisopropylidene-glucose (II) is prepared in liquid  $\text{NH}_3$  (which is then evaporated and replaced by  $\text{Et}_2\text{O}$ ; general method). (I) and MeI or  $\text{Me}_2\text{SO}_4$  give 97% of 3-methyl-diisopropylidene-glucose, b.p.  $105^\circ/0.3$  mm.,  $[\alpha]_D^{24} -34.2^\circ$  in EtOH; the 3-Et, b.p.  $115^\circ/0.8$  mm.,  $[\alpha]_D^{24} -25.75^\circ$  in  $\text{COMe}_2$ , and 3-Pr, b.p.  $120^\circ/1$  mm.,  $[\alpha]_D^{24} -29.2^\circ$  in  $\text{CHCl}_3$ , derivatives are similarly prepared in 90 and 30% yield using EtI(Br) or Pr-I. (I) and the requisite acyl chloride give diisopropylidene-glucose 3-acetate, m.p.  $62^\circ$ ,  $[\alpha]_D^{24} -38.5^\circ$  in  $\text{CHCl}_3$ , 3-benzoate, m.p.  $64^\circ$ ,  $[\alpha]_D^{24} -50.2^\circ$  in EtOH, and 3-p-toluenesulphonate, m.p.  $120^\circ$ ,  $[\alpha]_D^{24} -70.4^\circ$  in  $\text{CHCl}_3$ . (I) and  $\text{PCl}_3$  (1 mol.) give [after hydrolysis (75% EtOH)] diisopropylidene-glucose phosphite; with  $\frac{1}{2}$  mol. of  $\text{PCl}_3$ , tri(diisopropylidene-glucose) phosphite, m.p. about  $60^\circ$ ,  $[\alpha]_D^{24} -19^\circ$  in  $\text{CHCl}_3$ , results. (I) and  $\text{POCl}_3$  similarly afford mono- [also obtained from (II),  $\text{POCl}_3$ , and  $\text{C}_5\text{H}_5\text{N}$ ] and tri-(diisopropylidene-glucose) phosphate, m.p. about  $55^\circ$ ,  $[\alpha]_D^{24} -44.4^\circ$  in  $\text{CHCl}_3$ . Tri(diisopropylidene-glucose) arsenite and di(diisopropylidene-glucose) disulphide are prepared from (I) and  $\text{AsCl}_3$  and  $\text{S}_2\text{Cl}_2$ , respectively. (I) also reacts with  $\text{HgCl}_2$ ,  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{HgCl}$ ,  $\text{SbCl}_3$ ,  $\text{BiCl}_3$ ,  $\text{CPh}_3\text{Cl}$ , and acetobromoglucose. Carbohydrates containing free or potential CHO and CO are readily oxidised by I in liquid  $\text{NH}_3$ : RCHO thus gives  $\text{RCO}\cdot\text{NH}_2$ .

H. B.

**Preparation of  $\alpha$ -aldose acetates from acetylated glycosides.** R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2465—2466).— $\alpha$ -Methylmannoside tetra-acetate is converted by conc.  $\text{H}_2\text{SO}_4$  in  $\text{Ac}_2\text{O}$ -AcOH into  $\alpha$ -mannose penta-acetate; the change is followed polarimetrically at  $20^\circ$  and is unimol. after 20 min.  $\alpha$ -Glucose penta-acetate is obtained similarly from  $\beta$ -methyl-,  $\beta$ -phenylthio-, and  $\beta$ - $\beta'$ -naphthylthio-glucoside tetra-acetates, whilst  $\alpha$ -methyl- $\gamma$ -d-mannoside tetra-acetate gives a d-mannose penta-acetate, m.p.  $76^\circ$  (corr.),  $[\alpha]_D^{20} +89.6^\circ$  in  $\text{CHCl}_3$ . The changes with  $\beta$ -methyl-( $\beta$ -d-galactoside) penta-acetate and  $\beta$ -phenylthio-d-xyloside triacetate have been followed polarimetrically.

H. B.

**Synthesis of derivatives of glucose 2:3:6-tri-p-toluenesulphonate and their identification with the sugars obtained by fission of tri-p-toluenesulphonyl- and iododi-p-toluenesulphonyl-**

starch. K. HESS and W. EYKING (Ber., 1934, 67, [B], 1908—1916; cf. A., 1933, 1279).—4:6-Benzylidene- $\beta$ -methylglucoside 2:3-di-p-toluenesulphonate is converted by  $\text{MeOH}\cdot\text{HCl}$  (improved prep.) into  $\text{CHPh}(\text{OMe})_2$  and  $\beta$ -methylglucoside 2:3-di-p-toluenesulphonate (I), transformed by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  at  $50^\circ$  into  $\beta$ -methylglucoside 4:6-diacetate 2:3-di-p-toluenesulphonate, m.p.  $136$ — $137^\circ$ ,  $[\alpha]_D^{22} -24.1^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{21} -21.2^\circ$  in  $\text{COMe}_2$ ,  $[\alpha]_D^{21} -53.9^\circ$  in  $\text{C}_6\text{H}_6$ . (I) is converted by the successive action of  $\text{CPh}_3\text{Cl}$  and  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into 6-triphenylmethyl- $\beta$ -methylglucoside 4-acetate 2:3-di-p-toluenesulphonate, m.p.  $128$ — $131^\circ$ ,  $[\alpha]_D^{24} +5.9^\circ$  in  $\text{CHCl}_3$ ,  $+9.6^\circ$  in  $\text{COMe}_2$ ,  $-21.1^\circ$  in  $\text{C}_6\text{H}_6$ , which with  $\text{AcOH}\cdot\text{HBr}$  at  $0^\circ$  yields non-cryst.  $\beta$ -methylglucoside 4-acetate 2:3-di-p-toluenesulphonate (II),  $[\alpha]_D^{22} -15.8^\circ$  in  $\text{CHCl}_3$ ,  $-10.5^\circ$  in  $\text{COMe}_2$ . With  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  and  $\text{C}_5\text{H}_5\text{N}$  at  $50^\circ$  (II) affords  $\beta$ -methylglucoside 4-acetate 2:3:6-tri-p-toluenesulphonate (III), labile form, m.p.  $131$ — $132^\circ$ , stable variety, m.p.  $149$ — $150^\circ$ ,  $[\alpha]_D^{22} -13.9^\circ$  in  $\text{CHCl}_3$ ,  $-5.1^\circ$  in  $\text{COMe}_2$ ,  $-32.7^\circ$  in  $\text{C}_6\text{H}_6$ , also obtained by the successive action of  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  and  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  on (I). Treatment of (III) with NaI in  $\text{COMe}_2$  at  $120^\circ$  leads to 6-iodo- $\beta$ -methylglucoside 4-acetate 2:3-di-p-toluenesulphonate, m.p.  $162$ — $163^\circ$ ,  $[\alpha]_D^{23} +11.1^\circ$  in  $\text{CHCl}_3$ ,  $+3.1^\circ$  in  $\text{COMe}_2$ ,  $[\alpha]_D^{23} -17.9^\circ$  in  $\text{C}_6\text{H}_6$ , identical with the product of degradation of iodostarch tri-p-toluenesulphonate.

H. W.

**Determination of fructose in the presence of glucose and sucrose.** M. NORDLUND (Suomen Kem., 1934, 7, 95B).—A measured amount of solution is treated with I and  $N\text{-NaOH}$ . After 20 min. at room temp., the solution is acidified with  $5N\text{-H}_2\text{SO}_4$  and excess of I titrated with  $\text{NaHSO}_3$ . Solid  $\text{Pb}(\text{OAc})_2$  is added to ppt. the reaction products, and the solution filtered. A portion of the filtrate is used, after removal of excess of Pb with  $\text{K}_2\text{SO}_4$  if necessary, for determination of fructose, e.g., by the Bertrand method. The accuracy of this method is unaffected by presence of large amounts of peptone, OH-acids, or alcohols.

J. W. S.

**Decomposition of fructose by ultra-violet light in non-aqueous solution (methyl alcohol).** R. CANTIENI (Helv. Chim. Acta, 1934, 17, 1528—1529).—Fructose in pure MeOH is decomposed by ultra-violet light with evolution of gas, mainly CO. Addition of  $\text{H}_2\text{O}$  to MeOH causes more copious evolution of gas. Acceleration of the evolution of gas by addition of  $\text{H}_2\text{O}$  is relatively greater as the quantity of  $\text{H}_2\text{O}$  diminishes.

H. W.

**Decomposition of fructose in quartz light in presence of pyridine. Determination of pyridine in very dilute solution.** R. CANTIENI (Helv. Chim. Acta, 1934, 17, 1492—1493).—Fructose solutions containing  $<1\%$  of  $\text{C}_5\text{H}_5\text{N}$  become brown and form a brown ppt. without evolving gas when irradiated. Those containing  $>1\%$  of  $\text{C}_5\text{H}_5\text{N}$  become yellow and evolve gas in amounts which increase with decreasing concn. of  $\text{C}_5\text{H}_5\text{N}$ . The intensity of the yellow colour diminishes with diminishing concn. of  $\text{C}_5\text{H}_5\text{N}$ . The concn. at which gas evolution ceases lies between 0.1 and 1% of  $\text{C}_5\text{H}_5\text{N}$ , whereas that at which interaction ceases lies between 0.001% and



0.0001% of  $C_5H_5N$ . A possible method of determining minute amounts of  $C_5H_5N$  is indicated. H. W.

**Three crystalline hexa-acetates of  $d$ - $\alpha$ -mannoheptose.** E. MONTGOMERY and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2463—2464).—Contrary to previous results (A., 1924, i, 617), acetylation ( $Ac_2O-NaOAc$ ) of  $d$ - $\alpha$ -mannoheptose (I) gives  $\beta$ - $d$ - $\alpha$ -mannoheptose hexa-acetate (II), m.p. 107°,  $[\alpha]_D^{20} +34.1^\circ$  in  $CHCl_3$  (cf. *loc. cit.*), and aldehyde- $d$ - $\alpha$ -mannoheptose hexa-acetate (III), m.p. 146°,  $[\alpha]_D^{20} -34^\circ$  in  $CHCl_3$ . (II) is converted by conc.  $H_2SO_4$  in  $Ac_2O-AcOH$  into its  $\alpha$ -isomeride, m.p. 75—76°,  $[\alpha]_D^{20} +120.8^\circ$  in  $CHCl_3$ .  $d$ - $\alpha$ -Mannoheptose *Et mercaptal*, m.p. 188—190°,  $[\alpha]_D^{20} -11.9^\circ$  in  $H_2O$  [from (I),  $EtSH$ , and 36%  $HCl$ ], is acetylated ( $Ac_2O-C_5H_5N$  at 0°) to the hexa-acetate, m.p. 77°,  $[\alpha]_D^{20} -2.2^\circ$  in  $CHCl_3$ , which is converted by  $HgCl_2$  in aq.  $COMe_2 + CdCO_3$  into (III). (III) is also formed from methyl- $\alpha$ -mannoheptoside penta-acetate and conc.  $H_2SO_4$  in  $Ac_2O-AcOH$ .

H. B.

**Alkaline conversion of  $\beta$ -glucoheptose.** Y. KHOUVINE (Compt. rend., 1934, 199, 869—870; cf. A., 1934, 513).—Treatment of  $\beta$ -glucoheptose (I) with aq.  $Ca(OH)_2$  yields the same glucoheptulose as that obtained from the  $\alpha$ -isomeride. The  $\alpha$ - $d$ -glucoheptulose from (I) gives, on reduction,  $\alpha$ -glucoheptitol and  $\alpha$ - $d$ -glucoheptulitol.

A. G. P.

**Configuration of isosucrose (sucrose- $D$  of Pictet and Vogel) and a peculiarity of the  $\beta$ -glucosidase of mushrooms.** A. GEORG (Helv. Chim. Acta, 1934, 17, 1566—1574; cf. A., 1933, 260).—Hydrolysis (Zemplén) of isosucrose octa-acetate affords isosucrose (I), m.p. 179° (corr.) after softening at 175°,  $[\alpha]_D^{20} +32.7^\circ$  to  $+34.7^\circ$  in  $H_2O$  [Pictet and Vogel (A., 1928, 510, 741; 1929, 913) record m.p. 127°,  $[\alpha]_D^{20} +19.0^\circ$  in  $H_2O$ , whereas Irvine *et al.* (A., 1929, 603) give m.p. 194° after softening at 152°,  $[\alpha]_D^{20} +34.2^\circ$  in  $H_2O$ ]. Application of Hudson's rules indicates that (I) is  $\beta$ -glucopyranosido- $\alpha$ -fructofuranoside. Unexpectedly, (I) is not hydrolysed by the  $\beta$ -glucosidase of emulsin from sweet almonds (analogous cases are cited), but is affected by the invertase of *Aspergillus niger*, although much less rapidly than is sucrose; this is shown to be due to the presence of both  $\alpha$ - and  $\beta$ -glucosidase. Pure  $\beta$ -fructofuranosidase does not attack (I).

H. W.

**$\alpha$ -Glucosidase of yeast.** B. HELFERICH, U. LAMPERT, and G. SPARMBERG (Ber., 1934, 67, [B], 1808—1811).—In contrast with the behaviour of  $\beta$ -glucosidase of almonds, increase in fission by  $\alpha$ -glucosidase of yeast is not observed on passing from phenol- to saligenin- and thence to *o*-cresol- $\alpha$ - $d$ -glucoside, thus further emphasising the great difference between the two enzymes.  $\beta$ - $d$ -Glucose penta-acetate is converted by *o*-cresol and  $ZnCl_2$  at 125—130° into *o*-cresol- $\alpha$ - $d$ -glucoside tetra-acetate, m.p. 101—102° after softening,  $[\alpha]_D^{20} +155^\circ$  in  $CHCl_3$ , catalytically hydrolysed by  $NaOMe$  to *o*-cresol- $\alpha$ - $d$ -glucoside, m.p. 170—172°,  $[\alpha]_D^{20} +156^\circ$  in  $H_2O$ .  $\omega$ -Bromo-*o*-cresol- $\alpha$ - $d$ -glucoside tetra-acetate, m.p. 94—95.5° (corr.) after softening,  $[\alpha]_D^{20} +145.6^\circ$  in  $CHCl_3$ , is converted by  $Ag_2CO_3$  in  $COMe_2-H_2O$  and subsequent hydrolysis by  $NaOMe-MeOH$  into saligenin- $\alpha$ - $d$ -glucoside ( $\alpha$ -salicin),  $[\alpha]_D^{20} +118^\circ$  in  $H_2O$ .

H. W.

**Glucoside from madder.**—See A., 1934, 1420.

**Structure of populin.** N. K. RICHTMYER and E. H. YEAKEL (J. Amer. Chem. Soc., 1934, 56, 2495—2497).—Synthetic populin (I), prepared by Dobbin and White's method (A., 1904, i, 905), is methylated ( $Ag_2O, MeI$ ) to tetramethylpopulin, m.p. 134—135°,  $[\alpha]_D^{20} -31.7^\circ$  in  $CHCl_3$  (the  $Me_4$  derivative, m.p. 148—150°, is probably formed also), debenzoylated ( $MeOH-NaOMe$ ) to  $\omega : 2' : 3' : 4'$ -tetramethylsalicin, m.p. 137—138°,  $[\alpha]_D^{20} -46.4^\circ$  in  $CHCl_3$ , which is hydrolysed ( $2N-HCl$  in  $EtOH$ ) to 2 : 3 : 4-trimethylglucose. (I) is, therefore, 6'-benzoylsalicin. (I) is reduced ( $H_2, Pd-black, AcOH$ ) to deoxypopulin ( $\beta$ -*o*-cresolglucoside 6-benzoate), m.p. 148—149°,  $[\alpha]_D^{20} -13.3^\circ$  in  $C_5H_5N$ , also prepared from *o*-cresolglucoside, m.p. 162—163°,  $[\alpha]_D^{20} -68.4^\circ$  in  $H_2O$  (lit. +61.75°) [prepared (cf. A., 1934, 992) by reduction ( $H_2, Pd-black, H_2O$ ) of salicin], and  $BzCl$  in  $C_5H_5N$ .

H. B.

**Nitrogenous glycosides. III. Preparation of a simple cyanophoric glycoside.** L. R. BUERGER (J. Amer. Chem. Soc., 1934, 56, 2494—2495).—Acetobromoglucose and  $AgCN$  in xylene give 1-cyano- $d$ -glucose 2 : 3 : 4 : 6-tetra-acetate (I), m.p. 76°, converted by  $AcOH$  at 150° or  $Ac_2O$  at 200° into  $\beta$ -glucose penta-acetate. (I) is decomposed by digestion with 50%  $AcOH$ , 5% tartaric acid, or warm  $H_2O$ .

H. B.

**Present position of *Digitalis* chemistry.** W. BLADERGROEN (Chem. Weekblad, 1934, 31, 674—680).—A review.

**Colour reaction of digitoxin, gitoxin, and gitalin; application to colorimetric determination of these glucosides.** J. A. SÁNCHEZ (Semana Med., 1934, II, 399—402).—Digitoxin in  $AcOH$  is treated with a solution of vanillin in  $HCl$  and heated (100°). A red colour is formed and changes to a stable blue. Details for quant. use are given.

CH. ABS. (p)

**Fructose anhydrides. XV. Constitution of graminin I.** H. H. SCHLUBACH and K. KOENIG (Annalen, 1934, 514, 182—196).—Details are given for the extraction and purification of graminin (I),  $M$  (in  $H_2O$ ) 776—1183,  $[\alpha]_D^{20} -36.6^\circ$  (cf. Tanret, A., 1891, 661; Tillmans *et al.*, B., 1929, 70; use of the last method does not give a protein-free product), from rye flour. (I) is hydrolysed ( $N-H_2SO_4$  at 20°) at the same rate as irisin (A., 1933, 938); the product obtained after 91% hydrolysis has an aldose val. of 0.59% (cf. A., 1932, 1021). These results indicate that (I) is built up solely of fructose units. Swelling of (I) in  $C_5H_5N$  at 75° and subsequent treatment with  $Ac_2O$  gives graminin acetate (II),  $[\alpha]_D^{20} -7.2^\circ$  in  $CHCl_3$ ,  $M$  (in  $C_6H_6$ ) 2606—2792; the (I) recovered by hydrolysis ( $MeOH-NaOMe$ ) has a somewhat higher mol. wt. (1416—1537) than the original (I). These vals. indicate the presence of 9—10  $C_6$  units. Successive treatment of (II) with  $Me_2SO_4$  and 30%  $NaOH$  (in  $COMe_2$ ) and  $MeI-Ag_2O$  affords methylgraminin,  $[\alpha]_D^{20} -48^\circ$  in  $CHCl_3$ , hydrolysed ( $H_2C_2O_4$  in 70%  $EtOH$ ) to 1 : 3 : 4 : 6-tetramethyl-, (probably) 3 : 4 : 6-trimethyl-, b.p. 94°/0.1 mm.,  $[\alpha]_D^{20} +27.3^\circ$  in  $CHCl_3$ , and a dimethyl-fructose. A ring structure is suggested for (I).

H. B.



**Esterification of starch and its degradation products.** A. F. DAMANSKY (Ann. Chim., 1934, [xi], 2, 491—565).—Potato-starch (I) by Peiser's or Pringsheim's method gives poor yields (14—25%) of Ac derivatives with some degradation to biose. Haworth's and Friese's methods afford quant. yields of amylose triacetate (II). (I) with  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  at  $0^\circ$  or  $\text{AcCl}-\text{C}_5\text{H}_5\text{N}$  first at  $-20^\circ$  and then at  $70-80^\circ$  gives a mixture of diacetate (III) and some (II). Samec's amylopectin (IV) gives, particularly by  $\text{AcCl}$ , almost entirely (III), Ling and Nanji's (IV) also some (II). Amylose (V) gives entirely (III), whilst "sol. starch" (VI) gives an  $\text{Ac}_4$  derivative. The amount of (II) obtained from (I) is increased by previous heating of (I) in  $\text{H}_2\text{O}$  (e.g., 30% after 30 min. at  $90^\circ$ ). Since (III) is unaltered by further acetylation, it is concluded that (I) is a mixture of (IV) and (V); (V) is considered to be a degradation product formed during the isolation of (I), which, if pure, would consist entirely of (IV). Formation of (V) from (IV) renders a third OH group reactive, either by stereochemical change or by fission of a linking between glucose mols. 2% of (I) in 0.15% aq.  $\text{NaOH}$  at  $0^\circ$  gives after 3 days 3—4% of (V), and 40—50% are formed in 2 hr. at  $50^\circ$ ; in 0.5*N*- $\text{NaOH}$ -abs.  $\text{EtOH}$  2% of (V) are formed in 25 days at  $0^\circ$  and 3—4% in 4 days at  $50^\circ$ . 0.1—0.15*N*- $\text{NaOMe}$  in dry  $\text{MeOH}$ , however, does not form (V) at  $0^\circ$  or  $50^\circ$  from (I) or (IV), and is used to hydrolyse the acyl derivatives (12—15 days at  $0^\circ$ ); the process is catalytic, since esters are formed in quantity and  $\approx 30\%$  of the  $\text{NaOMe}$  is neutralised. The relationship of (II) and (III) to (V) and (IV) is thus established. The following gelatinisation temp. are determined viscosimetrically: (I)  $57.9^\circ$ , Samec's (IV)  $43.6^\circ$ , Ling and Nanji's (IV),  $45.9^\circ$ , (II) and other di-esters  $40.2-43.9^\circ$ ; the identity of the products recovered by hydrolysis of the esters is confirmed by this method. Results exactly similar to those given by  $\text{AcCl}$  are obtained with  $\text{BzCl}$  and cinnamoyl chloride in  $\text{C}_5\text{H}_5\text{N}$ . The following are described: tricinnamate of (V),  $[\alpha]_D^{25} -186^\circ$  in  $\text{CHCl}_3$ , sol. in  $\text{CHCl}_3$ , etc. [from (I), maize starch, or (IV) previously heated to  $90^\circ$ ], and the tribenzoate,  $[\alpha]_D^{25} +80.3^\circ$  in  $\text{CHCl}_3$ , sol. in  $\text{CHCl}_3$ , etc. [from (I) or (V)]; dicinnamate and dibenzoate of (IV), insol. in org. solvents. By separation of its benzylation products (VI) is shown to consist of (I) (2.4%), (V) (3%), amylose B (8.5%),  $[\alpha]_D^{25} +167.3^\circ$  in  $\text{H}_2\text{O}$ , non-reducing ( $\text{Bz}_3$  derivative, m.p.  $187^\circ$ ,  $[\alpha]_D^{25} +95.3^\circ$  in  $\text{CHCl}_3$ ) (reddish-brown colour with I), and a non-reducing biose (VII) (78.5%),  $[\alpha]_D^{25} +152.6^\circ$  in  $\text{H}_2\text{O}$  ( $\text{Bz}_3$  derivative, m.p.  $181^\circ$ ,  $[\alpha]_D^{25} +70.6^\circ$  in  $\text{CHCl}_3$ ). (VII) is not maltose, but is hydrolysed directly to glucose only; it gives a brown colour with I. R. S. C.

**Chemistry of cellulose.** H. STAUDINGER (Naturwiss., 1934, 22, 797—803, 815—819).—A lecture.

**Separation and fractional extraction of cellulose acetates.** L. CLÉMENT and C. RIVIÈRE (Bull. Soc. chim., 1934, [v], 1, 1075—1082).—Fractional pptn. of cellulose acetate in  $\text{COMe}_2$  with mixtures of  $\text{COMe}_2$  and  $\text{H}_2\text{O}$ , or fractional extraction with  $\text{MeOH}-\text{H}_2\text{O}$ ,  $\text{EtOH}-\text{H}_2\text{O}$ , or  $\text{EtOH}-\text{COMe}_2$ , leads to a no. of fractions differing considerably in chemical and physical properties, e.g., degree of acetylation, m.p., and solubility in many org. solvents. F. S. H. H.

**Preparation of *d*-glutamic acid.** Y. C. CHENG and W. H. ADOLPH (J. Chinese Chem. Soc., 1934, 2, 221—224).—Hydrolysis of wheat gluten (I) is facilitated and affords increased yields of glutamic acid hydrochloride when Sn, Ni, Pb, or Cu is used as catalyst. Peanut proteins and soya beans give nearly as good yields as (I). J. L. D.

**Catalytic hydrogenation of amides to amines.** B. WOJCIK and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 2419—2424; cf. A., 1934, 283).—Amines (primary, sec., and tert.) are formed in good yield by reduction [usually with  $\text{H}_2$  (200—300 atm.) at  $250^\circ$  in dioxan using a Cu—Cr oxide catalyst] of the appropriate amides. With  $\text{RCO}\cdot\text{NHR}'$  and especially  $\text{RCO}\cdot\text{NR}'_2$ , the following reactions occur:  $\text{RCO}\cdot\text{NR}'_2 + \text{H}_2 \rightarrow \text{CH}_2\text{R}\cdot\text{NHR}' + \text{R}'\text{H} + \text{H}_2\text{O}$ ;  $\text{RCO}\cdot\text{NR}'_2 + \text{H}_2 \rightarrow \text{RMe} + \text{NHR}'_2 + \text{H}_2\text{O}$ . The reaction  $\text{RCO}\cdot\text{NH}_2 + \text{H}_2 \rightarrow \text{CH}_2\text{R}\cdot\text{OH} + \text{NH}_3$  occasionally takes place; this change occurs almost exclusively on attempted reduction in aq. and  $\text{EtOH}$  media. The predominating secondary reaction is  $2\text{NH}_2\text{R} \rightarrow \text{NHR}_2 + \text{NH}_3$ ; hydrolysis, ammonolysis, and aminolysis of the amide and alkylation (by alcohol produced) of the amine may occur. The amides used are prepared from  $\text{RCO}_2\text{Et}$  and liquid  $\text{NH}_3$  or the appropriate amine at  $250^\circ$  in  $\text{H}_2$  (50—100 atm.) or from the  $\text{NH}_4$  or amine salt in dioxan at  $250^\circ$ .

Lauramide is thus reduced to 48% of *n*-dodecylamine (I) and 49% of *di-n*-dodecylamine (II), m.p.  $55-56^\circ$  (hydrochloride, m.p.  $207-208^\circ$ );  $\text{NH}_4$  laurate gives (I) (14%) and (II) (79%); heptamide affords 39% of mono- (III) and 58% of *di*- (IV) *n*-heptylamine;  $\alpha$ -phenylbutyramide yields  $\alpha$ -amino- $\beta$ -phenylbutane (72%) and material (23%), b.p.  $163-167^\circ/3-4$  mm.; salicylamide furnishes *o*-cresol (80%); tetrahydrofuroamide gives 60% of mono- and 33% of *di*-tetrahydrofurfurylamine;  $\gamma$ -hydroxyvaleramide (crude) affords valerolactone (74%) and  $\alpha$ -amino- $\delta$ -hydroxypentane (16%), b.p.  $119-121^\circ/8$  mm. (hydrochloride, m.p.  $107-110^\circ$ );  $(\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$  yields pyrrolidine (25%), 1- $\delta$ -aminobutylpyrrolidine (14%), and *N*- $\delta$ -aminobutylsuccinimide (15%), b.p.  $120-124^\circ/3$  mm. (hydrochloride, m.p.  $89-90^\circ$ ); *laur*- $\beta$ -phenylethylamine, m.p.  $73^\circ$ , furnishes  $\text{PhEt}$  (11%),  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$  (16%), (I) (13%), (II) (9%), and  $\beta$ -phenylethyl-*n*-dodecylamine (66%), b.p.  $182-184^\circ/2$  mm. (hydrochloride, m.p.  $232-233^\circ$ ); *laur*cyclohexylamine, m.p.  $85^\circ$ , gives mono- (15%) and *di*-cyclohexylamines, (I), (II) (24%), and cyclohexyl-*n*-dodecylamine (62%), b.p.  $158-159^\circ/2$  mm. (hydrochloride, m.p.  $204-205^\circ$ ); *lauranilide* affords  $\text{NH}_2\text{Ph}$  (29%),  $\text{NHPH}_2$  (5%), (I) (14%), (II) (2%), and *n*-dodecylaniline (37%), b.p.  $160-161^\circ/2$  mm. (hydrochloride, m.p.  $206^\circ$ ); *laur*-*n*-amylamide, m.p.  $78^\circ$ , yields *di-n*-amylamine (8%), (I) (15%), (II) (42%), and *n*-amyl-*n*-dodecylamine (35%), b.p.  $175-177^\circ/10$  mm. (hydrochloride, m.p.  $240-241^\circ$ ); *hepto*- $\beta$ -phenylethylamine, m.p.  $78^\circ$ , furnishes  $\text{PhEt}$  (5%), (III) (7%), (IV) (10%),  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$  (6%), and  $\beta$ -phenylethyl-*n*-heptylamine (56%), b.p.  $153-156^\circ/9$  mm. (hydrochloride, m.p.  $254-255^\circ$ ); *adip*-*n*-amylamide, m.p.  $161-162^\circ$ , gives *di-n*-amylamine (90%); 1-laurylpiperidine affords *n*-dodecyl alcohol (2%) and 1-*n*-dodecylpiperidine (92%), b.p.  $139-140^\circ/2$  mm. (hydrochloride, m.p.  $184-186^\circ$ ); 1-heptylpiperidine



yields heptyl alcohol (5%) and 1-*n*-heptylpiperidine (92%); 1- $\alpha$ -phenylbutyrylpiperidine, b.p. 145—146°/2 mm., furnishes  $\beta$ -phenylbutyl alcohol (32%) and  $\alpha$ -piperidino- $\beta$ -phenylbutane (65%), b.p. 134—135°/8 mm. (hydrochloride, m.p. 166—168°); 1-nonylpiperidine gives 1-*n*-nonylpiperidine (88%), b.p. 135—137°/11 mm. (hydrochloride, m.p. 186—187°); 1-furoylpiperidine affords tetrahydrofurfuryl alcohol (3%) and 1-tetrahydrofurfurylpiperidine (85%), b.p. 96—98°/9 mm. (hydrochloride, m.p. 180°); 1-benzoylpiperidine yields PhMe (79%) and CH<sub>2</sub>Ph-OH (3%); 1- $\beta$ -hydroxybutyrylpiperidine, b.p. 109—113°/9 mm., furnishes 1-butylpiperidine (56%); 1- $\beta$ -hydroxy- $\alpha$ -dimethylbutyrylpiperidine, b.p. 86—88°/3 mm., gives piperidine (29%) and 1-isobutylpiperidine (64%); *sebacylpiperidine*, b.p. 255—256°/2 mm., m.p. 59—60°, affords decane- $\alpha$ -diol (4%) and  $\alpha$ -*dipiperidinodecane* (94%), b.p. 181—183°/2 mm. (hydrochloride, m.p. 276—277°); succinylpiperidine yields (CH<sub>2</sub>)<sub>4</sub>(OH)<sub>2</sub> (15%) and  $\alpha$ -dipiperidinobutane (80%); *adipylpiperidine*, b.p. 221—223°/2 mm., m.p. 61—62°, furnishes (CH<sub>2</sub>)<sub>6</sub>(OH)<sub>2</sub> (16%) and  $\alpha$ -*dipiperidino*hexane (80%); *laurdiethylamide*, b.p. 166—167°/2 mm., gives (II) (30%) and *ethyl-n-dodecylamine* (64%), b.p. 124—129°/2 mm. (hydrochloride, m.p. 205—207°); *heptodiethylamide* affords (IV) (25%), *ethyl-n-heptylamine* (64%), b.p. 81—83°/16 mm. (hydrochloride, m.p. 188—190°), and *diethyl-n-heptylamine* (4%), b.p. 86—87°/16 mm. (hydrochloride, m.p. 105—106°); *N-n-amylsuccinimide*, b.p. 123—124°/3 mm., yields 1-*n*-amylpyrrolidine (79—88%); *N- $\beta$ -phenylethylsuccinimide*, m.p. 134°, furnishes PhEt (13%) and 1- $\beta$ -phenylethylpyrrolidine (65%), b.p. 113—115°/9 mm. (hydrochloride, m.p. 159—160°); *N-n-amylphthalimide* gives 3:4-hexahydrobenzopyrrolidine (V) (8%) and its 1-*n*-amyl derivative (52%), b.p. 104—106°/3 mm. (hydrochloride, m.p. 210—211°); *N- $\beta$ -phenylethylphthalimide* affords PhEt (22%), (V) (16%), and 1- $\beta$ -phenylethyl-3:4-hexahydrobenzopyrrolidine (39%), b.p. 167—168°/10 mm. (hydrochloride, m.p. 216—217°).

Piperidine (VI) and *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me at 250° in H<sub>2</sub> give *Ph piperidine-1-carboxylate*, b.p. 101—102°/3 mm., also prepared from (VI), PhOH, and CO<sub>2</sub> under similar conditions. *Bu<sup>n</sup> piperidine-1-carboxylate*, b.p. 98—99°/13 mm., is similarly obtained from (VI), Bu<sup>n</sup>OH, and CO<sub>2</sub>, whilst *n*-amylamine, PhOH, and CO<sub>2</sub> afford *Ph n-amylcarbamate*, b.p. 108—111°/5 mm.

H. B.

Action of hydrobromic acid on tri- $\beta$ -hydroxyethylamine and tetra- $\beta$ -hydroxyethylammonium bromide. V. PRELOG and Z. BLAŽEK (Coll. Czech. Chem. Comm., 1934, 6, 476—486).—The hydrobromide (I), m.p. 196.5°, of N(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>3</sub> and CH<sub>2</sub>Br·CH<sub>2</sub>·OH in hot EtOH give tetra- $\beta$ -hydroxyethylammonium bromide (II), cryst., hygroscopic (bromide of the Ac<sub>4</sub> derivative, m.p. 150.5°). Only three of the OH groups of (II) can be replaced by Br by use of HBr. (II) with HBr (9 mols. of 64% or 21 mols. of 71%) at 110° gives NN-di- $\beta$ -bromoethylmorpholinium bromide, m.p. 243° (corresponding picrate, m.p. 146.5°), and N-spirodimorpholinium bromide, m.p. 285° (decomp.) (corresponding picrate, m.p. 210°). When heated with 64% HBr first at 110° and then at 160—170°, (II) gives tri- $\beta$ -bromoethyl- $\beta$ -hydroxyethylammonium bromide (III), decomp. 228°, the hydro-

bromide (IV), m.p. 162°, of di- $\beta$ -bromoethyl- $\beta$ -hydroxyethylamine (picrate, m.p. 135.5°) (also formed by heating directly to 170°), and (at 160°) N- $\beta$ -bromoethylmorpholine hydrobromide (V), m.p. 222—224° (picrate, m.p. 134.5°). (IV) is best obtained by use of 25 mols. of 71% HBr at 160°, but also from (I), (II), or (III) and 3 mols. of 64% HBr, and from (I) and HBr·AcOH at 170°. (IV) and NH<sub>2</sub>Ph in hot MeOH give a substance, C<sub>12</sub>H<sub>20</sub>ON<sub>2</sub>Br<sub>2</sub>, m.p. 275° (decomp.) (picrate, m.p. 208°) (conc. alkali liberates a solid base), and N- $\beta$ -hydroxyethyl-di-( $\beta$ -phenylaminoethyl)amine hydrobromide, decomp. about 294°. (V) and 64% HBr at 170—200° give (·CH<sub>2</sub>Br)<sub>2</sub>, (IV), and NH(CH<sub>2</sub>·CH<sub>2</sub>Br)<sub>2</sub>·HBr, m.p. 209—210° (lit. 202—204°). (V) and NH<sub>2</sub>Ph in hot MeOH give N- $\beta$ -phenylaminoethylmorpholine (dihydrobromide, m.p. 223—224°; dipicrate, m.p. 192°).

R. S. C.

Configurative behaviour of  $\psi$ -leucine in the Walden inversion and elimination of halogen by dilute alkali from stereoisomeric  $\alpha$ -bromo- $\beta$ -dimethylbutyrylamino-acids. E. ABDERHALDEN, W. FAUST, and E. HAASE (Z. physiol. Chem., 1934, 228, 187—197).— $\alpha$ -Amino- $\beta$ -dimethylbutyric acid (*dl*- $\psi$ -leucine) was prepared from pinacolin, the formyl derivative, m.p. 210°, was resolved by brucine, and the products were hydrolysed by 10% HBr, giving l(+)- (I), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +10.01° in H<sub>2</sub>O, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -8.19° in 20% HCl, and d(-)- $\psi$ -leucine (II), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -10.15° in H<sub>2</sub>O, +8.36° in 20% HCl [C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub> derivative (III), m.p. 239—240°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +47.1° in EtOH]. The active formyl derivatives were converted into l(-)- (IV), m.p. 66°, b.p. 115—120°/12 mm., [ $\alpha$ ]<sub>D</sub><sup>25</sup> -14.4° in EtOH (acid chloride, b.p. 68—70°/10 mm., [ $\alpha$ ]<sub>D</sub><sup>25</sup> -14.7°), and d(+)- $\alpha$ -bromo- $\beta$ -dimethylbutyric acid (V), m.p. 70°, b.p. 115—120°/10 mm., [ $\alpha$ ]<sub>D</sub><sup>25</sup> +14.0° in EtOH (acid chloride, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +14.5°). Amination of (IV) and (V) regenerated (I) and (II) of the same configuration as the original material. When (II) was injected into a dog, (III) was isolated from the urine, hence the + form has the *l*-configuration. The following were synthesised from the acid chlorides and the appropriate NH<sub>2</sub>-acid ester: l(-)- $\alpha$ -bromo- $\beta$ -dimethylbutyryl-l(-)- (VI), [ $\alpha$ ]<sub>D</sub><sup>27</sup> +7.35°, and d(+)-tyrosine (VII), [ $\alpha$ ]<sub>D</sub><sup>27</sup> -53.6°, and l(+)-, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +5.37°, and d(-)- $\psi$ -leucine (VIII), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -14.8°; d(+)- $\alpha$ -bromo- $\beta$ -dimethylbutyryl-l(-)-tyrosine (IX), [ $\alpha$ ]<sub>D</sub><sup>27</sup> +51.8°, and d(+)-tyrosine (X), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -7.87°, and d(-)-, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -5.02°, and l(+)- $\psi$ -leucine, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +15.1° (all [ $\alpha$ ] in EtOH). Of these only (VI) and (VIII) are hydrolysed by trypsin. In the tyrosine series Br elimination by alkali occurs more rapidly with (VII) and (IX) than with (VI) and (X).

J. H. B.

Solubility of the stereoisomerides of cystine; identity of stone- and hair-cystine.—See A., 1934, 1381.

Additive compounds of halides of bivalent metals with organic bases. VIII.—See this vol., 49.

Additive compounds of alkali halides and organic bases.—See this vol., 48.

Acetylation of  $\alpha$ -amino- and  $\alpha$ -hydrazinosulphonic acids. H. J. BACKER and H. MULDER (Rec. trav. chim., 1934, 53, 1120—1127; cf. A., 1933,



702).—Acetylation ( $\text{Ac}_2\text{O}$  in  $\text{H}_2\text{O}$ ) of the Na salt of  $\alpha$ -aminoethane- $\alpha$ -sulphonic acid (from  $\text{MeCHO}$ , aq.  $\text{NaHSO}_3$ , and aq. 25%  $\text{NH}_3$  at about  $70^\circ$ ) gives Na  $\alpha$ -acetamidoethane- $\alpha$ -sulphonate.  $\alpha$ -Amino- $\alpha$ -phenylmethanesulphonic acid (from  $\text{PhCHO}$ ) similarly affords Na  $\alpha$ -acetamido- $\alpha$ -phenylmethanesulphonate, which is resolved through the strychnine salt; the d-,  $[\text{M}]_D^{25} +23^\circ$ , and l-,  $[\text{M}]_D^{25} -23.8^\circ$ , -Ba salts are described.  $\alpha$ -Amino- $\alpha$ -p-nitrophenyl- and - $\alpha$ -anisyl-methanesulphonic acids and K  $\alpha$ -acetamido- $\alpha$ -p-nitrophenyl- and - $\alpha$ -anisyl-methanesulphonates are described. The above  $\text{NH}_2$ -acids are all decomposed by aq. KCN, whereas the Ac derivatives are not. Na hydrazinodimethanesulphonate,  $(\cdot\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na})_2$  ( $\text{Ac}_2$  derivative), prepared from  $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$  and aq.  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , is converted by aq. KCN into hydrazinodiacetonitrile (yield about 5%), m.p.  $182-184^\circ$  (decomp.).  $\text{NHPh}\cdot\text{NH}_2$  and  $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$  similarly give K phenylhydrazinomethanesulphonate ( $\text{NO}$ - and  $\text{Ac}_2$  derivatives), converted by aq. KCN into a little phenylhydrazinodiacetonitrile, m.p.  $34-35^\circ$ . H. B.

**Dehydration of acid amides to nitriles.** C. H. KAO, J. Y. YEN, and S. L. CHIEN (J. Chinese Chem. Soc., 1934, 2, 240—242).—Amides are converted into nitriles best with  $\text{PCl}_5$  or  $\text{POCl}_3$  and NaCl.

J. L. D.

**Constitution of ascorbic acid. Action of sodium hypochlorite on  $\alpha$ -methoxy-acid amides.** R. G. AULT, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1934, 1722—1726).—(a)  $\text{OMe}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$  (I) (modified prep. from  $\text{OMe}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$ , b.p.  $92^\circ/0.03$  mm.), m.p.  $113-114^\circ$ , with aq.  $\text{NaOCl}$  at  $0^\circ$  or  $25^\circ$  gives  $\text{PhCHO}$ ,  $\text{NH}_3$ , and  $\text{CO}_2$ , but no  $\text{NaCNO}$  (II) (cf. A., 1934, 756). (b) In aq.  $\text{MeOH}$  45% of  $\text{OMe}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ , which is formed as intermediate product, is isolated; in  $\text{N-NaOH}$  at  $0^\circ$  this gives  $\text{PhCHO}$ ,  $\text{NH}_3$ , and  $\text{MeOH}$ , but no (II). 2 : 3 : 5-Trimethyl-*l*-arabonamide, *O*-methyl-lactamide (modified prep.), m.p.  $84^\circ$  (lit.  $79-81^\circ$ ), and 2 : 4-dimethyl-*d*-erythronamide with aq.  $\text{NaOCl}$  give similarly the aldehyde and  $\text{NH}_3$ , but no (II). The formation of (II) is thus characteristic of  $\alpha$ -OH-amides; it probably occurs by virtue of co-ordination, e.g.,  $\begin{matrix} \text{CHR}\cdot\text{OH} \\ | \\ \text{N}\cdot\text{CO} \end{matrix}$ .

In (a)  $\text{OMe}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}_2\text{H}$  is probably an intermediate product. R. S. C.

**Preparation of aldonic and saccharic acid amides in liquid ammonia.** J. W. E. GLATTFELD and D. MACMILLAN (J. Amer. Chem. Soc., 1934, 56, 2481—2482).—*dl*-Erythronamide, m.p.  $62.3^\circ$  [which could not be prepared by Weerman's method (A., 1917, i, 546)], is obtained in quant. yield when *dl*-erythronolactone is dissolved in a little liquid  $\text{NH}_3$  and the solution evaporated. The following are similarly prepared: *dl*- $\alpha\gamma$ -, m.p.  $118.5-119.5^\circ$ , and - $\beta\gamma$ -, m.p.  $90.7^\circ$ , -dihydroxybutyramides; *d*-, m.p.  $94.8^\circ$ ,  $[\alpha]_D^{20} +28.2^\circ$  in  $\text{H}_2\text{O}$ , and *l*-, m.p.  $94.8^\circ$ ,  $[\alpha]_D^{20} -28^\circ$  in  $\text{H}_2\text{O}$ , -erythronamides; *d*-galactonamide; *d*-gluconamide; *d*-mannonamide (from the  $\gamma$ - or  $\delta$ -lactone). Coumarin is unaffected by liquid  $\text{NH}_3$ .  $\gamma$ -Butyrolactone is also unaffected at the b.p.; ammonolysis occurs at room temp. in a sealed bomb. H. B.

**Carbamide phosphate.** C. MATIGNON and M. DODÉ (Bull. Soc. chim., 1934, [v], 1, 1114—1127).—

The physical and chemical properties of carbamide phosphate (I),  $\text{CO}(\text{NH}_2)_2\cdot\text{H}_3\text{PO}_4$ , m.p.  $117.5^\circ$ , are recorded. The salt  $3\text{CO}(\text{NH}_2)_2\cdot 2\text{H}_3\text{PO}_4$  was not obtained and the m.-p. curve of the system  $\text{CO}(\text{NH}_2)_2$ -(I) yields no evidence of the existence of any combination other than (I). F. S. H. H.

**Microchemistry of diethylbromoacetylcarbamide (Adaline).** M. WAGENAAR (Pharm. Weekblad, 1934, 71, 1261—1264).—Adaline gives characteristic micro-cryst. ppts. with  $\text{HNO}_3$ ,  $\text{AgNO}_3$  ( $\text{AgBr}$ ), and  $\text{Pt}(\text{SO}_4)_2$  [ $(\text{NH}_4)_2\text{PtBr}_6$ ]. S. C.

**Azido-dithiocarbonic acid. VIII. Guanidine trinitride and azido-dithiocarbonate.** J. CRAIK, K. H. BERGER, and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 2380—2381; cf. A., 1934, 735).— $\text{NH}_2\text{C}(\text{NH}_2)_2\cdot\text{HN}_3$ , m.p.  $93.5^\circ$ , and  $\text{NH}_2\text{C}(\text{NH}_2)_2\cdot\text{SH}\cdot\text{CS}\cdot\text{N}_3$ , decomp.  $88-90^\circ$ , have been prepared. E. S. H.

**Tautomeric transformations of certain organic phosphorus compounds.** A. E. ARBUZOV and A. I. RAZUMOV (J. Gen. Chem. Russ., 1934, 4, 834—841; cf. A., 1929, 1129).—The Na salt of Et  $\alpha$ -diisobutylphosphinoacetate, b.p.  $170-171^\circ/10$  mm., prepared from  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$  and  $\text{P}(\text{O}i\text{Bu}^\beta)_3$ , exists in three tautomeric forms, which react with MeI as follows:  $\text{PO}(\text{O}i\text{Bu}^\beta)_2\cdot\text{CHNa}\cdot\text{CO}_2\text{Et} + \text{MeI} \rightarrow$

$\text{PO}(\text{O}i\text{Bu}^\beta)_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$  (I) + NaI;

$\text{P}(\text{ONa})(\text{O}i\text{Bu}^\beta)_2\cdot\text{CH}\cdot\text{CO}_2\text{Et} + \text{MeI} \rightarrow$

$\text{PI}(\text{ONa})(\text{O}i\text{Bu}^\beta)_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} \rightarrow$   
 $\text{PO}(\text{ONa})(\text{O}i\text{Bu}^\beta)\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$  (II) +  $\text{Bu}^\beta\text{I}$ ;

$\text{PO}(\text{O}i\text{Bu}^\beta)_2\cdot\text{CH}\cdot\text{C}(\text{ONa})\cdot\text{OEt} + \text{MeI} \rightarrow$

$\text{PO}(\text{O}i\text{Bu}^\beta)_2\cdot\text{CHMe}\cdot\text{Cl}(\text{ONa})\cdot\text{OEt} \rightarrow$

$\text{PO}(\text{O}i\text{Bu}^\beta)_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Na}$  (III) + EtI. (I), b.p.  $165-168.5^\circ/7.5$  mm., is obtained in 43% yield, and (II) and (III) (not isolated) in 25% yields.  $\text{P}(\text{OEt})_3$  or  $\text{P}(\text{ONa})(\text{OEt})_2$  (IV) and  $\text{COPh}\cdot\text{CH}_2\text{Br}$  in  $\text{Et}_2\text{O}$  give a mixture of products, from which the ketone,

$\text{PO}(\text{OEt})_2\cdot\text{CH}_2\cdot\text{COPh}$  (V), b.p.  $174-176^\circ/2.5$  mm., is isolated. The Na salt of (V) with MeI in  $\text{Et}_2\text{O}$  yields the substance  $\text{PO}(\text{OEt})_2\cdot\text{CHMe}\cdot\text{COPh}$ , b.p.  $171-180^\circ/3$  mm. (IV) and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Ph}$  in  $\text{Et}_2\text{O}$  yield Ph  $\alpha$ -diethylphosphinoacetate, b.p.  $153.5-157^\circ/9$  mm., the Na salt of which reacts with MeI to give Ph  $\alpha$ -diethylphosphinopropionate, b.p.  $140-146^\circ/15$  mm. (50% yield), EtI, and other products.  $\text{PPh}_2\text{Cl}$  and  $\text{NaO}i\text{Bu}^\beta$  in  $\text{Et}_2\text{O}$  afford  $\text{PPh}_2\cdot\text{O}i\text{Bu}^\beta$ , b.p.  $188^\circ/15$  mm., which with  $\text{COMe}\cdot\text{CH}_2\text{Cl}$  at  $140^\circ$  gives  $\text{POPh}_2\cdot\text{CH}_2\cdot\text{COMe}$ , b.p.  $220-224^\circ/10$  mm., m.p.  $73^\circ$ , in which H is not replaceable by Na. R. T.

**Sodium cacodylate.** F. MARTIN (Bull. Sci. pharmacol., 1934, 41, No. 36, 21—28; Chem. Zentr., 1934, i, 3774—3775).—Chemically neutral Na cacodylate (I) reacts alkaline to phenolphthalein (II); if neutral to (II), 3% of free dimethylarsinic acid is present. To test for Na methylarsinate (III), 1 g. of (I) is dissolved in 5 c.c. of dil.  $\text{H}_2\text{SO}_4$ , and 2 drops of 10% KI are added. With  $\leq 0.1\%$  of (III), a ppt. forms on mixing. J. S. A.

**Radial esters of tetrathio-orthostannic acid.** II. H. J. BACKER and J. KRAMER (Rec. trav. chim., 1934, 53, 1101—1112; cf. A., 1933, 1274).—The following alkyl and aryl tetrathio-orthostannates,  $\text{Sn}(\text{SR})_4$ , are prepared from  $\text{SnCl}_4$  and  $\text{RSNa}$  as



previously described (*loc. cit.*): R=*n*-amyl, b.p. 162°/0.004 mm.; *n*-hexyl, decomp. on attempted distillation in cathode vac.; *n*-dodecyl, m.p. 35.5°; *n*-hexadecyl, m.p. 53—54°; allyl;  $\beta$ -methylallyl; cyclohexyl, m.p. 53—54° (crystallographic data given); Ph, m.p. 67°; *p*-tolyl, m.p. 100°; *p*-C<sub>6</sub>H<sub>4</sub>Cl, m.p. 189°; *p*-C<sub>6</sub>H<sub>4</sub>Br, m.p. 217°; *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>v</sup>, m.p. 106°; benzyl, decomp. on attempted distillation in cathode vac. (SH·CH<sub>2</sub>·CH<sub>2</sub>)<sub>2</sub>O (in EtOH-NaOEt) and SnCl<sub>4</sub> (in C<sub>6</sub>H<sub>6</sub>) give the spiro-compound,

$\text{Sn} \left( \begin{array}{c} \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} \right)_2$ , m.p. 124°. Sn(SAlk)<sub>4</sub> are oxidised [warm HNO<sub>3</sub> (*d* 1.1)] to SnO<sub>2</sub> and (SAlk)<sub>2</sub>. Sn(SEt)<sub>4</sub> and Sn(SPr <sup>$\beta$</sup> )<sub>4</sub> with EtOH-HgCl<sub>2</sub> give compounds of the composition C<sub>2</sub>H<sub>5</sub>ClSHg and C<sub>3</sub>H<sub>7</sub>ClSHg, respectively. SnPh<sub>2</sub>Br<sub>2</sub> (simplified prep.; cf. Chambers and Scherer, A., 1926, 629) and NaSPh in C<sub>6</sub>H<sub>6</sub> afford di(phenylthiol)diphenylstannane, SnPh<sub>2</sub>(SPh)<sub>2</sub>, m.p. 65—65.5°. Slow addition of 60% oleum to cold PhBu<sup>v</sup> (from C<sub>6</sub>H<sub>6</sub>, Bu<sup>v</sup>Cl, and a little AlCl<sub>3</sub>) gives *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>v</sup>·SO<sub>3</sub>H (*K* salt+H<sub>2</sub>O); the chloride, m.p. 83°, is reduced (Sn, conc. HCl) to *p*-tert.-butylthiophenol, b.p. 117°/10 mm. *p*-C<sub>6</sub>H<sub>4</sub>Cl·SH, *p*-C<sub>6</sub>H<sub>4</sub>Br·SH, and *p*-C<sub>6</sub>H<sub>4</sub>Me·SH are similarly prepared.

CH<sub>2</sub>:CH:CH<sub>2</sub>·SH, b.p. 67—69°, and CH<sub>2</sub>:CMe:CH<sub>2</sub>·SH, b.p. 93.5°/760 mm. (which polymerises readily), are prepared by hydrolysis (aq. NaOH) of NH<sub>2</sub>:C(NH)<sub>2</sub>:SR.

H. B.

**Configuration of bisdimethylglyoximediamine cobaltic salts.**—See this vol., 51.

**Action of niobium and tantalum pentachloride on organic compounds.** IV. H. FUNK (Ber., 1934, 67, [B], 1801—1804; cf. A., 1929, 1039).—NbCl<sub>5</sub> and TaCl<sub>5</sub> react readily with CH<sub>2</sub>Ac<sub>2</sub> with evolution of HCl and formation of compounds contaminated by the products of decomp. of CH<sub>2</sub>Ac<sub>2</sub>. The complication can be avoided by use of a suitable solvent (MeOH, EtOH) in small amount, but the products then contain OAlk. They are colourless to dark yellow, those containing Nb being darker than the corresponding Ta compounds and those derived from CH<sub>2</sub>AcBz darker than those obtained with CH<sub>2</sub>Ac<sub>2</sub>. They are much less sensitive to H<sub>2</sub>O than the parent chlorides. The following salts are described: NbCl<sub>2</sub>(OMe)<sub>2</sub>·C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>, m.p. 128—129°;

TaCl<sub>2</sub>(OMe)<sub>2</sub>·C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>, m.p. 113—115°;

NbCl<sub>2</sub>(OEt)<sub>2</sub>·C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>, m.p. 74—76°;

TaCl<sub>2</sub>(OEt)<sub>2</sub>·C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>, m.p. 63—65°;

NbCl<sub>2</sub>(OMe)<sub>2</sub>·C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>, m.p. 144—145°;

TaCl<sub>2</sub>(OMe)<sub>2</sub>·C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>, m.p. 138—139°;

NbCl<sub>2</sub>(OEt)<sub>2</sub>·C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>, m.p. 110—112°;

TaCl<sub>2</sub>(OEt)<sub>2</sub>·C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>, m.p. 114—116°.

H. W.

**Recent researches on the cyclane series.** M. GODCHOT (Bull. Soc. chim., 1934, [v], 1, 1154—1200).—A lecture.

**Thermal decomposition of cyclohexane hydrocarbons.** N. D. ZELINSKI, B. M. MICHAÏLOV, and J. A. ARBUZOV (J. Gen. Chem. Russ., 1934, 4, 856—865).—The yields of butadiene obtained by heating various hydrocarbons at 750° with or without H<sub>2</sub>O are: cyclohexene 65.2;  $\Delta^3$ -methylcyclohexene 56.4; cyclohexane 40; methyl- 34.8, and ethyl-cyclohexane 41.2; decahydronaphthalene 11.6 mol.-%; at the

same time, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and H<sub>2</sub> are produced in various proportions. Under analogous conditions,  $\Delta^1$ -methylcyclohexene affords isoprene in 36.2 mol.-% yield.

R. T.

**Raman effect and organic chemistry.**  $\gamma$ -cyclopentyl- $\Delta^{\alpha}$ -propine and its derivatives. B. GRÉDY (Compt. rend., 1934, 199, 1129—1131).—Mg cyclopentyl bromide and CH<sub>2</sub>Br·CBr:CH<sub>2</sub> give  $\beta$ -bromo- $\gamma$ -cyclopentyl- $\Delta^{\alpha}$ -propene, b.p. 75°/13 mm., converted by NaNH<sub>2</sub> in decahydronaphthalene at 150° into  $\gamma$ -cyclopentyl- $\Delta^{\alpha}$ -propine (I), b.p. 132.5—133.5°/760 mm. (Ag, Cu, and Na derivatives). The Mg derivative of (I) is transformed by trioxymethylene into  $\delta$ -cyclopentyl- $\Delta^{\beta}$ -butin- $\alpha$ -ol (II), b.p. 117°/14 mm., and by MeCHO into  $\varepsilon$ -cyclopentyl- $\Delta^{\gamma}$ -pentin- $\beta$ -ol (III), b.p. 114—115°/13 mm. Treatment of (I), (II), and (III) with Me<sub>2</sub>SO<sub>4</sub> and NaNH<sub>2</sub> in anhyd. Et<sub>2</sub>O affords, respectively,  $\delta$ -cyclopentyl- $\Delta^{\beta}$ -butine, b.p. 164—165°/760 mm.,  $\alpha$ -methoxy- $\delta$ -cyclopentyl- $\Delta^{\beta}$ -butine, b.p. 96—97°/15 mm., and  $\beta$ -methoxy- $\gamma$ -cyclopentyl- $\Delta^{\gamma}$ -pentine, b.p. 99.5°/17 mm. A cyclic nucleus separated by CH<sub>2</sub> from the C:C linking is without influence on the frequencies of the latter. The presence of cyclopentyl is characterised by a series of bands, and the band 1445, characteristic of CH<sub>2</sub>, is resolved into two rays 1429 and 1450 in all derivatives of (I).

H. W.

**Internal energy relationships and regularities of substitution among aromatic, carbocyclic compounds.** O. SCHMIDT (Ber., 1934, 67, [B], 1870—1887).—The line of reasoning is based on the work of London (A., 1927, 923; 1928, 344, 1077; 1929, 1397) whereby it is assumed that homopolar union depends on the coupling of two electrons of opposite spin and that under these conditions the energy of union constitutes the main part of the total energy; also, the twist vectors of the valency electrons of an atom are parallel. Hence, the twist vectors of the valency electrons of consecutive C atoms of a chain or ring with an even no. of C atoms are anti-parallel. A single C:C linking vicinal to a C:C union is strengthened, whereas the next is weakened, and the alternation of strengthening and weakening continues with diminishing intensity through the whole mol.; it is strongly pronounced at a distance of 2.5 Å. and probably obvious at 5 Å. The C:C linking consists of two spin-valencies, one of which is weaker than the other. The electrons concerned with the stronger linking, localised in the direction of the line of nuclear union, are designated *A* electrons, whereas the others, inclined thereto, are *B* electrons. The latter are more feebly united because further distant from one another. The potential of the *B* electrons inversely  $\propto$  to the distance. The *B* electrons at the terminations of a diameter of C<sub>6</sub>H<sub>6</sub> are anti-parallel, whereas those with parallel spin are located at similar positions in cyclooctatetraene (I). Vectorial addition in C<sub>6</sub>H<sub>6</sub> causes strong resultants directed inwards, whereas with (I) the effect is weak. Within the C<sub>6</sub>H<sub>6</sub> nucleus there is therefore a ring of 6 *B* electrons co-planar with the 6 atoms, held together in the *o*- and *p*-position by coupling of electron pairs with opposed spin. This is the cause of aromatic character. The energy of relationships



of aromatic hydrocarbons and their partly hydrogenated products are calc. The results are in accord with thermochemical data and permit simple explanation of the reaction relationships of complex aromatic compounds. The regularities of substitution are in harmony with the author's conceptions. H. W.

**Technical reactions. IV. Substitution rules in aromatic compounds.** O. SCHMIDT (Z. Elektrochem., 1934, 40, 765—770).—Theoretical.

E. S. H.

**Direct introduction of deuterium into benzene without heterogeneous catalysis.** C. K. INGOLD, C. G. RAISIN, and C. L. WILSON (Nature, 1934, 134, 734).—When  $C_6H_6$  is shaken with 90%  $H_2SO_4$  of enhanced  $H^2$  content part of the  $H^2$  is transferred to the  $C_6H_6$ , which gives  $H_2O$  on combustion. The amount of  $H^2$  transferred increases with time of shaking. Certain substitution products of  $C_6H_6$  undergo spontaneous exchange of their nuclear H atoms with the H of  $H_2O$  or acids more readily than does  $C_6H_6$  itself. The existence of an aromatic substitution depending on "normal" polarisation, *i.e.*, one corresponding with the ionisation, is thus demonstrated.

L. S. T.

**Direct introduction of deuterium into benzene.** J. HORIUTI and M. POLANYI (Nature, 1934, 134, 847).—A general mechanism for H exchange in unsaturated compounds involving the addition and subsequent elimination of  $H_2O$  or H halide is suggested. The interchange of H between  $C_6H_6$  and 90%  $H_2SO_4$  recently reported (preceding abstract) is regarded as a special case of this general principle.

L. S. T.

**Direct introduction of deuterium into benzene.** C. K. INGOLD, C. G. RAISIN, and C. L. WILSON (Nature, 1934, 134, 847—848).—Whilst the mechanism suggested by Horiuti and Polanyi (see above) often applies to unsaturated compounds it does not apply to the H exchange between aq.  $H_2SO_4$  and  $C_6H_6$ . This involves polarisations in which addition and subsequent removal of  $H_2SO_4$  occur.

L. S. T.

**Electrochemical chlorination of benzene.**—See this vol., 45.

**Reactive methyl group in toluene derivatives.**

II. *p*-Nitrobenzotribromide. C. H. FISHER (J. Amer. Chem. Soc., 1934, 56, 2469—2470).— $p\text{-NO}_2\cdot C_6H_4\cdot CHBr_2$  (I) and aq. NaOBr give *p*-nitrobenzotribromide (II), m.p. 86—87°, which is stable to hot MeOH and cold alkali, and is hydrolysed (boiling  $H_2O$  or, more rapidly, aq.  $Na_2CO_3$ ) to  $p\text{-NO}_2\cdot C_6H_4\cdot CO_2H$  (III). (II) and PhOH at 135—145° afford a little (I) and an alkali-sol. coloured substance. Condensation products are obtained from (II) and NPhMe<sub>3</sub>; (I) could not be isolated. (II) could not be dehalogenated by COMe<sub>2</sub> or COPhMe; treatment with  $N_2H_4$  in EtOH gives  $N_2$  (cf. Cox *et al.*, A., 1931, 1074). Prolonged treatment (8 days) of  $p\text{-C}_6H_4Me\cdot NO_2$  with NaOBr affords a little (III).  $CBR_2\cdot NO_2$  is formed by the action of NaOBr on 2 : 4- $C_6H_3Me(NO_2)_2$  and *s*- $C_6H_2Me(NO_2)_3$ . H. B.

**Fluoro-derivatives of butyltoluene and of butyl-*m*-xylene. Fluoronitro-derivatives with the**

odour of musk. G. DARZENS and A. LÉVY (Compt. rend., 1934, 199, 959—962).—3-Fluoro-5-*tert*-butyltoluene (I), m.p. 96—98°/25 mm., and 4-fluoro-5-*tert*-butyl-*m*-xylene (II), b.p. 97—98°/21 mm., are obtained from *m*- $C_6H_4FMe$  and 4-fluoro-*m*-xylene with  $Bu^tCl$  and  $AlCl_3$ , respectively. 2-Fluoro-5-*tert*-butyl-*m*-xylene (III), b.p. 100°/22 mm., is prepared through the borofluoride (cf. A., 1927, 654) from 2-nitro-5-*tert*-butyl-*m*-xylene. With conc.  $H_2SO_4\text{-}HNO_3$ , (I), (II), and (III) give, respectively, 2 : 4 : 6- $(NO_2)_3$ , m.p. 95°, 2 : 6-, m.p. 57.5°, and 4 : 6- $(NO_2)_2$ -derivatives, m.p. 89°, all of which possess the odour of musk.

J. L. D.

**Volume effect of alkyl groups in aromatic compounds. VI. Constitution of the iodo-*p*-cymene formed by direct iodination of the hydrocarbon.** S. N. GANGULY and R. J. W. LE FEVRE (J.C.S., 1934, 1697—1699; cf. A., 1934, 878).—Pure 2-aminocymene gives (diazo-reaction) 2-iodocymene (I), b.p. 122°/11 mm. [dichloride (II), m.p. 97°]. The Grignard reagent from 3-bromocymene affords *p*-cymene and a little 3-iodocymene, b.p. 125—126°/11 mm. (dichloride, m.p. 85—87°). Cymene,  $HIO_3$ , and I in hot EtOH give (I) (cf. lit. and A., 1933, 1153) and substances halogenated in the side-chain; the former was identified by prep. of (II) and of 3 : 5-dinitro-2-piperidino-*p*-cymene and by the  $[\alpha]$  therein of *l*-menthol (III). The  $[\alpha]$  of (III) is slightly lower in solution in the 3- than in the 2-halogenocymenes.

R. S. C.

**Preparation of styrene.** H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1934, 53, 1133—1138).—Pure styrene (I), b.p. 145—145.8°/760 mm., 48°/20 mm., m.p. —33°, is prepared from  $\beta$ -bromo- $\alpha$ -phenylethyl Et ether, b.p. 96—100°/15 mm. (from  $CH_2Br\cdot CHBr\cdot OEt$  and  $MgPhBr$ ), and Zn-Cu in 90% EtOH, and subsequent vac. distillation (partial polymerisation occurs at atm. pressure) over anhyd.  $Na_2SO_4$ . (I) can be kept for several months in the cold and darkness without polymerisation taking place. The physical consts. of (I), PhEt, and ethylcyclohexane are tabulated and compared with those in the lit.

H. B.

**Determination of the mol. wt. of polystyrenes.** A. SMAKULA (Angew. Chem., 1934, 47, 777—779).—The molar absorption coeff. at 260  $\mu$  for polystyrenes  $\propto$  mol. wt. deduced from val. of  $\eta$  (Staudinger).

A. G.

**Relation between constituents of Japanese acid earth and its catalytic action [on naphthalene].**—See this vol., 44.

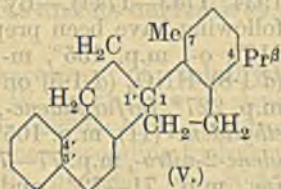
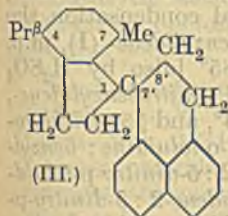
**Fluorene and triphenylmethane. XIII. Alcoholic potassium hydroxide as a reagent for fluorene hydrocarbons with a labile hydrogen atom.** A. A. VANSCHIEDT (J. Gen. Chem. Russ., 1934, 4, 875—884).—Hydrocarbons containing the cyclopentadiene ring give characteristic colorations with EtOH-KOH.

R. T.

**Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones. IV. Constitution of Diels' hydrocarbon, " $C_{25}H_{24}$ ," from cholesterol.** J. W. COOK, C. L. HEWETT, W. V. MAXNEORD, and (MISS) E. ROE (J.C.S., 1934, 1727—1738; cf. A., 1934, 766).—The

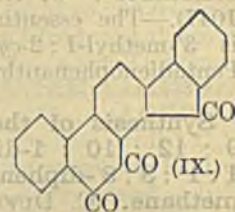


Grignard reagent from 3-bromo-*p*-cymene and  $\text{CH}_2\text{O}$  give 3-*p*-cymylcarbinol (not obtained pure), b.p. 143—144°/25 mm. (3:5-dinitrobenzoate, m.p. 85—86°), which with  $\text{SOCl}_2$  and  $\text{NPhMe}_2$  give 3-chloromethyl-*p*-cymene (I), b.p. 129—130°/25 mm. The Grignard reagent therefrom with 1-keto-1:2:3:4-tetrahydrophenanthrene gives an oil, which with  $\text{P}_2\text{O}_5$  at 145—150° yields a resin, b.p. about 260—270°/4—5 mm., dehydrogenated (Se) at 320—340° to 1-(3-*p*-cymylmethyl)phenanthrene, m.p. 115—116° [ $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$  complex, m.p. 134—135°], oxidised ( $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ ) to 1-3'-methyl-6'-isopropylbenzoylphenanthraquinone, m.p. 208—209° (phenazine, m.p. 187°). (I) and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  in  $\text{C}_6\text{H}_6$  give an ester, b.p. 195—200°/14 mm., which after hydrolysis yields at 180°  $\beta$ -3-(*p*-cymyl)propionic acid, m.p. 61—61.5°, dehydrated by  $\text{SnCl}_4$  at 120° to 7-methyl-4-isopropyl-1-hydrindone (II), m.p. 46—48°, b.p. 165—167°/15 mm. (phenylhydrazone, m.p. 96—97°). This with the Grignard reagent from  $\beta$ -1-naphthylethyl chloride affords 1-hydroxy-1-( $\beta$ -1'-naphthylethyl)-7-methyl-4-isopropyl-hydrindene, m.p. 115—116°, which with  $\text{KHSO}_4$  at 160° gives 3-( $\beta$ -1'-naphthylethyl)-4-methyl-7-isopropylindene, m.p. 92—93°, and with  $\text{H}_2\text{SO}_4\text{-AcOH}$  at 100°,  $\text{P}_2\text{O}_5$  at 160°, or  $\text{AlCl}_3$  in  $\text{CS}_2$  at 0° gives 7-methyl-4-isopropylhydrindene-1:7'-spiro-7':8'-dihydrophenalene (III), m.p. 82—83°. The Grignard reagent from

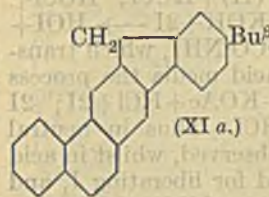


5-bromotetrahydronaphthalene and ethylene oxide give  $\beta$ -5-tetrahydronaphthylethyl alcohol, b.p. 120°/0.2 mm. (3:5-dinitrobenzoate, m.p. 128—129°), the chloride (IV) (by  $\text{SOCl}_2$  and  $\text{NPhMe}_2$ ), b.p. 155°/11—12 mm., of which with (II) gives (Grignard) 1-hydroxy-1-( $\beta$ -5'-tetrahydronaphthylethyl)-7-methyl-4-isopropyl-hydrindene, m.p. 114.5—115°, which, when dehydrated with  $\text{H}_2\text{SO}_4\text{-AcOH}$  at 100°, and then heated with Se at 320°, gives probably a little 5-methyl-8-isopropyl-naphthylfluorene, m.p. 198—200°, and much 7-methyl-4-isopropylhydrindene-1:1'-spiro(4':5'-benz)-hydrindene (V), an oil (picrate, m.p. 121.5—122°). Spiran formation in these dehydrogenations is prevented and yields in previous stages are improved if the  $\beta$ -position of the ethylenic linking is substituted. Thus,  $\text{CH}_2\text{Ph-CHMe-COCl}$  [prep. of the acid from  $\text{CH}_2\text{PhCl}$  and  $\text{CMeNa}(\text{CO}_2\text{Et})_2$ ] and  $\text{AlCl}_3$  give an 82% yield of 2-methyl-1-hydrindone (VI), which with  $\text{CH}_2\text{Ph-CH}_2\text{-MgCl}$  gives a carbinol, converted by distillation in vac. into 3- $\beta$ -phenylethyl-2-methylindene (80%), b.p. 170°/1 mm. (picrate, unstable), which with  $\text{AlCl}_3$  in  $\text{CS}_2$  at 0° gives 10-methyl-3:4:10:11-tetrahydro-1:2-benzfluorene, b.p. 159°/0.8 mm., dehydrogenated by Se at 310—320° to give a 65% yield of chrysofluorene, m.p. 182—183°. Previous samples of tetrahydrochrysofluorene contained some spiran. (IV) and the Grignard reagent from (IV) give 3-( $\beta$ -5'-tetrahydronaphthylethyl)-2-methylindene, m.p. 173°, b.p. 190°/0.3 mm. (picrate, m.p. 115°), which with  $\text{AlCl}_3$

in  $\text{CS}_2$  at 0° or  $\text{H}_2\text{SO}_4\text{-AcOH}$  at 100° gives 10-methyl-3:4:10:11:5':6':7':8'-octahydro-2':1'-naphtha-1:2-fluorene, m.p. 123.5—124°, b.p. 195°/0.4 mm., converted by Se at 310—320° or 400—420° to 2':1'-naphtha-1:2-fluorene (VII), sublimes at 300°/0.3 mm., m.p. 327—328° (preheated to 300°) (2:7-dinitro-anthraquinone complex, m.p. 249—251°), which with



$\text{Na}_2\text{Cr}_2\text{O}_7$  (best, an excess) in hot  $\text{AcOH}$  yields 2':1'-naphtha-1:2-fluorenone (VIII), m.p. 207—208°, sublimes at < 300°/0.3 mm., and some triketone (IX), m.p. 340—350° (decomp. from 280°), sublimes at 300—320°/0.3 mm. [also formed by oxidation of (VIII)]. (I) and  $\text{CMeNa}(\text{CO}_2\text{Et})_2$  in  $\text{C}_6\text{H}_6$  give an ester, b.p. 175°/2 mm., whence by hydrolysis and decarboxylation at 200°  $\beta$ -(3-*p*-cymyl)- $\alpha$ -methylpropionic acid, b.p. 160—162°/0.8 mm., was obtained. This acid with  $\text{SnCl}_4$  at 120° gives 2:7-dimethyl-4-isopropyl-1-hydrindone, b.p. 160°/16 mm., m.p. 46—46.5°, which with (IV) affords 3-( $\beta$ -5'-tetrahydronaphthylethyl)-2:4-dimethyl-7-isopropylindene, b.p. 218°/0.3 mm. (dipicrate, m.p. 119—119.5°), cyclised by  $\text{AlCl}_3$  or  $\text{H}_2\text{SO}_4\text{-AcOH}$  to 5:10-dimethyl-8-isopropyl-3:4:10:11:5':6':7':8'-octahydro-2':1'-naphtha-1:2-fluorene, b.p. 215—220°/0.3 mm., whence by Se at 310—325° was obtained 5-methyl-8-isopropyl-2':1'-naphtha-1:2-fluorene (X), m.p. 198°, sublimes at 230—240°/0.2 mm. (2:7-dinitroanthraquinone complex, m.p. 261—262°), which is not identical (mixed m.p.) with Diels' hydrocarbon,  $\text{C}_{25}\text{H}_{24}$  (XI), from cholesterol. Oxidation ( $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ ) of (X) affords 5-methyl-8-isopropyl-2':1'-naphtha-1:2-fluorenone, m.p. 197—198°. Absorption curves are given for (VII), (X), (XI), phenanthrene, and picene; the close similarity of those of the first three compounds indicates that (XI) has a ring system related to (VII). X-Ray spectra, however, show that (XI) has a longer mol. than (X), and it is suggested that (XI) may be 7-isobutyl-1':2'-naphtha-2:3-fluorene (XIa), the new ring system being produced by fission between C14 and C15 and



linking of C15 to C23 and of C21 to C12. Rearrangement of the ring structure during dehydrogenation is not observed with simple polycyclic hydroaromatic compounds, but is characteristic of the terminal 5-membered ring and labile side-chain of the sterols etc. It is caused by the high temp. used and not by any special reagent.

R. S. C.

Is Diels' hydrocarbon, " $\text{C}_{18}\text{H}_{16}$ ," a pure single substance? H. W. THOMPSON (Chem. and Ind., 1934, 1027—1028).—Diels' hydrocarbon, " $\text{C}_{18}\text{H}_{16}$ ," (from cholesterol), is recovered unchanged on distillation with Zn dust. Slow crystallisation from dil.



EtOH gave separation into two fractions, m.p. 150° and 142°. The former, recryst. repeatedly, showed m.p. 253° (12° depression with chrysene) and agreed with empirical formula  $C_{17}H_{12}$ . These facts suggest that " $C_{18}H_{16}$ " is a mixture. H. G. M.

Is Diels' hydrocarbon  $C_{18}H_{16}$  a pure single substance? J. W. COOK (Chem. and Ind., 1934, 1047).—The essential constituent of Diels'  $C_{18}H_{16}$  is 3'-methyl-1:2-cyclopentenophenanthrene. cyclo-Pentadienophenanthrene has not yet been synthesised. J. W. B.

Synthesis of the blue hydrocarbon  $C_{30}H_{16}$ , 9:12:10:1-diphenylenenaphthacene or 1:1':3:3'-diphenylenrubene, from dibenzoylmethane. C. DUFRAISSE and R. GIRARD (Bull. Soc. chim., 1934, [v], 1, 1359—1367).—The blue diphenylenrubene  $C_{30}H_{16}$  (I) obtained by prolonged action of  $PCl_5$  on  $CH_2Bz_2$  thus:  $CH_2Bz_2 - 4HCl \rightarrow$  yellow  $C_{30}H_{20}Cl_4$  (II)  $- 2HCl \rightarrow$  red dichlorodiphenylenrubene  $C_{30}H_{18}Cl_2$  (III)  $- HCl \rightarrow$  violet chlorophenylenrubene  $C_{30}H_{17}Cl$  (IV)  $- HCl \rightarrow$  (I), has an identical absorption spectrum (revised data; max. at 6100, 5650, and 5250 Å.), volatility (at 270—275°/0.01 mm.), and solubility, and gives the same reduction product, as a specimen of (I) obtained by the action of KOH at 325—330° on (IV) (A., 1933, 1284) in  $C_{10}H_8$ , or on (II) or (III), or obtained from  $\alpha\alpha$ -triphenyl- $\Delta^8$ -propinen- $\alpha$ -ol, thus confirming the structure previously assigned (Badoche, *ibid.*, 1154) to (I), and the elimination of 2Ph in the conversion of the colourless  $C_{42}H_{26}$  into (I). The absorption spectra of (III) and (IV) closely resemble, respectively, those of tetraphenyl- and diphenylphenylene-rubene. J. W. B.

(A) Halogenation of organic compounds. Bromination and iodination of aromatic amines by means of *N*-chloroamides. (B) Mechanism of iodination of organic compounds by means of chloroamides and oxidising agents. M. V. LICHOSCHERSTOV, B. I. TSIMBALIST, and A. A. PETROV (J. Gen. Chem. Russ., 1934, 4, 557—562, 622—628).—(A) Arylamines may be conveniently halogenated by the reaction  $NH_2 \cdot RH + MX + R' \cdot CO \cdot NHCl$  (I)  $\rightarrow$   $NH_2 \cdot RX + MCl + R' \cdot CO \cdot NH_2$  (II), where RH is an aromatic radical, R' is NHCl, Me, or some other radical, and MX is an alkali halide.

(B) In neutral solution the above reaction consists of the stages (I) +  $H_2O \rightarrow$  (II) + HOCl;  $HOCl + 2KI \rightarrow 2I + KCl + KOH$ ;  $KOH + 2I \rightarrow HOI + KI$ ; (II) + HOI  $\rightleftharpoons$   $H_2O + R' \cdot CO \cdot NHI$ , which transfers I to the compound. In acid media the process is (I) +  $2KI + AcOH \rightarrow$  (II) +  $KOAc + KCl + 2I$ ;  $2I + (I) + \cdot RH \rightarrow 2 \cdot RI + (I) + HCl$ . Thus in neutral solution liberation of I is not observed, whilst in acid solutions half of the (I) is used for liberating I, and iodination commences only after addition of further (I); the same effect is obtained by adding the theoretical amount of I, and half the total amount of (I), or by using  $K_2Cr_2O_7$ ,  $KIO_3$ , or  $KMnO_4$  in place of (I). R. T.

Fission of aryltrimethylammonium chlorides in aqueous solution by means of sodium amalgam. P. GROENEWOLD and R. ROBINSON (J.C.S., 1934, 1692—1697).—The % of salt decomp.,

$+NArMe_3Cl^- \rightarrow NArMe_2 + CH_4$  or  $\rightarrow ArH + NMe_3$ , and the % of reacting mols. giving  $NMe_3$  in the reductive fission of aryltrimethylammonium chlorides with 12 times the theoretical amount of 1% Na—Hg at 95—100° ( $CO_2$  stream) under standard conditions are, respectively, given in parentheses after each salt:  $Ar = Ph$ , m.p. 220° (decomp.) (picrate, m.p. 123—124°) (44—46; 71.1); *o*- (88—90; 62.9), *m*- (picrate, m.p. 108°) (61—63; 60.1), and *p*- $C_6H_4Me$  (picrate, m.p. 193—198°) (27—30; 30.8); *o*-, m.p. 140° (decomp.) (picrate, m.p. 125°) (34—37; 88.6), *m*-, m.p. 195° (decomp.) (picrate, m.p. 132.5—133.5°) (62.5—65.4; 64), and *p*- $C_6H_4OMe$ , m.p. > 200° (decomp.) (picrate, m.p. 176—177°) (65—68; 20.2); 3-, m.p. > 200° (decomp.) (picrate, m.p. 166—167°) (89—91; 92.5), and 4- $C_6H_4Ph$ , m.p. 205—208° (decomp.) (picrate, m.p. 153°) (93.5—96; 85.8), and 2-naphthyl, m.p. 173—174° (90—91; 94.7). With aq.  $Me_2SO_4$  on a steam bath *m*- $C_6H_4Ph \cdot NH_2$  affords 3-dimethylaminodiphenyl, b.p. 171—173°/12 mm. (methiodide, m.p. 182—183°; 6-*NO*-derivative, m.p. 121—122°). It is suggested that increased unsaturation of the aryl group facilitates the reaction by increasing the rate of fission between the N atom and the aromatic nucleus. J. W. B.

Orientation problems. I. Effect of nitro-groups in Schiff's bases. A. MCGOOKIN (J.C.S., 1934, 1743—1744).—By the usual condensation the following have been prepared: benzylidene- (I), m.p. 116°, *o*-, m.p. 155°, *m*-, m.p. 185° [also by  $H_2SO_4$  (*d* 1.8)— $HNO_3$  (*d* 1.5) on (I)], and *p*-nitrobenzylidene-, m.p. 227°, furfurylidene-, m.p. 153°, and  $\beta\beta\beta$ -trichloroethylidene- (II), m.p. 105°, 4-nitro-*o*-toluidine; benzylidene-2-nitro-, m.p. 77—78°, and -2:5-dinitro-*p*-toluidine, m.p. 71—72°, and furfurylidene-2:5-dinitro-*p*-toluidine, m.p. 208°. All are stable to acids, hydrolysis being effected only by heating with aq.  $NH_3$  (*d* 0.880) under pressure. With aq.  $KMnO_4$  (I) readily gives PhCHO and 4-nitro-*o*-toluidine, but in dry  $COMe_2$  a colourless solid is isolated, which gives no PhCHO until  $H_2O$  is added. With  $HNO_3$  (*d* 1.5) at 0° (II) gives a substance, m.p. 170°. J. W. B.

Rearrangement of alkyylanilines. VI. Mechanism of rearrangement. W. J. HICKINBOTTOM (J.C.S., 1934, 1700—1705).—When heated together at 100—115° ( $H_2O$  excluded),  $NPhMe_2$  and  $CPh_3Cl$  afford  $CHPh_3$  and *p*- $C_6H_4 \cdot NMe_2$  (methiodide, m.p. 206—207°),  $NPhMeAc$  at 140—150° similarly giving the *Ac* derivative, m.p. 191—192°, of *p*-triphenylmethylmethylaniline, m.p. 211—212° (prep. from  $NHPhMe \cdot HCl$  and  $CPh_3 \cdot OH$  in boiling  $AcOH$ ). Thermal decomp. of  $NHPhMe \cdot HBr$  at 305—310° gives up to 13.8% MeBr and a mixture of (mainly)  $NH_2Ph$  (11%) and *p*- $C_6H_4Me \cdot NH_2$ , whereas the HI salt gives only 2—6% of MeI and a mixture of *o*- and *p*- $C_6H_4Me \cdot NH_2$ . A general hypothesis, assuming the separation of an alkyl cation which reacts with a quinonoid form of the aniline, is developed to explain such migrations, and its extension to the rearrangements of  $NClPhAc$ ,  $NHPh \cdot OH$ , and  $(\cdot NHPh)_2$  is briefly discussed. J. W. B.

3-Halogeno-1-nitro-, -1-amino-, and -1-hydroxy-naphthalenes. H. H. HODGSON and R. L. ELLIOTT (J.C.S., 1934, 1705—1707).—With  $Cl_2$ — $AcOH$



at 100°, 4-nitroaceto- $\alpha$ -naphthalide gives its 2-Cl-derivative, m.p. 231°, converted by boiling 20% NaOH into 2-chloro-4-nitro- $\alpha$ -naphthol, m.p. 231°, and by boiling H<sub>2</sub>SO<sub>4</sub>-aq. EtOH into 2-chloro-4-nitro- $\alpha$ -naphthylamine (I), m.p. 249°, from which, by diazotisation, 3-chloro-1-nitronaphthalene, m.p. 105°, is obtained. With Br-PhNO<sub>2</sub> at room temp. 4-nitro- $\alpha$ -naphthylamine (II) gives its 2-Br-derivative (III), m.p. 250° (hydrobromide). (II) and Hg(OAc)<sub>2</sub> in hot AcOH afford a mercuriacetate [mercurichloride, m.p. 244° (decomp.); mercuribromide, m.p. 249° (decomp.); mercuriiodide, m.p. 259° (decomp.); mercurihydroxide], converted by the appropriate halogen into (I), (III), or the 2-I-derivative, all deaminated to the corresponding 3-halogeno-1-nitronaphthalene, suitable reduction of which affords 3-chloro-, m.p. 62° (hydrochloride, m.p. 219°; Ac, m.p. 197°, and Bz, m.p. 162°, derivatives), 3-bromo-, m.p. 70° (hydrochloride, m.p. 247°; Ac, m.p. 174°, and Bz, m.p. 166°, derivatives), and 3-iodo-, m.p. 84° (hydrochloride, m.p. 238°; Ac, m.p. 207°, and Bz, m.p. 174°, derivatives), - $\alpha$ -naphthylamine, from which, by the diazo-reaction, 3-chloro-(2:4-Br<sub>2</sub>-derivative, m.p. 112°), 3-bromo-, m.p. 61° (2:4-Br<sub>2</sub>-derivative, m.p. 133°), and 3-iodo-, m.p. 119° (2:4-Br<sub>2</sub>-derivative, m.p. 191°), - $\alpha$ -naphthol, are obtained.

J. W. B.

Catalytic action of Japanese acid earth. VI. Action on cyclohexylamine and its derivatives.—See this vol., 44.

Electrochemical preparation of tolylhydrazines. E. W. COOK and W. G. FRANCE (J. Amer. Chem. Soc., 1934, 56, 2225—2226).—The toluenediazonium chlorides yield the corresponding hydrazines (current efficiencies *o*-, 74.9; *p*-, 58.5; *m*-, 35.6%) when reduced with a Hg cathode at 5—6°. Ease of reduction does not appear to be related to the polar properties of the compounds.

E. S. H.

Preparation of 3:3'-ditrifluoromethylhydrazobenzene. M. GONZE (Bull. Acad. roy. Belg., 1934, [v], 20, 809—815).—3:3'-Ditrifluoromethylhydrazobenzene (I), m.p. 36.2°, is much more stable to heat, oxidation, and acids than (*m*-C<sub>6</sub>H<sub>4</sub>Me·NH)<sub>2</sub> (II), and is best prepared by reduction of (*m*-CF<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>·N)<sub>2</sub> (III), m.p. 82.5° (A., 1923, i, 292), with SnCl<sub>4</sub> and 2% EtOH-HCl. With HCl (I) gives (III), *m*-CF<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, and a solid, possibly the related tolidine. (All reductions in N<sub>2</sub> atm.)

F. S. H. H.

Derivatives of  $\beta$ -naphthoylhydrazine. H. GOLDSTEIN and A. STUDER (Helv. Chim. Acta, 1934, 17, 1485—1487).—The  $\beta$ -naphtholylhydrazones of PhCHO, *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, COMe<sub>2</sub>, and CPhMe have m.p. 230°, 228°, 143°, and 200°, respectively. With NaNO<sub>2</sub>,  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH·NH<sub>2</sub>·HCl affords  $\beta$ -naphthoazide, m.p. about 76° (violent decomp.), converted by 90% or 50% H<sub>2</sub>SO<sub>4</sub> into  $\beta$ -C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H and by boiling abs. EtOH into  $\beta$ -naphthylurethane.

H. W.

Occurrence of free radicals in chemical reactions. VIII. [Thermal fission of aryl- and acyl-azotriphenylmethanes.] H. WIELAND [with K. HEYMANN, T. TSATSAS, D. JUCHUM, G. VARVOGLIS, G. LABRIOLA, O. DOBBELSTEIN, and H. S. BOYD-BARRETT] (Annalen, 1934, 514, 145—181; cf. A., 1922,

i, 772; 1926, 61).—Decomp. of CPh<sub>3</sub>·N·NPh (I) in C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub> at 60—70° gives (CPh<sub>3</sub>·O)<sub>2</sub> (II) (50—60%), some PhOH, and a little Ph<sub>2</sub> (probably formed thus: CPh<sub>3</sub>·N·NPh + C<sub>6</sub>H<sub>6</sub> → N<sub>2</sub> + CHPh<sub>2</sub> + Ph<sub>2</sub>). Decomp. in PhMe and C<sub>5</sub>H<sub>5</sub>N affords C<sub>6</sub>H<sub>4</sub>MePh (*o*+*p*-) and phenylpyridine (probably 2+4-), respectively. Decomp. of (I) in CCl<sub>4</sub> at 55° and then at the b.p. gives PhCl and  $\alpha\alpha\alpha$ -trichloro- $\beta\beta\beta$ -triphenylethane (III), m.p. 237° (decomp.) [reduced (large excess of Zn dust, AcOH) to CPh<sub>3</sub>Me; a small amount of Zn dust leads to CPh<sub>3</sub>Me and (probably)  $\alpha\alpha\alpha\delta\delta\delta$ -hexaphenylbutane, m.p. 271°]; C<sub>6</sub>H<sub>6</sub>, CPh<sub>4</sub>, and CHPh<sub>3</sub> are formed in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> and CO<sub>2</sub> at 55—65°, whilst C<sub>6</sub>H<sub>6</sub>, CPh<sub>4</sub>, and CPh<sub>3</sub>·OH are produced in boiling H<sub>2</sub>O and CO<sub>2</sub>. Slow decomp. of (I) in presence of sand at 105—115°/high vac. gives C<sub>6</sub>H<sub>6</sub> (probably formed from Ph radicals), CPh<sub>4</sub>, and CHPh<sub>3</sub>. (I) and benzoquinone (IV) in C<sub>6</sub>H<sub>6</sub> and N<sub>2</sub> at 60—70° afford quinhydrone, phenylbenzoquinone (V), and *p*-C<sub>6</sub>H<sub>4</sub>(O·CPh<sub>3</sub>)<sub>2</sub>, thus showing the production of active H in the decomp. and phenylation (cf. above). (V) is also obtained from PhN<sub>2</sub>Cl, AgOAc, and (IV) in AcOH. Decomp. of CPh<sub>3</sub>·N·NBz (VI) in C<sub>6</sub>H<sub>6</sub> and CO<sub>2</sub> and subsequent treatment of the red solution (A) with Br gives a compound (Br content about 36%), hydrolysed (EtOH-KOH) to a Br-free acid containing about 12.5% N; the free radical produced thus contains N (cf. *loc. cit.*). The main product obtained by decomp. of (VI) is COPh·CPh<sub>3</sub> (VII); in one case, *p*-benzoyltriphenylmethane was isolated also. Decomp. of (VI) in C<sub>6</sub>H<sub>6</sub> is accelerated by O<sub>2</sub> and proceeds exothermally; (II) (about 10%), (VII), and small amounts of BzOH, CO<sub>2</sub>, and PhOH, but no Bz<sub>2</sub>O<sub>2</sub>, are produced: 2CPh<sub>3</sub>·N·NBz + O<sub>2</sub> → (CPh<sub>3</sub>·O)<sub>2</sub> + 2N·NBz. (II) is not produced when O<sub>2</sub> is passed into (A) (prepared in N<sub>2</sub>). No volatile product is obtained by decomp. of (VI) in presence of sand in a high vac. (VI) and Br in C<sub>6</sub>H<sub>6</sub> give BzBr and CPh<sub>3</sub>Br. The mol. heats of combustion at const. pressure of (I), (VI), and (VII) are 3171, 3238, and 3181 kg.-cal., respectively. The differing rates of decomp. of (I) and (VI) are decided by the tenacity of the C·N linking; decomp. of (I) is best represented as: CPh<sub>3</sub>·N·NPh → CPh<sub>3</sub> + [N·NPh] → Ph + N<sub>2</sub>.

$\alpha$ -1-Naphthyl- $\beta$ -triphenylmethylhydrazine, m.p. 183° (decomp.) (from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH·NH<sub>2</sub> and CPh<sub>3</sub>Cl in C<sub>6</sub>H<sub>6</sub>), is oxidised (Br-H<sub>2</sub>O in C<sub>6</sub>H<sub>6</sub>) to  $\alpha$ -naphthaleneazotriphenylmethane (VIII), m.p. 117° (decomp.), which decomposes in C<sub>6</sub>H<sub>6</sub> and N<sub>2</sub> at 50—60° or in presence of sand at 105—120°/high vac. to  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CPh<sub>3</sub>, C<sub>10</sub>H<sub>8</sub>, and CHPh<sub>3</sub>; in C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub>, 32.3% of (II) is produced. (VIII) in CCl<sub>4</sub> and N<sub>2</sub> at 55° gives (III) and 1-C<sub>10</sub>H<sub>7</sub>Cl; in H<sub>2</sub>O and CO<sub>2</sub> at 100°,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CPh<sub>3</sub>, C<sub>10</sub>H<sub>8</sub>, CPh<sub>3</sub>·OH, and 9-phenylfluorene result.  $\beta$ -Naphthaleneazotriphenylmethane, decomp. 114°, in CCl<sub>4</sub> and CO<sub>2</sub> at 50—70° affords (III) and 2-C<sub>10</sub>H<sub>7</sub>Cl; in C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub>, 29% of (II) results. Benzeneazotridiphenylmethane, decomp. 118°, heated in xylene gives a violet solution (the colour fades on keeping) from which CH(C<sub>6</sub>H<sub>4</sub>Ph)<sub>3</sub> (IX) is isolated; decomp. in "benzene," b.p. 120—150°, affords C<sub>6</sub>H<sub>6</sub>, whilst in C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub>, 28% of [C(C<sub>6</sub>H<sub>4</sub>Ph)<sub>3</sub>·O]<sub>2</sub> (X) results. Diphenylazotridiphenylmethane, m.p. 110° (decomp.), decomposes in xylene to (IX) and Ph<sub>2</sub>; in C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub>, 34% of (X) is formed.



*m*-Di(triphenylmethylhydrazino)benzene, m.p. 173° (decomp.) [from *m*-C<sub>6</sub>H<sub>4</sub>(NH·NH<sub>2</sub>)<sub>2</sub> and CPh<sub>3</sub>Cl in C<sub>5</sub>H<sub>5</sub>N], is oxidised [alkaline K<sub>3</sub>Fe(CN)<sub>6</sub> in CHCl<sub>3</sub>] to *m*-di(triphenylmethylazo)benzene, m.p. 127° (decomp.), which in C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub> at 72° gives (II), CPh<sub>3</sub>·OH, and resinous products; decomp. at 70°/vac. affords C<sub>6</sub>H<sub>6</sub> (from C<sub>6</sub>H<sub>4</sub> radicals) and CHPh<sub>3</sub>. 2:3-Di(triphenylmethylhydrazino)-, m.p. 198°, and 2:3-di(triphenylmethylazo)-, m.p. 148° (decomp.), -naphthalene are similarly prepared. 2:2'-Di(triphenylmethylhydrazino)diphenyl (XI), m.p. 185° (decomp.), is oxidised [K<sub>3</sub>Fe(CN)<sub>6</sub>] to (probably) the 2-hydrazino-2'-azo-derivative, m.p. 165° (decomp.); decomp. in xylene and subsequent treatment with O<sub>2</sub> gives (II) (= >1 CPh<sub>3</sub> group) and a hydrocarbon (? 2-triphenylmethyl-diphenyl), m.p. 171°. Oxidation (Br-H<sub>2</sub>O in CHCl<sub>3</sub>) of (XI) affords (probably) 3-bromo-2-triphenylmethylhydrazino-2'-triphenylmethylazodiphenyl, decomp. 139°, which decomposes in xylene to CHPh<sub>3</sub> and a compound, C<sub>31</sub>H<sub>23</sub>N<sub>2</sub>Br, m.p. 219—220° (darkening) [probably an *o*-phenyleneazine (cf. Tauber, A., 1896, i, 686)].

$\alpha$ -1-Naphthoyl- $\beta$ -triphenylmethylhydrazine, m.p. 187° (decomp.), is oxidised (aq. CaOCl<sub>2</sub> in CHCl<sub>3</sub> or Et<sub>2</sub>O) to  $\alpha$ -naphthoylazotriphenylmethane, m.p. 59° (decomp.), which decomposes readily in C<sub>6</sub>H<sub>6</sub> and N<sub>2</sub> at 30—35° to give (after atm. oxidation)  $\alpha$ -naphthoyltriphenylmethane (XII), m.p. 176° (also formed in absence of solvent), and in C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub> to (II), (XII), and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H.  $\beta$ -Naphthoylazotriphenylmethane, m.p. 65° (decomp.) [hydrazo-derivative, m.p. 173° (decomp.)], similarly affords  $\beta$ -naphthoyltriphenylmethane, m.p. 202°, alone or with (II) and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H; decomp. in C<sub>6</sub>H<sub>6</sub>+ (IV) at 50—70° gives quinhydrone. Succintriphenylmethylhydrazide, m.p. 241° (decomp.) [from (·CH<sub>2</sub>·CO·NH·NH<sub>2</sub>)<sub>2</sub> and CPh<sub>3</sub>Cl in aq. C<sub>5</sub>H<sub>5</sub>N], is oxidised (CaOCl<sub>2</sub>) to succinylbisazotriphenylmethane, m.p. 81—82° (decomp.), which decomposes in C<sub>6</sub>H<sub>6</sub> and N<sub>2</sub> at 20—50° to  $\beta$ -diketo- $\alpha\alpha\alpha\zeta\zeta$ -hexaphenylhexane, m.p. 220°, also formed with (II) in C<sub>6</sub>H<sub>6</sub>+O<sub>2</sub>. Terephthal-, m.p. 221° (decomp.), and *ox*-, m.p. 247° (decomp.), -triphenylmethylhydrazide and terephthalylbisazotriphenylmethane, m.p. 92° (decomp.), are similarly prepared. *Et p*-triphenylmethylhydrazinobenzoate, m.p. 152—153° (from *Et p*-hydrazinobenzoate, m.p. 115—116°, and CPh<sub>3</sub>Cl in C<sub>5</sub>H<sub>5</sub>N), is oxidised (Br-H<sub>2</sub>O in Et<sub>2</sub>O) to *p*-carbethoxybenzenediazotriphenylmethane, m.p. 107° (decomp.).  $\beta$ -Phenylpropionylazotriphenylmethane, m.p. 55—56° (decomp.), undergoes fission to  $\beta$ -phenylethyl triphenylmethyl ketone, m.p. 135°; in C<sub>6</sub>H<sub>6</sub>+O<sub>2</sub>, (II), CH<sub>2</sub>Ph·CH<sub>2</sub>·CO<sub>2</sub>H, and a little PhOH are also formed. Cinnamtriphenylmethylhydrazide, m.p. 182° (decomp.), is oxidised directly to CHPh·CH·CO·CPh<sub>3</sub> (XIII) by Br-H<sub>2</sub>O; with CaOCl<sub>2</sub>, (XIII) and a Cl-containing compound, m.p. 185—186°, result. Phenylpropionylazotriphenylmethane, m.p. 70° (decomp.), is prepared by oxidation [K<sub>3</sub>Fe(CN)<sub>6</sub>] of phenylpropionyltriphenylmethylhydrazide, m.p. 158—159° (from CPh<sub>3</sub>·C·COCl and CPh<sub>3</sub>·NH·NH<sub>2</sub> in Et<sub>2</sub>O).

Benzoylhydrazinodiphenylmethane, m.p. 179—180°, from NHBz·NH<sub>2</sub> and CHPh<sub>2</sub>Br in C<sub>5</sub>H<sub>5</sub>N, is oxidised (I in Et<sub>2</sub>O-CHCl<sub>3</sub>) to benzoylazodiphenylmethane, m.p. 96—98° (decomp.) (which rearranges in PhMe at 100° to CPh<sub>2</sub>·N·NHBz), thermal decomp. of which gives N<sub>2</sub> (75%) and a substance, C<sub>27</sub>H<sub>22</sub>O<sub>2</sub>N<sub>2</sub>, m.p. 257—259°

(decomp.). Acetylhydrazinodiphenylmethane, m.p. 137°, is oxidised (Br-H<sub>2</sub>O in CHCl<sub>3</sub>) to CPh<sub>2</sub>·N·NHAc; phenylhydrazinodiphenylmethane, m.p. 75—76°, could not be oxidised to CHPh<sub>2</sub>·N·NPh. H. B.

Decomposition of normal diazotates. Z. E. JOLLES and W. CAMIGLIERI (Atti Congr. naz. Chim., 1933, 4, 491—495).—The reaction 4PhN<sub>2</sub>OH = C<sub>24</sub>H<sub>18</sub>ON<sub>2</sub>+3N<sub>2</sub>+3H<sub>2</sub>O, which takes place with diazobenzene in alkaline solution, and the corresponding reactions for *p*- and *m*-toluidine (I), *o*- and *p*-anisidine, and *p*-phenetidine (II), were verified by measuring the N<sub>2</sub> evolved. The min. duration of the reactions varied from 3½ to 70 hr., and the N<sub>2</sub> evolved differed considerably from the calc. quantities only for (I) and (II). The observation of Heller (cf. A., 1908, i, 300), that PhN<sub>2</sub>Cl in alkaline solution was converted into PhOH, which coupled with more PhN<sub>2</sub>Cl to form trisbenzeneazophenol, was not confirmed, the decomp. of PhN<sub>2</sub>OH into PhOH or diazo-resin being governed by the alkali concn. R. N. C.

Amphoteric aromatic substitution. I. Reactions of sodium benzenediazoate and nitrosoacetanilide. W. S. M. GRIEVE and D. H. HEY (J.C.S., 1934, 1797—1806).—In the interaction of PhN<sub>2</sub>ONa (I) or NPhAc·NO (II) with PhX (X=H, Me, Cl, NO<sub>2</sub>, CO<sub>2</sub>Et, CHO), mesitylene (III), *m*-xylene (IV), and *o*-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub> (V) to give N<sub>2</sub> [and AcOH from (II)] and derivatives of the type Ph·C<sub>6</sub>H<sub>4</sub>X, Ph substitution always occurs in the *o*- and/or *p*-position to X, irrespective of whether X is a group normally *op*- or normally *m*-directing to cationoid reagents, and the reaction is not appreciably affected by the alkalinity of the medium. Since with (I) (V) gives only 4-nitro-3-methyldiphenyl, and the ratio nitrodiphenyls : methyldiphenyls is 4 : 1 when an equimol. mixture of PhNO<sub>2</sub> and PhMe (both in excess) is employed, substitution occurs more readily *op* to NO<sub>2</sub> than it does *op* to Me. It is suggested that the decomp. of (I) or (II) involves the production of free Ph radicals, which have amphoteric character, functioning as a cationoid or anionoid reagent at the reactive *op*-positions as occasion demands. In agreement with this view the velocity of N<sub>2</sub> evolution from (II) in homogeneous solution in C<sub>6</sub>H<sub>6</sub> (461), (IV) (466), PhMe (344), (III) (507), CCl<sub>4</sub> (405), PhOMe (522), PhNO<sub>2</sub> (502), PhCl (400), and AcOH (100) is unimol., the vals. of the unimol. velocity coeffs. (*k*×10<sup>5</sup> min.<sup>-1</sup>), given in parentheses, differing but slightly, since the essential reaction in all cases is the formation of free Ph; a similar mechanism is applied to the decomp. of diazonium salts. Only when (II) decomposes in C<sub>6</sub>H<sub>6</sub> or in MeOH (C<sub>6</sub>H<sub>6</sub> absent) is Ph<sub>2</sub> obtained, arising, in the latter case, from the reactions: 2Ph+MeOH → 2C<sub>6</sub>H<sub>6</sub>+CH<sub>2</sub>O (isolated as its 2:4-dinitrophenylhydrazone); Ph+C<sub>6</sub>H<sub>6</sub> → Ph<sub>2</sub>+H. Decomp. of (II) occurs in AcOH, H<sub>2</sub>O, or CCl<sub>4</sub> to give *p*-OH·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Ph, and in EtOAc, CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, and Et<sub>2</sub>O, although in these cases MeCHO is the only product identified. Decomp. of CH<sub>2</sub>Ph·NAc·NO in C<sub>6</sub>H<sub>6</sub>, PhMe, or PhCl occurs only after addition of K<sub>2</sub>CO<sub>3</sub>. The main products are CH<sub>2</sub>Ph·OAc and CH<sub>2</sub>·CHPh, a small yield of CH<sub>2</sub>Ph<sub>2</sub> (identified by oxidation to CPh<sub>2</sub>) being the only definite substitution product isolated. The 2:4-dinitrophenylhydraz-



ones of *p*-methyl-, m.p. 199—200°, and *p*-chloro-, m.p. 184—185°, -benzophenone are prepared. J. W. B.

**Esters of sulphurous acid. III. Metallic aryl sulphites.** W. VOSS and M. LAX (Ber., 1934, 67, [B], 1916—1919; cf. A., 1931, 462).—Powdered Na and PhOH are allowed to react in xylene and the solution is treated at 0° with SO<sub>2</sub>, whereby Na Ph sulphite is pptd. Na β-C<sub>10</sub>H<sub>7</sub> sulphite is prepared similarly. Both substances are very unstable towards H<sub>2</sub>O. Salts of aryl sulphites cannot therefore be intermediates in Bucherer's reaction. H. W.

Rotations of the nitrophenyl esters of disubstituted acetic and propionic acids and of the free acids.—See this vol., 14.

**Addition of phenols to aryl[alk]enes. Synthesis of phenylthymol and its isomerides.** J. B. NIEDERL and C. H. RILEY (J. Amer. Chem. Soc., 1934, 56, 2412—2414).—Equimol. quantities of CHPh:CHMe (from CHPhEt:OH and a trace of conc. H<sub>2</sub>SO<sub>4</sub> at 150°), *o*-cresol, and conc. H<sub>2</sub>SO<sub>4</sub> in AcOH give (probably) α-phenyl-β-4-hydroxy-3-methylphenylpropane (I), b.p. 200°/18 mm. (phenylcarbamate, m.p. 178°). α-Phenyl-β-2-hydroxy-5-methylphenylpropane (II), b.p. 215—220°/28 mm. (phenylcarbamate, m.p. 123°), and α-phenyl-β-2(or 4)-hydroxy-4(or 2)-methylphenylpropane ("phenylthymol" or "phenylisothymol") (III), b.p. 200—205°/22 mm. (phenylcarbamate, m.p. 125°), are similarly obtained from *p*- and *m*-cresol, respectively. The PhOH coeffs. (towards *S. aureus*) of (I), (II), and (III) are 59, 82, and < 10, respectively. H. B.

**Diphenyl and its derivatives; new asymmetric 2:2'-disubstituted derivatives of diphenyl.** L. MASCARELLI and D. GATTI (Atti Congr. naz. Chim., 1933, 4, 503—505).—*o*-Iodoanisole and *o*-C<sub>6</sub>H<sub>4</sub>I:NO<sub>2</sub> condense in presence of Cu powder to 2-nitro-2'-methoxydiphenyl, m.p. 80—81°, reduced (Sn, HCl) to 2-amino-2'-methoxydiphenyl, m.p. 80—81°. Diazotisation and treatment with KI gives 2-iodo-2'-methoxydiphenyl, m.p. 58—59°, with some diphenyleneiodonium iodide, in accordance with a characteristic reaction of 2-diazo-2'-substituted diphenyls with KI, which occurs when the 2'-substituting group is N<sub>2</sub>Cl, NO<sub>2</sub>, Cl, Br, I, or OMe, but not Me. 2-Methyl-2'-diazo-diphenyl is, however, decomposed by H<sub>2</sub>O to fluorene. R. N. C.

**Preparation and germicidal properties of 4-hydroxy-2-methylphenyl alkyl sulphides.** C. M. SUTER and J. P. MCKENZIE (J. Amer. Chem. Soc., 1934, 56, 2470—2471).—*m*-C<sub>6</sub>H<sub>4</sub>Me:OMe and conc. H<sub>2</sub>SO<sub>4</sub> (2 mols.) at room temp. give 74—86% of 3-methoxytoluene-6-sulphonic acid [*p*-toluidine salt, m.p. 204—205° (corr.)]; the chloride, b.p. 173—175°/17 mm. (cf. Haworth and Lapworth, A., 1924, i, 848), is reduced (method; Org. Synth., 1921, 1, 71) to 4-methoxy-2-methylthiophenol (I), b.p. 130—132°/22 mm. (cf. Shah et al., A., 1933, 1292) [Bz derivative, m.p. 78—79° (lit. 84°)]. 4-Methoxy-2-methylphenylthiolacetic acid has m.p. 72—73°. 4-Methoxy-2-methylphenyl Me, b.p. 145—147°/26 mm., Et, b.p. 150—151°/23 mm., Pr<sup>a</sup>, b.p. 162—163°/22 mm., Bu<sup>a</sup>, b.p. 173—175°/23 mm., and *n*-amyl, b.p. 165—167°/15 mm., sulphides, prepared from (I) as previously described (A., 1932, 1244), are demethylated to 4-hydroxy-2-

methylphenyl Me, b.p. 148—151°/15 mm. (13, 12, 10), Et, b.p. 159—163°/20 mm. (20, 50, 40), Pr<sup>a</sup>, b.p. 165—170°/20 mm. (23, 80, 80), Bu<sup>a</sup>, b.p. 180—186°/27 mm. (14, 100, 80), and *n*-amyl, b.p. 193—197°/24 mm. (8, 250, 200), sulphides, respectively; the nos. quoted in parentheses are the PhOH coeffs. towards *B. typhosus*, *S. aureus*, and *Strep. hæmolyticus*, respectively. H. B.

**Preparation of veratryl chloride and formation of the 9:10-dihydroanthracene nucleus.** P. CARRÉ and D. LIBERMANN (Compt. rend., 1934, 199, 791—793).—ClSO<sub>2</sub>Et is added to veratryl alcohol (I) and C<sub>5</sub>H<sub>5</sub>N in anhyd. Et<sub>2</sub>O and, after removal of C<sub>5</sub>H<sub>5</sub>N.HCl, SOCl<sub>2</sub> is introduced, whereby ClSO<sub>2</sub>Et and SO<sub>2</sub>Cl:CH<sub>2</sub>:C<sub>6</sub>H<sub>3</sub>(OMe)<sub>2</sub> are produced, the latter of which when distilled affords SO<sub>2</sub> and 3:4-dimethoxybenzyl chloride (II), b.p. 152—156°/10 mm., m.p. 48—49°, in 60—70% yield. (I) is transformed by conc. HCl mainly into 2:3:6:7-tetramethoxy-9:10-dihydroanthracene (III), m.p. 237°, also obtained through 3:4:3':4'-tetramethoxydiphenylmethane, m.p. about 70°, by the action of CH<sub>2</sub>O on veratrole in presence of HCl and ZnCl<sub>2</sub>. (II) is stable towards gaseous HCl, but readily converted by conc. HCl into (III), probably owing to hydrolysis to (I). Piperonyl alcohol and conc. HCl give the corresponding chloride and 2:3:6:7-bis(methylenedioxy)-9:10-dihydroanthracene. H. W.

**Preparation and germicidal properties of derivatives of 4-*n*-butylresorcinol.** M. L. MOORE, A. A. DAY, and C. M. SUTER (J. Amer. Chem. Soc., 1934, 56, 2456—2459).—4-Chlororesorcinol (I), b.p. 147°/18 mm., m.p. 105° (lit. 89°), prepared by Reinhard's method (A., 1878, 276), and SO<sub>2</sub>Cl<sub>2</sub> give the 4:6-Cl<sub>2</sub>-derivative, m.p. 112—113° (lit. 77° and 101°), which affords the known Me<sub>2</sub> ether. (I) could not be prepared by Clark's method (A., 1933, 270). 4-Butylresorcinol and SO<sub>2</sub>Cl<sub>2</sub> in Et<sub>2</sub>O give 6-chloro-4-butylresorcinol (II), m.p. 84—85° [also prepared from (I), Pr<sup>a</sup>CO<sub>2</sub>H, and ZnCl<sub>2</sub> at 125—135°], which with Cl<sub>2</sub> in Et<sub>2</sub>O affords the 2:6-Cl<sub>2</sub>-derivative, m.p. 124—125°. (II) is reduced (Clemmensen) to 6-chloro-4-*n*-butylresorcinol (III), m.p. 70—71°, also prepared (less satisfactorily) from SO<sub>2</sub>Cl<sub>2</sub> and 4-*n*-butylresorcinol (IV) (6-Br-, m.p. 67—68°, and 6-acetoxymercuri-, m.p. 164—165°, -derivatives). (IV) heated with aq. NaHCO<sub>3</sub> in CO<sub>2</sub> gives 2:4-dihydroxy-5-*n*-butylbenzoic acid (V), m.p. 172—173° (decomp.). Mercuration of (III) by Whitmore and Hanson's method (Org. Synth., 1925, 4, 13) affords the anhydro-compound, C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>ClHg, m.p. > 225°, converted (AcOH) into the 2-acetoxymercuri-, m.p. 153—154°, and thence (aq. EtOH-HCl) into the 2-chloromercuri-derivative (VI), m.p. 144—145°. (II) similarly gives a compound, C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>ClHg, m.p. 227—230°, convertible into the 2-chloromercuri-derivative, m.p. 218—220°. (IV) and an excess of Hg(OAc)<sub>2</sub> in EtOH afford a compound, C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>Hg<sub>2</sub>(?), m.p. > 230°. The m.p. of the Hg derivatives are uncorr.; all others are corr. Of several of the above compounds examined, (VI) possesses the highest PhOH coeff. (towards *B. typhosus* and *S. aureus*); (V) is inactive. H. B.

**Relation between chemical constitution and purgative action.** A. P. T. EASSON, J. HARRISON,



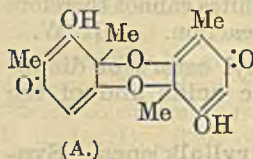
B. A. MACSWINEY, and F. L. PYMAN (Quart. J. Pharm., 1934, 7, 509—513).—Members of the two homologous series di-(*p*-hydroxyphenyl)- and di-(4-hydroxy-3-methylphenyl)-dialkyl-(or -aryl)-methanes were prepared by saturating mixtures of the appropriate aldehyde or ketone and an excess of PhOH or *o*-cresol with dry HCl and keeping at room temp. The following are new:  $\beta\beta$ -di-(*p*-hydroxyphenyl)-*n*-butane, m.p. 124—125°;  $\beta\beta$ -di-(*p*-hydroxyphenyl)-*n*-pentane, m.p. 150°;  $\alpha\alpha$ -di-(4-hydroxy-3-methylphenyl)-*n*-heptane, m.p. 86—87°;  $\beta\beta$ -di-(4-hydroxy-3-methylphenyl)-*n*-butane, m.p. 145—147°;  $\alpha\alpha$ -di-(4-hydroxy-3-methylphenyl)- $\alpha$ -phenylethane, m.p. 142—143°; 1:1-di-(4-hydroxy-3-methylphenyl)cyclohexane, m.p. 191—192°. The (2-)lactones, m.p. 127—129° and 167—168°, respectively, of 2-hydroxy-5-methoxy- and of 2:4-dihydroxy-4':4''-dimethoxy-triphenylacetic acid were prepared by heating benzoic acid with *p*-OH-C<sub>6</sub>H<sub>4</sub>-OMe and *pp'*-dimethoxybenzoic acid with *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, respectively.  $\alpha$ -(2-Hydroxy-5-methylphenyl)phthalide, m.p. 171°, was prepared by condensation of *p*-cresol with *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O followed by reduction. Most of the above have purgative properties. C. G. A.

**Derivatives of 1:2:3:4-tetrahydroxybenzene. III. Synthesis of dill apiole, and extension of the Dakin reaction.** W. BAKER, E. H. T. JUKES, and (in part) C. A. SUBRAHMANYAM (J.C.S., 1934, 1681—1684).—Gallacetophenone 3:4-Me<sub>2</sub> ether (improved prep.) is oxidised by 3% H<sub>2</sub>O<sub>2</sub> in 10% NaOH in H<sub>2</sub> (Dakin reaction) to 1:2-dihydroxy-3:4-dimethoxybenzene, converted by CH<sub>2</sub>:CH-CH<sub>2</sub>Br and anhyd. K<sub>2</sub>CO<sub>3</sub>-COMe<sub>2</sub> into its 2-allyl ether, isomerised at 165° into 1:2-dihydroxy-3:4-dimethoxy-5-allylbenzene, b.p. 160—173°/14 mm. (1:2-Me<sub>2</sub> ether, m.p. 25°, b.p. 145°/12 mm.), converted by CH<sub>2</sub>I<sub>2</sub>-COMe<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub> into its 1:2-CH<sub>2</sub>O<sub>2</sub>-derivative, identical with natural dill apiole. The following are similarly prepared: *pyrogallol methylene ether*, m.p. 65°, and 7-methoxy-8-acetyl-2-methylchromone, m.p. 161—162° (by Me<sub>2</sub>SO<sub>4</sub> on the 7-OH-derivative, A., 1934, 410). The Dakin reaction is readily applicable to OH-aryl ketones; thus resacetophenone with 6% H<sub>2</sub>O<sub>2</sub>-12% NaOH at 50° in H<sub>2</sub> gives 1:2:4-C<sub>6</sub>H<sub>3</sub>(OMe)<sub>3</sub> (I); 2:4-C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>-CO-CH<sub>2</sub>Ph gives CH<sub>2</sub>Ph-CO<sub>2</sub>H (II) (95%) and (after methylation) (I); ononctin gives *p*-OMe-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-CO<sub>2</sub>H (60%) and (I); homopiperonylresacetophenone affords  $\beta$ -piperonylpropionic acid (90%), and 2:4-C<sub>6</sub>H<sub>4</sub>(OH)(OMe)-CO-CH<sub>2</sub>Ph gives (II) (50% yield). J. W. B.

**Condensation of pyrocatechol with acetone.** W. BAKER (J.C.S., 1934, 1678—1681).—The compound C<sub>21</sub>H<sub>24</sub>O<sub>4</sub> (Fabinyi *et al.*, A., 1905, i, 591), best obtained by heating together *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> (I) (2 mols.), COMe<sub>2</sub> (3 mols.), AcOH, and conc. HCl on a steam-bath at atm. pressure [also from 2 mols. of (I), CO(CH<sub>2</sub>COMe)<sub>2</sub> (1 mol.), and AcOH-HCl], is 5:6:5':6'-tetrahydroxy-3:3:3':3'-tetramethylbis-1:1'-spirohydrindene (II) (Me<sub>4</sub> ether,  $\alpha$ -form, m.p. 158°, and  $\beta$ -form, m.p. indef.

125—158°, with conversion into the  $\alpha$ -form), converted by Br-AcOH into its 4:7:4':7'-Br<sub>4</sub>-derivative, m.p. 231° (decomp.) (lit., m.p. 130°), which, contrary to the lit., is stable to H<sub>2</sub>O at 100°. J. W. B.

**Phenol dehydrogenation. V. Dehydrogenation of trimethylphloroglucinol. Structure of cedron.** H. ERDTMAN (Svensk Kem. Tidskr., 1934, 46, 226—229).—The observations of Herzig *et al.* (A., 1914, i, 295) on cedron (I), C<sub>18</sub>H<sub>20</sub>O<sub>6</sub>, the product of dehydrogenation of trimethylphloroglucinol with FeCl<sub>3</sub>, are confirmed, but their structural conclusions do not accord with the facile reductive fission of (I), which is best represented as (A) and its tautomeric form, a mechanism of formation being suggested. The acidity is due to the system CO·C·C·OH. J. W. B.



**Effect of strain in cycloalkylcarbinols on their reactivity with benzene in presence of aluminum chloride.** R. C. HUSTON and K. GOODENOOT (J. Amer. Chem. Soc., 1934, 56, 2432—2434).—*cyclo*-Hexylcarbinol (1 mol.), C<sub>6</sub>H<sub>6</sub> (4—5 mols.), and AlCl<sub>3</sub> (0.66 mol.) at 75—80° give 7% of *cyclo*hexylphenylmethane (I), b.p. 239.5—241.5°/736 mm.; *cyclo*-pentylcarbinol similarly affords 45% of *cyclo*pentylphenylmethane (II), b.p. 234.5—236°/736 mm., and some *di*(*cyclo*pentylmethyl)benzene, m.p. 101.5—102°. (I) and (II) are not similarly produced at 25—35°. *cyclo*Butylcarbinol gives 29 and 21% of *cyclo*butylphenylmethane (III), b.p. 218—219°/736 mm., at 25—35° and 75—80°, respectively. The reactivity of the carbinols decreases (in accordance with expectation) with increase in the size of the ring; when the strain is min. the reactivity is of the same order as that of CH<sub>2</sub>Alk·OH. The mol. vols., parachors, and mol. refractions of (I), (II), (III), and allylbenzene are given. H. B.

**Purification of alcohols through their *p*-nitrobenzoates. *cis*-2-Decahydronaphthol.** W. HÜCKEL and K. KUMETAT (Ber., 1934, 67, [B], 1890—1893).—Difficulties are met in the purification of alcohols through their *p*-nitrobenzoates (I), since hydrolysis frequently occurs unexpectedly slowly, the small amounts of regenerated alcohol are contaminated with ketone, and the liquid is coloured yellow to red by azoxy- or azo-compounds. These are avoided by reducing (I) by H<sub>2</sub> in presence of EtOH-HCl-PtO<sub>2</sub> to the NH<sub>2</sub>-derivatives, which are hydrolysed by alkali. The separation of *cis*-, m.p. 18° (II), and *trans*-2- (III), m.p. 53°, from *trans*-2- (IV), m.p. 75°, -decahydronaphthol is described. (II) gives a *p*-nitrobenzoate, m.p. 77°, *p*-aminobenzoate, m.p. 155° [hydrochloride, m.p. 216° (decomp.)], and *H* succinate, m.p. 59°. (III) yields a *p*-nitrobenzoate, m.p. 112°, *p*-aminobenzoate, m.p. 118° [hydrochloride, m.p. 167—168° (decomp.)], and *H* succinate, m.p. 64°. The *p*-nitrobenzoate, m.p. 141°, and *p*-aminobenzoate, m.p. 103—104° [hydrochloride, m.p. 211—213° (decomp.)], of (IV) are described. *trans*-1-Decahydronaphthol, m.p. 49°, yields a *p*-aminobenzoate, m.p. 143° (hydrochloride, m.p. 180—182° (decomp.)). (II) exists in two forms, m.p. 18° and m.p. 31°, respectively, which very slowly pass into one another. Since they do not behave as nuclei, the



difference is not attributable to polymorphism and the existence of *d*+*l*- and *r*-forms is suggested. (II), almost free from (IV), is obtained by isomerisation of *cis*-2-decahydronaphthol, m.p. 105°, at 105–110° for 1 hr. in presence of Cu chromite and H<sub>2</sub> at 30 atm., whereby a mixture of *cis*-compounds readily separable through their H phthalates is produced. At 160° (IV) is also formed. H. W.

***p*-Nitrobenzyl esters of organic acids.** T. L. KELLY and M. SEGURA (J. Amer. Chem. Soc., 1934, 56, 2497).—*p*-Nitrobenzyl glutarate, m.p. 69°, adipate, m.p. 105.6°, suberate, m.p. 85°, azelate, m.p. 43.8°, itaconate, m.p. 90.6°, diphenate, m.p. 182.6°, *o*-benzoylbenzoate, m.p. 100.4°, *p*-cyanobenzoate, m.p. 189.2°, 3 : 5-dinitrobenzoate, m.p. 156.8°, *o*-bromobenzoate, m.p. 109.8°, *m*-chlorobenzoate, m.p. 107.2°, and *o*-, m.p. 110.8°, *m*-, m.p. 121°, and *p*-, m.p. 140.6°, -iodobenzoates are prepared by Reid's method (A., 1917, i, 333). Cryst. esters were not obtained from hexoic, octoic, nonoic, and decioic acids. H. B.

**Synthetic ephedrine [isomeride].** J. LAMBILLON (Bull. Soc. chim., 1934, [v], 1, 1411–1416).—CH<sub>2</sub>Ph·MgCl reacts with CH<sub>2</sub>Cl·CHCl·OEt to give [with (·CH<sub>2</sub>Ph)<sub>2</sub>] β-chloro-α-benzylethyl Et ether, b.p. 125°/12 mm., converted by the appropriate alkylamine at 100–110° into the corresponding β-methylamino-, b.p. 120–122°/12 mm. (hydrochloride; aurichloride) {together with some [OEt·CH(CH<sub>2</sub>Ph)·CH<sub>2</sub>]<sub>2</sub>NMe, b.p. 220°/12 mm.}, β-ethylamino-, b.p. 126°/vac., β-dimethylamino-, b.p. 123–124°/12 mm., and β-diethylamino-, b.p. 147°/20 mm., -derivatives. These are converted by HBr (*d* 1.78) at 75° into ephedrine analogues of the type CH<sub>2</sub>Ph·CH(OH)·CH<sub>2</sub>·NHR, and thus are obtained β-hydroxy-γ-phenylpropyl-methyl-, b.p. 137–138°/12 mm. (hydrochloride), and -ethylamine, b.p. 146–148°/12 mm. (hydrochloride).

J. W. B.

**Condensation of rosaniline with 1-chloro-2 : 4-dinitrobenzene.** A. E. PORAI-KOSCHITZ and E. I. MANDELSCHTAM (J. Gen. Chem. Russ., 1934, 4, 842–846).—Rosaniline and 1 : 2 : 4-C<sub>6</sub>H<sub>3</sub>Cl(NO<sub>2</sub>)<sub>2</sub> in AcOH or C<sub>6</sub>H<sub>5</sub>N give 4 : 4'-diamino-2'' : 4''-dinitrophenylfuchsonimide (I), m.p. 168–170° (98% yield), when heated for 5 hr. at 180–200°. (I) affords the corresponding 2'' : 4''-diamine (II), m.p. indef., on reduction (SnCl<sub>2</sub> or Zn–AcOH). (II) is an intense fast violet dye for wool, silk, or cotton (tannin). R. T.

**New isomeride of cholesterol.** R. DE FAZI (Atti Congr. naz. Chim., 1933, 4, 476–480; Chem. Zentr., 1934, ii, 257).—The substance, m.p. 141–143°, obtained by heating cholesterol (I) hydrochloride (m.p. 136–137°) with NaOAc in EtOH is now established as an isomeride of (I). It is also produced with allocholesterol (II) by the action of NaOAc on the hydrochloride, m.p. 124–126° (A., 1933, 710). From both hydrochlorides HCl is eliminated from adjacent C atoms yielding the same isomeride. Similarly (II) is obtained from the two hydrochlorides, m.p. 158.5° and 124–126°. A. G. P.

**Structure of cholesterol.** M. VANGHELOVICI (Chem. and Ind., 1934, 998).—Comparison of the structures of cholesterol (I) and squalene suggests that the second Me is at 9. The synthesis of (I) in the animal organism probably follows the course : carbohydrates

→ saturated fatty acids → unsaturated fatty acids → polyisoprenic-carotenoid compounds → (I). H. W.

**Photochemistry of ergosterol.** O. LINSERT (Med. u. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 281–287; Chem. Zentr., 1934, i, 3615).—A review. R. N. C.

**cycloPropane derivatives, and their reactions, in particular those of isomerisation.** N. J. DEMJANOV (J. Gen. Chem. Russ., 1934, 4, 762–777).—A review of the lit. is given. R. T.

**New products of condensation of glycerol with aromatic compounds.** P. P. SCHORIGIN and A. T. SMIRNOV (J. Gen. Chem. Russ., 1934, 4, 830–833).—Glycerol α-2 : 4 : 6-trinitrobenzoate, m.p. 140–142°, prepared from C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>·COCl and glycerol (I), yields C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>·OH and (I) on hydrolysis with aq. KOH, whilst on nitration glyceryl α-2 : 4 : 6-trinitrobenzoate βγ-dinitrate, m.p. 123°, is obtained. The prep. of the corresponding α-picrate is described. Phenyl-βγ-dihydroxypropylamine, m.p. 40–42°, b.p. 200–203°/7–8 mm., is prepared by boiling glyceryl monochlorohydrin in NH<sub>2</sub>Ph; under analogous conditions, CH<sub>2</sub>Cl·CH<sub>2</sub>·OH yields NPh·C<sub>2</sub>H<sub>4</sub>·OH and (NPh·CH<sub>2</sub>)<sub>2</sub>. R. T.

**Synthesis of tetrahydronaphthalenecarboxylic acids and naphthalenic hydrocarbons.** G. DARZENS and A. LÉVY (Compt. rend., 1934, 199, 1131–1133).—Successive treatment of CHPh(CO<sub>2</sub>Et)<sub>2</sub> with Na in PhMe and crotyl bromide in EtOH gives Et<sub>2</sub>phenylcrotylmalonate, b.p. 160–162°/2 mm., hydrolysed to the corresponding non-cryst. acid, which passes at 180° into phenylcrotylacetic acid (I), m.p. 55°, b.p. 158°/3 mm. (I) is very slowly converted by 85% H<sub>2</sub>SO<sub>4</sub> at room temp. (rise of temp. causes sulphonation) into 4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-1-carboxylic acid, m.p. 87°, which could not be dehydrogenated by S or Se without simultaneous loss of CO<sub>2</sub> with production of 1-C<sub>10</sub>H<sub>7</sub>Me. H. W.

**Action of acetic anhydride on β-naphthamidrazone.** H. GOLDSTEIN and F. CHASTELLAIN (Helv. Chim. Acta, 1934, 17, 1481–1482).—β-C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> is transformed into β-C<sub>10</sub>H<sub>7</sub>·CN (improved method), converted by HCl in EtOH into Et imino-β-naphthoate hydrochloride (I) in 85% yield. Successive treatment of (I) with NaOH and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O gives β-naphthamidrazone (II), C<sub>10</sub>H<sub>7</sub>·C(NH)<sub>2</sub>·NH·NH<sub>2</sub> or C<sub>10</sub>H<sub>7</sub>·C(NH<sub>2</sub>)<sub>2</sub>·N·NH<sub>2</sub>, which, contrary to Pinner, does not give β-C<sub>10</sub>H<sub>7</sub>·NH·NH<sub>2</sub> under the influence of Ac<sub>2</sub>O. (II) and cold Ac<sub>2</sub>O containing NaOAc give a Ac<sub>2</sub> derivative, C<sub>17</sub>H<sub>17</sub>O<sub>3</sub>N<sub>3</sub>, m.p. 186°, which passes when heated into AcOH and acetyl-β-naphthylmethyltriazole, m.p. 135°. H. W.

**α-Naphthylacetic acid.** A. HIGGINBOTTOM and W. F. SHORT (Rec. trav. chim., 1934, 53, 1141).—Crystallisation (from C<sub>6</sub>H<sub>6</sub>) of the acids obtained by oxidation (KMnO<sub>4</sub> in aq. EtOH at –1° to 0°) of 1-allylnaphthalene gives α-C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H (I) and a mixture, m.p. about 106° (cf. Keach, A., 1933, 948), of α-naphthylacetic acid (m.p. 132°, when regenerated from the anilide, m.p. 156°) and 10–20% of (I). H. B.

**Knoevenagel reaction.** H. LOHAUS (Annalen, 1934, 514, 137–144).—Exposure of a solution of



stable Et cinnamylideneacyanoacetate (I) in EtOH containing a little  $H_2SO_4$  to sunlight (in Pyrex glass) gives the labile form (II), since further exposure of the cryst. material recovered affords the *cyclobutane* derivative (III), m.p.  $125^\circ$ , of Reimer (A., 1911, i, 447; 1913, i, 1060); in EtOH alone, (I) similarly gives the open-chain dimeride (IV), m.p.  $165^\circ$ , of Reimer (*loc. cit.*). Rapid conversion of (II) into (I) occurs when its solution in EtOH-I is exposed to sunlight (in quartz).  $CHPh:CH:CHO$  (0.2 g.-mol.),  $CN\cdot CH_2\cdot CO_2Et$  (0.2 g.-mol.), EtOH (20 c.c.), and piperidine (V) (1 drop) at  $30-35^\circ$  (heat of reaction) give 71.5% of (I) [converted into (IV)]; twenty-fold increase in the amount of (V) results in a reaction temp. of  $65^\circ$  and a 60.4% yield of (II) [convertible into (III)]. Condensation occurs very slowly in presence of  $C_5H_5N$  and gives (I) (80.5% yield). An 11.6% yield of (I) (?) is obtained in the absence of condensing agent after 20 months. These results conform to the "regulating law" of Skrabal (A., 1912, ii, 33; 1922, ii, 488). Prolonged interaction of  $PhCHO$ ,  $CN\cdot CH_2\cdot CO_2Et$ , and (V) in the cold gives the labile  $CHPh:C(CN)\cdot CO_2Et$  (VI) (Bertini, A., 1901, i, 537); when the reaction mixture is made homogeneous with EtOH and kept at room temp. for 8 weeks the stable form (VII), m.p.  $51^\circ$ , begins to separate. (V) is considered to effect the change (VI)  $\rightarrow$  (VII). The production of (VII) using (V) in EtOH at  $15-25^\circ$  or  $45-48^\circ$  (according to the amount) or  $C_5H_5N$  (no solvent) probably involves the rapid rearrangement of the intermediate (VI). H. B.

**5-Chloroveratrylidenehippuric acid and some of its derivatives.** R. M. HANN (J. Washington Acad. Sci., 1934, 24, 464-466).—Hippuric acid and 5-chloroveratraldehyde with  $NaOAc\cdot Ac_2O$  give 5-chloroveratrylidenehippuric acid *azlactone*, m.p.  $161^\circ$ , hydrolysed ( $NaOH$ ) to 5-chloroveratrylidenehippuric acid (I), m.p.  $192^\circ$  (*Me*, m.p.  $135^\circ$ , and *Et* ester, m.p.  $104^\circ$ ; *amide*, m.p.  $213-214^\circ$ , and corresponding *imide*, m.p.  $286-287^\circ$ ). All m.p. except that of (I) are corr. H. G. M.

**Chaulmoogric acids and their derivatives.** L. TAUB (Med. u. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 295-302; Chem. Zentr., 1934, i, 3765).—Chaulmoogric acid undergoes decomp. on keeping even when pure, yellowing and forming  $HCO_2H$ . The *Et* ester is stable indefinitely. Hydnocarpic acid also decomposes on keeping. The use of mixed benzyl esters of the total fatty acids of chaulmoogra and hydnocarpus oils ("Antileprol By") is an improvement on the use of the *Et* esters.

J. S. A.

**Influence of cyclisation on the colour of molecules.** (MME.) RAMART-LUCAS (Bull. Soc. chim., 1934, [v], 1, 1133-1148).—The colour change which accompanies the cyclisation of an open-chain compound may be due to (1) changes in the chromophores due to an isomerisation or intramol. reaction, (2) an alteration in the relative positions of the chromophores, or (3) a change due to cyclisation alone. The change may be either bathochromic or hypsochromic and can be predicted in some cases.

The absorption spectra of phthalide, its mono- and di-aryl derivatives, of phthalein, its *Me* ether and *Na*

salt are discussed. On passing from an acyclic to a cyclic mol. containing one chromophore, if the chromophore is not modified and the valency angles remain about normal, the change of absorption should be small. The position of max. absorption of the following pairs of ketones is about the same:  $COEt$ , and *cyclohexanone*;  $COMeBu^r$  and camphor;  $COBu^r_2$  and fenchone. The change from  $A(CH_2)_nB$  (V)

( $n > 1$ ) to  $(CH_2)_n \begin{matrix} A \\ \diagdown \\ B \end{matrix}$  (VI) should be analogous to

that on passing from  $(EtA+EtB)$  (VII) to  $Et\cdot A\cdot B\cdot Et$  (VIII). If the absorptions of (V) [or (VII)] and (VIII) are known, that of (VI) can be predicted approx. Thus since the esterification of phenols produces a hypsochromic effect, the same effect should be observed on passing from coumaric acid to coumarin, and the curves for these substances show that this is the case. Similar predictions are verified by the curves for *o*- $NH_2\cdot C_6H_4\cdot CH_2\cdot CO_2H$  (IX),  $NHPhAc$  (X), and oxindole (XI), [(IX) $\rightarrow$ (XI), hypsochromic; (X) $\rightarrow$ (XI), bathochromic] and for allylbenzene, *isoallylbenzene*, and indene.

F. S. H. H.

**Reaction between  $\alpha$ -ketonic acids and  $\alpha$ -amino-acids.** R. M. HERBST and L. L. ENGEL (J. Biol. Chem., 1934, 107, 505-511).—In  $H_2O$  at  $100^\circ$   $\alpha$ -ketonic acids react with  $\alpha$ - $NH_2$ -acids thus:  $COR\cdot CO_2H + NH_2\cdot CHR'\cdot CO_2H \rightarrow CO_2H\cdot CR\cdot N\cdot CHR'\cdot CO_2H \rightarrow CO_2H\cdot CHR\cdot N\cdot CR'\cdot CO_2H \rightarrow NH_2\cdot CHR\cdot CO_2H + R'\cdot CHO + CO_2$ . Such action between  $AcCO_2H$  and  $NH_2\cdot CHPh\cdot CO_2H$  (I) [ $PhCHO$ , alanine (II),  $CO_2$ ], glycine [ $CH_2O$ ,  $CHO\cdot CO_2H$ , (II),  $CO_2$ ], phenylalanine (III) [ $CH_2Ph\cdot CHO$ , (II),  $CO_2$ ], *l*-aspartic acid, and *l*-cystine [both giving  $MeCHO$ , (II),  $CO_2$ ] is investigated quantitatively, the isolated products being given in brackets. No action occurs with  $NHMe\cdot CHPh\cdot CO_2H$  or  $NH_2\cdot CMe_2\cdot CO_2H$ .  $CH_2Ph\cdot CO\cdot CO_2H$  (IV) and (I) afford  $PhCHO$ ,  $CO_2$ , and (III), and  $\alpha$ -keto- $\gamma$ -hydroxy- $\beta$ -*diphenylvalerolactone*, obtained by self-condensation of (IV).

J. W. B.

***cycloHexanedicarboxylic acids of the tartaric acid type.*** W. HÜCKEL and U. LAMPERT (Ber., 1934, 67, [B], 1811-1816).—*Et cyclohexanone-2-carboxylate* is transformed by the successive action of  $NaCN$  and  $HCl$  into 1-hydroxycyclohexane-1:2-dicarboxylic acid (I), m.p.  $178^\circ$ , in 30% yield. The non-cryst. acid simultaneously obtained passes when distilled in vac. into  $\Delta^1$ -tetrahydro-*o*-phthalic anhydride (II), m.p.  $74^\circ$ , which is not obtained when homogeneous (I) is distilled, but is formed in 70% yield from (I) and  $Ac_2O$ . (II) is transformed by aq.  $Na_2CO_3$  followed by  $AgNO_3$  into *Ag*,  $\Delta^1$ -tetrahydro-*o*-phthalate, whence *Et*,  $\Delta^1$ -tetrahydro-*o*-phthalate, b.p.  $147^\circ/10$  mm. (I) and  $AcCl$  give 1-acetoxycyclohexane-1:2-dicarboxylic anhydride, m.p.  $98^\circ$  (corresponding acid, m.p.  $141^\circ$ ). The action of  $Cl_2\cdot H_2O$  on (II) dissolved in  $NaOH$ , followed by addition of  $AcOH$  and  $Pb(OAc)_2$ , leads to the salt,  $C_8H_9O_5ClPb$ , whence by means of conc.  $H_2SO_4$  in EtOH, 1-chloro-2-hydroxycyclohexane-1:2-dicarboxylic acid (III), m.p.  $186^\circ$ , is obtained. (III) is very readily transformed by  $H_2O$  into 1:2-dihydroxycyclohexane-1:2-dicarboxylic acid [cis-form (IV), m.p.  $184^\circ$ , not resolved by bases; trans-variety, m.p.  $178^\circ$  (decomp.)], which with brucine in EtOH



yields a *brucine* salt, m.p. 237°, whence a *d*-acid, m.p. 182°, and a *brucine* salt, m.p. 226°, whence an *l*-acid]. Treatment of (III) with dil. NaOH leads to non-cryst. 1:2-*oxidocyclohexene-1:2-dicarboxylic acid* (V) (*Ba*, *Pb*, and *fenchylamine*, m.p. 176°, salts). (V) and H<sub>2</sub>O give only (IV), whereas (V) and HCl-Et<sub>2</sub>O yield (III). (III) and warm AcCl afford 1:2-*diacetoxy-cyclohexane-1:2-dicarboxylic anhydride* (VI), m.p. 174°, 1:2-*diacetoxy-cyclohexane-1:2-dicarboxylic acid* (VII), m.p. 200°, and (?) 1-*chloro-2-acetoxy-cyclohexane-1:2-dicarboxylic acid*, m.p. about 160°. (VI) and (VII) are also obtained from the stereoisomeric (OH)<sub>2</sub>-acids with Ac<sub>2</sub>O or AcCl and (VI) from (VII) by AcCl. H. W.

**Isatogens and indoles. XV. *m*-Phenylenediacrylic acid.** P. RUGGLI and A. STAUB (Helv. Chim. Acta, 1934, 17, 1523—1527).—*m*-C<sub>6</sub>H<sub>4</sub>(CHO)<sub>2</sub> is converted by prolonged treatment with NaOAc and Ac<sub>2</sub>O at 150° into *m*-*phenylenediacrylic acid* (I), m.p. 280° (slight decomp.). Alternatively, CHCl(CO<sub>2</sub>Et)<sub>2</sub> is treated successively with NaOEt and *m*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub>, giving essentially Et<sub>2</sub> *m*-*xylylene-dichloromalonate*, hydrolysed and decarboxylated to non-cryst. *m*-*xylylenedi-α-chloropropionic acid*, which is transformed by boiling KOH-H<sub>2</sub>O into (I) [Me<sub>2</sub>, m.p. 132°, and Et<sub>2</sub>, m.p. 53.5°, esters]. H. W.

**Rotenone. XXXI. Synthesis of 2-hydroxy-4:5-dimethoxyphenylacetic acid.** L. E. SMITH and F. B. LAFORGE (J. Amer. Chem. Soc., 1934, 56, 2431).—The *azlactone*, red and yellow forms, m.p. 168°, from 4:5-*dimethoxy-2-methoxy-methoxybenzaldehyde*, m.p. 61° [from 2:4:5-C<sub>6</sub>H<sub>2</sub>(ONa)(OMe)<sub>2</sub>·CHO and CH<sub>2</sub>Cl·OMe in PhMe], is converted by successive hydrolysis (10% KOH), oxidation (H<sub>2</sub>O<sub>2</sub>), and steam distillation (of mixed acids to remove BzOH) into 2-*hydroxy-4:5-dimethoxy-phenylacetic acid*, m.p. 138°. H. B.

**Acetoacetic ester condensation. IX. Condensation of ethyl  $\gamma$ -isobutyryl- $\beta$ -phenylpropane- $\alpha$ -dicarboxylate.** R. F. B. COX and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 2459—2463).—Styryl Pr <sup>$\beta$</sup>  ketone (I) (0.34 mol.), CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> (II) (0.34 mol.), and EtOH-NaOEt (0.03 mol.) give Et  $\gamma$ -isobutyryl- $\beta$ -phenylpropane- $\alpha$ -dicarboxylate (III), b.p. 192—194°/7 mm., m.p. 42°, which with an equivalent amount of NaOEt at 125—130°/vac. (cf. A., 1934, 756) affords COMePr <sup>$\beta$</sup>  and CHPh:C(CO<sub>2</sub>Et)<sub>2</sub> (retrograde Michael) (II), Pr <sup>$\beta$</sup> CO<sub>2</sub>Et, CHPh:CH·CO<sub>2</sub>Et (IV), Pr <sup>$\beta$</sup> CO·CH<sub>2</sub>·CO<sub>2</sub>Et (V), 5-phenyl-2:2-dimethylcyclohexane-1:3-dione (VI) (Dieckmann and Kron, A., 1908, i, 388), and (probably) two *diisobutyryldiphenylcyclobutanes*, m.p. 155° (VII) and 180° (VIII) [presumably formed by dimerisation of (I)]. (III) is considered to undergo an internal acetoacetic ester condensation to Et 5-phenyl-2:2-dimethylcyclohexane-1:3-dione-4-carboxylate, which is then degraded to (VI), (IV), and (V); the results substantiate to the mechanism previously suggested (*loc. cit.*) for the acetoacetic ester condensation. (VI) is also obtained when Et 5-phenyl-2:2-dimethylcyclohexane-1:3-dione-4:6-dicarboxylate is heated with BzOH at 150°. (VII) is converted by Ac<sub>2</sub>O at 140° into (VIII) and an *isomeride*, m.p. 182°; (VIII) is similarly unaffected.  $\alpha$ -Methylstyryl Pr <sup>$\beta$</sup>  ketone, b.p. 140—141°/

12 mm., is prepared in 12% yield by Rupe and Hirschmann's method (A., 1931, 1050). H. B.

**Sulphite liquor lactone and tsuga-resinol.** H. EMDE and H. SCHARFNER (Naturwiss., 1934, 22, 743—744).—The sulphite liquor lactone of Holmberg, m.p. 256° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -54.5° in COMe<sub>2</sub>, is identified with Kawamura's tsuga-resinol and to it is assigned the constitution  $\begin{matrix} \text{CH}_2\text{R}-\text{CH}-\text{CO} \\ | \\ \text{CH}_2\text{R}-\text{CH}-\text{CH}_2 \end{matrix} > \text{O}$  [R=3:4-C<sub>6</sub>H<sub>3</sub>(OMe)·OH]. It is regarded as derived through a dehydrolactone by dimerisation and Cannizzaro reaction from coniferaldehyde. H. W.

**Lichen substances. XLIV. Salazinic and norstictinic acid. XLV. Identity of coccellic acid with barbatic acid.** Y. ASAHINA and F. FUJIKAWA (Ber., 1934, 66, [B], 1789—1792, 1793—1795).—XLIV. Very mild treatment of norstictic acid (I) with KOH-K<sub>2</sub>CO<sub>3</sub> yields K<sub>2</sub> *norstictinate* (+3H<sub>2</sub>O), from which (I) is regenerated by dil. HCl at 0°. Salazic acid (II) similarly affords K<sub>2</sub> *salazinate* (+3H<sub>2</sub>O), re-forming (II) when treated with dil. HCl. Similarity of absorption spectra indicates similar results with salazic acid  $\alpha$ -Me ether (III). The formation of red crystals on treatment with KOH appears to depend on the presence of free phenolic OH *o*- to CHO and of a lactol group in the second nucleus. Action of more conc. KOH on the red crystals leads to dark red or brown resins. The red salts are best represented by A [R=Me, ·CH<sub>2</sub>·OH, and ·CH<sub>2</sub>·OMe, respectively, in the cases of (I), (II), and (III)].

**XLV. Exhaustive extraction of the thalli of *Cladonia amaurocraea* with Et<sub>2</sub>O gives *l*-usnic acid, m.p. 203°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -487° in CHCl<sub>3</sub>, and coccellic acid (I), C<sub>19</sub>H<sub>20</sub>O<sub>7</sub> (instead of C<sub>20</sub>H<sub>22</sub>O<sub>7</sub>), m.p. 186—187°, proved identical with barbatic acid by comparison of the Me esters, m.p. 173°. Alkaline hydrolysis of (I) affords CO<sub>2</sub>,  $\beta$ -orcinol, and rhizonic acid, with which the coccellic acid of Hesse is probably identical. H. W.**

**Condensation of acraldehyde with cyclohexyl and aromatic rings.** E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1934, 4, 866—870).—Hexahydrobenzaldehyde and MeCHO in aq. COMe<sub>2</sub> in presence of KOH at 70° yield *hexahydrocinnamaldehyde* (I), b.p. 92—94°/4 mm. [*semicarbazone*, m.p. 179—180° (decomp.); *diacetate*, b.p. 122—124°/13 mm.], readily polymerising to a glassy product at 100°. (I) is oxidised by KMnO<sub>4</sub> to hexahydrobenzoic acid, whilst Ag<sub>2</sub>O affords hexahydrocinnamic acid. Piperonyl-acraldehyde is obtained in 15% yield by Ladenburg's method (A., 1895, i, 42). R. T.

**Synthesis of  $\gamma$ -resorcylaldehyde dimethyl ether.** D. B. LIMAYE (Proc. Indian Acad. Sci., 1934, A, 1, 163—165).—2:6-Dimethoxyphenylglyoxylic acid and NH<sub>2</sub>Ph at 180° give (3—5 min.) the anil, hydrolysed (aq. NaOH) to  $\gamma$ -resorcylaldehyde Me<sub>2</sub> ether, m.p. 98—99°, b.p. 285° (*semicarbazone*, m.p. 190°; yields 2:6-dimethoxycinnamic acid, m.p. 146—147°), which with AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> at 100° gives



$m\text{-C}_6\text{H}_4(\text{OH})_2$ , but under other conditions affords the OH- and  $(\text{OH})_2$ -aldehydes. R. S. C.

Some phenolic derivatives of lignin. L. LEMMEL (Bull. Soc. chim., 1934, [v], 1, 1082—1085).—The cresols heated at  $125^\circ$  with pine sawdust (previously extracted with  $\text{EtOH}\text{-C}_6\text{H}_6$ ) and a trace of HCl give *o*-, m.p.  $220\text{--}225^\circ$ , *m*-, m.p.  $210\text{--}220^\circ$ , and *p*-cresol-lignin,  $\{(\text{C}_6\text{H}_7\text{O})(\text{OMe})(\text{OH})[\text{C}_6\text{H}_3\text{Me}(\text{OH})]\}_x$ , decomp. above  $165^\circ$  ( $\text{Ac}_2$  derivatives, m.p.  $165\text{--}173^\circ$ ,  $160\text{--}165^\circ$ , and  $140\text{--}150^\circ$ , respectively).

F. S. H. H.

Reactions involving ring closure. K. ZIEGLER (Ber., 1934, 67, [A], 139—149).—A lecture.

H. W.

Reactions of *trans*- $\beta$ -decalone. I. E. LEHMANN and B. KRATSCHHELL (Ber., 1934, 67, [B], 1867—1870).—Chlorination of *trans*-2-ketodecahydronaphthalene yields, in addition to much non-cryst. matter, *trans*-3-chloro-2-ketodecahydronaphthalene (I), m.p.  $92^\circ$ , *trans*-dichloro-2-ketodecahydronaphthalene, m.p.  $137^\circ$ , and a hydrocarbon,  $\text{C}_{20}\text{H}_{26}$ , m.p.  $59^\circ$ . Treatment of (I) with boiling aq. NaOH affords the two forms of *trans*-3-hydroxy-2-ketodecahydronaphthalene, m.p.  $84^\circ$  (II) and m.p.  $134^\circ$  (III), respectively (corresponding oximes, m.p.  $183^\circ$  and m.p.  $192^\circ$ , respectively). (II) is oxidised by  $\text{KMnO}_4$  to cyclohexane-*trans*-1:2-diacetic acid, m.p.  $167^\circ$ . Reduction of (III) with Na-Hg in  $\text{MeOH}\text{-H}_2\text{O}$  affords 2:3-dihydroxydecahydronaphthalene, m.p.  $141^\circ$ . (III) is not acylated by *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  in  $\text{C}_6\text{H}_5\text{N}$ , which converts it into (II); under similar conditions (II) remains unchanged. (II) with 80%  $\text{H}_2\text{SO}_4$  at  $60^\circ$  yields *trans*-2-keto- $\Delta^3$ -octahydronaphthalene, b.p.  $126\text{--}127/12$  mm. (oxime, m.p.  $145^\circ$ ). (I), Na, and  $\text{CH}_2(\text{CO}_2\text{Et})_2$  in boiling  $\text{Et}_2\text{O}$  afford *Et*, *trans*-2-ketodecahydronaphthyl-3-malonate, b.p.  $162^\circ/0.5$  mm., whence the corresponding acid, m.p.  $149\text{--}150^\circ$ , and *trans*-2-ketodecahydronaphthyl-3-acetic acid, m.p.  $93^\circ$ .

H. W.

Acetophenone- $\omega$ -sulphonic acid, and phenylglyoxal- $\alpha$ -sulphonic acids. G. D. PARKES and S. G. TINSLEY (J.C.S., 1934, 1861—1864).—Phenacyl bromide and aq.  $\text{Na}_2\text{SO}_3$  give the Na salt of acetophenone- $\omega$ -sulphonic acid, m.p.  $73\text{--}75^\circ$  [ $\text{NH}_4$ , m.p.  $207^\circ$ ,  $\text{NH}_2\text{Ph}$ , m.p.  $181^\circ$ , and  $\text{NH}_2\text{NHPH}$ , m.p.  $208^\circ$  (decomp.), salts], which is liberated by passing HCl into the dry  $\text{Et}_2\text{O}$  suspension. By condensation with the appropriate  $\text{ArN}_2\text{Cl}$  are obtained: phenylglyoxal- (I), m.p.  $220^\circ$  (decomp.) [*Ba* salt, m.p.  $188^\circ$  (decomp.)], *p*-bromo- (II), m.p.  $240^\circ$  (decomp.), *o*-2:4-dibromo-, m.p.  $245^\circ$  (decomp.) [*Ba* salt, m.p.  $270^\circ$  (decomp.)], and *o*-2:4:6-tribromo- (III), m.p.  $210^\circ$  (decomp.) (also a labile form), *o*- (IV), m.p.  $238^\circ$  (decomp.), and *p*-nitro-, m.p.  $259^\circ$  (decomp.), *o*-4-bromo-2-nitro-, m.p.  $242^\circ$  (decomp.), *p*-chloro-, m.p.  $240^\circ$  (decomp.), *o*-2:4-dichloro-, m.p.  $248^\circ$  (decomp.), and *o*-2:4:6-trichloro-, m.p.  $217^\circ$ , phenylglyoxal- $\alpha$ -sulphonic acid, all of type  $\text{NHR}\cdot\text{N}\cdot\text{CBz}\cdot\text{SO}_3\text{H}$ . With  $\text{Br}\text{-AcOH}$  (I) gives successively (II), *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{N}\cdot\text{CBzBr}$ , and 2:4- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NH}\cdot\text{N}\cdot\text{CBzBr}$ ; (III) with  $\text{Br}$  gives 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}\cdot\text{N}\cdot\text{CBzBr}$ . Similarly are obtained  $\omega$ -bromophenylglyoxal-*o*-nitro-, m.p.  $128^\circ$ , and *o*-4-bromo-2-nitro-, m.p.  $185^\circ$ , phenylhydrazone [also by excess of

$\text{Br}\text{-AcOH}$  on (IV)]. Similar reactions with  $\text{Cl}_2$  give  $\omega$ -chlorophenylglyoxal-*p*-chloro-, m.p.  $133^\circ$ , *o*-2:4-dichloro-, m.p.  $106^\circ$ , and *o*-2:4:6-trichloro-, m.p.  $119^\circ$ , phenylhydrazone. J. W. B.

Structure of metal ketyls. II. Dissociation of alkali metal pinacolates to metal ketyls in liquid ammonia solution. C. B. WOOSTER. III. Mechanism of reactions with alkyl halides. C. B. WOOSTER and W. E. HOLLAND (J. Amer. Chem. Soc., 1934, 56, 2436—2438, 2438—2442).—II. Decomp. of the product (A) from  $\text{COPh}_2$  and Na (1 equiv.) in liquid  $\text{NH}_3$  solution with  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{Br}$  gives 5—15% of benzpinacol, indicating that (A) consists largely of  $\text{CPh}_2\cdot\text{ONa}$  (I) (cf. Bachmann, A., 1933, 505):  $(\cdot\text{CPh}_2\cdot\text{ONa})_2 \rightleftharpoons 2\text{CPh}_2\cdot\text{ONa}$ . The following results show that the change  $2\text{CPh}_2\cdot\text{ONa} \rightarrow \text{COPh}_2 + \text{CNaPh}_2\cdot\text{ONa}$  (II) (cf. A., 1929, 928) occurs to little or no extent. Addition of  $\text{CH}_2\text{Ph}\cdot\text{OH}$  (III) [which reacts rapidly (5 min.) with (II)] to (I) does not retard the reaction between (I) and  $\text{EtBr}$  (approx. 1 equiv.; added after 5 min.); reaction occurs more slowly with approx. 0.1 equiv. of  $\text{EtBr}$  [which does not promote reaction between (I) and (III)]. The results of Kraus and Bien (A., 1933, 1120) indicate that the anion  $\text{CR}_2\text{O}^-$  exists in liquid  $\text{NH}_3$ .

III.  $\text{MeOAc}$  (or  $\text{Et}_2\text{CO}_3$ ) reacts slowly with (I) in liquid  $\text{NH}_3$ ; (I) is probably hydrolysed by the ammonolysis products of the ester. Decomp. of (I) in liquid  $\text{NH}_3$  by slow addition of  $\text{EtBr}$  gives 88—99% of  $\text{COPh}_2$  (determined as oxime):  $2\text{CPh}_2\cdot\text{ONa} + \text{EtBr} \rightarrow \text{COPh}_2 + \text{CPh}_2\text{Et}\cdot\text{ONa} + \text{NaBr}$ . Rapid addition of  $\text{EtBr}$  with stirring affords only 20—45% of  $\text{COPh}_2$ . These results indicate that  $\text{COPh}_2$  is formed in a secondary reaction, which is suppressed during the rapid decomp. of (I):  $\text{CPh}_2\cdot\text{ONa} + \text{EtBr} \rightarrow \text{NaBr} + \text{C}_{15}\text{H}_{15}\text{O}$ ;  $\text{CPh}_2\cdot\text{ONa} + \text{C}_{15}\text{H}_{15}\text{O} \rightarrow \text{COPh}_2 + \text{CPh}_2\text{Et}\cdot\text{ONa}$ . Possible side reactions (leading to the production of Et ethers) are discussed; the OEt content of the residue [freed from  $\text{COPh}_2$  (19.9%)] from one experiment is not large enough to account for the diminution in the yield of  $\text{COPh}_2$ . The reaction mechanism suggested by Schlenk and Weickel (A., 1911, i, 545) is considered to be disproved. The product (?  $\text{CPh}_2\text{Br}\cdot\text{OEt}$ ) obtained from  $\text{CHPh}_2\cdot\text{OEt}$  and  $\text{Br}$  in  $\text{Et}_2\text{O}$  in presence of light (Hg-vapour lamp) gives  $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$  when treated with  $\text{NH}_2\cdot\text{OH}$  in alkaline solution.  $\text{CPh}_3$  does not react with  $\text{EtBr}$  in liquid  $\text{NH}_3$ . H. B.

Action of Grignard reagents on desyl chloride.

I. Aryl Grignard reagents. R. ROGER and A. MCGREGOR (J.C.S., 1934, 1850—1853).— $\text{CHPhClBz}$  (I) and  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  give mainly  $\text{CHPh}_2\cdot\text{CPh}_2\cdot\text{OH}$  and some  $\text{CHPh}_2\text{Bz}$ ; *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  gives *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHPhBz}$  and a substance (?)  $\text{C}_{22}\text{H}_{22}\text{O}_3$  (II), m.p.  $185^\circ$ , converted by heating at  $130^\circ/\text{vac.}$  into a mixture, m.p.  $45\text{--}75^\circ$ , from which  $\text{Bz}_2$  and  $\text{CH}_2\text{PhBz}$  (III) are isolated. With *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  (I) gives (II) and a mixture which seems to contain *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHPhBz}$ . Mechanisms are discussed, and since the intermediate formation of  $\text{CPh} > \text{O}$  may be involved, the following attempts were made to prepare it from (I) (Madelung *et al.*, A., 1932, 62). (I) with  $\text{KOH}$  gives only  $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$  and (III), converted



by  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  (IV) into *phenyl-p-tolylbenzyl-carbinol*, m.p. 89.5—90.5°. (I) with  $(\text{C}_6\text{H}_5\text{OH})_2$  and moist  $\text{Ag}_2\text{O}$  gave bidesyl and a little  $\text{CHPhBz}\cdot\text{OH}$ . Distillation of  $\alpha$ -methoxy- $\beta$ -diphenyloxan in  $\text{CO}_2$  at atm. pressure gives  $\text{MeOH}$ ,  $\text{Bz}_2$ , and a substance, m.p. 48—49°, converted by (IV) into a substance, m.p. 142—143°.  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHPhBz}$  boiled with (IV) gives  $\alpha\beta$ -*diphenyl- $\alpha\beta$ -di-*p*-tolylethan- $\alpha$ -ol*, m.p. 195—196°.

J. W. B.

#### Reactivity of unsymmetrical distyryl ketones.

W. P. JENNINGS and A. MCGOOKIN (J.C.S., 1934, 1741—1742).—By condensation of the appropriate styryl Me ketone and substituted  $\text{PhCHO}$  are obtained 4-*hydroxy-2-methoxy-*, m.p. 137°, 3:4'-*dimethoxy-*, m.p. 77—78°, 3- (I), m.p. 167°, and 4-*chloro-4'-hydroxy-* (II), m.p. 200—201°, and 3- (III), m.p. 115.5°, and 4-*chloro-4'-methoxy-* (IV), m.p. 157—157.5°, *-distyryl ketone*. Condensed with  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  (I), (II), (III), and (IV) give, respectively, *Et 3-p-hydroxyphenyl-5-m-*, m.p. 202° (*Me ether*, m.p. 121°), and *-5-p-chlorostyryl-*, m.p. 200°, *Et 3-m-*, m.p. 123°, and *3-p-chlorophenyl-5-p-methoxystyryl-*, m.p. 128°,  $\Delta^5$ -*cyclohexen-1-one-2-carboxylate*. J. W. B.

**Stereoisomerism of indones.** R. DE FAZI (Atti Congr. naz. Chim., 1933, 4, 481—482).—By the action of dry  $\text{Cl}_2$  on a  $\text{CHCl}_3$  solution of  $\beta$ -phenyl- $\alpha$ -ethylindone at  $-5^\circ$  to  $-10^\circ$  are obtained two stereoisomeric  $\alpha\beta$ -*dichloro- $\beta$ -phenyl- $\alpha$ -ethylhydrindones*, m.p. 92—94° and 115—116°, respectively. Similarly from  $\beta$ -phenyl- $\alpha$ -methylindone are obtained two  $\alpha\beta$ -*dichloro- $\beta$ -phenyl- $\alpha$ -methylhydrindones*, m.p. 92—93° and 110—111°, respectively. They are racemised by boiling with  $\text{Cu}$  in  $\text{MeOH}$  for 45 min. R. N. C.

**$\alpha$ -Oximino- and  $\alpha$ -amino-derivatives of *o*-hydroxypropiophenone.** H. L. MASON (J. Amer. Chem. Soc., 1934, 56, 2499—2500).—*o*- $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{COEt}$ ,  $\text{BuO}\cdot\text{NO}$ , and  $\text{HCl}$  in  $\text{Et}_2\text{O}$  give *o*-*benzoyloxyphenyl  $\alpha$ -oximinoethyl ketone*, m.p. 100—101°, which is hydrolysed (aq.  $\text{EtOH}$ - $\text{NaOH}$ ) to the *o*-*OH*-derivative, m.p. 85—88°, and reduced (method: Hartung and Munch, A., 1929, 1066) to *o*-*benzoyloxyphenyl  $\alpha$ -aminoethyl ketone*, m.p. 112—114° [*hydrochloride* ( $+0.5\text{H}_2\text{O}$ ), decomp. 180°]. H. B.

**Friedel-Crafts type reactions on diphenyl.** S. L. SILVER and A. LOWY (J. Amer. Chem. Soc., 1934, 56, 2429—2431).— $\text{Ph}_2$  or  $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{COMe}$ ,  $\text{AcCl}$ , and  $\text{AlCl}_3$  give 4:4'-*diacetyldiphenyl*.  $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$  (I) is similarly prepared using 1 mol. of  $\text{CH}_2\text{Cl}\cdot\text{COCl}$  (II) or  $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$ ; with an excess of (II), 4:4'-*di(chloroacetyl)diphenyl*, m.p. 228—229° [oxidised ( $\text{KMnO}_4$ ) to diphenyl-4:4'-*dicarboxylic acid* and  $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ], also obtained from (I) and (II), results.  $\text{Ph}_2$  and  $(\text{COCl})_2$  give *di-p*-diphenyl ketone and 4:4'-*diphenylbenzil*. *p*-*Benzenesulphonyldiphenyl*, m.p. 148.5° [oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to  $p\text{-PhSO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ ], and *di-p*-*diphenyl sulphoxide*, m.p. 207—208° [oxidised (10%  $\text{KMnO}_4$ ) to the sulphone], are prepared using  $\text{PhSO}_2\text{Cl}$  and  $\text{SOCl}_2$ , respectively. All the reactions are carried out in  $\text{CS}_2$ . Complex products are obtained from  $\text{Ph}_2$ ,  $\text{CH}_2\cdot\text{CHCl}$ , and  $\text{AlCl}_3$  in light petroleum at  $-5^\circ$  to  $5^\circ$ . H. B.

**New factor controlling certain chelations, with special reference to disubstitution in the res-**

**orcinol nucleus.** W. BAKER (J.C.S., 1934, 1684—1692).—Analysis of the physical and chemical properties of certain diacetyresorcinols indicates that chelation between the carbonyl-O (donor) and the H (acceptor) of the adjacent OH occurs only when the OH and Ac are united to 2 mutually doubly-linked C atoms of the  $\text{C}_6\text{H}_6$  nucleus (probably dependent on the electromeric effect), thus supplying confirmatory evidence that the aromatic character of  $\text{C}_6\text{H}_6$  is not dependent on the rapid alternation of double linkings (Mills *et al.*, A., 1931, 83). Thus the 2:4-Ac<sub>2</sub> derivative (I) is doubly chelated, whereas in the 4:6-Ac<sub>2</sub> compound (II), only simple chelation is possible. Such fixation of the position of the double linkings determines the position of further substitution: thus whereas rearrangement of 2-*O*-acetylresacetophenone (no fixation) by  $\text{AlCl}_3$  gives only (II) (usual *p*-migration), the 4-*O*-Ac derivative (double linkings fixed) affords a 45% yield of a mixture containing 58% of (I) (*Me*<sub>2</sub> ether, m.p. 65°, b.p. 187°/15 mm.) and 42% of (II), but on removal of the chelation reversion to *p*-migration occurs, since the 4-*O*-Ac derivative, m.p. 34°, of resacetophenone 2-*O*-Me ether (*isopæanol*, prep. with *pæanol* from  $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$  by rearrangement with  $\text{AlCl}_3$  in  $\text{PhNO}_2$ , or from  $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  and  $\text{MeCN}$  with  $\text{ZnCl}_2\text{-Et}_2\text{O-HCl}$ ), and subsequent methylation gives only the *Me*<sub>2</sub> ether of (II), the *Me*<sub>2</sub> ether of resacetophenone, and no (I). In the nitrophenols both O of the  $\text{NO}_2$  can act as donors in chelation with OH, whether the C atoms, to which the groups are attached, are united by a single or double linking. Thus 2-nitroresorcinol (III) is doubly chelated and no essential difference is observed in the properties of 2:4- and 2:6-dinitroresorcinols. In the disubstitution of resorcinol the 4-derivative is always formed first and, in the absence of the disturbing factors discussed above, the second substituent enters position 6, and the formation of dihalogeno-,  $(\text{CO}_2\text{H})_2$ ,  $(\text{SO}_3\text{H})_2$ , and  $(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2$  derivatives (all 4:6-) and of  $(\text{NO}_2)_2$ ,  $(\text{CHO})_2$  (both 2:4-), and bisazo-(2:4- or 2:6- according to conditions) (chelation fixing the position of the double linkings in the last three), are discussed on this basis. Nitration of resacetophenone with  $\text{HNO}_3$  (*d* 1.42) at 30—40° gives the 5- $\text{NO}_2$ -derivative, since oxidation (3%  $\text{H}_2\text{O}_2$ -*N*- $\text{NaOH}$  in  $\text{H}_2$ ) and subsequent methylation affords 5-nitrohydroxyquinol $\text{Me}_3$  ether. Nitro (Adams, A., 1919, i, 160) is 5-nitro-2-hydroxy-4-methoxyacetophenone, since its *Me*<sub>2</sub> ether, m.p. 180° (not the compound, m.p. 131°, *loc. cit.*), is identical with that of 5-nitroresacetophenone. With  $\text{HNO}_3$  (*d* 1.42) at 80° (II) gives its 2- $\text{NO}_2$ -derivative. J. W. B.

**Synthesis of methoxychalkones [methoxyphenyl styryl ketones] and methoxybenzylidene- $\beta$ -coumaranones from methoxyacetophenones and nitrobenzaldehydes.** D. PRICE and M. T. BOGERT (J. Amer. Chem. Soc., 1934, 56, 2442—2449).—2:3:4-( $\text{OMe}$ )<sub>3</sub> $\text{C}_6\text{H}_2\cdot\text{COMe}$  and  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in aq.  $\text{EtOH}$ - $\text{NaOH}$  give 2:3:4-*trimethoxyphenyl o-*, m.p. 125° (all m.p. are corr.), *m-*, m.p. 135°, and *p-*, m.p. 160.5°, *-nitrostyryl ketones*, which are reduced ( $\text{SnCl}_2$ ,  $\text{AcOH-HCl}$ ) to 2-2':3':4'-*trimethoxyphenylquinoline*, m.p. 105°, and 2:3:4-*trimethoxyphenyl m-*, m.p. 98°, and *p-*, m.p. 104°, *-aminostyryl ketone*, re-



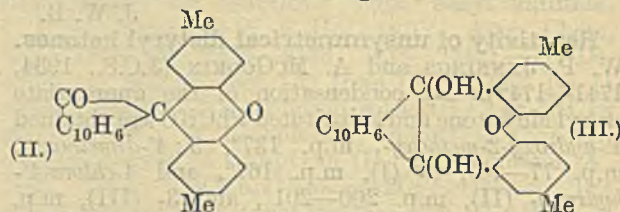
spectively. 2-Hydroxy-3:4-dimethoxyacetophenone (I) and *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO in MeOH-NaOMe give 2-hydroxy-3:4-dimethoxyphenyl β-hydroxy-β-*o*-nitrophenylethyl ketone (II), m.p. 132° [the *p*-NO<sub>2</sub>-isomeride (III) has m.p. 156°], which when heated above its m.p. affords 2-hydroxy-3:4-dimethoxyphenyl *o*-nitrostyryl ketone (IV), m.p. 163.5° [Ac derivative, m.p. 115°, prepared from (II) or (IV) (or a mixture) and Ac<sub>2</sub>O-NaOAc]. (I) and *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO in aq. EtOH-NaOH give 2-hydroxy-3:4-dimethoxyphenyl *m*-nitrostyryl ketone, m.p. 190.5° (Ac derivative, m.p. 99°), whilst crude (III) is dehydrated (Ac<sub>2</sub>O) to 2-hydroxy-3:4-dimethoxyphenyl *p*-nitrostyryl ketone, m.p. 188.5° (Ac derivative, m.p. 173.5°). 2-Acetoxy-3:4-dimethoxyphenyl αβ-dibromo-β-*o*-, m.p. 143.5°, -*m*-, an oil, and -*p*-, m.p. 148°, -nitrophenylethyl ketones (from the above Ac derivatives and Br in CHCl<sub>3</sub>) are converted by EtOH-KOH [independently of temp. (cf. von Auwers and Anschütz, A., 1921, i, 682)] into 2'- (V), m.p. 196—196.5°, 3'- (VI), m.p. 220°, and 4'- (VII), m.p. 265.5°, -nitro-5:6-dimethoxybenzylidenecoumaranone, respectively; (V) is accompanied by a Br-containing substance, m.p. 133°. (VII) is also prepared from 2-hydroxy-3:4-dimethoxyphenyl acyl chloride, m.p. 161.5° [from 1:2:3-C<sub>6</sub>H<sub>3</sub>(OMe)<sub>3</sub>, CH<sub>2</sub>Cl·COCl, and AlCl<sub>3</sub> in CS<sub>2</sub> under defined conditions; different conditions lead to 4:6-di(chloroacetyl)pyrogallol 2-Me ether, m.p. 154.5°], and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO in alkali. Reduction (SnCl<sub>2</sub>, AcOH-HCl) of (V), (VI), and (VII) at room temp. gives the corresponding NH<sub>2</sub>-derivatives, m.p. 211—212°, 205.5°, and 174°, respectively; at 100°, (V) gives (mainly) dimethoxycoumarinoline, m.p. 179° (cf. Feist and Siebenlist, A., 1927, 671).

H. B.

**Influence of chemical constitution on visible colour and other tinctorial properties in the case of structurally related methoxychalkones [methoxyphenyl styryl ketones] and methoxybenzylidenecoumaranones.** D. PRICE, A. DINGWALL, and M. T. BOGERT (J. Amer. Chem. Soc., 1934, 56, 2483—2486).—The 2:3:4-trimethoxyphenyl nitro- and amino-styryl ketones [absorption spectra curves for the *m*- (I) and *p*- (II) -NH<sub>2</sub>-derivatives given] (preceding abstract) and the 5:6-dimethoxy-nitro- and -amino-benzylidenecoumaranones [absorption spectra curves for the 3'- (III) and 4'- (IV) -NH<sub>2</sub>-derivatives given; that for (III) appears to be anomalous] (*loc. cit.*) are generally yellow (varying shades). (III), (IV), and the 2'-NH<sub>2</sub>-isomeride (V) are more intensely coloured than the NO<sub>2</sub>-derivatives [which resemble the OH-analogues (Felix and Friedländer, A., 1910, i, 278)]; all dissolve in conc. H<sub>2</sub>SO<sub>4</sub> to (usually) red solutions. There is not such a marked difference between (I) and (II) and the corresponding NO<sub>2</sub>-derivatives. The 2-hydroxy-3:4-dimethoxyphenyl nitrostyryl ketones (*loc. cit.*) are more intensely coloured than their Ac derivatives and the β-hydroxy-β-nitrophenylethyl ketones. Passage from (II) to (IV) is accompanied by a marked deepening in colour; no such effect is observed with (I) and (III). The position of the NH<sub>2</sub>-group has a much greater effect on the colour of the coumaranones than of the styryl ketones. (II), (IV), and (V) dye silk and wool (from dil. solutions in dil. AcOH) greenish-yellow, golden-yellow and orange-yellow, respectively.

H. B.

**Condensation of acenaphthenequinone with cresols and naphthols; cyclic pinacols.** I. MATEI and E. BOGDAN (Ber., 1934, 67, [B], 1834—1842).—Cautious addition of conc. H<sub>2</sub>SO<sub>4</sub> (6 equivs.) to a molten mixture of acenaphthenequinone (I) and *p*-cresol gives anhydro-8-keto-7:7-di-2'-hydroxy-5'-methylphenylacenaphthene (II), m.p. 333°, which is insol. in alkali and does not give an Ac derivative.



With 1 equiv. of conc. H<sub>2</sub>SO<sub>4</sub>, (I) and *p*-cresol afford anhydro-7:8-di-2'-hydroxy-5'-methylphenylacenaphthene-7:8-diol (III), m.p. 225° (or +1EtOH, 1AcOH, or 1PhMe, m.p. 191°, 136°, and 148°, respectively), which is insol. in alkali and transformed by conc. H<sub>2</sub>SO<sub>4</sub> into (II). (I), β-C<sub>10</sub>H<sub>7</sub>-OH, and a few drops of conc. H<sub>2</sub>SO<sub>4</sub> yield anhydro-8-keto-7:7-di-2'-hydroxynaphthylacenaphthene (IV), m.p. 337°, whereas in boiling EtOH containing HCl anhydro-7:8-di-2'-hydroxynaphthylacenaphthene-7:8-diol [+1EtOH or +1AcOH, m.p. 180—182° (decomp.)] is obtained, transformed by boiling AcOH containing conc. H<sub>2</sub>SO<sub>4</sub> into (IV). (I), and *m*-cresol in boiling EtOH-conc. HCl yield 8-keto-7:7-di-4'-hydroxy-2'-methylphenylacenaphthene, m.p. 165° (Ac<sub>2</sub> derivative, m.p. 229—230° after softening). Similarly (I) and *o*-cresol give 8-keto-7:7-di-4'-hydroxy-3'-methylphenylacenaphthene, m.p. 216—217° (Ac<sub>2</sub> derivative, m.p. 180°), whilst (I) and α-C<sub>10</sub>H<sub>7</sub>-OH yield 8-keto-7:7-di-4'-hydroxynaphthylacenaphthene, m.p. 218° (decomp.) [Ac<sub>2</sub> derivative, m.p. >192° (decomp.)].

H. W.

**Constitution of dypnopinacone.** D. IVANOV (Compt. rend., 1934, 199, 729—731; cf. A., 1933, 157).—Dypnopinacone (I) results from the condensation of dypnone with MgCl·CHPh·CO<sub>2</sub>MgCl or related substances which are agents for ketolic condensation. From this fact, and also from the presence of one OH and one CO in the mol., (I) is considered to be βδζ-triphenyl-γ-benzoyl-Δ<sup>βζ</sup>-heptadien-δ-ol.

R. N. C.

**Optical method for the study of reversible organic oxidation-reduction systems.** IV. Aryl-*p*-benzoquinones. V. *o*-Benzoquinones. D. E. KVALNES (J. Amer. Chem. Soc., 1934, 56, 2478—2481, 2487—2489).—IV. *p*-Benzoquinone (I) and the appropriate ArN<sub>2</sub>X in aq. EtOH-NaOAc at > room temp. give 55—85% of phenyl- (II), m.p. 114° (0.698), *p*-diphenyl-, m.p. 199° (0.719), β-naphthyl-, m.p. 173—174° (0.713), *p*-tolyl-, m.p. 138—139° (0.703), anisyl-, m.p. 120—121° (0.692), *p*-acetylphenyl-, m.p. 152—153° (0.715), *p*-carboxyphenyl-, m.p. 220—221° (decomp.), *p*-carbethoxyphenyl-, m.p. 123—124° (0.716), and *m*-, m.p. 105—107° (0.721), and *p*-, m.p. 137° (0.721), -nitrophenyl-*p*-benzoquinones. (II) and PhN<sub>2</sub>X (III) similarly give poor yields of 2:5-diphenyl- (IV), m.p. 214° (0.689), and tetraphenyl-, m.p. 311—315°, -*p*-benzoquinone. 2:5-Dichloro-*p*-benzoquinone and (III) (excess) in AcOH



afford 2 : 5-dichloro-3 : 6-diphenyl-*p*-benzoquinone, m.p. 208—209°, hydrolysed (MeOH-alkali) to the 2 : 5-(OH)<sub>2</sub>-derivative (polyporic acid). *p*-Xyloquinone and *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>X (1 mol.) give 3-*m*-nitrophenyl-, m.p. 123—124°, and a little 3 : 6-*di*-*m*-nitrophenyl-, m.p. 241—242°, -2 : 5-dimethyl-*p*-benzoquinone. Some 2-phenyl-, m.p. 110°, and a little 2 : 3-diphenyl-, m.p. 135—136°, -1 : 4-naphthaquinone are obtained from (III) and 1 : 4-naphthaquinone [the 2-*p*-carboxyphenyl derivative, m.p. 303—305° (decomp.), is prepared in good yield using *p*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>X; reductive acetylation of this gives 1 : 4-diacetoxy-2-*p*-carboxyphenyl-naphthalene, m.p. 200—201°]. 3-Phenyl-2 : 6-dimethyl-1 : 4-naphthaquinone, m.p. 114—115°, is prepared in poor yield. 3 : 4-*Di*-*p*-carboxyphenyl-1 : 2-naphthaquinone has m.p. 260—262°. The naphthaquinones are purified through the naphthaquinols. (IV) and Ac<sub>2</sub>O-conc. H<sub>2</sub>SO<sub>4</sub> give 1 : 2(? 3) : 4-triacetoxy-2 : 5-diphenylbenzene, m.p. 191—192°. Pure products could not be obtained from (I) and *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>X, 2 : 6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·N<sub>2</sub>X, and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·N<sub>2</sub>X; 2-methoxy-1 : 4-naphthaquinone does not react with (III). 2-Hydroxy-1 : 4-naphthaquinone and (III) give the 3-benzene-azo-derivative, m.p. 225—226° (decomp.). *p*-Diphenyl-, m.p. 177—178°,  $\beta$ -naphthyl-, m.p. 172—174°, *p*-tolyl-, m.p. 123°, *anisyl*-, m.p. 111—112°, *p*-acetylphenyl-, m.p. 192—193°, and *p*-carboxyphenyl- (anhyd. and +H<sub>2</sub>O), m.p. 230—231°, -quinols are described. The vals. quoted in parentheses after some of the above quinones are the relative oxidation potentials [(I)=0.711 volt] determined in C<sub>6</sub>H<sub>6</sub> by the method previously described (A., 1932, 947; 1934, 527); the normal potentials are also determined electrometrically in 70% EtOH.

V. The relative oxidation potentials of the following are determined polarimetrically in C<sub>6</sub>H<sub>6</sub> using the system *d*-camphor-10-sulphonyl-quinol and -quinone (improved prep.; cf. A., 1932, 947): (I)=0.711 volt; *o*-benzoquinone, 0.833; 4-chloro-, 0.810, 4-bromo-, 0.810, 4-methyl-, 0.796, 4-triphenylmethyl-, 0.804, 3 : 4-dimethyl-, 0.765, tetrachloro-, 0.860, and tetrabromo-, 0.860, -*o*-benzoquinones. The vals. are compared with those determined electrometrically in aq. solution. The effects of substituents are discussed briefly. 2 : 5 : 1-C<sub>6</sub>H<sub>3</sub>(OH)(OMe)·CHO is oxidised (method: Dakin, Proc. Chem. Soc., 1909, 194) to 4-methoxy-pyrocatechol, m.p. 48—50° (diacetate, m.p. 69—70°), oxidised (Ag<sub>2</sub>O, Et<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>) to 4-methoxy-*o*-benzoquinone (V), decomp. 88—90° (darkens at 85°). 4-Bromo-*o*-benzoquinone, m.p. 74—75°, is similarly prepared. The potentials of (V) and 3 : 5-dichloro-*o*-benzoquinone are 0.658 and 0.819 volt, respectively.

H. B.

Synthesis and properties of 2 : 7-tetramethyldiaminoanthraquinone, 2 : 7-tetramethyldiamino-10-hydroxy-10-phenylanthrone, and related compounds. D. C. R. JONES and F. A. MASON (J.C.S., 1934, 1813—1817).—Anthraquinone-2 : 7-disulphonic acid with KClO<sub>3</sub> in boiling dil. HCl affords a mixture of the 2 : 7-Cl<sub>2</sub>-derivative (I) and 2-chloroanthraquinone-7-sulphonic acid (*sulphonyl chloride*, m.p. 205°), converted by 33% aq. NHMe<sub>2</sub> at 185—190° into the Na salt of 2-dimethylaminoanthraquinone-7-sulphonic acid (*hydrochloride*), the Na salt of the -6-sulphonic acid and the Na salt of 2-diethyl-

aminoanthraquinone-7-sulphonic acid being similarly prepared. By heating (I) or the 2 : 6-Cl<sub>2</sub>-derivative with the appropriate 33% aq. NHR<sub>2</sub> and Cu powder at 180° are obtained 2-chloro-7-, m.p. 256°, and -6-dimethylamino-, m.p. 258°, and -7-diethylamino-, m.p. 254°, -anthraquinone, but with 50% aq. NHR<sub>2</sub> and Cu in C<sub>5</sub>H<sub>11</sub>·OH at 220° are obtained 2 : 7- (II), m.p. 317° (*Br*<sub>1</sub>-derivative, m.p. 234°), and 2 : 6-tetramethyldiamino-, m.p. 289°, and 2 : 7-tetraethyldiamino-, m.p. 285°, -anthraquinone. With H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> (II) gives a mixture of (NO<sub>2</sub>)<sub>1</sub>-derivatives, m.p. 260—282°, a compound, m.p. 264°, being obtained with warm 50% HNO<sub>3</sub>. Reduction of (II) with Sn-AcOH-conc. HCl gives 2 : 7-tetramethyldiamino-9(or 10)-anthrone (III), m.p. 180° (*Ac* derivative, m.p. 173°), oxidised by aq. FeCl<sub>3</sub> in boiling AcOH to 2 : 7 : 2' : 7'-octamethyltetraamino-9(10) : 9'(10')-dianthrone, m.p. 330°. With MgPhBr in Et<sub>2</sub>O or Na in boiling PhCl-PhMe (II) gives the dye salt from which the carbinol base, 2 : 7-tetramethyldiamino-10-hydroxy-10-phenylanthrone, m.p. 273° (*zincchloride*; hydrochloride in H<sub>2</sub>O has chief absorption band at 650 m $\mu$ , and strong absorption at 450 m $\mu$ ), is derived. Other dyes obtained by replacing PhCl by 1-C<sub>10</sub>H<sub>7</sub>Br, *p*-C<sub>6</sub>H<sub>4</sub>MeBr, *p*-C<sub>6</sub>H<sub>4</sub>Br·OMe, and MeI (*anthranol base*, m.p. 59—71°) are briefly described (no analytical data). With MgPhBr (III) gives 2 : 7-tetramethyldiamino-9(10)-hydroxy-9(10)-phenyldihydroanthracene, m.p. 190°. 3 : 3'-Tetramethyldiaminodiphenylmethane with 40% CH<sub>2</sub>O-15% HCl at 90° gives 2 : 7-tetramethyldiamino-9 : 10-dihydroanthracene, m.p. 198°.

J. W. B.

Scammonium resin. K. H. BAUER and R. JUNGE (Arch. Pharm., 1934, 272, 841—848).—Scammonin (I) with H<sub>2</sub>SO<sub>4</sub> in EtOH or MeOH gives the *Et*, m.p. 46°, b.p. 123°/4 mm., or *Me* ester, m.p. 49—50°, respectively, of scammonic acid (II), C<sub>15</sub>H<sub>30</sub>(OH)·CO<sub>2</sub>H, m.p. 68° (*Ba* salt), and *d*-CHMeEt·CO<sub>2</sub>H (III). With Ba(OH)<sub>2</sub> (I) yields (II) and (III). Scammonic acid (IV) (equiv. wt. about 1060) does not give (II) on acid hydrolysis; it contains 4 monosaccharide residues (I-titration), of which 2 are glucose (V) (quant. fermentation). > 1 mol. of (V) is obtained by hydrolysis of (IV) with emulsin, but no rhodose (VI) is liberated. (IV) is thus probably (II)-(VI)-rhamnose-(V)-(V), the OH of (II) being linked glucosidically. In (I) the CO<sub>2</sub>H groups of (II) and (III) are esterified. Only these ester linkings are affected by Ba(OH)<sub>2</sub>, but H<sub>2</sub>SO<sub>4</sub> hydrolyses also the glucosidic linkings.

R. S. C.

Resinols. III.  $\alpha$ - and  $\beta$ -Amyrone oxides and their derivatives. F. S. SPRING and T. VICKERSTAFF (J.C.S., 1934, 1859—1861).—Oxidation (BzO<sub>2</sub>H in CHCl<sub>3</sub> at 0°) of  $\alpha$ - and  $\beta$ -amyrone gives  $\alpha$ -, m.p. 183°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +125° in CHCl<sub>3</sub>, and  $\beta$ -, m.p. 234°, -amyrone oxides II; those previously described (A., 1934, 776) are now designated  $\alpha$ - and  $\beta$ -amyrone oxides I.  $\beta$ -Amyrin acetate is similarly oxidised to an oxide (I), m.p. 293° [identical with the previously described (A., 1933, 1299) "oxy- $\beta$ -amyrin acetate"], also prepared by acetylation (Ac<sub>2</sub>O-KOAc) of  $\beta$ -amyrin oxide (II) and by Rollett and Bratke's method (A., 1923, i, 588). Hydrolysis (KOH in EtOH-C<sub>6</sub>H<sub>6</sub>) of (I) gives (II), which is also formed by oxidation (BzO<sub>2</sub>H in CHCl<sub>3</sub> at 0°) of  $\beta$ -amyrin; (II) is the "oxy- $\beta$ -amyrin" of Rollett



and Bratke (*loc. cit.*) and Spring (A., 1933, 1299). The "oxy- $\beta$ -amyrone" of Rollett and Bratke (*loc. cit.*) is now termed  $\beta$ -amyrone oxide III. The "oxy- $\alpha$ -amyryn" of Vesterberg (A., 1892, 290) is oxidised ( $\text{CrO}_3$ , AcOH at  $70^\circ$ ) to  $\alpha$ -amyrone oxide I. H. B.

**Digitalis glucosides. VIII. Degradation of the lactone side-chain of digitoxigenin.** W. A. JACOBS and R. C. ELDERFIELD (Science, 1934, 80, 434).—Oxidation of the *sec.*-OH group with  $\text{CrO}_3$  converts  $\alpha$ -digitoxanoldiacid into the keto-acid, *digitoxanon diacid*,  $\text{C}_{22}\text{H}_{34}\text{O}_5$ ; reduction (Clemmensen) yields *digitoxandiacid*,  $\text{C}_{22}\text{H}_{36}\text{O}_4$ . The  $\text{Me}_2$  ester on treatment with a Grignard reagent followed by  $\text{CrO}_3$  oxidation is degraded with the loss of 3 of the original C atoms of the lactone side-chain to the monobasic acid  $\text{C}_{20}\text{H}_{32}\text{O}_2$ , m.p. 219—219.5° (*Me* ester, m.p. 97—98°; *Et* ester, m.p. 76.5—77.5°), which may be identical with  $\alpha$ -tiocholanic acid. L. S. T.

[Pterosantalol.] H. LEONHARDT and W. BUSCKE (Ber., 1934, 67, [B], 1888—1889; cf. A., 1934, 1007).—A question of priority (cf. Raudnitz, *ibid.*, 1223). H. W.

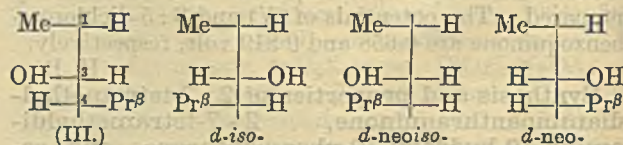
Dehydration of linalool and structure of the terpene obtained thereby. B. A. ARBUSOV and V. S. ABRAMOV (Ber., 1934, 67, [B], 1942—1946).—Linalool is dehydrated by distillation at 150—160°/150—160 mm. in presence of a trace of I, giving 33.7% of a hydrocarbon (I), b.p. 51—51.5°/8.5 mm.  $\alpha$ -Naphthaquinone and (I) in EtOH give 7- $\delta$ -methyl- $\Delta^7$ -pentenyl-5 : 8 : 9 : 10-tetrahydroanthraquinone, m.p. 58.5—59.5°, dehydrogenated to 7- $\delta$ -methyl- $\Delta^7$ -pentenyl-anthraquinone, m.p. 80—81.5°, which is oxidised by  $\text{HNO}_3$  (*d* 1:1) at  $170^\circ$  and subsequently at 200—220° to anthraquinone-2-carboxylic acid, m.p. 285—286° (*Et* ester, m.p. 144°). (I) is therefore identical with myrcene. (I) adds maleic anhydride readily, giving a non-cryst. anhydride, b.p. 186—191°/8 mm., transformed into an acid,  $\text{C}_{14}\text{H}_{20}\text{O}_4$  (II), m.p. 111—113.5°. Ozonisation of (II) gives  $\text{COMe}_2$  and an acid approximating to tetrahydrobenzene-1 : 2-dipropionic acid. Attempted isomerisation of (II) by HBr gave non-cryst. products. It is therefore possible that (I) contains small amounts of an isomeric hydrocarbon of the limonene type which hampers the purification of *isohexenyltetrahydrophthalic* acid and the products of its isomerisation. H. W.

**Syntheses in sesquiterpene series. I.** A. E. BRADFIELD, E. R. JONES, and J. L. SIMONSEN (J.C.S., 1934, 1810—1812).—*l*-Tetrahydrocarvone,  $[\alpha]_{5461} -20.3^\circ$ ,  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ , and Zn in  $\text{C}_6\text{H}_6$  give *Et* 2-hydroxy-2-menthylacetate, b.p. 144—148°/12 mm.,  $[\alpha]_{5461} -18^\circ$  (free acid, m.p. 77—78°), dehydrated ( $\text{KHSO}_4$  at 180—200°) to *Et* 2-menthylideneacetate, b.p. 133—136°/12 mm.,  $[\alpha]_{5461} -59.3^\circ$ , which is reduced ( $\text{H}_2$ , Pd-norit, EtOH) to *Et* 2-menthylacetate (I), b.p. 125—126°/12 mm.,  $[\alpha]_{5461} +7.2^\circ$  [free acid (II), b.p. 162—166°/12 mm. (*p*-toluidide, m.p. 133°)]. Bouveault reduction of (I) affords  $\beta$ -2-menthylethyl alcohol, b.p. 126—131°/12 mm.,  $[\alpha]_{5461} +9.8^\circ$ , the bromide (III), b.p. 126°/12 mm., of which with  $\text{CN}\cdot\text{NaMe}(\text{CO}_2\text{Et})_2$  gives *Et*  $\beta$ -2-menthylethylmethylmalonate, b.p. 193°/12 mm. Hydrolysis ( $\text{MeOH}\text{--KOH}$ ) and subsequent decarboxylation at 165—200° affords

$\gamma$ -2-menthyl- $\alpha$ -methylbutyric acid (IV), b.p. 160—163°/2 mm.,  $[\alpha]_{5461} +25^\circ$  in  $\text{CHCl}_3$  [*p*-toluidide, m.p. 142° (sinters at 139°)]. Traces of a ketonic product are obtained from (IV) and  $\text{P}_2\text{O}_5$  in  $\text{Et}_2\text{O}$  or xylene and from the chloride, b.p. 154—157°/12 mm., and  $\text{AlCl}_3$  in  $\text{CS}_2$ . (III) is converted ( $\text{NaI}$ ,  $\text{COMe}_2$ ) into the iodide and thence ( $\text{EtOH}\text{--KCN}$ ) into  $\beta$ -2-menthylpropionitrile, b.p. 141—146°/14 mm., which with  $\text{EtOH}\text{--H}_2\text{SO}_4$  gives *Et*  $\beta$ -2-menthylpropionate (V), b.p. 145—151°/16 mm.,  $[\alpha]_{5461} +17.3^\circ$ . This and  $\text{MgMeI}$  afford  $\gamma$ -2-menthyl- $\alpha$ -dimethylpropyl alcohol, b.p. 144—147°/17 mm.,  $[\alpha]_{5461} +35^\circ$  in  $\text{CHCl}_3$ , which is dehydrated ( $\text{KHSO}_4$  at  $180^\circ$ ) to a mixture, b.p. 127—128°/19 mm., of  $\delta$ -2-menthyl- $\beta$ -methyl- $\Delta^2$ - and - $\Delta^3$ -butenes, since ozonolysis gives  $\text{CH}_2\text{O}$ ,  $\text{COMe}_2$ , (II), and impure  $\beta$ -2-menthylethyl *Me* ketone, m.p. 127—129°/17 mm. (2 : 4-dinitrophenylhydrazones, m.p. 113°). The mol. refractions of the above compounds are all normal except those of (I) and (V), which show an exaltation of approx. 1 unit. H. B.

**Menthone series. XIII. Relative molecular configurations of menthols and menthylamines.** J. READ and W. J. GRUBB (J.C.S., 1934, 1779—1783).

—The ratios of the reaction velocities of *l*-menthylamine (I) and *d*-neomenthylamine (II) are determined by allowing equimol. mixtures to react with 0.67 mol. of various  $\text{ArCOCl}$  in  $\text{CHCl}_3$ +aq. NaOH at  $25^\circ$  (with stirring); the resulting product is analysed polarimetrically. In each case, (II) reacts somewhat faster than (I). Similar competitive reaction of equimol. mixtures of various pairs of menthols in  $\text{C}_5\text{H}_5\text{N}$  at  $25^\circ$  shows that *l*-menthol (III) reacts much more rapidly than *dl*-neomenthol (IV). With  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$  [which can be used to separate a mixture of (III) and (IV)], the mean relative rates of reaction are: menthols 16.5, *isomenthols* 12.3, *neomenthols* (V) 3.1, *neomenthols* (VI) 1. If these differences are due to steric hindrance, then OH(3) and H(4) must be assigned a *trans*-configuration in (V) and (VI). This conclusion is supported by the formation of a predominance of *neomenthol* (VII) in the reduction of menthone (A., 1934, 413), and by the more rapid esterification (as above) of *trans*- than *cis*-cyclohexane-1 : 2-diol monobenzoate. The production of  $\Delta^3$ -menthene by dehydration of (V) and (VI) [and from the neo-amines and  $\text{HNO}_2$  by way of (VII)] must be due to *trans*-elimination of  $\text{H}_2\text{O}$  between OH(3) and H(4), assuming that H(2) is unaffected. Modified configurations are now assigned as follows :



Analogous configurations ( $\text{NH}_2$  replacing OH in above formulæ) are assigned to the menthylamines; the results with (I) and (II) are, incidentally, at variance.

The following reference compounds are described : *o*-, m.p. 188.5°,  $[\alpha]_{\text{D}} -62.9^\circ$  [all rotations are in  $\text{CHCl}_3$  at  $17.5^\circ$ ], *m*-, m.p. 135°,  $[\alpha]_{\text{D}} -59.4^\circ$ , and *p*-, m.p. 170°,  $[\alpha]_{\text{D}} -53.8^\circ$ , -nitrobenzoyl-, 3 : 5-dinitrobenzoyl-, m.p. 193°,  $[\alpha]_{\text{D}} -60^\circ$ , and  $\beta$ -naphthoyl-, m.p. 180.5°,  $[\alpha]_{\text{D}} -51.9^\circ$ , -*l*-menthylamines; *o*-, m.p. 183°,



$[\alpha]_D +36.5^\circ$ , m., m.p.  $131^\circ$ ,  $[\alpha]_D +18.7^\circ$ , and p., m.p.  $151^\circ$ ,  $[\alpha]_D +16.1^\circ$ , -nitrobenzoyl-, 3:5-dinitrobenzoyl-, m.p.  $164^\circ$ ,  $[\alpha]_D +22.6^\circ$ , and  $\beta$ -naphthoyl-, m.p.  $165^\circ$ ,  $[\alpha]_D +5.4^\circ$ , -d-neomenthylamines. H. B.

[Isomerisation of  $\alpha$ -pinene to an aliphatic terpene (*alloocimene*).] B. A. ARBUSOV (Ber., 1934, 67, [B], 1946; cf. A., 1934, 658).—The identity of the product obtained from  $\alpha$ -pinene with *alloocimene* is confirmed by comparison of the additive compounds formed with maleic anhydride. H. W.

Spontaneous resolution of pinenenitrolbenzylamine. M. DELÉPINE, R. ALQUIER, and (Mlle.) F. LANGE (Bull. Soc. chim., 1934, [v], 1, 1250—1252).—Pinenenitrolbenzylamine crystallises from EtOH in enantiomorphous crystals, which, when separated by hand, have  $[\alpha] +76^\circ$  and  $-91.6^\circ$ , respectively (cf. A., 1889, 1071). R. S. C.

Racemisation in the camphene transformation. S. S. NAMETKIN and A. I. SCHAVRIGIN (J. Gen. Chem. Russ., 1934, 4, 847—855).—Racemisation taking place during the transformation of camphene into isoborneol, or vice versa, and in other analogous cases, is explained by a combination of Nametkin and Brüssov's (A., 1928, 132) and Wagner's rearrangements. R. T.

New methods in stereochemistry. I. Preparation of *d*- and *l*-borneol. II. Resolution of *dl*-menthol. J. CLARK and J. READ (J.C.S., 1934, 1773—1775, 1775—1779).—I. Successive treatment of *d*-borneol (I), m.p.  $200-201^\circ$ ,  $[\alpha]_D +21.5^\circ$  in EtOH, with Na and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  in  $\text{C}_5\text{H}_5\text{N}$  gives impure (III) (below), m.p.  $70-72^\circ$ ,  $[\alpha]_D +34^\circ$  in EtOH, converted ( $\text{SOCl}_2$ ) into the chloride (II), b.p.  $130-135^\circ/13$  mm. (I) and (II) in  $\text{C}_5\text{H}_5\text{N}$  afford (after repeated crystallisation from aq. MeOH and MeOH) *d*-bornyl *d*-bornoxyacetate, m.p.  $72^\circ$ ,  $[\alpha]_D +63.3^\circ$  in  $\text{CHCl}_3$ , hydrolysed (1% EtOH-KOH) to optically pure (I), m.p.  $204.5-205^\circ$ ,  $[\alpha]_D +37.6^\circ$  in PhMe, and *d*-bornoxyacetic acid (III), m.p.  $76^\circ$ ,  $[\alpha]_D +59.1^\circ$  in EtOH (which can be used repeatedly in an improved process). *l*-Borneol (IV), m.p.  $190-197^\circ$ ,  $[\alpha]_D -33.6^\circ$  in EtOH, is similarly converted into crude *l*-bornoxyacetyl chloride, b.p.  $140-143^\circ/17$  mm., and thence into impure, m.p.  $55-60^\circ$ , and pure, m.p.  $72^\circ$ ,  $[\alpha]_D -63.3^\circ$  in  $\text{CHCl}_3$ , *l*-bornyl *l*-bornoxyacetate; subsequent hydrolysis (as above) gives optically pure (IV), m.p.  $205^\circ$ ,  $[\alpha]_D -37.9^\circ$  in PhMe, and *l*-bornoxyacetic acid, m.p.  $76^\circ$ ,  $[\alpha]_D -59^\circ$  in EtOH. The (II) prepared (as above) from a specimen of (I) with  $[\alpha]_D +28.4^\circ$  in EtOH, with *l*-menthol in  $\text{C}_5\text{H}_5\text{N}$  affords optically impure *l*-menthyl *d*-bornoxyacetate, an oil,  $[\alpha]_D -17.9^\circ$  in  $\text{CHCl}_3$ . The corresponding *d*-bornyl, b.p.  $206-208^\circ/0.5$  mm.,  $[\alpha]_D -37.7^\circ$  in  $\text{CHCl}_3$ , and *l*-bornyl *l*-menthoxyacetate,  $[\alpha]_D -76.1^\circ$  in  $\text{CHCl}_3$  [from (IV) and *l*-menthoxyacetyl chloride in  $\text{C}_5\text{H}_5\text{N}$ ], cannot be applied effectively to the purification of impure (I) and (IV).

II. *l*-Menthyl chloroacetate, b.p.  $136^\circ/13$  mm., m.p.  $39-40^\circ$ ,  $[\alpha]_D -77.5^\circ$  in  $\text{CHCl}_3$  [from *l*-menthol (V) and  $\text{CH}_2\text{Cl}\cdot\text{COCl}$  in  $\text{C}_6\text{H}_6$ ], and *l*-menthylamine (VI) at  $140^\circ$  give *l*-menthyl *l*-menthylaminoacetate (VII), m.p.  $63^\circ$ ,  $[\alpha]_D^{19.6} -105.3^\circ$  in  $\text{CHCl}_3$  [*N*-Ac (VIII), *N*-Bz (IX), m.p.  $96^\circ$ , *N*-*p*-nitrobenzoyl, m.p.  $146^\circ$ , and

*N*-3:5-dinitrobenzoyl, m.p.  $170^\circ$ , derivatives; hydrochloride, m.p.  $69^\circ$ ; sulphate (X), m.p.  $191^\circ$ ; oxalate, m.p.  $168.5^\circ$ ]. Et *l*-menthylaminoacetate [from (VI) and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$  in  $\text{C}_6\text{H}_6$ ] has b.p.  $139^\circ/10$  mm.,  $[\alpha]_D -56.1^\circ$  in  $\text{CHCl}_3$ . *dl*-Menthyl chloroacetate, b.p.  $130^\circ/9.5$  mm., and (VI) at  $120-130^\circ$  afford *dl*-menthyl *l*-menthylaminoacetate (XI), a waxy solid,  $[\alpha]_D -43^\circ$  in  $\text{CHCl}_3$ , repeated crystallisation of which from MeOH gives *d*-menthyl *l*-menthylaminoacetate (XII), m.p.  $82^\circ$ ,  $[\alpha]_D -2^\circ$  in  $\text{CHCl}_3$  [*N*-Ac (XIII), m.p.  $95^\circ$ , *N*-Bz, m.p.  $106-107^\circ$ , *N*-*p*-nitrobenzoyl, m.p.  $146^\circ$ , and *N*-3:5-dinitrobenzoyl, m.p.  $131^\circ$ , derivatives; sulphate, m.p.  $176^\circ$ ]. Hydrolysis (1% EtOH-KOH) of (VIII) affords *N*-acetyl-*l*-menthylaminoacetic acid (XIV), m.p.  $154^\circ$ ,  $[\alpha]_D -43.6^\circ$  in  $\text{CHCl}_3$ , which is attacked only slowly by hot 50%  $\text{H}_2\text{SO}_4$  or 10% NaOH; *N*-benzoyl-*l*-menthylaminoacetic acid, m.p.  $118^\circ$ , is similarly obtained from (IX). Hydrolysis of (XII) gives *l*-menthylaminoacetic acid, m.p.  $191^\circ$ ,  $[\alpha]_D -61.5^\circ$  in  $\text{CHCl}_3$ , and *d*-menthol (XV), b.p.  $98^\circ/12$  mm., m.p.  $42-43^\circ$ ,  $[\alpha]_D +50.6$  in EtOH (yield 36.6% based on *dl*-menthol originally used). Crystallisation (from  $\text{COMe}_2$  and EtOH- $\text{COMe}_2$ ) of the sulphate of (XI) gives pure (X) [hydrolysed to (V) in 65.2% yield]; basification of the residue and subsequent crystallisation from MeOH affords (XII) [and thence (XV) in 55.9% yield]. The *N*-Ac derivative of (XI), prepared by acetylation of (XI) or from *dl*-menthol, (XIV), and  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$ , on fractional recrystallisation from MeOH gives (XIII) [and thence (XV) in 7.5% yield]. (XIV) is decomposed by  $\text{SOCl}_2$  in absence of solvent. *l*-Menthylamine H phthalate heated at  $150^\circ/360$  mm. affords *phthal-l*-menthylimide, m.p.  $109^\circ$ ,  $[\alpha]_D -18.9^\circ$  in  $\text{CHCl}_3$ , hydrolysed (5% EtOH-KOH) to *phthal-l*-menthylamic acid, m.p.  $171^\circ$ ,  $[\alpha]_D -71.8^\circ$  in  $\text{CHCl}_3$ , which is readily dehydrated ( $\text{SOCl}_2$ ; HCl) to the imide. H. B.

Chemistry and pharmacology of campherol and related compounds. Y. SAHASHI, K. TAKEUCHI, T. SHIMAMOTO, T. IRI, and T. TAKEBE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 47—109).—Fractionation by  $\text{Et}_2\text{O}$  of additive compounds of "campherol" from campher-fed dog's urine with  $\text{CaCl}_2$  in dry  $\text{C}_6\text{H}_6$  yields *trans*- (but not *cis*-) $\pi$ -(8- or 9-) (20%), 3- (15%), and 5-hydroxycampher (55%). With (I) from rabbit's urine, 3- and 5- but not  $\pi$ -hydroxycampher (II) are present. *p*-Diketocamphane, m.p.  $208-210^\circ$  (uncorr.) (A., 1921, i, 257), prepared by various methods, differs in  $[\alpha]$  with the solvent used. Further details of the prep. of 5-hydroxycampher (A., 1934, 659) are given; with  $\text{Ac}_2\text{O}$  it yields 5-acetoxycampher, b.p.  $149-150^\circ/25$  mm. [semicarbazide, m.p.  $223-224^\circ$  (uncorr.)]. Acetylation of *d*- $\pi$ -bromocampher (J.C.S., 1895, 67, 382) affords *d*- $\pi$ -acetoxycampher, b.p.  $125^\circ/4-5$  mm. [semicarbazide, m.p.  $233^\circ$  (uncorr.)], hydrolysed to (II), m.p.  $234^\circ$ ,  $[\alpha]_D^{17} +64^\circ$  in abs. EtOH. Oxidation of (II) gives  $\pi$ -apocampher-7-carboxylic acid, m.p.  $246^\circ$  (uncorr.), and -aldehyde, m.p.  $204-205^\circ$  (uncorr.) (semicarbazide, decomp.  $>300^\circ$ ).  $\beta$ -(10)-Bromocampher (J.C.S., 1902, 81, 1462) acetylates to  $\beta$ -acetoxycampher, b.p.  $128-130^\circ/3-4$  mm. [semicarbazide, m.p.  $163^\circ$  (uncorr.)], converted by



EtOH-KOH into  $\beta$ -hydroxycamphor (III), m.p. 216° (uncorr.) [semicarbazide, decomp. 213° (uncorr.)] (cf. J.C.S., 1913, 103, 63). (III) with AcOH-CrO<sub>3</sub> at low temp. yields  $\beta$ -apocamphor-1-aldehyde, m.p. 203—205° (uncorr.) [semicarbazide, m.p. 247° (uncorr.); disemicarbazide, m.p. 240° (uncorr.)], and, mainly, the  $\beta$ -hydroxycamphor ester of ketopinic acid, m.p. 164°. The cardiotoxic action and toxicity of camphor, 3-, 5-,  $\pi$ -, and 10-hydroxycamphor,  $\pi$ -camphorcarboxylic acid, etc. indicate that (III) is the only compound to exhibit stimulating action without any initial systolic depression. The bearing of the data on the action of "vitacamphor" (cf. Tamura *et al.*, B., 1932, 960; A., 1930, 955; 1932, 948) is discussed.

F. O. H.

**Active racemates. Fusion curve of mixtures of  $d$ - $\alpha$ -chloro- and  $\alpha$ -bromo-camphor- $\pi$ -sulphonamide.** M. DELÉPINE, L. LABRO, and (MLLE.) F. LANGE (Bull. Soc. chim., 1934, [v], 1, 1252—1255).— $d$  and  $l$ - (I)  $\alpha$ -Bromocamphor- $\pi$ -sulphonyl chloride, m.p. 140° (lit. 136—137°), [ $\alpha$ ]<sub>D</sub> 130—131° in CHCl<sub>3</sub>, give a *racemate*, m.p. 121° (eutectic m.p. 116.5°). (I) and  $d$ - $\alpha$ -chlorocamphor- $\pi$ -sulphonyl chloride, [ $\alpha$ ]<sub>D</sub> +111—112° in CHCl<sub>3</sub>, are isomorphous and give an "active racemate" (II), [ $\alpha$ ]<sub>D</sub> -18.8° (calc. 18°).  $d$ - (III) and  $l$ - $\alpha$ -Chloro-, m.p. 149—150°, and  $\alpha$ -bromocamphor- $\pi$ -sulphonamide (IV), m.p. 145—146°, give *racemates*, m.p. 154.5° and 175° with eutectic m.p. 135° and 137.5°, respectively. (III) and  $l$ - (IV) give an "active racemate" (V), m.p. 160.5° (eutectic m.p. 132°), [ $\alpha$ ] -18°, also obtained from (II). (V) is less sol. than its components. "Active" and ordinary racemates are thus strictly analogous. R. S. C.

**Caryophyllenes.** I. W. C. EVANS, G. R. RAMAGE, and J. L. SIMONSEN (J.C.S., 1934, 1806—1810).—Blue  $\beta$ -caryophyllene nitrosite (Deussen and Lewisohn, A., 1907, i, 945) is reduced (Na, EtOH) to aminodihydro- $\beta$ -caryophyllene (I) (Semmler and Mayer, A., 1912, i, 120), b.p. 138—143°/2 mm. [3:5-dinitrobenzoate, m.p. 172—173° (softens at 163°)], which is probably a mixture of stereoisomerides. (I) is reduced (H<sub>2</sub>, Pd-norit, EtOH) to aminotetrahydro- $\beta$ -caryophyllene, b.p. 140—142°/12 mm., [ $\alpha$ ] -29.1°, converted by HNO<sub>3</sub> and subsequent dehydration (KHSO<sub>4</sub> at 190°) into dihydro- $\beta$ -caryophyllene, b.p. 118—121°/14 mm., [ $\alpha$ ]<sub>5461</sub> -47.15°, which differs from the isomeric dihydrocaryophyllenes of Deussen (A., 1928, 70). Humulene ( $\alpha$ -caryophyllene) nitrosochloride (II) and boiling C<sub>3</sub>H<sub>5</sub>N give a mixture of products from which a nitrosohumulene (III), m.p. 126—127°, separates. (III) [which is probably identical with the compound, m.p. 128—129°, obtained by Deussen *et al.* (A., 1909, i, 813) from (II) and NaOEt or NaOPr] is reduced (Na, EtOH) to aminodihydrohumulene, b.p. 141—142°/11 mm., [ $\alpha$ ]<sub>5461</sub> -0.64° (hydrochloride, m.p. 257°; Ac derivative, m.p. 142°; picrolonate, m.p. 232°), which is apparently homogeneous. Oxidation [KMnO<sub>4</sub>, COMe<sub>2</sub> followed by HNO<sub>3</sub> ( $d$  1.165) on acid fraction] of  $\gamma$ -caryophyllene, conversion of the acidic product into Me ester, fractionation, and subsequent hydrolysis gives *as*-dimethylsuccinic, *cis*-norcaryophyllenic (IV), C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>, m.p. 125—127° (sinters at 118°), [ $\alpha$ ]<sub>5461</sub> +137° in CHCl<sub>3</sub>, and *cis*-caryophyllenic acid,

C<sub>9</sub>H<sub>14</sub>O<sub>4</sub>, m.p. 80—81° (sinters at 76°), [ $\alpha$ ]<sub>5161</sub> +13.56° in CHCl<sub>3</sub> (cf. Ruzicka *et al.*, A., 1931, 735). (IV) affords a liquid anhydride, is stable to HCl at 120°, and is converted by successive treatment with PCl<sub>5</sub>, Br (at 120°), MeOH, and EtOH-KOH into *dehydro-norcaryophyllenic acid*, m.p. 193°. (IV) is probably a methylcyclopentanedicarboxylic acid. H. B.

**Structure of [the compound] C<sub>7</sub>H<sub>12</sub>O<sub>2</sub> from the hydrogenation of furylacraldehyde.** M. FARLOW, H. E. BURDICK, and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 2498—2499).—The compound previously described (A., 1934, 416) as 1:5-dioxaoctahydroindene is (probably) 1:9-dioxa-5-spiroonane,

$$\begin{array}{c} \text{CH}_2\text{-CH}_2 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{-CH}_2 \\ | \quad | \\ \text{O} \quad \text{O} \end{array}$$
 (cf. Fittig and Strom, A., 1892, 813), since it is converted by HI into di- $\gamma$ -iodopropyl ketone, which is reduced (Zn, EtOH) to COPr<sub>2</sub> and with piperidine gives di- $\gamma$ -piperidinopropyl ketone. H. B.

**Synthetical experiments in chromone group.** XIII. Hydroxy-2-styrylchromones. K. C. GULATI, S. R. SETH, and K. VENKATARAMAN. XIV. Action of sodamide on 1-acyloxy-2-acetonaphthones. H. S. MAHAL and K. VENKATARAMAN. XV. Synthesis of formnonetin, daidzein, and  $\beta$ -baptigenin. H. S. MAHAL, H. S. RAI, and K. VENKATARAMAN (J.C.S., 1934, 1765—1767, 1767—1769, 1769—1771).—XIII. 7-Methoxy-2-methylchromone, conveniently prepared from 2-hydroxy-4-methoxyacetophenone, Na, and EtOAc, is converted into 7-methoxy-, m.p. 189—190°, and 7:4'-dimethoxy-, m.p. 144°, -2-styrylchromone. Resacetophenone, CH<sub>2</sub>PhCl, and anhyd. K<sub>2</sub>CO<sub>3</sub> in COMe<sub>2</sub> give 2-hydroxy-4-benzoyloxyacetophenone, m.p. 111°, converted (method; A., 1932, 520) into 7-benzoyloxy-2-methyl- (I), m.p. 137°, and -2-styryl- (II), m.p. 161°, -chromone. (II) is debenzylated (AcOH-HBr) to 7-hydroxy-2-styrylchromone, m.p. 239°. (I) and *p*-CH<sub>3</sub>Ph·O·C<sub>6</sub>H<sub>4</sub>·CHO (III) give the dibenzyl ether, m.p. 176°, of 7:4'-dihydroxy-2-styrylchromone, m.p. 332° (diacetate, m.p. 183°). Contrary to Sen and Ghosh (J.C.S., 1920, 117, 61), phloracetophenone (IV), m.p. (anhyd. or +H<sub>2</sub>O), 219° [2:4-dinitrophenylhydrazine, m.p. 280° (decomp.); Ac<sub>3</sub> derivative, m.p. 103°], is not obtained from *s*-C<sub>6</sub>H<sub>3</sub>(OH)<sub>3</sub>, AcOH, and ZnCl<sub>2</sub>; a compound, C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>, m.p. > 290° (decomp.), is formed. (IV), CH<sub>2</sub>PhCl, and K<sub>2</sub>CO<sub>3</sub> in COMe<sub>2</sub> give (probably) 2:6-dihydroxy-4-benzoyloxy-3-benzylacetophenone, m.p. 121°, since it does not undergo a smooth styryl ketone or  $\beta$ -diketone condensation. (IV) and Ac<sub>2</sub>O-NaOAc afford 5:7-dihydroxy-3-acetyl-2-methylchromone (V), m.p. 252°, and its diacetate, m.p. 131°. Hydrolysis (10% Na<sub>2</sub>CO<sub>3</sub>) of (V) and subsequent acidification gives 5:7-dihydroxy-2-methylchromone, m.p. 279° (lit. 290°) (7-benzyl ether, m.p. 148°, which does not react with PhCHO); the preceding results differ from those of Canter *et al.* (A., 1931, 962). 7-Benzoyloxy-5-methoxy-2-methylchromone, m.p. 156°, and (III) give a substance, C<sub>32</sub>H<sub>26</sub>O<sub>5</sub>, m.p. 181°.

XIV. 1-Hydroxy- $\beta$ -naphthyl *o*-methoxystyryl ketone, m.p. 155° [acetate, m.p. 93°; dibromide, m.p. 157°, converted by EtOH-KOH into a compound, C<sub>20</sub>H<sub>14</sub>O<sub>3</sub>, m.p. 252° (decomp.)], is prepared from 2:1-C<sub>10</sub>H<sub>6</sub>·Ac·OH (VI) and *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO in EtOH-



KOH. 2:1-C<sub>10</sub>H<sub>6</sub>Ac·OBz and NaNH<sub>2</sub> in Et<sub>2</sub>O at > 22° followed by decomp. of the solid reaction product with dil. AcOH give 1-hydroxy-β-naphthyl phenacyl ketone, m.p. 147°, converted by conc. H<sub>2</sub>SO<sub>4</sub> at room temp. into α-naphthaflavone, m.p. 157°. 2-Acetyl-α-naphthyl o-methoxybenzoate, m.p. 115° [from (VI) and o-OMe·C<sub>6</sub>H<sub>4</sub>·COCl in C<sub>5</sub>H<sub>5</sub>N], is similarly converted into 1-hydroxy-β-naphthyl o-methoxyphenacyl ketone, m.p. 113°, and thence by EtOH-conc. H<sub>2</sub>SO<sub>4</sub> into 2'-methoxy-α-naphthaflavone, m.p. 164° [sulpho-derivative, m.p. 326° (decomp.), formed using conc. H<sub>2</sub>SO<sub>4</sub> alone]. 2-Acetyl-α-naphthyl 2:4-dimethoxy-, m.p. 126°, and 3:4:5-trimethoxy-, m.p. 143°-benzoates similarly give 1-hydroxy-β-naphthyl 2:4-dimethoxy-, m.p. 133°, and 3:4:5-trimethoxy-, m.p. 142°, phenacyl ketone, respectively, convertible into 2':4'-dimethoxy-, m.p. 214°, and 3':4':5'-trimethoxy-, m.p. 224°, α-naphthaflavone, respectively.

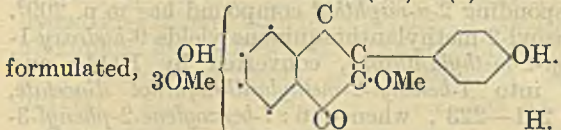
XV (cf. A., 1934, 660, 1107). 2-Hydroxy-4-benzyl-oxyphehyl p-methoxybenzyl ketone, m.p. 103° [from the 2:4-(OH)<sub>2</sub>-derivative, CH<sub>2</sub>PhCl, and anhyd. K<sub>2</sub>CO<sub>3</sub> in COMe<sub>2</sub>], HCO<sub>2</sub>Et, and Na give the benzyl ether, m.p. 182°, of 7-hydroxy-4'-methoxyisoflavone (formononetin) (VII), m.p. 257° (cf. Wessely et al., A., 1933, 614). The Ac derivative, m.p. 170° (lit. 164—165°), of (VII) and HI (d 1.7) in Ac<sub>2</sub>O at 140° afford 7:4'-dihydroxyisoflavone (daidzein), m.p. 322° (darkens > 310°) [Ac<sub>2</sub> derivative, m.p. 187° (sinters at 184°) (lit. 182°)] (cf. Baker et al., A., 1933, 510; Wessely et al., loc. cit.). 2-Hydroxy-4-benzyl-oxyphehyl 3:4-methylendioxybenzyl ketone, m.p. 94° (sinters at 86°) [from ψ-baptigenetin (Späth and Schmidt, A., 1929, 1458), CH<sub>2</sub>PhCl, and K<sub>2</sub>CO<sub>3</sub> in COMe<sub>2</sub>], HCO<sub>2</sub>Et, and Na give the benzyl ether, m.p. 168°, of 7-hydroxy-3':4'-methylendioxyisoflavone (ψ-baptigenin), m.p. 292—293° (darkens > 288°) [lit. 298—299° (vac.) and 303—304°] [Ac derivative, m.p. 176° (lit. 173°)]. H. B.

**Chromone chlorides and dichromylenes.** A. SCHÖNBERG and S. NICKEL (Ber., 1934, 67, [B], 1795—1798; cf. A., 1931, 1305).—8-Methylflavone is readily converted by (·COCl)<sub>2</sub> into the corresponding chloride, which with Cu powder in boiling PhMe affords 2:2-diphenyl-8:8'-dimethyldichromylene, m.p. 240°. Similarly, 8-methoxy-1-thioflavone successively yields the chloride and 8:8'-dimethoxy-2:2'-diphenyl-1:1'-dithiodichromylene, m.p. 292—293°. Reduction of xanthone in AcOH containing Ac<sub>2</sub>O and NaClO<sub>4</sub> by activated Zn wool gives the diperchlorate of 9:9'-dihydroxydixanthyl, converted by MgPhBr or LiPh in Et<sub>2</sub>O into dixanthylene. H. W.

**Components of *Matteucia orientalis*. Optically active flavanones.** S. FUJISE and T. KUBOTA (Ber., 1934, 67, [B], 1905—1908; cf. A., 1933, 832).—The difficulties met in the attempted identification of demethoxymatteucinol (I) with synthetic 5:7-dihydroxy-6:8-dimethylflavanone (II) are explained by the observation that the natural material is optically active. Matteucinol (IV) (improved prep. from the roots of *M. orientalis*) has m.p. 175.5°, [α]<sub>D</sub><sup>25</sup> —39.47° in COMe<sub>2</sub> (Me ether, m.p. 103—103.5°, [α]<sub>D</sub><sup>14</sup> —7.80° in COMe<sub>2</sub>), whilst the data, m.p. 202.5°, [α]<sub>D</sub><sup>25</sup> —50.00° in COMe<sub>2</sub>, and m.p. 112—112.5°, [α]<sub>D</sub><sup>11</sup> —22.47°, respectively, are recorded for (I) and its Me ether. (I) gives an oxime, m.p. 210—211°, [α]<sub>D</sub><sup>25</sup> —62.1° (corresponding

r-oxime, m.p. 232°), whilst the oxime of (III) has m.p. 202°, [α]<sub>D</sub><sup>18</sup> —33.1° (corresponding r-oxime, m.p. 228—229°). After being racemised by conc. H<sub>2</sub>SO<sub>4</sub> the natural materials and their Me ethers are identical with the corresponding synthetic substances. H. W.

**New flavone dye.** W. KARRER (Helv. Chim. Acta, 1934, 17, 1560—1565).—Thapsin (I), C<sub>19</sub>H<sub>18</sub>O<sub>8</sub>, m.p. 224°, is obtained as by-product of the extraction of digitoxin from (?) *Digitalis thapsi*, L. It contains 2 OH and 4 OMe. (I) is converted by Me<sub>2</sub>SO<sub>4</sub> and NaOH into dimethylthapsin, prisms, m.p. 130°, or rhombohedra, m.p. 129°, transformed by boiling KOH-EtOH into p-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and 2-hydroxy-3:4:5:6:ω-pentamethoxyacetophenone (II), m.p. 66—67°. Since ethylation of (I) gives diethylthapsin, dimorphous, m.p. 130°, hydrolysed to p-OEt·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and 2-hydroxytetramethoxyethoxyacetophenone (III), m.p. 63—64°, the C<sub>6</sub>H<sub>6</sub> nucleus carries only 1 OH. Methylation of (II) yields 2:3:4:5:6:ω-hexamethoxyacetophenone, b.p. 210°/14 mm., oxidised by KMnO<sub>4</sub> to (impure) pentamethoxyphenylglyoxylic acid, whilst similar treatment of (III) leads to pentamethoxyethoxyacetophenone, b.p. 208°/14 mm., oxidised to an acid which differs from (IV). (I) is therefore



H. W.

**Dibenzfuran [diphenylene oxide]. III. Nuclear substitutions.** H. GILMAN, G. E. BROWN, W. G. BYWATER, and W. H. KIRKPATRICK (J. Amer. Chem. Soc., 1934, 56, 2473—2477).—2-Acetamido- (I) or 2-diacetamido- (II) diphenylene oxide and Br (1 mol.) in AcOH give 3-bromo-2-acetamidodiphenylene oxide, m.p. 194°; the free base, m.p. 129° (hydrochloride, decomp. 236°), is de-aminated to 3-bromodiphenylene oxide (III) and converted by aq. NH<sub>3</sub>+CuBr at 190° into 2:3-diaminodiphenylene oxide (IV) (quin-oxaline, m.p. 184—185°). (I) or (II) and HNO<sub>3</sub> in AcOH afford 3-nitro-2-acetamidodiphenylene oxide, m.p. 196° [described by Borsche and Schacke (A., 1924, i, 161) as the Ac<sub>2</sub> derivative], which on hydrolysis and reduction gives (IV). 3-Aminodiphenylene oxide is prepared from the 3-Br-derivative (V), aq. NH<sub>3</sub>, and CuCl at 200—210°; its Ac<sub>2</sub> derivative (VI) and Br in AcOH give the Ac<sub>1</sub> derivative, m.p. 240—241°, of 2-bromo-3-aminodiphenylene oxide, m.p. 172—173°, also convertible [as for (V)] into (IV). (VI) and fuming HNO<sub>3</sub> in AcOH afford 2-nitro-3-acetamidodiphenylene oxide (Brumberg, Diss., Göttingen, 1925), which on hydrolysis and reduction gives (IV). Diphenylene oxide (VII) and Cl<sub>2</sub> (1 mol.) in AcOH at 60° afford the 3-Cl-derivative, also prepared from (VII) and PCl<sub>5</sub>; with Cl<sub>2</sub> (excess) in CCl<sub>4</sub> at 40°, the 3:6-Cl<sub>2</sub>-derivative, m.p. 185°, is formed. (VII) and I (1 mol.) in conc. HNO<sub>3</sub>+CHCl<sub>3</sub> give the 3-I-derivative, m.p. 112°; with 2 mols. of I in the hot, the 3:6-I<sub>2</sub>-derivative, m.p. 173°, results. 2-Nitrodiphenylene oxide and Br in AcOH at 70° give 3-bromo-7-nitrodiphenylene oxide (VIII), m.p. 250.5—251.5°, also prepared [together with a little of the 2NO<sub>2</sub>-isomeride, m.p. 154.5—155.5°], from (III) and HNO<sub>3</sub> (d 1.52) in AcOH. 3:7-Diaminodiphenylene oxide is obtained by reduc-



tion of 7-nitro-3-aminodiphenylene oxide [from (VIII), aq.  $\text{NH}_3$ , and  $\text{CuCl}$  at 208—210°] or from 3-bromo-7-aminodiphenylene oxide, m.p. 133—134°, aq.  $\text{NH}_3$ , and  $\text{CuBr}$  at 205°. 2-Bromodiphenylene oxide and  $\text{HNO}_3$  (*d* 1.5) in  $\text{AcOH}$  give (probably) the 7- $\text{NO}_2$ -derivative, m.p. 251°, converted by aq.  $\text{NH}_3 + \text{CuBr}$  at 200° into (probably) 7-nitro-2-aminodiphenylene oxide, m.p. 133°.

H. B.

Supposed aryloxyperihydrofurananthroxyls as derivatives of benzoylene- $\beta\beta'$ -benzofuran. II. R. SCHOLL and J. DONAT (Ber., 1934, 67, [B], 1919—1922; cf. A., 1933, 508).—Re-examination has been made of the following "aryloxyperihydrofurananthroxyls," now shown to be derivatives of benzoylene- $\beta\beta'$ -benzofuran. Anthraquinone-1-carboxyl chloride and  $\text{PhOMe}$  in presence of  $\text{FeCl}_3$  at 130° give 1-anisoylanthraquinone, transformed by  $\text{Na}_2\text{S}_2\text{O}_4$  in boiling aq.  $\text{EtOH}$  into 9-hydroxy-1-anisoylanthrone, which yields 6:7-benzoylene-2-anisyl- $\beta\beta'$ -benzofuran, m.p. 182°, with conc.  $\text{H}_2\text{SO}_4$ . 1-*p*-Tolylanthraquinone, m.p. 205—206°, similarly affords 6:7-benzoylene-2-*p*-tolyl- $\beta\beta'$ -benzofuran, m.p. 186°. Diphenyl anthraquinonyl ketone, m.p. 234—235°, yields 6:7-benzoylene-2-*p*-diphenyl- $\beta\beta'$ -benzofuran, m.p. 220°. The corresponding 2- $\alpha$ -naphthyl compound has m.p. 209°. 1-Benzoyl-2-methylanthraquinone yields 9-hydroxy-1-benzoyl-2-methylanthrone, converted by  $\text{KOAc}$  and  $\text{Ac}_2\text{O}$  into 1-benzoyl-2-methylanthraquinol diacetate, m.p. 221—223°, whence 6:7-benzoylene-2-phenyl-3-methyl- $\beta\beta'$ -benzofuran, m.p. 206°.

H. W.

Rotenone. XXX. Non-crystalline constituents of derris root. H. L. HALLER and F. B. LAFORGE (J. Amer. Chem. Soc., 1934, 56, 2415—2419).—The material extracted by light petroleum (b.p. 30—60°) from the ground root is freed from toxicarol by extraction of its  $\text{Et}_2\text{O}$  solution with aq. 5%  $\text{KOH}$ ; the  $\text{Et}_2\text{O}$  solution is then conc. and kept at 0°, when rotenone (I) separates. Evaporation of the residual solution gives amorphous "deguelin concentrate" (II), which contains 60—63% of (I) + deguelin (III) [as determined by Gross and Smith's method (A., 1934, 1017)]. Treatment of (II) with  $\text{MeOH-KOH}$  in  $\text{H}_2$  affords 38.2% of optically inactive (III); successive treatment of the residue (after extraction of its  $\text{Et}_2\text{O}$  solution with 2%  $\text{KOH}$ ) with air in  $\text{MeOH-KOH}$  and  $\text{EtOH-H}_2\text{SO}_4$  gives (mainly) dehydrorotenone, some dehydrodeguelin, and a little of a compound,  $\text{C}_{19}\text{H}_{14}\text{O}_6$ , m.p. 240—250°. Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOAc}$ ) of (II) affords tetrahydroroteneone (dihydroroteneonic acid), 19.1% of  $\beta$ -dihydroroteneone (dihydrodeguelin) (IV),  $[\alpha]_D^{20} - 104^\circ$  in  $\text{C}_6\text{H}_6$ , and (after treatment with  $\text{MeOH-KOH}$  in  $\text{H}_2$ ) about 15% of optically inactive (IV). (II), therefore, contains < 19% of optically active (III). The *l*-deguelin of Takei *et al.* (A., 1934, 194) is probably *dl*-deguelin contaminated with a little (I). Isoroteneone (V),  $[\alpha]_D^{20} - 74.6^\circ$  in  $\text{C}_6\text{H}_6$ , +13° in dioxan, is racemised by  $\text{EtOH-KOH}$  in  $\text{H}_2$ ; (V) obtained by hydrolysis ( $\text{EtOH-H}_2\text{SO}_4$ ) of acetylisorotenone (A., 1932, 950) has  $[\alpha]_D^{20} - 21.1^\circ$  in  $\text{C}_6\text{H}_6$ .

H. B.

Hydrogenation of derivatives of pyridine. H. ADKINS, L. F. KUICK, M. FARLOW, and B. WOJCIK (J. Amer. Chem. Soc., 1934, 56, 2425—2428).— $\text{C}_5\text{H}_5\text{N}$  and the following derivatives of  $\text{C}_5\text{H}_5\text{N}$  are reduced ( $\text{H}_2$  (150—300 atm.); usually Raney Ni; occasionally

no solvent, but usually in  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ , dioxan, or methylcyclohexane; 100—200°] to the corresponding piperidines: 2-Me, 2- and 4-Ph, 2- $\text{CH}_2\text{Ph}$ , 2- $\text{CH}_2\text{Ph}\cdot\text{CH}_2$ ; 3- $\text{CO}_2\text{Et}$ , 3- $\text{CO}_2\text{Bu}$ , 2: 6-Me<sub>2</sub>, 2: 6-Ph<sub>2</sub>, 2: 6-di- $\beta$ -phenylethyl, 6-Ph-2-Me, 2- $\gamma$ -phenylpropyl, 2- $\delta$ -phenylbutyl, 2: 3- and 2: 6-( $\text{CO}_2\text{Et}$ )<sub>2</sub>, 3- $\text{CO}_2\text{Et}$ -2: 6-Me<sub>2</sub>, and 3-Ac (which gives 3-ethyl- and 3- $\alpha$ -hydroxyethyl-piperidines); the 2: 6-derivatives are reduced most readily. Reduction of  $\text{Et}$  pyridine-3-carboxylate in  $\text{EtOH}$  gives  $\text{Et}$  piperidine-3-carboxylate, b.p. 79—80°/4 mm. (cf. McElvain and Adams, A., 1924, i, 417), and some of its 1-Et derivative, b.p. 113—116°/19 mm. (hydrochloride, m.p. 143°).  $\text{Et}$  piperidine-2: 3-dicarboxylate [hydrochloride, m.p. 200—202° (decomp.)] has b.p. 119—121°/3 mm. (cf. Clemo *et al.*, A., 1932, 178).  $\text{Et}$  2: 6-dimethylpiperidine-3-carboxylate, b.p. 93—95°/10 mm. (hydrochloride, m.p. 162—163°), and *Bu* pyridine-3-carboxylate, b.p. 119—120°/8 mm., and piperidine-3-carboxylate, b.p. 83—86°/2 mm., are new. Reduction ( $\text{H}_2$ ,  $\text{Cu-Cr}$  oxide,  $\text{EtOH}$  at 250°) of  $\text{C}_5\text{H}_9\text{N}[\text{CH}_2]_n\text{CO}_2\text{Et}$  to  $\text{C}_5\text{H}_{10}\text{N}[\text{CH}_2]_n\text{CH}_2\text{OH}$  occurs when  $n=1$  or 4, to a much smaller extent when  $n=3$ , but not when  $n=2$ .

H. B.

2-Aminopyridine series. II. Action of phthalic anhydride and salicyloyl chloride on 2-aminopyridine. K. FEIST and J. SCHULTZ (Arch. Pharm., 1934, 272, 785—791; cf. A., 1934, 417).—2-Aminopyridine (I) and  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  at 180° give the *H* phthalate, m.p. 120°, and *N*-2-pyridylphthalimide (II), m.p. 225° (perbromide,  $\text{XBr}_2$ , m.p. 162°; periodide,  $\text{XI}_3$ , m.p. 128°), the constitution of which is proved (i) by its resistance to hydrogenation, and (ii) by its formation also from  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{S}$ ,  $o\text{-C}_6\text{H}_4(\text{COCl})_2$ , or  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NH}$ . (II) and cold, aq.  $\text{NaOH}$  give *N*-2-pyridylphthalamic acid, m.p. 169° (*Na* salt, m.p. > 300°), which cannot be esterified, but regenerates (II) at the m.p. or when heated in 95%  $\text{EtOH}$  or  $\text{AcCl}$ . 6-Amino- $\alpha$ -picoline gives similarly the *H* phthalate, m.p. 168°, and *N*-6- $\alpha$ -picolinophthalimide, m.p. 192.5°.  $o\text{-OAc-C}_6\text{H}_4\text{COCl}$  and (I) in  $\text{Et}_2\text{O}$  give a mixture of 2-salicyloyl-, m.p. 203°, and 2-acetylsalicyloyl-amidopyridine, m.p. 140°, indifferent to hydrogenation.

R. S. C.

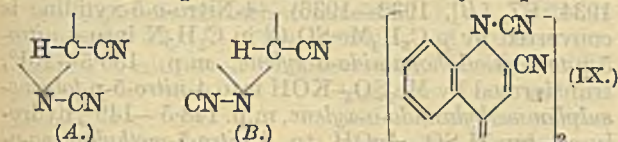
Amino-acids and related compounds. VIII. Electrolytic oxidation of histamine and histidine. Y. TAKAYAMA and H. OEDA (J. Chem. Soc. Japan, 1934, 55, 649—654; cf. A., 1933, 1127).—On electrolytic oxidation, histamine yields  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{CO}(\text{NH}_2)_2$ , and  $\beta$ -alanine; histidine (I) similarly yields  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_2(\text{CO}_2\text{H})_2$  (II), and a melanin-like substance. Aspartic acid is suggested as an intermediate in the formation of (II) from (I).

CH. ABS. (r)

Quinoline dicyanide. Stereochemistry of ter-valent nitrogen. O. MUMM, H. LUDWIG, and (in part) D. H. LU and R. RADENHAUSEN (Annalen, 1934, 514, 34—60).—6-Methoxyquinoline (I) (2 mols.),  $\text{CNBr}$  (1 mol.), and anhyd.  $\text{HCN}$  (rather > 2 mols.) in cold  $\text{C}_5\text{H}_6$  give (I) hydrobromide and a dicyanide (II),  $\text{C}_7\text{H}_7\text{ON}_2$ , m.p. 85—87°, which is converted by dil.  $\text{EtOH-NH}_3$  into an isomeride, m.p. 169—170°; 3-methylquinoline (III) similarly affords analogous dicyanides, m.p. 139° (IV) and 125° (V), respectively. Dicyanides could not be obtained from 2- and 4-



methyl- or 2- and 4-phenyl-quinolines; the last-named gives 2-hydroxy-1-cyano-4-phenyl-1:2-dihydroquinoline, m.p. 150° (cf. below).  $\alpha$ -Naphthquinoline similarly affords (at 150°) the 4-CN-derivative, m.p. 154—156°, hydrolysed (conc. HCl at 150°) to  $\alpha$ -naphthquinoline-4-carboxylic acid, m.p. 278° (decomp.), which is oxidised (alkaline  $\text{KMnO}_4$ ) to pyridine-2:3:4-tricarboxylic acid (VI). 4-Cyano-2-phenyl-, m.p. 138°, and 4-cyano-8-methyl-quinoline, m.p. 140—141° [corresponding acid, m.p. 276° (decomp.; darkens at 260°), also oxidised to (VI)], are similarly prepared from 2-phenyl- and 8-methyl-quinoline, respectively. The primary (more fusible) (VII) and *sec.* (less fusible) (VIII) quinoline dicyanides (A., 1914, i, 574) are both hydrolysed (conc. HCl at 150°) to quinoline-2-carboxylic acid [hydrochloride (+ $\text{H}_2\text{O}$ ), m.p. 202°]; the  $\beta$ -naphthquinoline dicyanides (*loc. cit.*) similarly afford  $\beta$ -naphthquinoline-2-carboxylic acid (hydrochloride). (VII) and (VIII) are considered to be *cis.* (A) and *trans.* (B) forms of 1:2-dicyano-1:2-dihydroquinoline. (VII) or (VIII) and I in  $\text{EtOH}-\text{C}_5\text{H}_5\text{N}$  give the compound (IX), m.p. 347°, and a little 2-cyanoquinoline



(X). (IX) and Br in AcOH afford 2:2'-dicyano-4:4'-diquinolyl, m.p. 306°, hydrolysed (conc. HCl at 130°) to 4:4'-diquinolyl-2:2'-dicarboxylic acid (+ $2\text{H}_2\text{O}$ ), m.p. 232° [diamide, m.p. 355—356°, obtained from (IX) and cold conc.  $\text{H}_2\text{SO}_4$ ], which when heated at 200—210° gives 4:4'-diquinolyl picrate, m.p. 262—263° (Clemons and Perkin, A., 1924, i, 1103). (IX) and conc.  $\text{HNO}_3$  in AcOH afford 2:2'-diketo-1:1'-dicyano-1:2:1':2'-tetrahydro-4:4'-diquinolyl, m.p. 334°, hydrolysed (conc. HCl at 130°) to 2:2'-dihydroxy-4:4'-diquinolyl, m.p. 397—399°. (VII) or (VIII) and I in  $\text{CHCl}_3$ +anhyd. NaOAc give (X). (VII) heated with AcOH affords quinoline (XI); similarly, (II) gives (I), (IV) yields (III), but (VIII) and (V) furnish 2-keto-1:2:3:4-tetrahydroquinoline (cf. *loc. cit.*) and its 3-Me derivative, m.p. 130°, respectively. Conversion of (VII) into (VIII) can be effected with  $\text{NH}_2\text{R}$ ,  $\text{NHR}_2$ , or  $\text{NR}_3$  but not with  $\text{EtOH}-\text{KOH}$  or acids; the change (VIII)  $\rightarrow$  (VII) has not been realised.

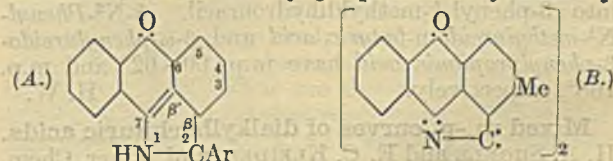
(XI) (1 mol.) and  $\text{CNBr}$  (1 mol.) in moist  $\text{Et}_2\text{O}$  or  $\text{C}_6\text{H}_6$  give 2-hydroxy-1-cyano-1:2-dihydroquinoline (XII), m.p. 117°; in the absence of moisture di-(1-cyano-1:2-dihydro-2-quinolyl) ether (XIII), m.p. 150°, results. (XII) and (XIII) are converted by dil. HCl or 20%  $\text{HClO}_4$  into (XI) and by 70%  $\text{HClO}_4$  into 1-cyanoquinolinium perchlorate, m.p. 194°. The following are similarly prepared: 2-hydroxy-1-cyano-6-methyl-1:2-dihydroquinoline, m.p. 120°, the corresponding ether, m.p. 139°, and perchlorate, m.p. 191°; 2-hydroxy-1-cyano-1:2-dihydro- $\beta$ -naphthquinoline (XIV), m.p. 121°, the corresponding ether (XV), m.p. 132°, and perchlorate, m.p. 200°; hydroxy-N-cyano-dihydroacridine and the corresponding ether. (XV) heated with the appropriate AlkOH gives the Me, m.p. 159°, Et, m.p. 128.5°, and Pr, m.p. 72°, ethers of (XIV). H. B.

Synthesis of *periquinolinazole* (N-N). I. Attempted synthesis of tetrahydro*periquinolinazole*. S. N. CHAKRAVARTI and K. GANAPATI (J. Annamalai Univ., 1934, 3, 223—228).—The formyl derivative of *N*-aminodihydrocarbostyryl (I) [from (I) and  $\text{HCO}_2\text{H}$  at 180—200°] with  $\text{POCl}_3$  in boiling PhMe gives a hydrochloride, m.p. 205—206°, of an oily base, reduced by Zn-dil. HCl to dihydrocarbostyryl, no cyclisation being effected. Condensation with  $\text{CH}_2\text{O}$  under usual conditions also failed. With  $\text{BzCl}$  and  $\text{C}_5\text{H}_5\text{N}$  (I) gives its Bz derivative, m.p. 168.9°, converted by  $\text{P}_2\text{O}_5$  in boiling PhMe into a substance, m.p. 212°. An improved prep. of quinoline-8-carboxylic acid by  $\text{CrO}_3$ -30%  $\text{H}_2\text{SO}_4$  oxidation of 8-methylquinoline is described. J. W. B.

Manufacture of carbazole compounds.—See B., 1934, 1095.

3:6-Dialkoxy-10-alkylacridinium derivatives with various types of amino-group in the 9 position. III. Mechanism of reaction of 9-chloro-3:6-dialkoxy-10-alkylacridinium chloride. K. ISHIMURA (J. Chem. Soc. Japan, 1934, 55, 716—730).—Hydrolysis of 9-chloro-3:6-dialkoxy-10-alkylacridinium chlorides gives both the corresponding hydroxides (I) and 9-hydroxy-3:6-dialkoxy-10-alkylacridinium hydroxides (II). The stabilities of (I)  $\propto$  their dissociation consts. and inversely  $\propto$  stability of (II). CH. ABS. (r)

Supposed aryl*peripyrroloanthroxylys* as derivatives of benzoylene- $\beta\beta'$ -benzopyrrole and the violet products of reduction of 1-cyanoanthraquinones. R. SCHOLL, O. BÖTTGER, and E. STIX (Ber., 1934, 67, [B], 1922—1931).—The recognition of the supposed aryloxy*perihydrofurananthroxylys* as derivatives of benzoylene- $\beta\beta'$ -benzofuran (A., 1933, 508; this vol., 92) implies the consideration of the *pyrroloanthroxylys* (formerly *pyrroloanthranolazyls*) as derivatives of benzoylene- $\beta\beta'$ -benzopyrroles (cf. A). This view is supported by fresh analyses; it explains the solubility in  $\text{NH}_3$  and NaOH, the behaviour on oxidation and reduction, and the titration with  $\text{CrO}_3$ . The aryl*peripyrroloanthranolazyls* (A., 1928, 773) with  $\text{Ar}=\text{Ph}$ ,  $\text{C}_6\text{H}_4\text{Me}$ ,  $m\text{-C}_6\text{H}_3\text{Me}_2$ ,  $\text{C}_6\text{H}_4\text{OMe}$ ,  $\text{C}_6\text{H}_4\text{Cl}$ , the *N*-Me and Bz derivative with  $\text{Ar}=m\text{-C}_6\text{H}_3\text{Me}_2$ , and the aryl-2-methyl



derivatives with  $\text{Ar}=\text{Ph}$  and  $p\text{-C}_6\text{H}_3\text{Me}_2$  are re-described in accordance with A as 6:7-benzoylene-2-aryl- $\beta\beta'$ -benzopyrroles, their 1 Me and Bz derivative and 6:7-benzoylene-2-aryl-3-methyl- $\beta\beta'$ -benzopyrroles. The oxylammonium or oxylum salts are oxonium or  $\text{NH}_4$  salts.

Mild reduction of 1-cyano-2-methylantraquinone by Zn dust and dil.  $\text{NH}_3$  leads, as with  $\text{Na}_2\text{S}_2\text{O}_4$ , to 1-cyano-2-methylantraquinol. With conc.  $\text{NH}_3$  for a long period at room temp. or for a short time in boiling solution the product is 6:7-benzoylene-3-methyl- $\beta\beta'$ -benzopyrrole (I), decomp.  $> 200^\circ$  (isolated



through the *perchlorate*), oxidised by amyl nitrite in boiling  $\text{PhNO}_2$  to the *substance B*, decomp. about  $300^\circ$ . Treatment of (I) in  $\text{COMe}_2$  with  $\text{Me}_2\text{SO}_4$  and 20%  $\text{NaOH}$  gives 6 : 7-benzoylene-1 : 3-dimethyl- $\beta\beta'$ -benzopyrrole, m.p. about  $187^\circ$  after softening (*perchlorate*). 1-Cyanoanthraquinone gives non-cryst. 6 : 7-benzoylene- $\beta\beta'$ -benzopyrrole, oxidised by amyl nitrite in  $\text{PhNO}_2$  to the *substance C*,  $\text{C}_{30}\text{H}_{14}\text{O}_2\text{N}_2$ , m.p.  $508\text{--}509^\circ$  after darkening at about  $490^\circ$  when rapidly heated. H. W.

**Synthesis of paraberine. I. Synthesis of 8 : 17-diketo-6 : 17-dihydroparaberine.** S. N. CHAKRAVARTI and K. GANAPATI (J. Annamalai Univ., 1934, 3, 208—215).—When heated with  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  isocoumarincarboxylic acid (Bamberger *et al.*, A., 1894, i, 192) affords *N*-benzylisocarbostyryl-3-carboxylic acid [1-keto-2-benzyl-1 : 2-dihydroisoquinoline-3-carboxylic acid], m.p.  $207^\circ$ , the chloride of which is converted by  $\text{AlCl}_3$  in  $\text{PhNO}_2$  into 8 : 17-diketo-6 : 17-dihydroparaberine,  $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{CH}_2\text{C}\text{--}\text{CO} \\ \text{CO}\text{--}\text{N}\text{--}\text{CH}_2 \end{array}\right\rangle\text{C}_6\text{H}_4$ , m.p.  $189^\circ$  (*oxime*, m.p.  $306^\circ$ ), which could not be reduced to tetrahydroparaberine (I).  $\text{NH}_2\cdot\text{CH}(\text{CH}_2\text{Ph})_2$  (or its formyl derivative) could not be converted into (I) by ring closure with  $\text{CH}_2\text{O}$ . J. W. B.

**$\beta$ -Ureidocarboxylic acids and dihydrouacils. I.  $\beta$ -Phenylureidocarboxylic esters and 3-phenyldihydrouacils.** K. MORSCH (Monatsh., 1934, 64, 333—340).— $\text{PhNCO}$  in  $\text{Et}_2\text{O}$  is added to the  $\text{NH}_2$ -ester in  $\text{Et}_2\text{O}$ , whereby the  $\omega$ -phenylureido-ester is obtained in 85—95% yield; it is converted by  $\text{HCl}$  into the corresponding dihydrouacil. The following transformations are recorded :

$\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  into *Me*  $\beta$ - $\text{N}^2$ -phenyl- $\text{N}^1$ -methylureidopropionate, m.p.  $58\text{--}59^\circ$ , and thence into 3-phenyl-1-methyldihydrouacil, m.p.  $130\text{--}131\text{--}5^\circ$ ; *Et*  $\beta$ - $\text{N}^2$ -phenyl- $\text{N}^1$ -methylureido-*n*-butyrate, m.p.  $111\text{--}112\text{--}5^\circ$ , whence 3-phenyl-6-methyldihydrouacil, m.p.  $209\text{--}209\text{--}5^\circ$ ;  $\text{NHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  into *Et*  $\beta$ - $\text{N}^2$ -phenyl- $\text{N}^1$ -methylureido-*n*-butyrate, m.p.  $67^\circ$ , whence 3-phenyl-1 : 6-dimethyldihydrouacil, m.p.  $154^\circ$ . *Et*  $\beta$ - $\omega$ -phenylureido- $\beta$ -phenylpropionate, m.p.  $116\text{--}117\text{--}5^\circ$ , and *Et*  $\beta$ - $\text{N}^2$ -phenyl- $\text{N}^1$ -methylureido- $\beta$ -phenylpropionate, m.p.  $102\text{--}102\text{--}5^\circ$ , are described.  $\text{PhNCO}$  and an alkaline solution of  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  yield a non-cryst. product transformed by dil.  $\text{HCl}$  into 3-phenyl-1-methyldihydrouacil.  $\beta$ - $\text{N}^2$ -Phenyl- $\text{N}^1$ -methylureido-*n*-butyric acid and  $\beta$ - $\omega$ -phenylureido- $\beta$ -phenylpropionic acid have m.p.  $60\text{--}62^\circ$  and m.p.  $168^\circ$ , respectively. H. W.

**Mixed m.-p. curves of dialkylbarbituric acids.** H. A. SHONLE and E. C. KLEIDERER (J. Amer. Chem. Soc., 1934, 56, 2489—2490).—M.-p. curves for the following pairs of dialkylbarbituric acids are given: (i) 5-ethyl-5- $\alpha$ -ethylpropyl- and 5-ethyl-5- $\alpha$ -methylbutyl-, (ii) 5- $\alpha$ -ethylpropyl-5-allyl- and 5- $\alpha$ -methylbutyl-5-allyl-, (iii) 5-ethyl-5-isoamyl- and 5-ethyl-5- $\alpha$ -methylbutyl- (optically active). H. B.

**Barbituric acids containing a sec.-amyl group.** H. A. SHONLE (J. Amer. Chem. Soc., 1934, 56, 2490—2491).—The 5-alkyl-5- $\alpha$ -ethylpropylbarbituric acids previously prepared (A., 1930, 1047) contain some of the 5- $\alpha$ -methylbutyl derivative (cf. Tabern and Volwiler, A., 1934, 783). Further details are given for

the prep. of 5- $\alpha$ -ethylpropyl-, m.p.  $196\text{--}197\text{--}5^\circ$ , 5-ethyl-5- $\alpha$ -ethylpropyl-, m.p.  $161\text{--}161\text{--}5^\circ$ , 5- $\alpha$ -ethylpropyl-5-allyl-, m.p.  $131\text{--}132^\circ$ , and 5- $\alpha$ -methylbutyl-5-allyl-, m.p.  $99\text{--}100^\circ$ , -barbituric acids.  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{CH}_2\text{Et}$  has m.p.  $43\text{--}45^\circ$  (lit.  $32\text{--}35^\circ$ ). Pharmacological data are given. H. B.

**Antineuritic vitamin.**—See A., 1934, 1415.

**6 : 7-Dimethyl- and 1 : 3 : 6 : 7-tetramethylalloxazine.** R. KUHN and H. RUDY (Ber., 1934, 67, [B], 1826—1829).—Condensation of 4 : 5-diamino-*o*-xylene hydrochloride (I) with alloxan in  $\text{H}_2\text{O}$  leads to 6 : 7-dimethylalloxazine, decomp.  $360^\circ$  after darkening at  $335^\circ$ , identical in cryst. form, absorption spectrum, colour reactions, and fluorescence with the  $\text{Na}_2\text{CO}_3$ -sol. product (II) of the degradation of lumilactoflavin. It is transformed by  $\text{CH}_2\text{N}_2$  into 1 : 3 : 6 : 7-tetramethylalloxazine, m.p.  $252^\circ$  (corr.), also obtained from (I) and dimethylalloxan and from (II), thus confirming the structure of (II). H. W.

**Synthesis of 6 : 7 : 9-trimethylflavin (lumilactoflavin).** R. KUHN and K. REINEMUND (Ber., 1934, 67, [B], 1932—1936).—4-Nitro-*o*-5-xylidine is converted by  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  in  $\text{C}_5\text{H}_5\text{N}$  into 4-nitro-5-*p*-toluenesulphonamido-*o*-xylene, m.p.  $150\text{--}151^\circ$ , transformed by  $\text{Me}_2\text{SO}_4\text{-KOH}$  into 4-nitro-5-*p*-toluenesulphonmethylamido-*o*-xylene, m.p.  $148\text{--}149^\circ$ , hydrolysed by  $\text{H}_2\text{SO}_4\text{-AcOH}$  to 4-nitro-5-methylamino-*o*-xylene (I), m.p.  $139^\circ$ . (I) is reduced by  $\text{SnCl}_2$  and conc.  $\text{HCl}$  to 4-amino-5-methylamino-*o*-xylene (II), m.p.  $79\text{--}80^\circ$ , the dihydrochloride, decomp.  $180\text{--}185^\circ$  when rapidly heated, of which condenses with alloxan tetrahydrate (III) in  $\text{H}_2\text{O}$  at  $50\text{--}60^\circ$  to 6 : 7 : 9-trimethylflavin (lumilactoflavin) [also  $+0\text{.}5\text{HCO}_2\text{H}$ ], (II) and (III) in  $\text{EtOH}$  at  $15\text{--}20^\circ$  yield alloxanyl-4-amino-5-methylamino-*o*-xylene, m.p.  $251\text{--}252^\circ$  (decomp.), transformed by boiling  $2\text{N}\text{-Na}_2\text{CO}_3$  into 2-keto-1 : 6 : 7-trimethyl-1 : 2-dihydroquinoxaline-3-carboxylic acid, m.p.  $214^\circ$  (decomp.), which passes by loss of  $\text{CO}_2$  into 2-keto-1 : 6 : 7-trimethyl-1 : 2-dihydroquinoxaline, m.p.  $176^\circ$ ; these substances are identical with those obtained by the alkaline degradation of lumilactoflavin. H. W.

**Synthesis of 6 : 7-dimethyl-9-*n*-amylflavin.** R. KUHN and F. WEYGAND (Ber., 1934, 67, [B], 1941—1942).—4-Nitro-*o*-5-xylidine is heated at  $140^\circ$  with  $n\text{-C}_5\text{H}_{11}\text{I}$  and the product is reduced by  $\text{SnCl}_2\text{-AcOH-HCl}$  to 4-amino-5-*n*-amylamino-*o*-xylene, which, with excess of alloxan in boiling  $\text{AcOH}$ , affords 6 : 7-dimethyl-9-*n*-amylflavin, decomp.  $295\text{--}300^\circ$  (corr.). H. W.

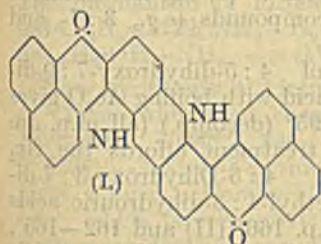
**Syntheses of substances resembling lactoflavin. II.** P. KARRER, E. SCHLITTLER, K. PFAEHLER, and F. BENZ (Helv. Chim. Acta, 1934, 17, 1516—1523; cf. A., 1934, 1233).—Colamine,  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ , and anhyd.  $\text{NaOAc}$  at  $100\text{--}120^\circ$  yield *o*-nitrohydroxyethylaniline, m.p.  $76^\circ$ , reduced (Pt and  $\text{H}_2$ ) to the diamine, which with alloxan tetrahydrate (I) yields 9- $\beta$ -hydroxyethylisalloxazine (II), m.p.  $310^\circ$  (decomp.) after becoming discoloured about  $300^\circ$ . Since irradiation of (II) in neutral or alkaline solution causes formation of alloxazine and methylisalloxazine, the presence of 1 OH in the  $\beta$ -position is sufficient to induce the typical flavin photo-sensitiveness. 5-Chloro-4-nitro-*o*-xylene, from 4-nitro-*o*-5-xylidine



(Sandmeyer), is converted by  $\alpha$ -aminopropane- $\beta$ - $\gamma$ -diol and anhyd. NaOAc at 125—130° into 4-nitro-5- $\beta$ - $\gamma$ -dihydroxypropylamino-*o*-xylene, m.p. 102°, which is reduced and condensed with (I) to 6:7-dimethyl-9- $\beta$ - $\gamma$ -dihydroxypropylisalloxazine, m.p. about 294° (decomp.) after darkening. *p*-C<sub>6</sub>H<sub>4</sub>BrAc is reduced (Clemmensen) to *p*-C<sub>6</sub>H<sub>4</sub>BrEt, transformed by HNO<sub>3</sub> (*d* 1.49) at  $\gt$  0° into a mixture of NO<sub>2</sub>-compounds, b.p. 132—134°/9 mm., which with NH<sub>3</sub>-EtOH at 150° yields 3-nitro-4-aminoethylbenzene (III), b.p. 126—130°/0.4 mm. (III) is reduced (SnCl<sub>2</sub> and HCl) and condensed with (I) to 6(or 7)-ethylalloxazine. The fluorescence colours of alloxazine derivatives are so characteristic that they may be used for purposes of identification. H. W.

**Ovoflavin e.** P. KARRER and K. SCHÖPP (Helv. Chim. Acta, 1934, 17, 1557—1558).—Irradiation of ovoflavin (I), from dry, technical ovalbumin, in 75% MeOH leads to 6:7-dimethylalloxazine. (I) therefore contains the 3-ring skeleton of lactoflavin (II), but the identity of the sugar-like side-chains in (I) and (II) remains unestablished. H. W.

**N-Dihydrobenzanthroneazine.** E. J. MÜLLER (Ber., 1934, 67, [B], 1799—1800).—*N*-Dihydroanthroneazine is converted by glycerol and H<sub>2</sub>SO<sub>4</sub> at 120°



into the compound (I), which does not yield a vat with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, is largely unchanged by molten alkali at 300°, but decomposed at 400°, and is oxidised by conc. H<sub>2</sub>SO<sub>4</sub> to the azine. Anthroneazine could not be transformed into

benzanthroneazine. Indanthrene in presence of NH<sub>2</sub>Ph does not yield a cryst. product, although the formation of a dihydroazine is established. H. W.

**Dicarbazyls.** VI. **Synthesis of 1:1'-dicarbazyl.** (MISS) H. G. DUNLOP, T. F. MACRAE, and S. H. TUCKER (J.C.S., 1934, 1672—1678).—2:2'-Diaminodiphenyl (I), 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Cl (II), and anhyd. K<sub>2</sub>CO<sub>3</sub> at 140° for 4 hr. give 80% of 2:2'-di-(2':4'-dinitroanilino)diphenyl (III), brick-red, m.p. 238—241° (corr.) (yellow 1:1-compound with C<sub>5</sub>H<sub>5</sub>N); at 190° for 10 min. (cf. Le Fèvre, A., 1929, 705), a 60% yield of (III) results, whilst at 140° for 5 min., 10% of 2-amino-2'-(2'':4'':dinitroanilino)diphenyl (IV), m.p. 168—170° (corr.; slight softening at 162°), is obtained. (IV) is also prepared in 38% yield from (I), (II) (slight excess), and K<sub>2</sub>CO<sub>3</sub> in xylene. The *salicylidene* derivative, m.p. 181—182.5° (corr.), of (IV) is probably the (III) of Le Fèvre (*loc. cit.*). Carbazole, (II), and K<sub>2</sub>CO<sub>3</sub> at 170—180° give *N*-2':4'-dinitrophenylcarbazole, m.p. 188—190° [the substance described as this by Le Fèvre (*loc. cit.*) is probably (III)]. (III) is reduced (EtOH-NH<sub>4</sub>HS) to 2:2'-di-(4'-nitro-2''-aminoanilino)diphenyl, m.p. 126°, converted by NaNO<sub>2</sub> in AcOH into 2:2'-di-(5''-nitro-1'':2'':3'':benztriazolyl)diphenyl, m.p. about 140°, reduction of which gives unworkable products. *p*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H (V) (from *p*-C<sub>6</sub>H<sub>4</sub>ClMe and Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in aq. AcOH-H<sub>2</sub>SO<sub>4</sub>) and warm HNO<sub>3</sub> (*d* 1.5) afford 4-chloro-3-nitrobenzoic acid [*amide*, m.p. 153—154°, dehydrated

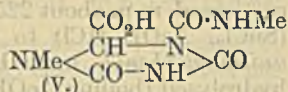
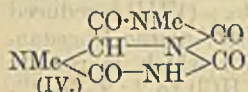
(P<sub>2</sub>O<sub>5</sub> at 170°) to 4-chloro-3-nitrobenzotrile (VI), m.p. 101° (lit. 110°)], also obtained from (VI) and boiling HNO<sub>3</sub> (*d* 1.42). *p*-C<sub>6</sub>H<sub>4</sub>Cl·CN (VII) and HNO<sub>3</sub> (*d* 1.51) give (VI); nitration is slower with HNO<sub>3</sub> (*d* 1.5) and does not occur with HNO<sub>3</sub> (*d* 1.49). (VII) and boiling HNO<sub>3</sub> (*d* 1.42) afford (V). *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> and (V) are nitrated by HNO<sub>3</sub> (*d* 1.48), indicating that the directing power of CN is  $<$  that of Cl or CO<sub>2</sub>H. (I), (VI), and K<sub>2</sub>CO<sub>3</sub> at 160—185° give 2:2'-di-(2''-nitro-4''-cyanoanilino)diphenyl (VIII), m.p. 243—248° (1:1-compounds with C<sub>5</sub>H<sub>5</sub>N, PhNO<sub>2</sub>, and C<sub>6</sub>H<sub>6</sub>); at 150° or in xylene, 2-amino-2'-(2''-nitro-4''-cyanoanilino)diphenyl, m.p. 143° [which with (VI) affords (VIII)], is obtained. (VIII) is hydrolysed (AcOH—conc. HCl at 200°) to 2:2'-di-(2''-nitro-4''-carboxyanilino)diphenyl, m.p.  $>$  300°, which with Cu-bronze at 320° in an evacuated Pyrex tube gives 2:2'-di-*o*-nitroanilinodiphenyl (IX). Hydrolysis (EtOH—NaOH at 160°) of (VIII) affords a compound, m.p.  $>$  300°, and 3:4-(NH<sub>2</sub>)(OH)C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H; with HNO<sub>3</sub>, a polynitrocompound, m.p. about 225°, results. (VIII) is reduced (SnCl<sub>2</sub>, AcOH—HCl) to 2:2'-di-(2''-amino-4''-cyanoanilino)diphenyl, m.p. 194—197°, which is readily hydrolysed (boiling AcOH—conc. HCl) to 2:2'-di-(2''-amino-4''-carboxyanilino)diphenyl (X), m.p. 280° (decomp.; softens at 265° and blackens at 275°). (X) is decarboxylated (as above) to 2:2'-di-*o*-aminoanilinodiphenyl, the intermediate in the synthesis (A., 1934, 86) of 1:1'-dicarbazyl. 2:2'-Di-(5''-cyano-1'':2'':3''-benztriazolyl)diphenyl, m.p. 269°, heated at 320° gives (probably) 6:6'-dicyano-1:1'-dicarbazyl, m.p. 305—307°; hydrolysis (EtOH—NaOH at 160°) affords 2:2'-di-(5-carboxy-1'':2'':3''-benztriazolyl)diphenyl, m.p.  $>$  330°.

Contrary to Le Fèvre (*loc. cit.*), complete absence of steric hindrance during *NN'*-disubstitution is considered not to be proved. The steric effect is often negligible in comparison with the polar effect; thus, (IX) can be acetylated, whereas (III) cannot (under same conditions). Furthermore, the ease of acetylation and ethylation of NPh<sub>2</sub>, *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NPh, and 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NPh [which with Et<sub>3</sub>SO<sub>4</sub> and KOH in EtOH (not COMe<sub>2</sub>) gives a little of the *N*-Et derivative] decreases in the order quoted. H. B.

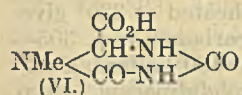
**Theobromuric acid degradation of theobromine.** H. BILTZ [with M. HEYN, H. MUNDT, and P. DAMM] (Ber., 1934, 67, [B], 1856—1866).—The varying results obtained in analysis of the product of the action of Cl<sub>2</sub> on theobromine suspended in boiling CHCl<sub>3</sub> free from EtOH are due to the presence of 1/3CHCl<sub>3</sub>, which is somewhat readily lost. The solvent-free substance is *N*-2:4:5:5-tetrachloro-1-methyl- $\Delta^2$ -iminazolyl-*N*-methylcarbamide-*N'*-carboxyl chloride, NMe·CCl<sub>2</sub> > CCl=N > CCl·NMe·CO·NH·COCl. It is converted by H<sub>2</sub>O into theobromuric acid [*N*-methyl-*N*-2:5-diketeto-1-methyl- $\Delta^3$ -iminazolyl-4-carbamide-*N'*-carboxylic acid] (I), NMe·CO > CO—N > C·NMe·CO·NH·CO<sub>2</sub>H. This constitution explains its ready conversion by warm H<sub>2</sub>O into CO<sub>2</sub>, methylparabanic acid, and NHMe·CO·NH<sub>2</sub> and the greater stability of the Me (II), m.p. 202°, and Et<sub>2</sub>, m.p. 210°, esters and of the NH<sub>4</sub>, m.p. 125° (decomp.), and Na, m.p. 105—106°



(decomp.), salts. The presence of NH in (I) is shown by the transformation of (II) into the *Ag* salt, converted by MeI and a little  $Ag_2O$  into *Me N-methyltheobromurate*, decomp. 175—177°, reduced by HI to (?) 3-methylhydantoin, m.p. 184—185°, and oxidised by  $K_2Cr_2O_7$  and  $H_2SO_4$  to a substance,  $C_8H_{10}O_5N_4$ , m.p. 205° (slight decomp.). Hot conc. HCl or hot  $NH_3-H_2O$  transforms (I) into  $N^1N^3$ -dimethyl-*s-dicarbamyl-carbamide* (III),  $NH_2 \cdot CO \cdot NMe \cdot CO \cdot NH \cdot CO \cdot NHMe$ , m.p. 200—201° (converted by boiling 20% into  $NH_2Me$  and *N-methylcyanuric acid*, m.p. 290°), and  $NH_4$ -dimethylureidoglycollate,  $NH_2 \cdot CO \cdot NMe \cdot C(OH)(CO_2NH_4) \cdot NH \cdot CO \cdot NHMe$ , m.p. 196—197°. Reasons are advanced against the symmetrical formula for (III) proposed by Fischer *et al.* Reduction of (I) with HI leads to hydrotheobromuric anhydride (IV), m.p. 264° (decomp.), or hydrotheobromuric acid (+ $H_2O$ ) (V). The identity of (IV) with 1:7-dimethylspirohydantoin and of its Me derivative with the corresponding 1:3:7-Me<sub>3</sub> compound is ex-



cluded, and the observation that (V) does not possess the lability of (I) indicates the absence of  $CO_2H$  attached to N. General considerations of the course of the reduction lead to the structures shown for (IV) and (V), according to which (IV) is not a true anhydride



of (V), a conclusion supported by the observation that esters cannot be obtained from it in the same manner as from (V). The constitution (V) readily explains the transformation, best by  $Na_2CO_3$ , of (V) by loss of  $NH_2Me$  and  $CO_2$  into theuric acid, which is therefore (VI).

H. W.

**Synthesis of pyridylpyrazoles.** G. R. CLEMO and T. HOLMES (J.C.S., 1934, 1739—1741).—Et pyridine-3-carboxylate (I), EtOAc, and EtOH-NaOEt at 77° give Et nicotinoylacetate ( $\beta$ -keto- $\beta$ -3-pyridylpropionate) (II), b.p. 125—135°/1 mm., hydrolysed (10%  $H_2SO_4$ ) to 3-pyridyl Me ketone, b.p. 106°/12 mm. (*oxime*, m.p. 130.5°). (II) and  $CH_2Cl \cdot CHCl \cdot OEt$  in aq.  $NH_3$  (or  $NH_2Me$ ) afford  $\gamma$ -keto- $\beta$ -carbethoxy- $\gamma$ -3-pyridylbutaldehyde, m.p. 116°, which reduces aq.  $NH_3-Ag_2O$ , restores the colour to Schiff's reagent, and is unaffected by EtOH- $NH_3$  or -HCl. (II) and  $NHPh \cdot NH_2$  in AcOH at 100° afford 1-phenyl-3-(3'-pyridyl)-5-pyrazolone, m.p. 188°. 3-(3'-Pyridyl)-5-pyrazolone, m.p. 268° [from (II) and  $N_2H_4 \cdot H_2O$  in MeOH], and  $POCl_3$  at 180° give 5-chloro-3-(3'-pyridyl)pyrazole, m.p. 190°, which with fuming  $HNO_3$  affords the 4- $NO_2$ -derivative, m.p. 220.5°. This is reduced (red P and 20% HI at 170°) to 4-amino-5(or 3)-(3'-pyridyl)pyrazole (III), m.p. 176° [*dipicrate*, m.p. 205°; *Ac derivative*, m.p. 183° (*dihydrochloride*, m.p. 254°)]. The *hydrazide*, m.p. 260°, of 5-(3'-pyridyl)pyrazole-3-carboxylic acid (*Et ester*, m.p. 170°) [prepared by Gough and King's method (A., 1933, 616)] and amyl nitrite in aq. EtOH-HCl give (after subsequent treatment with EtOH) Et 5-(3'-pyridyl)pyrazole-3-carbamate [*dihydrochloride* (+EtOH), m.p. 302° (after loss of EtOH at 126°)], which is hydrolysed (conc. HCl) to 3-amino-5-(3'-pyridyl)pyrazole (IV) (*hydrochloride*,

m.p. 301°; *Ac derivative*, m.p. 308—309°; *dipicrate*, m.p. 219°). (IV) is identical with the supposed (III) of Gough and King (A., 1932, 68; *loc. cit.*; cf. Lund, A., 1933, 840). The nitro-5-(3'-pyridyl)pyrazole produced during  $HNO_3$ -oxidation of nicotine is, therefore, the 3-derivative; introduction of  $NO_2$  occurs before the formation of the final pyrazole ring (cf. Gough and King, *loc. cit.*).  
H. B.

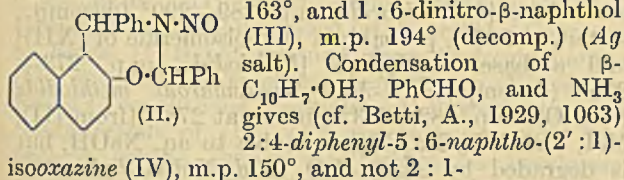
**Action of acetic anhydride on uric acid glycols and their ethers.** Introduction. H. BILTZ. I. 1:3-, 3:7-, and 7:9-Dimethyl- and 7:9-diethyl-uric acid [glycols]. H. BILTZ and L. LOEWE (J. pr. Chem., 1934, [ii], 141, 218—224, 225—240).—Introduction. The dialkyl ethers of uric acid glycols [4:5-dihydroxy-4:5-dihydric acids] are not converted by boiling  $Ac_2O$  into *spirodihantoin*s (I); acetylation occurs at position 7 (in the case of the 1:3-Me<sub>2</sub> derivative, 5-alkoxy-1:3-dimethylisouric acid is formed). Similarly, the 5-alkyl ethers do not give (I); acetylation occurs at  $C_4 \cdot OH$  and then at  $>N_3 \cdot H$ , but prolonged treatment causes fission of the  $N_3-C_4$  linking and the production of 5-alkoxyhydantamides. 9-Methyl- and 3:9-dimethyl-uric acid glycols are acetylated at  $>N_7 \cdot H$ ; subsequent rearrangement into (I) occurs. (I) are not obtained from the 7-substituted compounds (e.g., 3:7- and 7:9-Me<sub>2</sub>).

I. Short treatment of 4:5-dihydroxy-7:9-dimethyl-4:5-dihydric acid with boiling  $Ac_2O$  gives an *Ac derivative*, m.p. 195° (decomp.) (all m.p. are corr.); more prolonged treatment affords the *Ac<sub>2</sub> derivative*, m.p. 165°. 4:5-Dihydroxy-3:7-dimethyl- (I) and -7:9-diethyl-4:5-dihydric acids afford *Ac<sub>2</sub> derivatives*, m.p. 166° (II) and 162—165°, respectively; *Ac<sub>1</sub> derivatives* could not be prepared. (II) is hydrolysed (conc. aq.  $NH_3$ ) to (I); with MeOH- and EtOH- $NH_3$ , the 5-Me ether (III) (*Na salt*, decomp. 90—120°; 4-*Ac derivative*, m.p. 180°) and 5-*Et ether* (IV), respectively, of (I) are produced. Prolonged treatment of (I) with  $Ac_2O$  gives 5-acetoxy-3:7-diacetyl-1-methylhydantamide,  $CO \cdot NMe \cdot C(OAc) \cdot CO \cdot NHAc$ , m.p. 150—152°; (III) and (IV) similarly afford 5-methoxy-, m.p. 126°, and 5-ethoxy-, m.p. 151°, -3:7-diacetyl-1-methylhydantamide, respectively. 4:5-Dihydroxy-1:3-dimethyl-4:5-dihydric acid (V) and  $Ac_2O$ -conc.  $H_2SO_4$  give the *Ac<sub>2</sub> derivative*, m.p. 160—165° (decomp.), converted by boiling  $Ac_2O$  into 5-acetamido-5-acetoxy-1:3-dimethylbarbituric acid (VI), m.p. 180° (decomp.) (also prepared from acetyl-1:3-dimethyluramil and  $Cl_2$  in  $Ac_2O$ ), and by anhyd. EtOH into 4-acetoxy-5-ethoxy-1:3-dimethyl-4:5-dihydric acid, m.p. 175—180° (becoming red), decomp. 190°. (VI) and EtOH similarly give 5-acetamido-5-ethoxy-1:3-dimethylbarbituric acid, m.p. about 210°, reduced (conc. HI) to 1:3-dimethyluramil; an analogous reaction does not occur with MeOH. The Me<sub>2</sub> and Et<sub>2</sub> ethers of (V) are converted by  $Ac_2O$  into 5-methoxy-, m.p. 207°, and 5-ethoxy-, m.p. 195°, -1:3-dimethyl- $\Delta^{4,9}$ -isouric acid, respectively.  
H. B.

**Optical absorption of porphyrins.**—See this vol., 10.



Action of nitrous acid on phenyl-2-hydroxy- $\alpha$ -naphthylmethylamine. II. N. AHMED and M. G. HEMPHILL [with F. E. RAY] (J. Amer. Chem. Soc., 1934, 56, 2403—2405; cf. A., 1933, 155).—The compound previously obtained (A., 1932, 263) from phenyl-2-hydroxy- $\alpha$ -naphthylmethylamine (I) and  $\text{HNO}_2$  is now shown to a mixture of 3-nitroso-2:4-diphenyl-5:6-naphtho-(2':1')-isooxazine (II), m.p.



163°, and 1:6-dinitro- $\beta$ -naphthol (III), m.p. 194° (decomp.) (Ag salt). Condensation of  $\beta$ - $\text{C}_{10}\text{H}_7\text{OH}$ ,  $\text{PhCHO}$ , and  $\text{NH}_3$  gives (cf. Betti, A., 1929, 1063) 2:4-diphenyl-5:6-naphtho-(2':1')-isooxazine (IV), m.p. 150°, and not 2:1-OH- $\text{C}_{10}\text{H}_6\text{CHPhNCHPh}$ . (IV) could not be methylated; with  $\text{HNO}_2$  it gives (II), whilst its *Ac* derivative, m.p. 170°, is hydrolysed (cold conc.  $\text{HCl}$ ) to 2:1-OH- $\text{C}_{10}\text{H}_6\text{CHPhNHAc}$ , which is methylated to the *Ac* derivative of phenyl-2-methoxy- $\alpha$ -naphthylmethylamine (V) (A., 1933, 1157) [*N*- $\text{CO}_2\text{Et}$  derivative (VI), m.p. 132°, obtained by methylation ( $\text{Me}_2\text{SO}_4$ , aq.  $\text{EtOH}$ - $\text{KOH}$ ) of the *N*- $\text{CO}_2\text{Et}$  derivative, m.p. 201°, of (I)]. (IV) and  $\text{N}_2\text{O}_3$  in  $\text{PhMe}$  give (III). (V) is converted by  $\text{HNO}_2$  into the corresponding carbinol. The mechanism of formation of (II) from (I) is:  $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{CHPh}\cdot\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{PhCHO} + \beta\text{-C}_{10}\text{H}_7\text{OH} + \text{NH}_3 \rightarrow \text{(IV)} \rightarrow \text{(II)}$ . H. B.

New synthesis of ricinine. J. REITMANN (Med. u. Chem. Abh. med.-chem. Forschungsstätten I.G. Farbenind., 1934, 2, 384—388; Chem. Zentr., 1934, i, 3597).—3-Nitro-4-pyridone with  $\text{PCl}_5$  and  $\text{POCl}_3$  gives 3-nitro-4-chloropyridine, m.p. 45°, b.p. 95°/5 mm., which is converted by  $\text{NaOMe}$  into 3-nitro-4-methoxypyridine (I), m.p. 73°, b.p. 127°/1 mm., with some 3-nitro-*N*-methyl-4-pyridone (II), m.p. 233°. (I) is converted into (II) at 170°. (I) is reduced by  $\text{Fe}$  and aq.  $\text{AcOH}$  to 3-amino-4-methoxypyridine, which by diazotisation and  $\text{CuCN}$  and  $\text{NaCN}$  gives 3-cyano-4-methoxypyridine (III), m.p. 124°. Ricinine is obtained from (III) by addition of  $\text{Me}_2\text{SO}_4$  and oxidation with  $\text{K}_3\text{Fe}(\text{CN})_6$ . R. N. C.

Alkaloids of *Anabasis aphylla*. X. Reduction of aphyllidine. A. OREKHOV and S. NORKINA [with T. MAXIMOVA] (Ber., 1934, 67, [B], 1845—1849; cf. A., 1932, 405).—Aphyllidine (I),  $\text{C}_{15}\text{H}_{22}\text{ON}_2$ , after purification through the perchlorate, m.p. 210—212°,  $[\alpha]_D^{25} +15.0^\circ$  in  $\text{MeOH}$ , has m.p. 112—113°,  $[\alpha]_D^{25} +6.50^\circ$  in  $\text{MeOH}$ ; the hydrochloride has m.p. 235—237°,  $[\alpha]_D^{25} +30.0^\circ$  in  $\text{H}_2\text{O}$ . (I) is strongly unsaturated; it combines with  $\text{Br}$  in ligroin- $\text{CHCl}_3$  with loss of  $\text{HBr}$  and production of bromoaphyllidine, m.p. 150—152° (hydrobromide, m.p. 210—211°; perchlorate, m.p. 234—235°), which is not reduced by  $\text{Zn}$  dust- $\text{AcOH}$  or  $\text{H}_2$  ( $\text{PtO}_2$ ) and is stable towards boiling  $\text{KOH}$ - $\text{MeOH}$ . Electrochemical reduction of (I) in 50%  $\text{H}_2\text{SO}_4$  at  $\text{Pb}$  electrodes leads to pachycarpine (II) (identified by the methiodide, hydriodide, dipicrate, and perchlorate). Catalytic hydrogenation ( $\text{PtO}_2$ ) of (I) slowly affords aphylline (III) at room temp., whereas at 80—90° (II) is produced. (I), (III), anagyrene, and lupanine are, therefore, derivatives of (+)-sparteine, whereas matrine, sophocarpine, and sophoridine belong to a different series. H. W.

Lupine. VIII. Alkaloids of *Lupinus palmeri*, S. Wats. J. F. COUCH (J. Amer. Chem. Soc., 1934, 56, 2434—2436; cf. A., 1934, 310).—Details are given for the extraction of lupinine (I) (hydrochloride, m.p. 207—209°; hydriodide, m.p. 140—141°; aurichloride, m.p. 211—213°; platinichloride, m.p. 166—166.5°; methiodide, m.p. 295—296°; methochloride, m.p. 212—213°; picrate, m.p. 136—137° and 196—197°; phenylcarbamate, m.p. 98—99°; d-camphorsulphonate, m.p. 181—182°), tetralupine (II),  $\text{C}_{19}\text{H}_{19}\text{ON}$ , m.p. 81—83°,  $[\alpha]_D^{25} +4.63^\circ$  [d-camphorsulphonate (+ $\text{H}_2\text{O}$ ), m.p. 164—165°], and pentalupine,  $\text{C}_{16}\text{H}_{30}\text{ON}_2$ , b.p. 175—182°/2 mm., from the air-dried plant; sparteine could not be found. (II) is isomeric with (I) and is not identical with isolupinine, m.p. 77—79° [from (I) and  $\text{Na}$  in  $\text{C}_6\text{H}_6$ ]. H. B.

*Sophora* alkaloids. VI. Bases of high b.p. from the foliage of *Sophora pachycarpa*. Sophoridine and sophocarpine. A. OREKHOV, M. RABINOVITSCH, and R. KONOVALOVA (Ber., 1934, 67, 1850—1855; cf. A., 1933, 617).—Sophocarpine (I) and sophocarpidine are isolated from the bases of high b.p. obtained from the foliage of *Sophora pachycarpa*. The proportion is approx. the same as in the alkaloid mixture from the seeds, which differs therefore from that of the foliage only in the absence of pachycarpine. Interaction of (I) or sophoridine (II) (from *S. alopecuroides*) with  $\text{CNBr}$  or  $\text{MgMeI}$  or under the conditions of the Hofmann degradation gives unchanged material or non-characteristic products. Electrochemical reduction of (I) in 50%  $\text{H}_2\text{SO}_4$  at a  $\text{Pb}$  cathode yields a volatile, cryst. base,  $\text{C}_{15}\text{H}_{26}\text{N}_2$ , b.p. 153—154°/5 mm.,  $[\alpha]_D^{25} -26.2^\circ$  in  $\text{EtOH}$  (dimethiodide, m.p.  $\gt 260^\circ$ ). Similar treatment of (II) gives a non-cryst. base,  $\text{C}_{15}\text{H}_{26}\text{N}_2$ , b.p. 172—173°/4 mm.,  $[\alpha]_D^{25} -37.1^\circ$  in  $\text{EtOH}$  (dimethiodide, m.p.  $\gt 260^\circ$ ). H. W.

Samandarine, the principal alkaloid in the poison of fire and alpine salamanders. C. SCHÖPF and W. BRAUN (Annalen, 1934, 514, 69—136).—The crude poison (method of isolation described) from *Salamander maculosa* and *S. atra* is digested with pepsin- $\text{HCl}$  at 37° during 13—16 days, the acidic solution is extracted with peroxide-free  $\text{Et}_2\text{O}$  [which removes oil and a sterol, probably  $\text{C}_{30}\text{H}_{52}\text{O}$ , m.p. 139° (sinters at 120°) (acetate, m.p. 107—108°)], and then basified (aq.  $\text{NH}_3$ ). Subsequent extraction with  $\text{Et}_2\text{O}$  gives samandarine (I),  $\text{C}_{19}\text{H}_{31}\text{O}_2\text{N}$  (cf. Faust, A., 1900, i, 186; Gessner and Craemer, A., 1930, 1204), + $\text{H}_2\text{O}$  (from aq.  $\text{COMe}_2$ ), + $\text{MeOH}$  (from  $\text{MeOH}$ ), m.p. 187—188°,  $[\alpha]_D^{25} +43.7^\circ$  in  $\text{COMe}_2$  {*N*-*NO*-derivative (? +0.5 $\text{EtOH}$ ), decomp. 111—113°, re-solidifying with m.p. 164—165°; *O*-*Ac*<sub>1</sub> derivative [hydrochloride, m.p. 300—302° (decomp.)], obtained during attempted reduction ( $\text{Zn}$  dust,  $\text{AcOH}$ ) of (I); *ON*-*Ac*<sub>2</sub>, m.p. 167—168°, *O*-*HCO* (+ $\text{H}_2\text{O}$ ), m.p. 148—150°, and *ON*-(*HCO*)<sub>2</sub>, m.p. 256—258°, derivatives}, and amorphous products [from which (I) is separated as its hydrochloride, m.p. 321—322°]. (I) is also obtained from the "substances III, IV, VIII, and IX" of Gessner and Craemer (*loc. cit.*). The samandaridine of Faust (*loc. cit.*) was not found; the samandarine of Netolitzky (A., 1904, i, 770) is probably impure (I). (I) contains 2 active H (Zere-



vitinov in PhOMe at 95°: general procedure). The presence of a *sec.*-OH in (I) is shown by its oxidation (CrO<sub>3</sub>, dil. H<sub>2</sub>SO<sub>4</sub>) to *samandarone* (II), C<sub>19</sub>H<sub>29</sub>O<sub>2</sub>N, m.p. 191—192° (sinters at 189°) (*N*-Bz derivative, m.p. 249—250°;  $\alpha$ -, m.p. 277—278°, and  $\beta$ -, m.p. 288—289°, *oximes*). (I) and MgMeI in Et<sub>2</sub>O give *methylsamandiol* (III), C<sub>20</sub>H<sub>35</sub>O<sub>2</sub>N, m.p. 170—172° [*hydrochloride*, m.p. 288—289°; *Ac*<sub>3</sub> derivative (+H<sub>2</sub>O), m.p. 188—190°], oxidised [as (I)] to *methylsamandione*, C<sub>20</sub>H<sub>31</sub>O<sub>2</sub>N, H<sub>2</sub>O, m.p. 124—126° (sinters at 118°) [*dioxime*, decomp. 268—270° (sinters at 265°); *N*-Me derivative *methiodide* (+2H<sub>2</sub>O), m.p. 258—260° (decomp.)]. (I) and MgPhBr afford *phenylsamandiol* (IV), C<sub>22</sub>H<sub>37</sub>O<sub>2</sub>N, 0.5MeOH, m.p. 194—196° [*hydrochloride*, decomp. 314—316° (sinters at 311°); *Ac*<sub>3</sub> derivative, m.p. 95—102° (decomp.; sinters at 60°)], which contains 3 active H. The production of (III) and (IV) indicates that the second O of (I) is present as >CH·O·C<, which with MgRX

gives >CH·OH CR<. (I) probably also contains 3 reduced C-rings; CMe groups are present, since oxidation of (I) by Kuhn and L'Orsa's method gives 1.07 mols. of AcOH. (IV) is oxidised [as (I)] to  $\alpha$ -*phenylsamandione* (V), C<sub>25</sub>H<sub>33</sub>O<sub>2</sub>N, m.p. 184—185° [*hydrochloride* (+0.5H<sub>2</sub>O), m.p. 250—252° (decomp.)]; *N*-Ac derivative, m.p. 232—233°; *semicarbazone*, m.p. 236—237° (decomp.; sinters at 234°); *oxime*, m.p. 203—204° (decomp.; sinters at 198°)], which contains 1 active H, and the isomeric  $\beta$ -*phenylsamandione* (VI), m.p. 112—113° (sinters at 106°) [*hydrochloride*, m.p. 275—277° (decomp.)]; *N*-Ac derivative, m.p. 194—195°. (V) and (VI) afford the same *dioxime*, m.p. 227—228° (decomp.; sinters at 224°) [*Ac* derivative, m.p. 149—151° (decomp.; sinters at 142°)] (which is formed only in strongly alkaline solution); they are probably stereoisomerides. Rearrangement of (V) or (VI) could not be effected with NaOEt or 3% H<sub>2</sub>SO<sub>4</sub>. (V), MeI, and 1.5*N*-Na<sub>2</sub>CO<sub>3</sub> give some *N*-methyl- $\alpha$ -*phenylsamandione*, (mainly) its *methiodide* (VII) (+H<sub>2</sub>O), m.p. 192—194° (decomp.; sinters at 190°), and small amounts of *de-N*-dimethyl- $\alpha$ -*phenylsamandione* (VIII), C<sub>27</sub>H<sub>37</sub>O<sub>2</sub>N, m.p. 216—217° (sinters at 206°) [*methiodide* (+MeOH), m.p. 256—258°], and the isomeric *isode-N*-dimethyl- $\alpha$ -*phenylsamandione*, m.p. 146° (sinters at 140°) [*methiodide hydriodide* (+0.5MeOH), m.p. 219—220° (decomp.; sinters at 216°)]. (VII) is degraded by aq. NaOH or Ag<sub>2</sub>O to (VIII) and an amorphous base [*methiodide*, C<sub>28</sub>H<sub>40</sub>O<sub>2</sub>NI (+MeOH), m.p. 269—270° (sinters at 266°)]. *N*-Methylsamandarine *methiodide* (+H<sub>2</sub>O), m.p. 271—272° [from (I), MeI, and aq. Na<sub>2</sub>CO<sub>3</sub>], is unaffected by aq. alkali, but is converted by Ag<sub>2</sub>O-H<sub>2</sub>O into *de-N*-dimethylsamandarine (IX), C<sub>21</sub>H<sub>35</sub>O<sub>2</sub>N, m.p. 190—191°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -121.3° in EtOH [*hydrochloride*, m.p. 275—276° (decomp.; sinters at 270°)], which contains 1 active H, and a little *N*-methylsamandarine, not obtained cryst., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -21.1° in C<sub>5</sub>H<sub>5</sub>N [*hydrochloride*, m.p. 300—302° (decomp.); *perchlorate*, m.p. 250—254° (decomp.; sinters at 220°)]. The *methiodide* (+H<sub>2</sub>O), m.p. 320—321°, of (IX) is similarly converted into (mainly) (IX). Reduction (H<sub>2</sub>, colloidal Pd, dil. AcOH) of (IX) gives a *dihydro*-derivative (X), m.p. 149—150° [*Ac* derivative, m.p. 93—94° (sinters at 88°); *methiodide*, m.p. 321—322°, con-

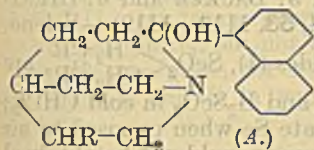
verted by Ag<sub>2</sub>O-H<sub>2</sub>O into (mainly) (X)]. (IX) and 3% H<sub>2</sub>SO<sub>4</sub> at 100° (bath) afford *hydroxydihydrode-N*-dimethylsamandarine (XI), C<sub>21</sub>H<sub>37</sub>O<sub>3</sub>N, m.p. 167—168° (sinters at 165°) [*perchlorate* (+0.5EtOH), m.p. 222—225° (sinters at 216°); *hydrochloride* (XII), m.p. 270—271° (decomp.) (sinters at 265°); *Ac* derivative, m.p. 141—143° (sinters at 139°)], which contains 2 active H; the products from the Zerevitinov reaction are a base [*hydrochloride*, m.p. 289—290° (decomp.; sinters at 287°), probably a stereoisomeride of (XII)] and a base, C<sub>22</sub>H<sub>41</sub>O<sub>3</sub>N [*hydriodide*, m.p. 273—275° (decomp.)]. *N*-Methylsamandarine *methiodide* (+H<sub>2</sub>O), m.p. 282—283° (sinters at 278°) [from (II), MeI, and 10% Na<sub>2</sub>CO<sub>3</sub>], is stable to aq. NaOH, but is degraded by Ag<sub>2</sub>O-H<sub>2</sub>O to *de-N*-dimethylsamandarine (XIII), C<sub>21</sub>H<sub>33</sub>O<sub>2</sub>N, m.p. 147—148° [*hydriodide*, decomp. 260—262° (sinters at 257°); *methiodide*, m.p. 323° (slight decomp.; sinters at 320°), similarly converted into (XIII) and (mainly) a neutral resin, which is reduced (H<sub>2</sub>, Pd, dil. AcOH) to a *dihydro*-derivative, m.p. 144—146°, [ $\alpha$ ]<sub>D</sub><sup>21</sup> -159° in 2*N*-AcOH [*hydriodide*, m.p. 268—270° (slight decomp.)]; *oxime*, m.p. 246—247° (sinters at 237°)], also prepared by oxidation (CrO<sub>3</sub>, dil. H<sub>2</sub>SO<sub>4</sub>) of (X). (XIII) and 3% H<sub>2</sub>SO<sub>4</sub> at 100° (bath) give *hydroxydihydrode-N*-dimethylsamandarine (XIV), m.p. 139—140° (sinters at 135°) [*hydriodide*, decomp. 245—248° (sinters at 239°)], which contains 1 active H, also prepared by oxidation of (XI). (XIII) is reduced (Na, EtOH) to (IX) (thus showing that the double linking is not  $\alpha\beta$  to the CO) and a product, which when treated with 3% H<sub>2</sub>SO<sub>4</sub> and then oxidised gives *samandesone* (XV), C<sub>21</sub>H<sub>33</sub>O<sub>3</sub>N, m.p. 190—192° (sinters at 188°) [*oxime*, m.p. 274—276° (sinters at 273°)]. (XV) is also prepared by energetic oxidation (CrO<sub>3</sub>, dil. H<sub>2</sub>SO<sub>4</sub>) of (XI) and (XIV); it is unaffected by boiling 2*N*-NaOH (in which it is sol.) or 50% KOH, and is not acetylated by Ac<sub>2</sub>O-NaOAc. The Zerevitinov reaction with (XV) gives only a little CH<sub>4</sub>; a base, C<sub>24</sub>H<sub>45</sub>O<sub>3</sub>N, m.p. 175—176°, is formed. Reduction (Na, EtOH) of (XV) affords *samandesol* (XVI), C<sub>21</sub>H<sub>35</sub>O<sub>3</sub>N, m.p. 170—172° (sinters at 168°), which is isomeric with (XIV), and *samandesolic acid* (XVII), C<sub>21</sub>H<sub>37</sub>O<sub>4</sub>N, H<sub>2</sub>O, m.p. 208—210° (decomp.) (sinters at 205°). (XVI) and (XVII) are also obtained from (XV) and EtOH-NaOEt. (XVI) and MgMeI (Zerevitinov) give a base, C<sub>23</sub>H<sub>43</sub>O<sub>3</sub>N, m.p. 223—224°. H. B.

**New tropan derivative from coca leaves.** O. WOLFES and O. HROMATKA (Merck's Jahresber., 1934, 47, 45—53; Chem. Zentr., 1934, ii, 1307).—A *dihydroxytropan*, C<sub>8</sub>H<sub>15</sub>O<sub>2</sub>N [probably (I)], m.p. 209—209.5°, [ $\alpha$ ]<sub>D</sub><sup>27</sup> -22° in EtOH (*hydrochloride*, CH<sub>2</sub>—CH—CH<sub>2</sub> [ $\alpha$ ]<sub>D</sub><sup>27</sup> +1.75° in H<sub>2</sub>O; *picrate*, | CH<sub>2</sub>—CH—CH<sub>2</sub> decomp. 253°), is isolated from the alkaloid fractionless sol. in Et<sub>2</sub>O than tropine and  $\psi$ -tropine. On benzylation (I) yields a *bis*(benzoyloxy)tropan [*sulphate*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +52.1° in EtOH; *mono-hydrochloride*, m.p. (+2H<sub>2</sub>O) 115°, (anhyd.) 205°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +41.8° in aq. EtOH; *nitrate*, m.p. 197°]. Reduction of (I) with HI and red P yields tropan; with POCl<sub>3</sub>, (I) affords a *tropen oxide*, b.p. 188°/752 mm. [*picrate*, m.p. 177° (decomp.)].

H. N. R.



**Cinchona alkaloids. XXIX. Stereochemical investigations. IV. Hydrocinchonine of H. Emde and epicinchonine of J. Suszko and A. Tomanek.** P. RABE, H. HAEUSZLER, and W. HOCHSTÄTTER (Annalen, 1934, 514, 61—68).—The dihydrocinchonine (=hydrocinchotoxin) (I), m.p. 112°, of Emde (A., 1932, 759) is impure *epihydrocinchonidine* (II) [prep. from hydrocinchonidine (III) and 25% HCl described (cf. *loc. cit.*)]. Contrary to Emde, (I) is not produced from hydrocinchonine (IV) and 25% HCl; *epihydrocinchonine* (V) results. Emde's conclusions regarding the stereochemical configuration of (II)—(V) are thus invalid. The present results confirm the structures previously assigned (A., 1932, 289). The *epicinchonine* of Suszko and Tomanek (A., 1933, 288) is considered to be *heterocinchonine* (A, R=CH<sub>2</sub>CH<sub>2</sub>). This is reduced (H<sub>2</sub>, Pd-black, 3% H<sub>2</sub>SO<sub>4</sub>) to the *dihydro*-derivative (VI) (A, R=Et), m.p. 202—203°,  $[\alpha]_D^{25} +152.9^\circ$  in 99% EtOH,



the *p*-toluenesulphonate, m.p. 167° (decomp.), of which is obtained from (IV) and *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl in C<sub>5</sub>H<sub>5</sub>N (cf. *loc. cit.*), and is converted by KOBz in EtOH into the benzoate, oil, of (VI). The bromide (A, R=Et, OH=Br) (which is neutral towards litmus) is obtained (no details) as a by-product from (IV) and PBr<sub>5</sub>; hydrolysis gives (VI). H. B.

**Alkaloids of calumba root. V. Absorption spectra of the alkaloids of calumba root and of some derivatives of berberine.** K. FEIST, W. AWE, and H. ETZRODT (Arch. Pharm., 1934, 272, 817—826; cf. A., 1932, 177).—The prep. of *palmatinium* (I), m.p. 240—242° (decomp.), and *jatro-rhizinium iodide* (II), m.p. 210—212° (decomp.), from calumba root (III) is described. The quaternary sulphates of berberine and the alkaloids of (III) are reduced to the *tert.* bases by amalgamated Zn and AcOH. Corydaline and Hg(OAc)<sub>2</sub> lead to 2:3:11:12-tetramethoxy-16-methyl-8:9:16:17-tetradehydroberbinium (8:9:16:17-tetradehydro-corydalinium iodide (IV), m.p. about 230° (decomp.). The absorption spectra of berberinium iodide (V), (I), (II), and the iodide of the new alkaloid from (III) (*loc. cit.*) are very similar (max. at 265 and 335 m $\mu$ ), but (V) differs by not showing also a subsidiary max. at 280 m $\mu$ . 16:17-Dihydrodeoxyberberine and 9-CH<sub>2</sub>Ph, - $\psi$ -CH<sub>2</sub>Ph, and -*o*-C<sub>6</sub>H<sub>4</sub>Me derivatives give a broad band below 315 m $\mu$  (max. 290 m $\mu$ ), but the corresponding reduced (III) alkaloids have no absorption above 305 m $\mu$  and a max. at about 280 m $\mu$ . The absorptions of 9-*m*-tolyldeoxyberberine and its hydriodide differ somewhat, which supports the view that the ethylenic linking wanders during salt formation. The absorption spectra of oxyberberine and "oxypalmatine" (modified preps.) are similar, showing a max. at 340 and a min. at 285 m $\mu$ ; the effect of the CO group is thus very pronounced. R. S. C.

**Reduction in morphine series. IV. *allo*- $\psi$ -Codeine.** R. E. LUTZ and L. SMALL (J. Amer. Chem. Soc., 1934, 56, 2466—2468).—*allo*- $\psi$ -Codeine (I)

(Speyer and Krauss, A., 1923, i, 1115) [salicylate, m.p. 202°; *hydrochloride*, m.p. 256—258° (decomp.)] is reduced (hydrochloride; H<sub>2</sub>, PtO<sub>2</sub>, AcOH) to 80% of the non-phenolic *dihydroallo- $\psi$ -codeine* (II), m.p. 78—79°,  $[\alpha]_D^{25} -105^\circ$  in EtOH [*H tartrate* (+2H<sub>2</sub>O), m.p. 124—125°, re-solidifying with m.p. 160—163°; *hydriodide*, m.p. 255° (decomp.); *perchlorate* (+3H<sub>2</sub>O), m.p. 265—270°], 18% of *tetrahydroallo- $\psi$ -codeine* (III), m.p. (anhyd.) 145.5°,  $[\alpha]_D^{25} -58^\circ$  in EtOH [*perchlorate* (+H<sub>2</sub>O), m.p. 102—104°; *methiodide*, m.p. 241—242° (decomp.)], and a trace of *tetrahydrodeoxycodeine* (IV). Reduction (H<sub>2</sub>, Pd-CaCO<sub>3</sub>, EtOH) of (I) affords approx. equal parts of (II) and (III). Reduction (Na, EtOH) of (I) gives 36% of the phenolic *dihydroallo- $\psi$ -codeine*, not obtained *cryst.* [*perchlorate* (+H<sub>2</sub>O), m.p. 145—147°; *methiodide*, m.p. 247—248° (decomp.)], and 44% of the previously described (A., 1934, 1117) mixture (V) of *dihydrodeoxycodeines-B* and *-C*. (IV) and (V) probably result from 1:6 addition of H<sub>2</sub> to (I); the intermediate *deoxycodeine-A* is then reduced. The *methiodide* of (II) is converted by hot alkali into the non-phenolic *dihydro- $\zeta$ -methylmorphimethine*, m.p. 99°,  $[\alpha]_D^{25} +117^\circ$  in EtOH [*salicylate*, m.p. 175°], hydrogenated to the non-phenolic *tetrahydro- $\zeta$ -methylmorphimethine*, m.p. 110°,  $[\alpha]_D^{25} -26^\circ$  in EtOH [*salicylate*, m.p. 175—175.5°]. Phenolic *tetrahydro- $\zeta$ -methylmorphimethine* (*hydriodide*, m.p. 249°), prepared by Speyer and Krauss' method (*loc. cit.*), is hydrogenated to the hexahydro-derivative [*hydriodide*, m.p. 279—281° (decomp.)] of  $\zeta$ -methylmorphimethine (Speyer and Koulen, A., 1925, i, 59) [*H tartrate* (+2H<sub>2</sub>O), m.p. 99—101° (decomp.); *perchlorate* (+H<sub>2</sub>O), m.p. 117—118°; *salicylate* (+H<sub>2</sub>O), m.p. 118—120°]. All m.p. are corr.

H. B.

**Oxidation of strychnine.** A. BERNARDI (Atti Congr. naz. Chim., 1933, 4, 389—396; Chem. Zentr., 1934, ii, 251).—Oxidation of strychnine (I) in AcOH by CrO<sub>3</sub> yields a product C<sub>42</sub>H<sub>42</sub>O<sub>8</sub>N<sub>4</sub>, m.p. 301—302°, which on reduction again gives colour reactions of (I).

A. G. P.

**Arsenated phenoxyalkanols.** L. A. SWEET and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 2409—2412).—*p*-OH·C<sub>6</sub>H<sub>4</sub>·AsO<sub>3</sub>H<sub>2</sub> and CH<sub>2</sub>Cl·CH<sub>2</sub>·OH in *N*-NaOH give  $\beta$ -*p*-*arsinophenoxyethyl alcohol* (I), m.p. 147—148° (softens at 127°) [*Na salt* (+2H<sub>2</sub>O); *nitrate* (II), m.p. 145°], which with HNO<sub>3</sub> (*d* 1.5) and conc. H<sub>2</sub>SO<sub>4</sub> at 20° affords  $\beta$ -2-*nitro-4-arsinophenoxyethyl nitrate* (III), m.p. 217—218° (decomp.; softens > 160°), hydrolysed (2.5*N*-HCl) to  $\beta$ -2-*nitro-4-arsinophenoxyethyl alcohol* (IV) [*3-nitro-4- $\beta$ -hydroxyethoxyphenylarsinic acid*], m.p. 138°. (IV) is reduced [Fe(OH)<sub>2</sub>, dil. NaOH] to  $\beta$ -2-*amino-4-arsinophenoxyethyl alcohol* (V) (+H<sub>2</sub>O), m.p. 96—98°, m.p. (anhyd.) 156—157° [*Na salt*; *anhydride*, m.p. 208—210° (decomp.); softens at 145—150°]; *hydrochloride*, m.p. 171—172° (decomp.); *N-Ac derivative*, m.p. 207° (decomp.). (I) and HNO<sub>3</sub> (*d* 1.5) in conc. H<sub>2</sub>SO<sub>4</sub> at 95° give  $\beta$ -2:6-*dinitro-4-arsinophenoxyethyl alcohol*, m.p. 212—215° (decomp.) [*nitrate*, m.p. 188—189°; corresponding (NH<sub>2</sub>)<sub>2</sub>-derivative, m.p. 205° (decomp.)], and 3:5-*dinitro-4-hydroxyphenylarsinic acid*, m.p. > 275°. (I) and HNO<sub>3</sub> (*d* 1.5) at 25—30° for 24 hr. afford 2-*nitro-4-arsinophenoxyacetic acid*, m.p. > 250° (*Me*



ester, m.p. 225—226°), which is reduced to 3-hydroxy-1:4-benzisooxazine-6-arsinic acid (Newbery *et al.*, A., 1929, 83). Hydrolysis (6*N*-HCl) of a mixture of (II) and (III) gives 2-chloro-4-arsinophenoxyethyl alcohol, m.p. 141° [nitrate, m.p. 205° (decomp.; softens at 136°)] [formed from (I) and Cl<sub>2</sub> from HCl+HNO<sub>3</sub>], and (IV) (removed by reduction). 4-β-Hydroxyethoxyphenylarsenoxide and its 3-Cl- and 3-NH<sub>2</sub>-derivatives, all m.p. > 250°, are prepared by reduction (H<sub>2</sub>SO<sub>4</sub>, HI) of the corresponding arsenic acids. 3-Amino-4-β-hydroxyethoxyphenyldichloroarsine hydrochloride has m.p. 174°. 3:3'-Dinitro-4:4'-di-β-hydroxyethoxyarsenobenzene and its dinitrate are prepared by reduction (25% H<sub>3</sub>PO<sub>2</sub> at 95°) of (IV) and (III), respectively; (V) similarly gives 3:3'-diamino-4:4'-di-β-hydroxyethoxyarsenobenzene. γ-p-Arsinophenoxypropyl alcohol, m.p. 146° [2-NO<sub>2</sub>-derivative (nitrate, m.p. 207°); 2-NH<sub>2</sub>-derivative hydrochloride, m.p. 136°], is prepared [as (I)].

H. B.

**Arsenicals derived from 6-nitro-β-naphthylamine.** L. A. SWEET and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 2408—2409).—6-Nitro-2-naphthylarsinic acid, prepared by the usual method from 6-nitro-β-naphthylamine (Bz derivative, m.p. 206°), is reduced [Fe(OH)<sub>2</sub>] to 6-amino-2-naphthylarsinic acid (Ac and N-CO<sub>2</sub>Et derivatives), which with (CH<sub>2</sub>)<sub>2</sub>O in 0.5*N*-Na<sub>2</sub>CO<sub>3</sub> gives 6-β-hydroxyethylamino-2-naphthylarsinic acid. All the above have m.p. > 250°. 2:6-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)<sub>2</sub> has m.p. 220°. H. B.

**Constitution of nearsphenamine.** W. J. C. DYKE and H. KING (J.C.S., 1934, 1707—1718).—Na formaldehydesulphoxylate and the appropriate NH<sub>2</sub>Ar in H<sub>2</sub>O and N<sub>2</sub> at 50—80° give Na anilino- (I), *o*-toluidino- (II) (tetrahydrate), *o*- (III) and *p*-carboxyanilino- (tetrahydrates), and 2-hydroxy-5-carbomethoxyanilino- (IV) (+3.5H<sub>2</sub>O), -N-methylenesulphoxylates. Na 2-hydroxy-5-carbomethoxyanilino-N-methylenesulphite (V) (+2H<sub>2</sub>O) is prepared using OH·CH<sub>2</sub>·SO<sub>2</sub>Na. (I)–(IV) do not reduce methylene-blue (VI) to any appreciable extent in neutral NaOAc-buffered solution in O<sub>2</sub>-free N<sub>2</sub>. (VI) is reduced to the extent of 71% by (IV) in aq. EtOH–NaOAc at 70—75°; in almost boiling 0.1*N*-AcOH, about 90% reduction occurs: NHR·CH<sub>2</sub>·O·SONa + (VI) ⇌ NHR·CH<sub>2</sub>·O·SO<sub>2</sub>Na + leuco-(VI). (IV) absorbs 0.1*N*-I until 90% of the S is converted into SO<sub>4</sub><sup>2-</sup>; a small amount of (V) (which is not acted on by I except in presence of acid) is probably first formed, viz.: (i) (subsidiary) NHR·CH<sub>2</sub>·O·SONa + I<sub>2</sub> → NHR·CH<sub>2</sub>·O·SO<sub>2</sub>Na + HI; (ii) (main) NHR·CH<sub>2</sub>·O·SONa + HI → NH<sub>2</sub>R + OH·CH<sub>2</sub>·O·SONa  $\xrightarrow{I_2}$  CH<sub>2</sub>O + Na<sub>2</sub>SO<sub>4</sub>. These results completely invalidate the conclusions of all previous workers [except possibly Freedman (cf. B., 1926, 767)] on the quant. action of I on nearsphenamine (VII) [which consumes 7.2 I (As:As requires 8), a considerable proportion of which is used in forming SO<sub>4</sub> at the expense of AsO<sub>3</sub>H<sub>2</sub> (which then reverts to AsO:RAsO<sub>3</sub>H<sub>2</sub> + 2HI → RAsO + I<sub>2</sub> + 2H<sub>2</sub>O)]. Unlike (I)–(IV), (VII) reduces (VI) in neutral solution at room temp.; this is attributed to activation by the As:As group, which does not take part in the reaction. Na diaminodihydroxyarsenobenzene-NN'-dimethylenesulphite has no action on (VI) at room

temp.; reduction (ascribed to As:As) occurs on warming. Little reaction (which is catalysed by light) occurs between (VI) and OH·CH<sub>2</sub>·O·SONa at room temp.; quant. oxidation occurs at approx. *p*<sub>H</sub> 3 and 100°.

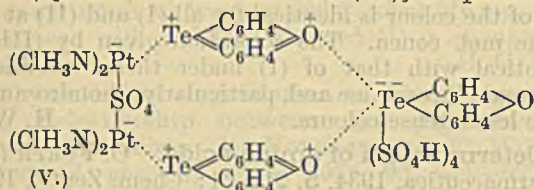
Determinations of As, total S (by Elvove's method, B., 1926, 27), S [by titration with (VI)], and free SO<sub>4</sub> in various commercial samples of (VII), and of As, S (Elvove), S [(VI)], and Na in the products obtained by pptn. from aq. solutions with AcOH in absence of O<sub>2</sub> (apparatus used described) show that some samples contain ·NH·CH<sub>2</sub>·O·SONa groups only, whilst others also contain ·NH·CH<sub>2</sub>·O·SO<sub>2</sub>Na; all the samples contain uncombined salts. The analogous results obtained with products synthesised (as standards) from salvarsan base and OH·CH<sub>2</sub>·O·SONa (2 mols.), OH·CH<sub>2</sub>·SO<sub>2</sub>Na (2 mols.), and an equimol. mixture of the two salts are given. H. B.

**Cyclic selenones.** H. J. BACKER and J. STRATING (Rec. trav. chim., 1934, 53, 1113—1119).—Seleno-Δ<sup>3</sup>-cyclopentene 1:1-dioxides (I), SeO<sub>2</sub> <  $\begin{matrix} \text{CH}_2 \cdot \text{CR} \\ \text{CH}_1 \cdot \text{CR}' \end{matrix}$  are obtained from (CH<sub>2</sub>·CR·)<sub>2</sub> and H<sub>2</sub>SeO<sub>3</sub> in cold CHCl<sub>3</sub>; (I) are unstable and liberate Se when exposed to air and light. Similar compounds could not be obtained from butadiene and αβγδ-tetramethyl- and αδ-dimethyl-βγ-diethyl-butadienes. The following are described: 3-methyl-, m.p. about 67° (decomp.) (from isoprene); 3:4-dimethyl-, m.p. about 66° (decomp.) [from (CH·CMe)<sub>2</sub>]; 3-tert.-butyl-, m.p. about 81—82° (decomp.) (from CH<sub>2</sub>·CMe·CH·CH<sub>2</sub>); 3:4-ditert.-butyl- (II), m.p. 132° (decomp.); 3-phenyl-, m.p. 90° (decomp.); 3:4-diphenyl-, m.p. 89—90° (decomp.), and 3-chloro-4-methyl-, m.p. about 110° (decomp.) (from CH<sub>2</sub>·CCl·CMe·CH<sub>2</sub>), -seleno-Δ<sup>3</sup>-cyclopentene 1:1-dioxides. (II) and SO<sub>2</sub> in Et<sub>2</sub>O give a compound, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>Se, m.p. about 143° (decomp.); C<sub>12</sub>H<sub>22</sub>O<sub>6</sub>Se + SO<sub>2</sub> + H<sub>2</sub>O + O → C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>SSe. H. B.

**Interpretation of the phenoxtellurine dibisulphate reaction with platinous compounds. Micro-analysis of platinum and tellurium.** H. D. K. DREW (J.C.S., 1934, 1790—1797).—Phenoxtellurine dibisulphate (I) is ground with (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub> or K<sub>2</sub>PtCl<sub>4</sub> and the product then triturated successively with cold H<sub>2</sub>O, conc. H<sub>2</sub>SO<sub>4</sub>, and cold H<sub>2</sub>O; subsequent extraction with boiling AcOH and drying at 105° in air gives the black phenoxtellurium platichloride (II), C<sub>12</sub>H<sub>8</sub>OCl<sub>4</sub>TePt (alternative structures discussed), which is decomposed by aq. HCl or aq. KCl to phenoxytellurine dichloride (III) and H<sub>2</sub>PtCl<sub>4</sub> or K<sub>2</sub>PtCl<sub>4</sub>, respectively. (III) and Ag<sub>2</sub>O in H<sub>2</sub>O afford phenoxtellurine oxide, which when heated gives phenoxtellurine and Ph<sub>2</sub>O. Some (II) is also produced from (I) and Magnus' green salt, probably owing to the dissociation, [Pt(NH<sub>3</sub>)<sub>4</sub>]PtCl<sub>4</sub> → [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> + PtCl<sub>2</sub>. Plati-ammines and Pt<sup>IV</sup> salts do not give colours with (I). The product from (I) and β-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (IV) is extracted with cold 75% (vol.) H<sub>2</sub>SO<sub>4</sub>; cautious addition of H<sub>2</sub>O to the resulting solution ppts. the purplish-black triphenoxtellurium tetrabisulphate diamminodichloroplatosulphate (V) (dotted lines represent ionised linkings). (V) is decomposed by warm H<sub>2</sub>O to phenoxtellurine salts, H<sub>2</sub>SO<sub>4</sub>, and (IV); with warm AcOH or cold Ac<sub>2</sub>O,



phenoxtellurine sulphate, (II), and a ppt. of (VI) (below) [mixed or combined with (IV)] are produced.



Impure *diamminodichloroplatosulphuric acid* (VI),  $\text{H}_2[\text{Pt}(\text{NH}_3\text{Cl})_2 \cdot \text{SO}_4 \cdot \text{Pt}(\text{NH}_3\text{Cl})_2]$ , black, is prepared from (IV) and fairly conc.  $\text{H}_2\text{SO}_4$ ; use of too conc.  $\text{H}_2\text{SO}_4$  gives (probably)  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2\text{SO}_4$ . (VI) is decomposed by aq.  $\text{NaCl}$  to (IV). The results support the view that the relationship between the  $\alpha$ - and  $\beta$ -plato-diammine dichlorides is not merely that between *trans*- and *cis*-isomerides but is also structural;  $\alpha$ -(IV) does not form compounds of the types (V) and (VI). (I) forms purple complexes with  $\text{PAr}_3$ ,  $\text{AsAr}_3$ , and  $\text{SbAr}_3$ , but not with  $\text{NAr}_3$  or  $\text{BiAr}_3$ .

Details are given for the micro-determination of Pt, Te, Cl, and S in substances containing all 4 elements. H. B.

**Mixtures of casein and native ox serum-albumin.** M. FREEMAN (Austral. J. Exp. Biol., 1934, 12, 155—160).—When casein is pptd. near its isoelectric point in presence of serum-albumin the ppt. is partly sol. in 1% aq.  $\text{NaCl}$ . The sol. fraction, which contains less P than the original casein and somewhat resembles euglobulin, increases in amount as the  $p_{\text{H}}$  of pptn. is increased. W. O. K.

**Ultra-violet absorption spectra of certain denatured proteins.** C. S. HICKS and H. F. HOLDEN (Austral. J. Exp. Biol., 1934, 12, 91—97).—The ultra-violet absorption of various proteins undergoes considerable change when the protein is denatured by EtOH or in alkaline solution; hot denaturation in acid solution has little effect except with serum-albumin, when secondary chemical changes may occur. W. O. K.

**Allocation of free amino-groups in proteins and peptides.** S. GURIN and H. T. CLARKE (J. Biol. Chem., 1934, 107, 395—419).—By the action of  $\text{PhSO}_2\text{Cl-NaOH}$  on the  $\text{NH}_2$ -acid are obtained the *benzenesulphonyl* derivatives of *dl*-phenylalanine, m.p. 127—128°, *dl*-methionine, m.p. 104°, and *l*-histidine, m.p. 236° (decomp.),  $[\alpha]_{\text{D}}^{25} -27.2^\circ$  in 0.1N-NaOH. Such derivatives are readily characterised as their cryst.  $\text{Bu}^a$  esters. The  $\text{Bu}^a$  esters of benzenesulphonyl-glycine, m.p. 26—27°, *dl*-alanine, m.p. 113°, *l*-leucine, m.p. 50—51°,  $[\alpha]_{\text{D}}^{25} -16.1^\circ$  in 95% EtOH, *dl*-alanylglycine, m.p. 76.5°, *glycyl-dl*-alanine, m.p. 101°, and *glycyl-l*-leucine, m.p. 107°, and the  $\text{Bu}^a_2$  esters of benzenesulphonyl-*d*-glutamic acid, m.p. 58—59°,  $[\alpha]_{\text{D}}^{25} 0^\circ$  in EtOH, and *i*- $\beta$ -hydroxyglutamic acid, m.p. 76° ( $\text{Bu}^a_1$  ester, m.p. 169—170°), are new. Hydrolysis of such derivatives of simple dipeptides with 50%  $\text{HCO}_2\text{H}$  containing a little conc.  $\text{HCl}$  at 90—100° proves that under such conditions complete fission of the peptide linkings can be effected without hydrolysis of the  $\cdot\text{SO}_2\text{Ph}$ , and hence this method is applied to determine the location of free  $\text{NH}_2$  in various

polypeptides. Thus hydrolysis of the *benzenesulphonyl* derivative, m.p. 123°, of oxidised glutathione affords, after esterification,  $\text{Bu}^a$  benzenesulphonyl-glutaminate, confirming the location of the free  $\text{NH}_2$  in the glutamic acid residue. The benzenesulphonyl derivative of gelatin (I) (S, 2.0%; control 0.20%:  $\text{NH}_2\text{-N}/\text{total N}=0.1$ ; control 4.0;  $p_{\text{H}}$  titration curve with glass electrode shifted as for deaminised gelatin) affords a hydrolysate from which is isolated a 50% yield of the *Cu* salt of  $\epsilon$ -benzenesulphonyl-*d*-lysine, characterised as its *phenylhydantoin* (II), m.p. 138°,  $[\alpha]_{\text{D}}^{25} -31.4^\circ$  in 95% EtOH, identical with a specimen synthesised thus: hydrolysis of its  $\epsilon$ -Bz derivative (Karrer *et al.*, A., 1926, 603) affords the phenylhydantoin of *d*-lysine, isolated as its *platinichloride*, m.p. 210—211° (decomp.), converted by grinding with finely-divided Ag and treatment with  $\text{PhSO}_2\text{Cl-NaOH}$  into (II), which is different from  $\epsilon$ -phenylureido- $\alpha$ -benzenesulphonyl-*d*-lysine, m.p. 145°,  $[\alpha]_{\text{D}}^{25} +11.9^\circ$  in 95% EtOH [prepared by  $\text{PhNCO}$  and  $\alpha$ -benzenesulphonyl-*d*-lysine (III), m.p. 249—251° (decomp.),  $[\alpha]_{\text{D}}^{25} -22.8^\circ$  in 0.1N-NaOH, obtained by *N*-NaOH hydrolysis of its  $\epsilon$ -Bz derivative, m.p. 168° (from  $\text{PhSO}_2\text{Cl}$  and  $\epsilon$ -benzoyl-*d*-lysine)]. Hydrolysis ( $\text{HCl}$ ) of the *dibzenesulphonyl* derivative of *d*-lysine affords (III). At least 50% of the free  $\text{NH}_2$  in (I) is due to the  $\epsilon$ - $\text{NH}_2$  in lysine, and  $\approx 0.5\%$  of the free  $\text{NH}_2$ -N can be allocated to  $(\text{NH}_2)_1$ -acids. J. W. B.

**Electric furnace with automatic temperature regulation for semi-micro-determination of carbon and hydrogen (ter Meulen).** B. HEINEMANN (Chem.-Ztg., 1934, 58, 991—992).—An apparatus is described and advantages are enumerated.

E. S. H.

**Argentometric semi-micro-determination of chlorine and bromine in organic substances.** B. BROBAŃSKI (Z. anal. Chem., 1934, 99, 108—109).—Polemical against Hölischer (A., 1934, 671).

J. S. A.

**Determination of chlorine in presence of bromine in organic substances.** F. Böck and G. Lock (Chem. Fabr., 1934, 7, 406—407).—Modified technique for Rose's method is described. The mean error is  $< 0.0002$  g.

E. S. H.

**Determination of small amounts of organic arsenic compounds in air.** M. JUREČEK (Coll. Czech. Chem. Comm., 1934, 6, 468—475).—Volatile As compounds are removed from air by sorption on  $\text{SiO}_2$  gel; the gel is then heated under  $\text{MgO}$ , covered with  $\text{Na}_2\text{O}_2\text{-Na}_2\text{CO}_3$ . Dusts of As compounds are absorbed from air by washing with  $\text{COMe}_2$  or  $\text{Et}_2\text{O}$ ; the solution is evaporated and the residue heated with  $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}_2$ . The aq. extract of the melt or the diluted acid solution is reduced and the  $\text{AsH}_3$  formed determined colorimetrically; suitable apparatus is described.

R. S. C.

**Determination of carbonyl compounds by means of 2:4-dinitrophenylhydrazine.** H. A. IDDLIES and C. E. JACKSON (Ind. Eng. Chem. [Anal.], 1934, 6, 454—456).—An aq. solution of the CO-compound is allowed to react with an excess of a saturated solution of 2:4-dinitrophenylhydrazine in 2N-HCl (I) at 0° for 1 hr. The ppt. is washed with (I) and dried in a vac. The average yields obtained with the follow-



ing are given in parentheses: MeCHO (95.04), COMe<sub>2</sub> (97.49), COMeEt (97.87), COMePr<sup>c</sup> (98.29), PhCHO (99.15), *p*- (99.39) and *o*-OH·C<sub>6</sub>H<sub>4</sub>CHO (98.7), *o*-OMe·C<sub>6</sub>H<sub>4</sub>CHO (100.2), vanillin (102.18%). S. C.

**Determination of aldehydes by the hydrogen sulphite method.** A. E. PARKINSON and E. C. WAGNER (Ind. Eng. Chem. [Anal.], 1934, 6, 433—436).—More accurate results are obtained by adding the aldehyde H sulphite (I) solution to an excess of I and back-titrating immediately with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. If (I) dissociates too rapidly at room temp. the solution is cooled in ice before and during contact with I. The following aldehydes were tested and the % purity of the samples is given in parentheses: CH<sub>2</sub>O (100), MeCHO (98.9), EtCHO (98.6), Pr<sup>c</sup>CHO (98.5), Pr<sup>β</sup>CHO (95.8), Bu<sup>c</sup>CHO (96.3), Bu<sup>β</sup>CHO (97.6), *n*-C<sub>6</sub>H<sub>13</sub>·CHO (97.2), PhCHO (97.1), acetal (97.2), *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO (96.1), vanillin (97.3), piperonal (100.6). Unsatisfactory results were obtained with paraldehyde, croton- and cinnam-aldehydes. S. C.

**Determination of lactic acid in presence of methylglyoxal.** J. O. GIRŠAVIČIUS and P. A. HEYFETZ (Biochem. Z., 1934, 274, 95—96).—The method of Simon and Neuberg (A., 1931, 662) is favoured. P. W. C.

**Determination of amino-acids and polypeptides.** E. CHERBULIEZ and A. HERZENSTEIN (Helv. Chim. Acta, 1934, 17, 1440—1443).—Blood serum (1 c.c.) is treated with so much powdered (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> that the vol. attains 1.5 c.c. and then with saturated (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> until the vol. is 4 c.c. After thorough shaking the mixture is passed through a dry filter and 1 c.c. of the filtrate is boiled for 2 min. with 0.2 c.c. of 1% aq. ninhydrin. The mixture is shaken with amyl alcohol until the aq. solution is perfectly clear and the alcoholic extract is agitated with 0.5% NaOH until it is pure blue in colour. The intensity is matched against that of a standard solution obtained from glycine. Under these conditions the reaction is sp. for the group ·CO·CH(NH<sub>2</sub>)· and hence is shown by all NH<sub>2</sub>-

acids (I) and the polypeptides (II) derived from them, by α-NH<sub>2</sub>-aldehydes and -ketones (III). The intensity of the colour is identical for all (I) and (II) at the same mol. concn. The coloration given by (III) is identical with that of (I) under these conditions, whereas glucosamine and, particularly, chondrosamine give less intense colours. H. W.

**Determination of amino-acids.** O. FURTH (Sci. Pharmaceutica, 1934, 5, 21—24; Chem. Zentr., 1934, i, 3600).—A review of recent work. R. N. C.

**Identification of aromatic nitro-compounds by optical crystallographic methods.** E. S. DAVIES and N. H. HARTSHORNE (J.C.S., 1934, 1830—1836).—Crystallographic data are given for 20 NO<sub>2</sub>-compounds. Some binary and ternary mixtures of these compounds were rapidly identified under the polarising microscope. R. S. C.

**Determination of *m*-cresol.** A. WADA and I. KAWAI (J. Soc. Chem. Ind. Japan, 1934, 37, 702B).—An improvement of Raschig's process for determining *m*-cresol as its (NO<sub>2</sub>)<sub>3</sub>-derivative (A., 1900, ii, 694) is described. H. N. R.

**Determination of nicotine by the silicotungstic acid method.** N. H. PIZER (J.S.C.I., 1934, 53, 356—357T).—The method is trustworthy for solutions containing from 0.1% to 0.005% of nicotine. Ignition of the nicotine silicotungstate at 1000° gives const. wt.

**Determination of quinine hydrobromide by the cupro-hydrogen bromide reaction.** G. DENIGES (Bull. Soc. Pharm. Bordeaux, 71, 251—254; Chem. Zentr., 1934, ii, 1343).—A simple colour reaction for the detection of Br' in the presence of quinine is described; the process may be made quant. H. N. R.

**Alkaloidal reagents. V. Aconite alkaloids.** J. C. MUNCH and H. J. PRATT (J. Amer. Pharm. Assoc., 1934, 23, 968—973).—The behaviour of aconitine, benzoylaconine, and aconine towards 71 alkaloidal reagents is recorded. Aconite alkaloids are excreted chiefly into the liver. A. E. O.

## Biochemistry.

**Case of deficient acclimatisation to low oxygen pressure.** J. BARCROFT, R. H. E. ELLIOTT, F. R. FRASER, W. HERKEL, B. H. C. MATTHEWS, and M. TALAAT (J. Physiol., 1934, 82, 369—376).—A normal subject kept in a reduced O<sub>2</sub> partial pressure for 5 days attained a poor degree of acclimatisation, alveolar O<sub>2</sub> pressure and total metabolism falling and CO<sub>2</sub> pressure remaining high. The O<sub>2</sub> dissociation curve was shifted to the right. The arterial blood at the end of the experiment was > 65% saturated with O<sub>2</sub>. R. N. C.

**Anhydrase activity of the blood and coelomic liquid of invertebrates.** M. FLORKIN (Bull. Acad. roy. Belg., 1934, [v], 20, 922—930).—A method is described for determination of the relative anhydrase activity, which catalyses the liberation of CO<sub>2</sub> from blood, of various body-fluids. This enzyme has been found in the blood of Annelids, but not in Arthropods or Molluscs. H. G. R.

**Direct chemical determination of "carb-amino-bound" carbon dioxide in hæmoglobin solution.** J. K. W. FERGUSON and F. J. W. ROUGHTON (Proc. Physiol. Soc., J. Physiol., 1934, 81, 21—22P).—Much CO<sub>2</sub> in blood is not pptd. by alkaline BaCl<sub>2</sub>. The proportion is higher in reduced than in oxy-hæmoglobin solutions. Carbamino-compounds are probably important in the transport of CO<sub>2</sub>. CH. ABS. (p)

**Determination of hæmoglobin in blood.** B. DEUTSCH (Biochem. Z., 1934, 274, 299—304; cf. Dénes, A., 1933, 174).—The hæmoglobin (I) content of blood is determined spectrophotometrically, without loss of accuracy, after (I) is converted into hæmochromogen. W. McC.

**Fluorescence of the blue pigments of the blood of the wrass.** M. FONTAINE (Compt. rend. Soc. Biol., 1934, 117, 420—422).—In ultra-violet light the



pigments show a red fluorescence (I) and the absorption spectrum shows a band at 665—631  $m\mu$ . The (I) spectrum shows bands at 666.5 and at 516  $m\mu$ . By treatment with *N*-KOH, the red (I) is changed to green.

H. G. R.

**Physiological degradation of blood-pigment.**  
**IV. Relationship between the pigments of blood and urine.** R. NOTHAAS and F. WIDENBAUER (*Z. ges. exp. Med.*, 1934, 93, 644—652).—The production from hæmin of a substance having the same chemical and physical properties as urochrome-B (I) is described. (I) is a derivative of hæmoglobin.

NUTR. ABS. (m)

**Bilirubin in the serum of vertebrates.** B. VARELA-FUENTES and A. MUNILLA (*Compt. rend. Soc. Biol.*, 1934, 117, 555—557).—Bilirubin has been found in small quantities in dog- and ewe-serum (I) and in considerable quantities in horse-(I). It is not present in rabbit-, pigeon-, guinea-pig-, hen-, pig-, duck-, or turkey-(I).

H. G. R.

**Differentiation of the pigments of human blood-serum.** F. VERZAR, H. SÜLLMANN, and A. VISCHER (*Biochem. Z.*, 1934, 274, 7—15).—A method for the differentiation of serum-pigments which depends on the spectrophotometric determination of total absorption, of absorption of bilirubin (I) (as azo-dye), of lipochromes sol. in light petroleum [carotene (II) and xanthophyll ester (III)], and of an "X" fraction of pigments (xanthophyll, flavin, and EtOH-sol., light petroleum-insol. non-diazotisable pigment) is elaborated and applied to a no. of normal and pathological sera. Of the total absorption of normal serum, 74% is due to (I), 8% to (II), 3% to (III), and 15% to the "X" fraction.

P. W. C.

**Clinical colour measurements. XII. Spectrophotometric pigment analysis of blood-serum, with respect to the bilirubin and carotene spectra.** L. HEILMEYER and H. TOOP (*Z. ges. exp. Med.*, 1934, 80, 603—632; *Chem. Zentr.*, 1934, i, 3774).—Bilirubin is identified from the extinction curve as the principal yellow pigment of normal and pathological sera, with absorption max. at 460  $m\mu$ . Carotenoid pigments, traces of hæmoglobin, and an unidentified yellow pigment are also present.

J. S. A.

**State of combination of protein degradation products on passage into the blood.** B. LUSTIG (*Biochem. Z.*, 1934, 274, 313—319).—Determination of N in the filtrate from heat-coagulated blood-sera (I) to which degradation products of protein have previously been added shows that about 25% of added proto- and deuto-albumoses, a much smaller proportion of peptone, and no  $NH_2$ -acids are adsorbed by the serum-proteins (II). (I) kept for 24 hr. before treatment lose  $\frac{1}{3}$  of their adsorbing power (III). Longer keeping leads to no further diminution of (III). (III) is unaffected when (I) are heated at 38° for several hr. or inactivated by heating for 1—2 hr. at 60°. Different (I) have different (III). (III) is greatly reduced by dilution to half concn. and destroyed by further dilution. After a meal rich in protein (I) have increased (III). It is the globin fraction of (II) which is responsible for (III).

W. McC.

**Determination of creatinine (and creatine) in blood.** O. FOLIN (*Z. physiol. Chem.*, 1934, 228, 268—272).—A criticism of Lieb and Zacherl's method (A., 1934, 543). The author's method is described.

J. H. B.

**Formation of acetylcholine in serum and embryonal extract.** R. AMMON and H. KWIAKOWSKI (*Pflüger's Archiv*, 1934, 234, 269—272; *Chem. Zentr.*, 1934, ii, 1330).—The results of previous workers are confirmed. Hydrolysis of acetylcholine is inhibited by use of a Ringer's solution containing eserine.

H. N. R.

**Ammonia content and formation in blood.**  
**XI. J. K. PARNAS** (*Biochem. Z.*, 1934, 274, 158—162).—A table shows the amount of  $NH_3$ -N eliminated from 3 samples of human blood as determined by the author's distillation method both with Folin's oxalate-carbonate buffer (I) and with borate buffer (II). In the first distillation with (II) much less  $NH_3$  is obtained than with (I), and on carrying out a second distillation with (II) the amount of  $NH_3$  falls to nil, whereas with (I) a further significant amount is obtained. (II) therefore removes completely the  $NH_3$  present and further  $NH_3$  formation is small. Long keeping with (II) leads to the formation of a small amount of  $NH_3$ .

P. W. C.

**Alkali reserve and fat content of the blood.** R. F. OGILVIE (*Edinburgh Med. J.*, 1934, 41, 448—451).—In rabbits the acid-base balance in blood does not control the fat content of the blood or its migration from the fat depôts.

CH. ABS. (p)

**Cholesterol content and cholesterolytic power of the serum of the aged.** M. ECK and J. DESBORDES (*Compt. rend. Soc. Biol.*, 1934, 117, 428—429).—The sera of atheromatous cases are frequently supersaturated with cholesterol.

H. G. R.

**Cholesterolytic power of serum in a study of the metabolism of cholesterol.** M. ECK and J. DESBORDES (*Compt. rend. Soc. Biol.*, 1934, 117, 429—431; cf. preceding abstract).—Cholesterol (I) is dissolved by serum in a definite proportion, influenced by various factors, so that (I) may be deposited in the arterics and may then be redissolved, possibly in excess.

H. G. R.

**Relation between the cholesterolytic power of a serum and its protein content.** M. ECK and J. DESBORDES (*Compt. rend. Soc. Biol.*, 1934, 117, 615—618).—The power (I) of a serum to dissolve excess cholesterol (II) is dependent on the ratio (III) of the total serum-protein pptd. by NaCl to the amount of (II) carried down by the pptn. In normal sera, (I) is zero when (III) is 50—65, becoming positive and negative, respectively, when (III) rises above or falls below these limits. (I) rises as the protein/urea-N ratio falls. The relation between (I) and (III) does not hold in pathological cases.

R. N. C.

**Maternal and foetal oxalæmia.** F. P. DONEDDU (*Arch. Farm. sperim.*, 1934, 58, 201—232).—Blood- $H_2C_2O_4$  rises slightly during the first four months of pregnancy, and falls suddenly in the fifth, then rises gradually to the ninth, when it falls sharply again. It rises considerably during parturition (I), falling again in puerperium.  $H_2C_2O_4$  in the umbilical cord



is high compared with blood- $\text{H}_2\text{C}_2\text{O}_4$ ; it is lower in premature than in normal (I), and seems to be related to the wt. and length of the foetus. Some results in pathological cases are given. R. N. C.

**Micro-determination of lactic acid in blood.** M. BOURDEAU (J. Pharm. Chim., 1934, [viii], 20, 342—353).—Neutralised serum freed from albumins and globulins is oxidised in a special apparatus (A., 1934, 384) with dil.  $\text{KMnO}_4$  solution in presence of  $\text{MnSO}_4$ , when lactic acid is converted into  $\text{MeCHO}$ , which is collected in Nessler's reagent. The latter is finally reoxidised with 0.5 c.c. of 0.05*N*-I, the excess being titrated with 0.005*N*- $\text{Na}_2\text{S}_2\text{O}_3$ . Ketones or  $\beta$ -hydroxybutyric acid do not interfere. S. C.

**Micro-determination of acetone in blood.** O. CANTONI (Biochem. Z., 1934, 274, 45—50).—A colorimetric method based on Frommer's reaction is described. P. W. C.

**Colorimetric determination of blood-sugar by the Creceleius-Serfert method.** L. ARNOLD (Med. Welt, 1934, 8, 364; Chem. Zentr., 1934, i, 3627).—The method is suitable for clinical purposes. A. G. P.

**Significance of phosphoric esters in the course of blood-glycolysis. I. Degradation of hexose phosphates to triose phosphates as the first stage of glycolysis. Formation of fructose phosphate from glucose and glyceraldehyde by intact erythrocytes. Explanation of the Harden-Young fermentation equation.** Z. DISCHE (Biochem. Z., 1934, 274, 51—74).—Washed erythrocytes convert glucose into a fructose phosphate (I) probably identical with the Harden-Young ester. (I) is then degraded by a rapid reaction to triose phosphate and subsequently by a slow reaction to lactic acid. Glucose phosphate (II) is not converted into (I), but probably is degraded to glyceraldehyde and  $\text{CO}(\text{CH}_2\text{-OH})_2$  phosphates, intact cells converting the latter into lactic acid and hæmolysed cells into (I). Degradation of (II) is reversible, erythrocytes being able to synthesise (II) from glyceraldehyde and glucose.  $\text{CO}(\text{CH}_2\text{-OH})_2$  is not esterified under these conditions. P. W. C.

**Glass electrode for determining the  $p_{\text{H}}$  of venous blood.** I. HARRIS, E. L. RUBIN, and W. J. SHUTT (J. Physiol., 1934, 81, 147—152).—A modified electrode is designed to avoid glycolysis and change of  $p_{\text{H}}$  in the sample, loss of  $\text{CO}_2$ , and variation of temp. CH. ABS. (p)

**Influence of neutral salts on the ultrafilterability of serum-calcium.** L. BRULL, R. POVERMAN, and A. LAMBRECHTS (Compt. rend. Soc. Biol., 1934, 108, 1165—1166; Chem. Zentr., 1934, i, 3759).—The ultrafilterability of serum-Ca is raised by neutral salts according to their position in Hofmeister's ion series,  $\text{SO}_4^{--}$  and  $\text{K}^+$  being most effective. J. S. A.

**Variations in serum-magnesium.** L. VELLUZ and J. VELLUZ (Compt. rend. Soc. Biol., 1934, 117, 417—418).—In 92% of the normal cases examined serum-Mg varied between 18 and 22 mg. per 1000 c.c. and showed no variation with age. H. G. R.

**Regulation of the mineral composition of the blood in the crayfish (*Astacus fluviatilis*, L.).**

M. BOGUCKI (Arch. internat. Physiol., 1934, 38, 172—179).—The mineral content of the normal blood-serum is Cl 6.21, Ca 0.48, Mg 0.06, Na 3.49, and K 0.11 mg. per ml. When the fish is placed in sea- $\text{H}_2\text{O}$  the concn. of the electrolytes in the hæmolymph increases with the concn. of the sea- $\text{H}_2\text{O}$ . As long as the proportion of sea- $\text{H}_2\text{O}$  is  $> 50\%$  the ratio of the different ions remains unchanged. The degree of hydration of the muscles diminishes with the increase of the concn. of the external medium, although the wt. of the fish remains const. NUTR. ABS. (m)

**Micro-determination of sulphate in plasma.** E. ØLLGAARD (Biochem. Z., 1934, 274, 181—188).— $\text{SO}_4^{--}$  in  $> 2$  c.c. of blood-serum or -plasma (but not in whole blood) is determined (error 5%), after deproteinisation with  $\text{CCl}_3\text{-CO}_2\text{H}$ , by pptn. with freshly prepared  $\text{COMe}_2$  solution of benzidine, dissolution of the ppt. in aq. EtOH containing  $\text{NH}_4\text{Cl}$  and  $\text{MgCl}_2$ , and immediate titration with 0.02*N*- $\text{BaCl}_2$  using Na rhodizonate as indicator. A blank determination must be made. Large amounts of  $\text{PO}_4^{--}$  do not interfere. W. McC.

**Determination of bromine in blood and in animal tissues.** I. BELLUCCI [with L. BALDANZI] (Gazzetta, 1934, 64, 696—702).—The org. matter is ashed and the I and Br are then determined as described in A., 1934, 1321. O. J. W.

**Determination of iodine in blood and thyroid gland.** I. BELLUCCI and R. VIGNI (Gazzetta, 1934, 64, 634—643).—After destruction of org. matter with KOH and  $\text{H}_2\text{O}_2$ , KI is extracted with EtOH and oxidised with alkaline  $\text{KMnO}_4$ ,  $\text{HNO}_2$  is destroyed with urea and AcOH, and after addition of  $\text{H}_2\text{SO}_4$  and KI, the I is titrated with 0.002*N*- (for blood) or 0.004*N*- $\text{Na}_2\text{S}_2\text{O}_3$  (for thyroid), with  $\text{CS}_2$  as indicator. The method will measure  $10^{-5}$  g. of I in 100 c.c. of blood. R. N. C.

**Determination of fibrinogen and thrombin.** J. O. W. BARRATT (J. Physiol., 1934, 80, 422—428).—Fibrinogen (I) is determined by measuring the coagulation time of a dil. citrated plasma to which thrombin (II) has been added. Human plasma is used as standard. (II) is determined by means of the time of clotting when the unknown (II) solution and normal human citrated plasma are mixed in proportions just sufficient to convert all (I) into fibrin with no excess of (II). CH. ABS. (p)

**Mechanism of the anticoagulant action of azo-dyes in blood-clotting.** A. St. G. HUGGETT (Quart. J. Pharm., 1934, 7, 372—378).—The azo-dyes chlorazol-sky-blue FFS (Chicago-blue 6B) and chlorazol-fast-pink BKS act as anticoagulants by inhibiting the action of thrombokinase and thrombase. C. G. A.

**Anticoagulating properties of gold and other salts.** A. LUMIÈRE and S. SONNERY (Compt. rend. Soc. Biol., 1934, 117, 443—444).—The thiosulphates of the alkalis and alkaline earths, particularly Na and Mg, are most effective in preventing the coagulation of blood. Whereas the thio-derivatives of Pb, Zn, and Sn are anticoagulants, other salts (except citrates) are not. H. G. R.



**Combination of tetanus- and diphtheria-toxin with blood-proteins.** E. KYLIN (Arch. exp. Path. Pharm., 1934, 177, 93—102).—Tetanus toxin (I) in Ringer's solution migrates cataphoretically towards the anode at a velocity  $>$  that of the blood-proteins (separated by cataphoresis). The migration of (I) is diminished by human serum, (I) tending to accompany the slowly moving globulin and to leave the more rapidly migrating albumin (II) (I)-free. Diphtheria (I) behaves similarly, although at high concns. it partly migrates with (II). The results indicate that the transport function of serum-proteins holds for bacterial (I). F. O. H.

**Separation of haptens by adsorption on inorganic colloids.** H. RUDY (Klin. Woch., 11, 1312—1313; Chem. Zentr., 1934, i, 3874).—Wassermann extracts can be adsorbed from a mixture of brain (I) and heart extracts (II) with  $\text{Al}(\text{OH})_3$ . Spirochæte extracts can be adsorbed from a mixture with (I) by kaolin, and from one with (II) by kaolin and fuller's earth. R. N. C.

**Immuno-chemistry of the pyrazolone series.** H. ERLÉNMEYER and E. BERGER (Arch. exp. Path. Pharm., 1934, 177, 116—118).—Of a series of pyrazolone derivatives (I), only those with the grouping  $\cdot\text{NPh}\cdot\text{NMe}\cdot$  functioned as a hapten in sp. antibody-formation in horse-serum as indicated by the inhibition of flocculation with the appropriate antigen of fowl-serum and (I). This immuno-property is correlated with the antipyretic action. F. O. H.

**Total and thyroxine-iodine of the lion's thyroid.** L. BLANCHARD (Bull. Soc. Chim. biol., 1934, 16, 1372—1373).—The left gland of a lion's thyroid contained 0.0683 g. of total and 0.0219 g. of thyroxine-I per 100 g. of fresh tissue. A. L.

**Mol. wt. of thyroglobulin.** M. HEIDELBERGER and T. SVEDBERG (Science, 1934, 80, 414).—At  $p_H$  4.8—11.3 the sedimentation const. (I) of pig thyroglobulin (II) is  $19.2 \times 10^{-13}$ , indicating a mol. wt. of approx.  $8 \times 10^5$ . At  $p_H$  3, (II) is incompletely split into two components, for the lighter of which (I) is approx.  $10 \times 10^{-13}$ . At  $p_H$  12, there is a similar fission. Human thyroglobulin has essentially the same (I) as (II). L. S. T.

**Carotenoids of the integuments of some insects.** E. LEDERER (Compt. rend. Soc. Biol., 1934, 117, 413—416).—The femur of *Ædipoda* contains a mixture of pigments similar to that of the wings, whilst the blue wings of *O. cœrulescens* contain only traces of carotenoid (I). The pigment of the red elytrons of the Coleopter *Mylabris* is not a (I). H. G. R.

**Glycogen and total carbohydrate content of the human heart.** H. BLUME (Beitr. path. Anat., 1934, 93, 20—35).—The % of glycogen (I) in the ventricles and in the septum of the normal human heart are practically identical; some time after death small differences were detected due to unequal glycogenolysis. In long-standing cardiac hypertrophy, (I) storage is increased in the affected part. (I) is more conc. in the infant than in the adult heart. The total carbohydrate of the adult hearts examined (at various times after death) was 0.45—1.46 g. per

100 g. of wet tissue, of which about 70% was (I); in infants probably more (I) is present. A (I) content  $>$  1.5 g. per 100 g. is regarded as pathological. *Post-mortem* glycogenolysis is most rapid during the first 5 hr.; after  $3\frac{1}{2}$  hr. about 50%, and after 9 hr. 90% of the original (I) disappears. Within 3 hr. of death it is possible to compute the amount of original (I), but not subsequently. NUTR. ABS. (b)

**Structure and origin of corpora lutea in some of the lower vertebrata.** J. T. CUNNINGHAM and W. A. M. SMART (Proc. Roy. Soc., 1934, B, 116, 258—281). H. G. R.

**Bombicesterol.** W. BERGMANN (J. Biol. Chem., 1934, 107, 527—532).—The unsaponifiable portion (1.5—1.6%) of the chrysalis oil of *Bombyx mori* contains, in addition to a large hydrocarbon fraction, 33% of sterols, isolated as their 3 : 5-dinitrobenzoates. Separation by the usual bromination of their acetates affords cholesterol (I) (85%) and sitosterols (II) (15%), no trace of bombicesterol (III) (Menozzi *et al.*, A., 1908, i, 265) being detected. (III) is probably a mixture of (I) and (II). J. W. B.

**Changes in the acid-base coefficient of meat during storage.** I. A. SMORODINCEV and N. N. KRYLOVA (Bull. Soc. Chim. biol., 1934, 16, 1344—1351).—The factors *A* and *B* of the acid-base ratio *A/B* (I) (cf. A., 1934, 322) of meat change in opposite directions during autolysis, (I) increasing to a max. val. 5—6 times that given after 1 hr. After 72 hr. at 4° or 48 hr. at 36°, (I) becomes const. at a val. three times that shown in 1 hr., but at both temp. the process follows the same course. The addition of acid accelerates the process. A. L.

**Determination of reduced glutathione in tissue.** L. BINET and G. WELLER (Bull. Soc. Chim. biol., 1934, 16, 1284—1296).—A method for the determination of reduced glutathione (I) in tissue by pptn. with Cd lactate from the  $\text{CCl}_4\cdot\text{CO}_2\text{H}$  extract is described. To the ppt. I is added, and the excess titrated with aq.  $\text{Na}_2\text{S}_2\text{O}_3$ . The results by this method indicate a lower (I) content than that given by other methods. The method may be used when ascorbic acid and ergothionine are present, and a modification to avoid interference by cysteine is suggested. A. L.

**Comparison of the surface tension of lymph and blood of the dog.** N. L. COSMOVICI and P. JITARIU (Compt. rend. Soc. Biol., 1934, 117, 520—521).— $\gamma$  of lymph-plasma is  $>$  that of the corresponding blood-plasma, but those of whole lymph and blood are practically the same. H. G. R.

**Pytalín content of human saliva.** A. GERHARD (Z. klin. Med., 124, 153—167; Chem. Zentr., 1934, ii, 452—453).—Saliva (I) is obtained by the method of Delhougne; maltose (II) is determined by the Willstätter-Waldschmidt-Leitz-Hesse method. There is no relation between the quantity of enzyme used and the (II) formed for as much as 50—60 mg. of (II). The most favourable results are obtained with 1 c.c. of (I) diluted to 1 : 8. With this material in young normal subjects 48—133 mg. of (I) are obtained; the vals. fluctuate considerably in pathological cases. Fluctuations are also dependent on



age, young men tending to have a lower ptyalin content. R. N. C.

**Chlorine content of gastric juice.** G. DELRUE and J. VAN DAMME (Compt. rend. Soc. Biol., 1934, 117, 488—490).—When the secretion of acid is small total Cl is const., but this increases with increased secretion of acid. H. G. R.

**Chloride concentration of gastric secretion from fundic pouches and from the intact whole stomach.** C. M. WILHELMJ, L. C. HEINRICH, I. NEIGUS, and F. C. HILL (Amer. J. Physiol., 1934, 108, 197—202).—Stomach fluid comprises (a) fundic secretion containing 578 mg. of Cl per 100 c.c. irrespective of rate of secretion or  $p_{\text{H}}$  of gastric contents, (b) pyloric and mixed duodenal secretions containing 340 mg. per 100 c.c. CH. ABS. (p)

**Elimination of iodine in human colostrum and milk.** A. W. ELMER and W. RYCHLIK (Compt. rend. Soc. Biol., 1934, 117, 530—532).—I in colostrum increases after the first day and is const. in the milk ( $20-47 \times 10^{-6}$  g. per 100 c.c. per 24 hr.). H. G. R.

**Effect of salts on cell permeability as shown by studies of milk secretion.** (A) G. L. PESKETT. (B) S. J. FOLLEY and G. L. PESKETT (Proc. Roy. Soc., 1933, B, 114, 167—180; 1934, B, 116, 396—402).—A. A definite correlation between the ratio of Na to diffusible Ca in the blood and that of solids-not-fat to fat in milk was observed in cows. It is suggested that variations in these salts affect the relative permeability of the mammary cell membranes to lipins and non-lipins.

B. This has been confirmed in cows of different breeds and is suggested as the factor governing the difference in milk composition between the breeds. H. G. R.

**Relation between quantity of milk, absolute fat production, and the percentage of fat in milk.** J. KRÍŽENECKÝ (Vestn. czechoslov. Akad. Zemed., 1934, 10, 6—8; Chem. Zentr., 1934, ii, 155).—Relationships for different breeds of cows show close correlation between milk yield and fat yield. A. G. P.

**Influence of the stage of lactation on fat determination by the Gerber method.** J. LYONS and M. O'SHEA (Sci. Proc. Roy. Dublin Soc., 1934, 21, 123—131).—A low val. for the fat content of cow's milk towards the end of lactation is due to the presence of a fraction in the form of very small globules. This amounts to about  $4\frac{1}{2}$  lb. for a 45-week period. P. G. M.

**Arachidonic acid in butter-fat.** A. W. BOSWORTH and E. W. SISSON (J. Biol. Chem., 1934, 107, 489—496).—By fractionation of the Me esters of the fatty acids from butter, a "C<sub>20</sub>" fraction was obtained which contained stearic, behenic, and arachidonic (I) acids [(I) separated as octabromide], but no arachidic acid. Linoleic and linolenic acids cannot be detected as tetra- and hexa-bromides, respectively, in presence of (I), since (I) forms isomeric bromides with similar properties. A. E. O.

**Effect of feeding irradiated dried yeast on the yield and composition of milk with special reference to its nutritional value.** F. DUSCH

(Diss., Techn. Hochschule, München, 1933, 112 pp.).—Feeding of the yeast slightly increases the fat content of milk and definitely increases solids-not-fat. Sp. gr., acidity, catalase, reductase, and leucocyte contents and rennin test are unaltered. The vitamin-D content of the milk is increased so that 0.5 g. of butter-fat prevents rickets in rats. No detectable rise in the antineuritic factor occurs. The growth factor appears to increase. NUTR. ABS. (m)

**Sugar content of bile.** Z. ASZÓDI (Biochem. Z., 1934, 274, 146—153).—Bile of fasting dogs contains a reducing substance, the amount of which increases after a carbohydrate diet and after adrenaline, decreases after insulin, and is little altered by a flesh or fat diet. Bile undergoes glycolysis. The reducing substance is probably glucose. P. W. C.

**Does glycogen occur often in urine?** F. N. SCHULZ and H. BECKER (Arch. Pharm., 1934, 272, 795—796).—Cappenberg's evidence (A, 1934, 797) that this is the case is invalid, the tests applied not being sp. R. S. C.

**Evaluation of urinary glucose.** A. CASTILLA (Bol. Soc. Quim. Peru, 1934, 1, 49—50).—Urinary analyses must relate to the whole output of the 24-hr. day. Iodometric determination of sugar was satisfactory. E. L.

**Pentose produced during chronic pentosuria.** P. BALINT (Biochem. Z., 1934, 274, 305—312).—The pentose had  $[\alpha]_{\text{D}}^{20} +32.4^{\circ}$  (*p*-bromophenylhydrazine, m.p. 128—129°; osazone, m.p. 162—163°). It was probably  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CH}_2\cdot\text{OH}$ . W. McC.

**Renal excretion of sucrose, xylose, urea, and inorganic sulphates in normal man; comparison of simultaneous clearances.** N. M. KEITH, M. H. POWER, and R. D. PETERSON (Amer. J. Physiol., 1934, 108, 221—228).—Relative clearances were in the descending order sucrose, xylose, urea, and inorg. SO<sub>4</sub>". CH. ABS. (p)

**Urea excretion and renal function.** T. BJERING (Acta Med. Scand., 1934, 82, 213—227).—There is a const. relationship in human patients between the concn. index of urea and of creatinine (I) in the same individual during variations of the (I) concn. from 10 to 150 and between blood-urea vals. of 13—90 mg. per 100 ml. The ratio of the max. clearance of urea to that of (I) is therefore const. in the same individual and, within the known limits of the (I) concn., independent of the diuresis. Provided the blood-urea is const., the urea content of the reabsorbed fluid remains const. and independent of the concn. index so long as this index is < 150. NUTR. ABS. (b)

**Economy of water in renal function referable to urea.** J. L. GAMBLE, C. F. MCKHANN, A. M. BUTLER, and E. TUTHILL (Amer. J. Physiol., 1934, 109, 139—154).—The requirement of H<sub>2</sub>O for renal elimination of substances is additive except where urea is a constituent. CH. ABS. (p)

**Creatinine clearance as a measure of glomerular filtration in dogs, with particular reference to the effect of diuretic drugs.** L. F. DAVENPORT, M. N. FULTON, H. A. VAN AUKEN, and R. J. PARSONS (Amer. J. Physiol., 1934, 108, 99—106).—Constancy



of normal creatinine excretion is undisturbed by exercise, diet, diuresis, or disease. CH. ABS. (p)

**Effect of magnesium halides on the  $p_H$  of urine.** P. DELBET and FRANCICEVIC (Bull. Acad. Méd., 1934, 108, 1470—1475; Chem. Zentr., 1934, i, 3760). The urine of cancerous, but not normal, subjects showed variation between  $p_H$  5 and 7 in one day; the cancerous condition tends towards alkalosis.  $\text{NaHCO}_3$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{AlCl}_3$  affect the  $p_H$  by direct transport, whilst Mg halides produce a sp. indirect acidifying effect. J. S. A.

**Urobilin excretion and destruction of blood.** A. LICHTENSTEIN (Nederland. Tijdschr. Geneesk., 1934, 78, 1522).—The average excretion (I) of urobilin (II) in the faeces of an average European of 70 kg. wt. is 135—150 mg. daily; in a Javanese, (wt. about 55 kg.) it was 75—80 mg. This lower rate of excretion may be due to diet poor in animal protein, since in healthy European vegetarians (I) of (II) is 75.4 mg. daily. Constipated individuals show low (I) of (II). Determination of (I) of (II) cannot be used to calculate the average time of survival of the red blood-corpusele. NUTR. ABS. (m)

**Pathological skin pigmentation and "pigment-vitamins."** P. MORAWITZ (Klin. Woch., 1934, 13, 324—327; Chem. Zentr., 1934, i, 3762).—Prolonged treatment of Addison's disease with adrenal cortex often produces a disappearance of pigmentation without affecting the other symptoms. Similarly, administration of sweet-orange- or lemon-juice to a scorbutic patient with a chloasma-like melanosis (I) causes the disappearance of (I), suggesting a connexion between (I) and avitaminosis-C. R. N. C.

**Chloride, carbohydrate, and water metabolism in adrenal insufficiency and other conditions.** H. SILVETTE (Amer. J. Physiol., 1934, 108, 535—544).— $\text{H}_2\text{O}$  retention and salt loss in muscles of adrenalectomised animals are related to deficiency of glucose and glycogen in the tissues. CH. ABS. (p)

**Presence of the anti-anæmic factor in preparations of dried stomach from the cardia, fundus, and pyloric regions.** E. MEULENGRACHT (Ugeskr. Laeger, 1934, 96, 179—187; Acta Med. Scand., 1934, 82, 352—374).—Powder from the fundus (pig) (defatted and dried) region is inactive; that from the pyloric region is strongly active. The anti-anæmic factor appears to be associated with the function of the pyloric glands (I). In pernicious anæmia the mucous membrane of the stomach is more or less atrophic and its secretory function impaired. Hence the disease may be due to atrophy and inactivity of (I). NUTR. ABS. (m)

**Guinea-pig as a hæmatopoietic test animal.** J. W. LANDSBERG and M. R. THOMPSON (J. Amer. Pharm. Assoc., 1934, 23, 964—968).—The active constituent of liver extract producing a reticulocyte response in the guinea-pig is not readily destroyed by heating. A. E. O.

**Calcium in beriberi and in fowls with similar symptoms due to calcium deficiency.** H. Y. OH (W. Chosen Med. Assoc., 1934, 24, 40—41).—Patients

with beriberi (I) have low serum-Ca, and show marked clinical improvement after intravenous injections of 20 ml. of 5% aq.  $\text{CaCl}_2$  daily. A condition resembling (I) in fowls kept on a low-Ca diet containing vitamin-B is relieved by Ca injections. Ca deficiency is an important factor in the etiology of (I). NUTR. ABS. (m)

**Biochemical control of cancer.** M. COPISAROW (Chem. and Ind., 1934, 1047—1048).—Recent results indicate that protracted enzyme depletion causes suppressed oxidation and resultant formation of carcinogenetic dehydrogenated products *in situ*. Corrective measures therefore involve (1) inhibition of tumour formation, (2) inactivation of unsaturated carcinogenetic substances, (3) counteraction of conditions detrimental to normal enzyme equilibrium, and (4) restoration of the glutathione oxidation-reduction. Substances possessing such properties are  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}$ , methylthionine chloride,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{S}_4\text{O}_6$ , colloidal S,  $\text{Ph}_2\text{SO}$ , and cysteine sulphoxide. J. W. B.

**Retention of glyoxalines in cardio-renal conditions.** M. LOEPER, M. PERRAULT, and A. LESURE (Compt. rend. Soc. Biol., 1934, 117, 433—435).—Retention of glyoxalines in cardio-renal affections, particularly in cases of œdema, with striking elimination at the crises, is demonstrated. H. G. R.

**Glyoxaline compounds in spinal fluids.** M. LOEPER, M. PERRAULT, E. BLOY, and A. LESURE (Compt. rend. Soc. Biol., 1934, 117, 576—578).—Glyoxaline compounds are found in large quantities in cerebrospinal fluid in pregnancy, in cases of nervous reaction with spinal hypertension, and in acute meningitis. In normal and other pathological conditions they are absent, or present only in traces. R. N. C.

**Glyoxalinæmia of parenteral origin.** M. LOEPER, M. PERRAULT, and A. LESURE (Compt. rend. Soc. Biol., 1934, 117, 578—579).—Glyoxalinæmia (I) occurs in many pathological conditions, produced probably by fever, release of leucocyte debris, destruction of erythrocytes, and from tissue-protein. Injection of serum increases (I) and also glyoxalinuria. Ascitic fluid in cirrhotics contains glyoxaline compounds even when albumin and cellular elements are low. R. N. C.

**Effect of adrenaline on the alimentary lipæmia of diabetes.** M. SULLIVAN and P. CAMERON (Amer. J. Med. Sci., 1934, 187, 457—462).—In diabetes, adrenaline depresses the curve of increasing blood-fat (Ruckert's method) following fat ingestion. NUTR. ABS. (b)

**Action of hexose diphosphate and phosphates on the diabetic organism.** V. S. ILJIN, N. N. JAKOVLEV, and V. M. VESSELKINA (Z. ges. exp. Med., 1934, 93, 679—684).—Subcutaneous injection of Na hexose diphosphate (I) or intravenous administration of a phosphate mixture ( $p_H$  7.0) produces in cats with partial pancreatectomy a reduction in blood-sugar, an increase in the lactacidogen (II) content of the muscles, but no significant change in the glycogen. The increase in (II) is very much less marked in completely pancreatectomised cats. The action of (I) is explained by the production of inorg. phosphate,



the effect of which on the diabetic animal is only partly accounted for by the increase in (II).

NUTR. ABS. (m)

**Does glycosuria influence the silicon in the pancreas and liver?** A. S. E. VON HERMANY (Münch. med. Woch., 1934, 81, 554; Chem. Zentr., 1934, i, 3760).—CaSiO<sub>3</sub> gel lowers blood- and urine-sugar. It is suggested that diabetes is due to a lowering of the SiO<sub>2</sub> content of the pancreas and liver.

J. S. A.

**Behaviour of blood-sugar during sulphur (sulfosin) treatment of dementia praecox.** S. IZIKOWITZ (Acta Med. Scand., 1934, 82, 567—578).—The blood-sugar decreased 5.5 hr. after injection of sulfosin; during the later period of fever hyperglycaemia was observed.

NUTR. ABS. (b)

**Methylglyoxal in infantile food disorders; relations with avitaminosis-B<sub>1</sub>.** G. POPOVICIU and N. MUNTEANU (Compt. rend. Soc. Biol., 1934, 115, 897—899).—In a no. of cases of summer infantile food disorders, AcCHO (I) in varying quantities was excreted in the urine. On recovery, (I) excretion ceased. No (I) was excreted in cases of avitaminosis-B<sub>1</sub> which were free from summer food disorders.

R. N. C.

**Acid-base equilibrium in patients with convulsions.** J. MADSEN (Compt. rend. Soc. Biol., 1934, 117, 625—630).—The mean  $p_H$  of the nocturnal urine in starvation of epileptic patients (I) is 6.05 as compared with 5.83 in controls (II). The matutinal alkaline tide, which rises steadily to the neutral point in (II), fluctuates towards the alkaline side in (I). Ingested NaHCO<sub>3</sub> is excreted more rapidly in (I) than in (II).

R. N. C.

**Ammonia content of the urine in convulsive patients.** J. MADSEN (Compt. rend. Soc. Biol., 1934, 117, 630—633).—Total urinary N is practically identical in normal persons (I) and epileptics (II). Urinary NH<sub>3</sub> at a const.  $p_H$  in (II) is > in (I).

R. N. C.

**Ratio of acids and ammonia in the urine of normal persons and convulsive patients.** J. MADSEN (Compt. rend. Soc. Biol., 1934, 117, 633—635).—The ratios NH<sub>3</sub>/inorg. acid, NH<sub>3</sub>/SO<sub>4</sub><sup>''</sup>, and NH<sub>3</sub>/org. acid are all increased in the urine of epileptics as compared with normal persons.

R. N. C.

**Causes of alimentary glycosuria in infective diseases.** N. A. NIELSEN (Acta Med. Scand., 1934, 82, 306—310).—In rabbits, fever, unaccompanied by toxæmia, does not affect the glycaemic response to administered glucose. The alimentary glycosuria of acute infectious disease is therefore caused by toxic liver damage.

NUTR. ABS. (n)

**Carbohydrate metabolism in infectious fevers.** S. LEITES, L. S. LIFSCHITZ, and A. ODINOV (Z. ges. exp. Med., 1934, 93, 803—815).—In febrile infections (I), oral and intravenous administration of glucose are followed by a more prolonged rise of blood-sugar (II) with no hypoglycaemic phase (III). (III) becomes very marked during the fall of the temp. Intravenous injection of adrenaline produces a very slight rise in (II) and occasionally a fall; its effect is not changed by previous administration (oral or intravenous) of

glucose. Fever has no definite effect on the glycaemic reaction to 10 units of insulin. In (I) utilisation and storage of carbohydrate are impaired as a result of defective cellular metabolism and hypofunction of the islet tissue.

NUTR. ABS. (m)

**Hæmochromatosis.** J. H. SHELDON (Lancet, 1934, 227, 1031—1036).—A lecture.

L. S. T.

**Creatine metabolism in children with hypothyroidism.** H. G. PONCHER, M. B. VISSCHER, and H. WOODWARD (J. Amer. Med. Assoc., 1934, 102, 1132—1135).—Hypofunction of the thyroid causes decrease or complete cessation of creatine excretion, which can be restored to normal by administration of thyroid extract.

NUTR. ABS. (m)

**Modifications of phosphorus, sodium, and nitrogen-exchange in the blood in renal and thyroid deficiency.** R. MESSINA (Arch. Farm. sperim., 1934, 58, 187—199).—In rabbits with UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> nephritis (I) total and inorg. P and Na fall slowly and steadily, whilst the N exchange also diminishes. Thyroidectomy (II) causes similar diminutions whilst with (I) and (II) together the fall is more considerable in all cases.

R. N. C.

**Basal metabolism and impedance angle in thyrotoxicosis and myxœdema.** J. D. ROBERTSON and A. T. WILSON (Lancet, 1934, 227, 1158—1159).—In Graves' disease the impedance angle (I), an electrical property of the body (J. Inst. Elect. Eng., 1933, 73, 203), deviates from the normal. Administration of I produced a fall in pulse and basal metabolic rates but no alteration in (I). In myxœdema (I) is normal and treatment with thyroid extract produced no change.

L. S. T.

**Hyperthyroxinæmia in thyrotoxicosis.** A. W. ELMER, W. RYCHLIK, and M. SCHEPS (Compt. rend. Soc. Biol., 1934, 117, 533—534).—In exophthalmic goitre thyroxine (I)-I is increased and varies between 8.5 and 16.1 × 10<sup>-8</sup> g. per 100 c.c. in the peripheral venous blood and the total (I) between 0.75 and 1.25 mg.

H. G. R.

**Transmission of influenza by a filterable virus.** T. FRANCIS, jun. (Science, 1934, 80, 457—459).—Previous observations (A., 1933, 1071) on the transfer of a filterable transmission agent from human cases of epidemic to ferrets are confirmed. Experiments with mice also indicate that the disease is produced by a filterable virus.

L. S. T.

**Enzoötic marasmus. Iron content of kidney, liver, and spleen.** E. J. UNDERWOOD (Australian Vet. J., 1934, 10, 87—92).—The Fe content of all three organs in diseased sheep and calves was > normal. The absence from the diet of some factor necessary for the utilisation of Fe in the body is indicated as the cause of the disease.

CH. ABS. (p)

**Diurnal changes in liver during pregnancy.** T. W. GOODWIN and G. M. HIGGINS (Amer. J. Physiol., 1934, 108, 567—572).—Changes in wt. and in glycogen and H<sub>2</sub>O contents of livers of pregnant rats (I), after feeding, resemble those of normal animals except that peak vals. occur earlier and the glycogen recovered at the peak is less in (I).

CH. ABS. (p)



**Residual reducing substances of the blood in puerperium.** E. BRANDSTRUP (*Acta Med. Scand.*, 1934, **82**, 329—337).—During the first 10 days of the puerperium lactose is not present in the blood in demonstrable amounts. NUTR. ABS. (m)

**Chemotherapy. I. Action of sodium formaldehydesulphoxylate in bacterial infections.** S. M. ROSENTHAL (*U.S. Pub. Health Rep.*, 1934, **49**, 908—911).—Subcutaneous injection of the sulphoxylate (I) gave a high degree of protection of mice against pneumococci (II). Death occurred only with dosages of 4 g. per kg. (I) produced no bactericidal or bacteriostatic effects in broth cultures of (II).

CH. ABS. (p)

**Change in the antirachitic activity of orthophosphoric acid by esterification with phenol.** R. LECOQ and M. L. BARBAN (*Compt. rend.*, 1934, **199**, 1255—1257).—Phenolic esterification decreases the antirachitic potency of  $H_3PO_4$ . Na phosphite,  $Ph_3PO_4$ , and guaiacol phosphate or phosphite do not relieve rickets, but  $Na_3PO_4$  (2%) does. J. L. D.

**Chemotherapy of syphilis and other infectious diseases. I. Experimental chemotherapy of preparation No. 1717, formaldehydesulphoxylate of 3-amino-4-hydroxyphenylarsinic acid.** G. W. RAIZISS, M. SEVERAC, and A. KREMENS (*J. Chemotherapy*, 1934, **11**, 34—45).—Prep. and properties are described. Efficiency against syphilis is > that of tryparsamide and approx. equal to that of acetarsone.

CH. ABS. (p)

**Changes in serum-proteins in general paralysis and correlations with serological reactions.** A. PRUNELL and J. GALMES (*Compt. rend. Soc. Biol.*, 1934, **117**, 551—552).—Wassermann and Kahn reactions progressively decrease as the serum-globulin increases and are often negative when this reaches 5—6 g. per 100 c.c.

H. G. R.

**Effect of hyperglobulinæmia on the Wassermann and Kahn reactions.** A. PRUNELL (*Compt. rend. Soc. Biol.*, 1934, **117**, 552—554; cf. preceding abstract).—The ppt. obtained in the Kahn reaction is independent of the globulin (I) and does not contain X. Paralytic serum (II) with a negative Wassermann reaction and an increased content of (I) has a lytic power > that of normal (II).

H. G. R.

**Manometric determination of oxygen uptake and carbon dioxide evolution of tissue sections.** H. RUSKA (*Arch. exp. Path. Pharm.*, 1934, **177**, 38—41).—An improved type of vessel suitable for use in Warburg's manometric method is described.

F. O. H.

**Mechanism of intracellular oxido-reduction.** P. JOYET-LAVERGNE (*Compt. rend.*, 1934, **199**, 1159—1161).—The catalysis of intracellular oxido-reductions is due to the conjoint action of glutathione and vitamin-A.

H. W.

**Capillaroscopy and acid-base equilibrium in mental work.** R. MESSINA (*Arch. Farm. sperim.*, 1934, **58**, 242—251).—Mental fatigue from prolonged study is accompanied by a fall in blood- $p_H$  and N exchange.

R. N. C.

**Viscosity of protoplasm.** A. M. FREDERIKSE (*Chem. Weekblad*, 1934, **31**, 593—595).—Methods

which have been used for determining the viscosity ( $\eta$ ) of protoplasm are reviewed. In order to obtain a val. representative of the undisturbed living material it is necessary to calculate  $\eta$  from measurements of Brownian movement; improved methods are outlined. Measurements with *Amœba verrucosa* show  $\eta$  to be different in different parts of the cells and to depend greatly on the physiological conditions prevailing at the time of the measurement. Narcotics in small quantities reduce, and in larger quantities increase,  $\eta$ , particularly of the ectoplasm. H. F. G.

**Viscosity and plasticity in muscle.** H. J. JORDAN (*Chem. Weekblad*, 1934, **31**, 590—593).—Smooth muscle is regarded as a colloidal system consisting of micelles surrounded by a viscous liquid, contraction involving first an elastic deformation of the micelles and then plastic propagation. The interrelationships of the elastic and plastic changes are discussed.

H. F. G.

**Relationships between the chemical and physical processes in muscular contraction.** O. MEYERHOF (*Ann. Inst. Pasteur*, 1934, **53**, 565—590).—A lecture.

**Chemical changes associated with muscular contraction in normal and adrenalectomised animals.** O. COPE, A. B. CORKILL, H. P. MARKS, and S. ОСНОА (*J. Physiol.*, 1934, **82**, 305—320).—The formation of lactic acid from glycogen and hexose phosphates by muscle extracts (I) shows no great differences between (I) from normal (II) and adrenalectomised cats (III). When stimulated anaerobically and isometrically the isometric coeffs. (IV) for lactic acid in (II) and (III) are similar, but (IV) for phosphagen (V) in (III) is > in (II), whilst the heat coeff. is decreased in (III), and the muscle performs less work, this decrease being probably due to its diminished capacity to resynthesise (V). During activity the rate of (V) breakdown is decreased.

R. N. C.

**Rôle of phosphocreatine in fundamental chemical changes in contracting mammalian muscle.** J. SACKS and W. C. SACKS (*Amer. J. Physiol.*, 1934, **108**, 521—527).—In rabbits fed with oats the alkali reserve of tissues decreased, and the amount of base liberated by hydrolysis of phosphocreatine (I) and conversion into hexose phosphate is equiv. to the lactic acid formed in muscle contraction. (I) tends to preserve a const.  $p_H$ .

CH. ABS.

**Transformation of adenosinetriphosphoric acid (adenyl pyrophosphate) in the isolated frog heart.** A. N. PARSCHIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 630—633).—Perfusion of the isolated frog heart with Ringer's solution results in a change in the adenyl pyrophosphate (I) content. NaF,  $CH_2I-CO_2H$ , and KCN have practically no effect on the rate of change of (I).

J. L. D.

**Phospholipin content and activity in muscle.** W. R. BLOOR and R. H. SNIDER (*J. Biol. Chem.*, 1934, **107**, 459—470).—By comparison of skeletal muscles of different extent of usage in the same animal and of the same muscle (I) in different animals subject to different amounts of use, it is found that the more used (I) has a higher phospholipin content



(II) than less used (I). Similar but smaller differences are found in cholesterol content (III) so that the (II) to (III) ratio is  $>$  in more used (I). Smooth (I) (gizzard and stomach) has normal (II) but high (III). The I val. is the same in much- or little-used (I).

C. G. A.

**Sources of energy in muscular work performed in anaërobic conditions.** R. MARGARIA and H. T. EDWARDS (Amer. J. Physiol., 1934, 108, 341—348).—Lactic acid production from glycogen is one probable source of energy corresponding with approx. 66% of anaërobic work. CH. ABS. (p)

**Anaërobic breakdown of carbohydrate in the isolated frog ventricle.** R. GADDIE and C. P. STEWART (J. Physiol., 1934, 80, 457—479).—Frog ventricle (I) exhausted by contracting in the absence of  $O_2$  repeatedly recovers on addition of glucose and mannose to the perfusion fluid. Fructose, galactose, various pentoses and other sugars, glycogen, glycine, and alanine are ineffective. Oleate and linoleate cause a little recovery at first, but the effect cannot be repeated. Partial recovery (II) is caused by AcCHO and glyceraldehyde, the latter being eventually toxic.  $AcCO_2H$  (III), glycerophosphate (IV), and dihydroxyacetone added separately have no effect, but (III) and (IV) together cause partial (II). Contraction of (I) in the absence of  $O_2$  is inhibited by  $CH_2I\cdot CO_2H$  and  $CH_2Br\cdot CO_2H$  and not restored by washing. Addition of glutathione (V) and cysteine prevent this inhibition, and partial (II) of an already affected heart is effected with (V). (I) which have been treated with  $CH_2I\cdot CO_2H$  and partly restored by (V) are poisoned by addition of glucose, perhaps because a toxic breakdown product of it accumulates under these conditions. Dil. aq.  $Na_3AsO_3$  slowly stops the contractions in  $N_2$  but not in  $O_2$ ; addition of glucose and reduced (V) restores them.

There are probably two paths of glucose breakdown in the heart, one through AcCHO and one through (III). NUTR. ABS. (m)

**Existence of two types of lactic fermentation in dog's muscle.** E. AUBEL and E. SIMON (Compt. rend. Soc. Biol., 1934, 117, 400—402).—Lactic acid is formed from hexose diphosphate in two ways. After the production of triose phosphate, in one case AcCHO is the intermediate product, in the other an equilibrium of Wurmser's type occurs. H. G. R.

**Influence of muscular work on urinary lipase.** K. MATOBA (Arch. Igakkai Zasshi, 1933, 40, 1528).—Urinary lipase (I) in meat-fed rats is more resistant to quinine and more sensitive to atoxyl and NaF than that of rice-fed rats. Increased (I) during muscular work is not derived from the blood.

CH. ABS. (p)

**Ammonia content and ammonia formation in muscle. XXI. Inhibition of ammonia formation by various alkaline buffer solutions.** T. MANN and P. OSTERN (Biochem. Z., 1934, 274, 154—157).—Deamination of adenylic acid by muscle deaminase is inhibited with increasing  $p_H$ , but to a different extent with different buffers. Thus the deamination at  $p_H$  8.85 is reduced to 20% with  $PO_4^{4-}$  and borate buffer, but only to 70% by veronal-carbonate buffer. P. W. C.

**Occurrence of decomposition products of chlorophyll. II. Decomposition products of chlorophyll in stomach walls of herbivorous animals.** P. ROTHEMUND, R. R. McNARY, and O. L. INMAN (J. Amer. Chem. Soc., 1934, 56, 2400—2403; cf. A., 1933, 168).—Extraction of the mucous membrane of the third and fourth stomachs of freshly-killed cows with  $COMe_2$  and subsequent fractionation of the  $Et_2O$ -sol. pigments with 0.35—38% HCl gives small amounts of deuterio- and proto-porphyrins (both formed by decomp. of blood-pigment), phylloerythrin (obtained in max. amount), phæo-purpurin 18, phæophorbide  $\alpha$ , and phæophytin (detected spectroscopically). These compounds have a definite erythropoietic effect on rats when administered *per os* in small doses (0.1—2 mg. per rat per day). H. B.

**Metabolic rate, blood-sugar, and the utilisation of carbohydrate.** H. T. EDWARDS, R. MARGARIA, and D. B. DILL (Amer. J. Physiol., 1934, 108, 203—209).—The R.Q. in man during severe exercise (I), designed to deplete the carbohydrate store, did not, even at the beginning, indicate that carbohydrate was the sole fuel. With continued (I) the R.Q. fell to a val. which represented an energy metabolism mainly of fat. It rose again after ingestion of glucose, but not until some time after the max. hyperglycæmia had been attained. With alternating rates of work the R.Q. rose when the rate was increased. The blood-sugar remained at the normal resting level during continuous (I). A difference between the rates at which the usage and mobilisation of glucose are diminished on stopping exercise may explain the hyperglycæmia resulting from discontinuous severe (I). NUTR. ABS. (b)

**Blood-sugar curve after administration of glucose in children.** S. A. SIWE (Jahrb. Kinderheilk., 1934, 142, 344—350).—In children, especially in young and nervous children, a marked hypoglycæmic phase frequently occurs  $1\frac{1}{2}$ — $2\frac{1}{2}$  hr. after oral administration of glucose (I) (1 g. per kg. of body-wt.). In severe rickets, the fasting blood-sugar level is often high, and oral administration of (I) may produce a flat curve which is abnormally sustained. The response of healthy young children, however, to (I) ingestion is normally very variable. NUTR. ABS. (b)

**Variation in sugar content of blood and urine after administration of glucose.** A. SZEPESHELYI (Arch. wiss. pr. Tierheilk., 1934, 67, 405—409).—The blood-sugar curve after ingestion of various amounts of glucose following a 24-hr. fast had its max. after 45—75 min. in dogs and after 105—150 min. in horses, reaching the original level after 135—180 and 210—360 min., respectively. The assimilation limit for dogs was 12—13 g. per kg. of body-wt. and that for horses 11—12 g. NUTR. ABS. (b)

**Influence of exercise on the blood-sugar, especially in connexion with glucose ingestion.** B. STRANDELL (Acta Med. Scand., 1934, Suppl. 55, 245 pp.).—If the ingestion of glucose (I) in man is immediately followed by exercise of long duration the hyperglycæmic response is considerably diminished or replaced by a fall in blood-sugar (II). This is due to



increased removal of (I) from the blood rather than to deficient absorption from the intestine. If exercise is begun when the glycaemic response to ingested (I) is at its max., the (II) level falls rapidly, but rises again if the exercise is discontinued. This latter rise is due to absorption of (I) remaining in the gut. Discontinuation of fasting exercise is often followed by a transitory rise in (II), probably due to hepatic glycogenolysis partly caused by adrenaline secretion. Subcutaneous adrenaline administration, however, has little effect on the (II) curve during exercise. NUTR. ABS. (b)

**Sugar threshold and renal function.** I, II. T. BJERJING and P. IVERSEN (*Acta Med. Scand.*, 1934, **82**, 193—212, 228—250).—I. The renal threshold is defined as that sugar concn. of the blood (or glomerular filtrate) at which the glucose (I) concn. of the re-absorbed fluid passes over from a higher level than that of the blood to a lower one, or conversely. Two threshold vals. must be considered, one for the rising and another for the falling blood-sugar (II) curve.

II. At the same (II) level, (I) re-absorption in the kidney is less with a falling (II) curve than with a rising one. The (I) concn. and total (I) excretion in the urine are dependent both on the (II) level and on the concn. index. When the latter remains const., changes of (II) concn. are paralleled by those of the urine, but an increased (I) excretion may be accompanied by a fall in the concn. index. In acidosis the tubules are poisoned so that the re-absorption of (I) is decreased. NUTR. ABS. (b)

**Glucose tolerance and the glycogen storage capacity of the dog.** W. L. BUTSCH (*Amer. J. Physiol.*, 1934, **108**, 639—642).—Continuous intravenous injection of glucose in the dog caused the liver-glycogen to increase until a level of 20% was reached, when the sugar tolerance of the animal markedly decreased. The muscle-glycogen attained a level of 3—4%. The time necessary to reach this max. was decreased by increasing the rate of administration of glucose. NUTR. ABS. (b)

**Effect of diet on the distribution of glycogen in the skeletal muscle of the rat.** M. SAHYUN, R. SIMMONDS, and H. WORKING (*Amer. J. Physiol.*, 1934, **108**, 708—712).—The glycogen content of the muscles varied directly with the quantity of carbohydrate fed. The gastrocnemius contained about 18% more glycogen than the quadriceps femoris, triceps brachii, and pectoralis major. A variation occurred from animal to animal. The right leg gave vals. > the left, which is unexplained. NUTR. ABS. (b)

**Glycogen metabolism in the rat after partial hepatectomy.** K. MACKENZIE (*Caduceus*, 1933, **12**, 105—112).—After removal of 30—50% of the liver of the rat, insulin more readily produces hypoglycaemic symptoms, and the % but not the total increase in liver-glycogen is greater. NUTR. ABS. (b)

**Carbohydrate exchange in splenectomised animals.** R. DEL ZOPPO (*Arch. Farm. speriment.*, 1934, **58**, 175—186).—Blood-sugar (I) is raised considerably 7—8 days after splenectomy (II), but returns to normal after approx. 21 days. The glycaemic curve (III) is higher and more extended during the hyperglycaemic

period. The (III) resulting from administration of adrenaline is also higher after (II), this increase persisting even when (I) has returned to normal.

R. N. C.

**Intermediary metabolism of carbohydrates from angiostomy data.** I. E. S. LONDON, E. F. IVANENKO, and M. J. PROCHOBOVA (*Z. physiol. Chem.*, 1934, **228**, 243—248).—AcCHO (I) and AcCO<sub>2</sub>H (II) were determined in the inflowing and outflowing blood of various organs of the dog, fasting, and after administration of glucose. There is no parallelism between the curves for (I) and (II). The highest vals. for (I) and (II) are given by the brain sinus. (I) is probably an intermediary metabolic product of glucose, (II) definitely so. J. H. B.

**Significance of bile acids in carbohydrate metabolism.** XXI (ii). **Glycolysis and degradation of glycogen in liver and muscle following administration of cholic acid and adenylypyrophosphoric acid.** K. WATANABE (*Biochem. Z.*, 1934, **274**, 268—273; cf. A., 1933, 88).—Administration of cholic acid (I) to rabbits causes increase, whilst that of adenylypyrophosphoric acid (II) (from rabbit muscle) causes decrease, in the glycogen content of the liver (III) and muscle (IV). Lactic acid production in (III) and (IV) is restricted by administration of (I) and increased by that of (II). (I) and (II) act antagonistically. W. McC.

**Bile acids and carbohydrate metabolism.** XXXII. **Influence of bile acids on liver-glycogenesis and on [H<sup>+</sup>] of urine.** K. OHASHI (*J. Biochem. Japan*, 1934, **20**, 319—326).—The *p*<sub>H</sub> of rabbit's urine gradually decreases during hunger to a min. val., when a slight increase sometimes occurs; it subsequently increases on subcutaneous injection of Na cholate. A similar phenomenon occurs with liver-glycogenesis. F. O. H.

**Biochemistry of carbohydrates.** V. **Micro-determination of chondroitinsulphuric acid in cartilage.** VI. **Chondroitinsulphuric acid in cartilage and bone.** T. MIYAZAKI. VII. **Enzyme hydrolysing glucosamine.** VIII. **Distribution and renal threshold of glucosamine after injection into animals.** K. KAWABE. IX. **Fermentation of chondroitinsulphuric acid by *B. pyocyaneus*.** Pyocyanine. T. MIYAZAKI. X. **Fate of glucosamine in the animal body.** K. KAWABE. XI. **Constitution and specific enzyme of benzoylglycuronic acid.** H. MASAMUNE (*J. Biochem. Japan*, 1934, **20**, 211—222, 223—231, 233—241, 243—251, 287—292, 293—310, 311—317).—V. Dried cartilage (I) (approx. 5 mg.) is hydrolysed with *N*-HCl (10 c.c.) for 30 min., the hydrolysate is evaporated to dryness, and glucosamine (II) in the residue determined colorimetrically by alkali and Ehrlich's reagent (A., 1931, 1081; cf. A., 1932, 532).

VI. The content of chondroitinsulphuric acid (III) (determined approx. by the reducing val. after hydrolysis) varies with the type of (I), viz., hyalin->elastic->fibro-(I); that of costal (I) is low owing to early ossification. With rabbits, the incidence of rickets increases (approx. ×3) the (III) content of the femur.

VII. An enzyme hydrolysing (II) occurs in the



lung, kidney, intestinal mucosa, pancreas, and, to a smaller extent, blood and gastric mucosa of rabbits, dogs, and cats, but not of guinea-pigs. Injection of (II) appears to increase the body-content of the enzyme.

VIII. (II) hydrochloride orally administered to rabbits (2 g. per kg. body-wt.) appears only in traces in the blood, but is excreted in the urine, a max. occurring 5—7 hr. after ingestion; the renal threshold is very low. Subcutaneous administration produces rapid excretion, the blood level being max. 2—3 hr. after injection. Temporary accumulation occurs in the liver, kidney, and mucosa of stomach and intestine.

IX. *B. pyocyaneus*, *Streptococcus hæmolyticus*, and *Staphylococcus flavus* hydrolyse (III) with liberation of a reducing substance but not of  $\text{SO}_4^{''}$ . Pyocyanine is formed, its solution in HCl giving absorption bands at 470, 380, and 275  $\mu$ .

X. Subcutaneous injection of (II) into normal rabbits produces liver-glycogenesis to an extent < that occurring after administration of the equiv. amount of glucose. The urinary lactic acid,  $[\text{H}^+]$ , and urea levels increase, but the total N, including that due to excreted (II), is < the total N administered; fructose is not excreted.

XI. Benzoylglucuronic acid (IV) treated with aq.  $\text{NaHCO}_3$  exhibits mutarotation, whilst no Bz is liberated (cf. A., 1926, 1056); the Bz is probably attached to C2 or C4.  $\text{CHCl}_3\text{-H}_2\text{O}$  extracts of kidney contain an enzyme (optimum  $p_{\text{H}}$  5.4—5.8, inactivated at 80°) which hydrolyses (IV). Differences in the rates of hydrolysis of tributyrin and (IV) by various enzyme preps. indicate that the enzyme is not an esterase.

F. O. H.

Food value of mannitol and sorbitol in relation to the balance of the ration. R. LECOQ (Compt. rend., 1934, 199, 894—896).—When comprising 35% of a pigeon's ration, mannitol (I) and sorbitol are completely utilised and in the case of (I) the vitamin-B (II) requirement is reduced. With 66% in the ration nutritional disturbances occur and polyneuritis intervenes however great the supply of (II). A. G. P.

Utilisation of inulin from *Arctium lappa* and certain soluble inulins by the rat. C. J. CARR and J. C. KRANTZ, jun. (Proc. Soc. Exp. Biol. Med., 1934, 31, 675—678).—No significant differences are noted in the absorption and utilisation of the insol. inulin from burdock root and in the sol. inulins from the roots of camas and wild onion.

NUTR. ABS. (m)

Carbonic acid assimilation by animal cells. W. LOELE (Virchow's Archiv, 286, 167—169; Chem. Zentr., 1934, i, 3602).— $\text{MeCHO}$  occurs in alkaline solutions of glycine and  $\text{H}_2\text{O}_2$  after passage of  $\text{CO}_2$ .

A. G. P.

Acetaldehyde and trimethylamine in human pulmonary expiration. W. LIBBRECHT and L. MASSART (Compt. rend. Soc. Biol., 1934, 117, 495—496).— $\text{MeCHO}$  and  $\text{NMe}_3$  have been detected in expired air after absorption in  $\text{H}_2\text{O}$ . H. G. R.

Relationship between oxygen consumption and nitrogen metabolism. IV. C. W. BALDRIDGE (Arch. Int. Med., 1934, 54, 517—539).—In dogs

the  $\text{O}_2$  consumption is decreased during recovery from acute hæmorrhagic anæmia. Blood transfused into dogs is lost from the peripheral circulation, during which time the basic metabolic rate is increased. The pigment of hæmolyzed blood is rapidly excreted and is accompanied by an increase in gaseous metabolism (whether the blood is hæmolyzed *in vivo* or obtained from another animal). Phloridzin diabetes in dogs is accompanied by a great increase in endogenous protein catabolism and  $\text{O}_2$  consumption, followed by a marked storage of N. C. G. A.

Protein and energy metabolism of wild and albino rats during prolonged fasting. F. G. BENEDICT and E. L. FOX (Amer. J. Physiol., 1934, 108, 285—294).—Wild rats have the higher basal metabolism. Towards the end of fasting protein metabolism increased, the animals deriving increased proportions of total heat from proteins. The effect was greater in wild rats. CH. ABS. (p)

Relative value of proteins in feeding. E. F. TERROINE (Compt. rend. Soc. Biol., 1934, 117, 574—576).—A criticism of Lesné and Clément's work.

R. N. C.

In what form is protein of food resorbed? I. E. S. LONDON and N. KOTSCHNEV (Z. physiol. Chem., 1934, 228, 235—242).—The arterial and portal blood (I) of angiotomised dogs was analysed for polypeptide-(II) and  $\text{NH}_2\text{-N}$  after introduction of various types of protein (III) into the stomach. (III) is resorbed as a mixture of  $\text{NH}_2\text{-acids}$  and (II), the proportion varying with the (III). In fistula dogs the gastric (IV) and small-intestinal chyme (V) was examined. The (II) quotients of (I) and (V) are similar (65%); that of (IV) is higher (88%). The products of (III) digestion pass unchanged through the intestinal wall into the portal vein. The  $\text{NH}_2\text{-acids}$  in the portal blood resorbed from the small intestine are found chiefly in the corpuscles, the (II) in the plasma. After exercise there is a decrease in resorption, a decrease in  $\text{NH}_2\text{-acids}$ , and an increase in (II) of the plasma, with only small changes in the erythrocyte-(II) quotient. J. H. B.

Chemistry of the intestine. I. Intestinal juice. II. Perfusion of the intestine with urea. III. Perfusion of the intestine with glycine. IV. Perfusion of the small intestine with *D*-alanine. G. IKEDA (J. Biochem. Japan, 1934, 20, 253—259, 261—269, 271—278, 279—285).—I. Juice from the upper part of the small intestine (I) of pilocarpinised dogs with fistulæ contained (average of 2 samples) 2.34% of solids, the inorg. (0.96%) including K (0.05%), Na (0.32%), Cl (0.47%), Ca, Mg, S, P, and Si and the org. (1.38%) urea,  $\text{NH}_3$ ,  $\text{NH}_2\text{-acids}$ , creatine, and creatinine.

II. Normal blood (II) perfused through an isolated loop of (I) shows a decrease in urea-N and an approx. corresponding increase in  $\text{NH}_3\text{-N}$ . With (II)+added urea, the decrease in urea-N is much > the increase in  $\text{NH}_3\text{-N}$ .

III. The  $\text{NH}_2\text{-N}$  of (II) perfused through (I) is approx. normal; the  $\text{NH}_3\text{-N}$  slightly increases. With (II)+added glycine, the  $\text{NH}_2\text{-N}$  is greatly diminished, whilst the increase in  $\text{NH}_3\text{-N}$  is more marked; a volatile acid is also formed. Glycine is subsequently



found in the muscle and mucosa of (I). With both types of perfusion, the urea-N decreases.

IV. The greater part of *d*-alanine added to (II) perfused through (I) is decomposed in an unknown manner, small amounts being fixed in the tissue or converted into lactic acid. F. O. H.

Feeding experiments with mixtures of highly purified amino-acids. VI. Relation of phenylalanine and tyrosine to growth. M. WOMACK and W. C. ROSE (J. Biol. Chem., 1934, 107, 449—458).—Phenylalanine is an essential dietary component for rats and cannot be replaced by tyrosine. C. G. A.

Metabolic effect of cystine. C. DOLFF (Z. ges. exp. Med., 1934, 93, 532—540; Chem. Zentr., 1934, ii, 88).—Peroral and parenteral administration of cystine (I) causes a lowering of blood-sugar  $\alpha$  the amount of (I) to a max. of 23%, an increase of total N in urine, and a decrease below normal in the tissues. R. N. C.

Oxidation of the sulphur of the acetyl and formyl derivatives of *d*- and *l*-cystine in the animal body. V. DU VIGNEAUD, H. S. LORING, and H. A. CRAFT (J. Biol. Chem., 1934, 107, 519—525).—Acetyl- and formyl-*d*-cystine, unlike the corresponding derivatives of *l*-cystine, are, in the rabbit, far more resistant to oxidation than the parent acid. A. E. O.

Comparative availability of *d*- and *l*-histidine for growth. G. J. COX and C. P. BERG (J. Biol. Chem., 1934, 107, 497—503).—*d*-Histidine is rather less efficient than *l*-histidine in promoting growth of rats when fed as a supplement to a histidine-deficient diet. A. E. O.

Origin of specific dynamic action. I. ABELIN (Naturwiss., 1934, 22, 758).—From fresh organs (liver and kidney) of animals which have been fed with meat shortly before death, an active protein-free extract can be isolated, which when injected into rats subcutaneously promotes heart and respiratory activity, a sensitiveness towards high external temp., and sometimes increased perspiration. It is suggested that after taking up proteins, a highly active substance is formed in the organs, which assists in the sp. dynamic action. A. J. M.

Course of specific-dynamic increase in metabolism. M. CARMENA (Arch. exp. Path. Pharm., 1934, 177, 85—92).—The basal metabolism of men frequently varies from day to day. Ingestion of meat produces a regular increase in O<sub>2</sub> consumption [indicating heat-formation due to the sp. dynamic action (I)] and a return to normal vals. with some subjects, whilst in others the curve is irregular; for each person, (I) due to protein is remarkably const. F. O. H.

Deaminating power of the lungs. L. BINET and D. BARGETON (Compt. rend., 1934, 199, 1245—1247).—The NH<sub>3</sub>-N in the blood-perfusate of an isolated lung increases from 1.09 to 3.04 mg. N per 100 c.c. during 3 hr. Alanine in the fluid is deaminated to A<sub>2</sub>CO<sub>3</sub>H. Concurrently, the R.Q. falls from about 1 to 0.68 in 3 hr. J. L. D.

Purine metabolism. III. Fate of guanosine and adenosine in the dog. L. R. CERECEDO and

F. W. ALLEN (J. Biol. Chem., 1934, 107, 421—424).—Guanosine (I) and adenosine (II) up to 3 g. are completely metabolised.  $\frac{1}{2}$  to  $\frac{2}{3}$  of the N of (I) is metabolised to allantoin (III), the remainder increasing the urinary urea (IV), this being > can be accounted for by the NH<sub>2</sub> of (I). (II) causes a similar increase of (III), but no more (IV) than is accounted for by deamination. It seems that (I) but not (II) is broken down beyond the (III) stage. C. G. A.

Nitrogen metabolism. Series 2. U. LOMBROSO (Arch. internat. Physiol., 1934, 38, 404—415).—A reply to Terroine's criticism of the postulation of an "azote injustifié" (N not determined by Kjeldahl method and loss through skin, intestinal putrefaction, and in collecting excreta) to explain the discrepancy between N balance and body-wt. balance. NUTR. ABS. (b)

Nitrogen metabolism. Series 2. I. Nutritive value of ammonium salts. G. SARZANA and A. GATTO (Arch. internat. Physiol., 1934, 38, 416—427).—The addition of org. NH<sub>3</sub> salts to a diet rich in carbohydrates, vitamins, salts, and lipins, but poor in protein, and of such a nature as to produce a gradual and progressive fall in wt. of albino rats, was incapable of conserving wt. or permitting longer survival. NUTR. ABS. (b)

Metabolic rhythm. Daily variations in the temperature of the body and the excretion of water, nitrogen, urea, and urobilin in the urine. E. FORSGREN and R. SCHNELL (Acta Med. Scand., 1934, 82, 155—169).—In two afebrile cases agreement was found between the daily variations in body-temp. and excretion of total N, urea, urobilin, and H<sub>2</sub>O. The course of the curves was relatively independent of meal times and of sleep. The administration of an antipyretic to a febrile case affected only the temp. curve. NUTR. ABS. (b)

Cyclic changes in the lipin content of the liver of the rat. B. OHLSSON and G. BLIX (Skand. Arch. Physiol., 1934, 69, 182—188).—Independently of food intake, the neutral fat content of the rat-liver in the morning is > in the evening. There is no cyclic change in phosphatides or H<sub>2</sub>O. NUTR. ABS. (b)

Esterification of cholesterol during absorption from the intestine. E. FRÖLICHER and H. SÜLLMANN (Biochem. Z., 1934, 274, 21—33).—Normal intestinal lymph of rabbits contains free (I) and esterified (II) cholesterol in the ratio of 1 : 1. During absorption of (I) from the intestine, both the (I) and (II) contents of the lymph are increased. Esterification must therefore occur during absorption. The cholesterol (especially (I)) content of the lymph is also increased after absorption of a pure fat diet due to accelerated passage of (I) back to the intestine for excretion. P. W. C.

Fate of plant sterols in the animal organism. I. H. DAM and U. STARUP (Biochem. Z., 1934, 274, 117—121).—Phytosterol (I) after intravenous injection in oil emulsions into rabbits can be detected by a considerable increase in the m.p. of the sterol acetate of the liver and lung, but not of the brain. Stored (I) is not esterified and very slowly disappears. (I) administered to rats by mouth causes a slight increase in



the m.p. of body-sterol acetate and with rabbits in 1 case gave a slight but in 2 cases no increase.

P. W. C.

**Change of xanthophylls in the body after absorption from the intestine.** H. SÜLLMANN and A. VISCHER (Biochem. Z., 1934, 274, 16—20).—After administration to man of egg-yolk [which contains a large amount of xanthophylls (I) and only traces of carotene and (I) ester], an increase occurs in the light petroleum-sol. fraction of the serum, but there is no increase in free (I). (I) are therefore changed during absorption and in part esterified.

P. W. C.

**Digestion of foods. IV. Digestion of synthetic fats. II.** S. SUZUKI and K. NISHINA (J. Agric. Chem. Soc. Japan, 1934, 10, 510—516).—The real digestion coeff. (I) of tripalmitin (II) is intermediate between that of triolein and tristearin. With large administration of (II) the difference between the apparent and the real (I) was small.

CH. ABS. (p)

**Metabolism of isolated fat-tissue. I. Tissue of normal and starved animals.** H. RUSKA and T. OESTREICHER (Arch. exp. Path. Pharm., 1934, 177, 42—52).—The protoplasm of the fatty tissue (I) of rat's testes and epidermis (II) has an  $O_2$  uptake, respectively, 50 and 90% of that of the liver. The R.Q. of normal (I) is  $> 1.0$  and indicates aerobic glycolysis. Starvation causes periodic increases in the respiration (III) and N and fat content of (I) which can be correlated with the disappearance of fat from the depôts; the R.Q. (in Ringer's solution) of (II) during max. (III) is  $< 1.0$ .

F. O. H.

**Oxidation of metabolites. III. Mechanism of the oxidation of fatty acids in an alkaline phosphate-hydrogen peroxide system.** E. J. WITZMANN (J. Biol. Chem., 1934, 107, 475—487; cf. A., 1926, 270).—When many fatty acids are treated with  $H_2O_2$  and  $Na_2HPO_4$  at  $p_H$  8—9 the chief product is  $CO_2$  [83.3% from decanoic acid (I)], together with  $AcOH$  [6.3% from (I)] and  $MeCHO$  and other  $CHI_3$ -yielding substances.  $AcOH$  is the only volatile acid formed, being resistant to oxidation, and  $COMe_2$  and homologues are almost entirely absent. Crotonic acid (II) and  $Pr-CO_2H$  (III) yield both  $COMe_2$  and  $AcOH$ ;  $OH-CHEt-CO_2H$  (IV) yields much  $AcOH$ ; and  $OH-CHMe-CH_2-CO_2H$  (V) much  $COMe_2$ . At  $p_H$  6—7, (III) and (V) are similarly oxidised, but (II) behaves as if largely composed of (IV). The mechanism of the oxidation of the  $C_4$  acids is discussed in the light of the above results.

A. E. O.

**Nutrition with edible tubers. I. Effects of common edible tubers and polished rice on breeding.** T. TAKAHASHI and H. YOKOYAMA (J. Agric. Chem. Soc. Japan, 1934, 10, 451—458).—When fed to rats in the proportion of 20 parts of dry powdered tuber to 100 parts of polished rice, potato, sweet potato, taro, and yam did not improve growth. Radish produced rapid increases in wt., but the life cycle was shortened. Carrot prolonged life, but the live-wt. increase was slow.

CH. ABS. (p)

**Effect of feeding rations varying in their mineral, vitamin, and protein contents on growth, reproduction, and lactation of dairy**

**cattle.** I. R. JONES (Minutes 18th Ann. Meeting Amer. Dairy Sci. Assoc., 1932, 46—54).—Customary rations containing sufficient Ca and P for growth were inadequate for satisfactory reproduction. Administration of cod-liver oil in addition to steamed bone flour did not further improve reproduction, but increased yields of milk and butter-fat. CH. ABS. (p)

**Mineral metabolism of horses and cows.** O. BANG and C. R. DAHM (Skand. Arch. Physiol., 1934, 69, 1—32).—When receiving dry hay as sole ration the horse excretes in the urine two thirds, the dry cow only one fortieth, of the total Ca excreted. In neither animal is there any appreciable amount of P in the urine. Both have a negative Ca balance (I) which is not affected by addition to the ration of  $H_2SiO_3$ , which should not, therefore, be taken into account in calculating the acid-base equiv. of the ration. In the cow addition of 200 g. of sucrose daily improves the Ca (I). In a cow giving 5 litres of milk per day and showing negative Ca and P (I), addition of sugar has no effect, but addition of wheat bran results in positive Ca and P (I). Changing the ration to green lucerne gives a positive P but a negative Ca (I). In a horse fed on bran alone and showing negative P and Ca (I), addition of  $NaHCO_3$  improves the Ca (I) but has little effect on the P (I). Addition of  $Ca_3(PO_4)_2$  causes equilibrium with respect to Ca and P.

NUTR. ABS. (m)

**Mineral metabolism. XXXI. Minimum mineral requirements of cattle. II.** P. J. DU TOIT, A. I. MALAN, and J. W. GROENEWALD (Onderstepoort J. Vet. Sci., 1934, 2, 565—606).—Daily requirements for (2 gal.) milk productions were Cl 14 g.,  $Na_2O$  15 g.,  $K_2O$  0.38 g. The Na content of S. African pastures is often  $<$  min. requirements. Mg deficiency is probably not important in animal nutrition.

CH. ABS. (p)

**Effect of addition of minerals and sucrose to milk diet on growth, fertility, and lactation in the rat.** H. L. KEIL, H. H. KEIL, and V. E. NELSON (Amer. J. Physiol., 1934, 108, 215—220).—Female rats on a milk diet supplemented with  $CuSO_4$  and  $FeCl_3$  grow almost as well as those on a stock ration, but reproduction (I) does not proceed beyond the 2nd generation (II). Addition of the Daniels and Hutton salt mixture (III) (B., 1925, 331) allowed normal growth (IV), but (I) proceeds only to the 5th (II). Of the constituents of (III), only  $MnSO_4$  permits favourable (IV) and (I) to the 3rd (II). The addition of sucrose gives results that are poorer than on milk, Fe, and Cu alone.

NUTR. ABS. (m)

**Agriculture, cows, and magnesium.** P. DELBET (Bull. Acad. Méd., 1934, 111, 393—415; Chem. Zentr., 1934, i, 3760).—The Mg content of foodstuffs is considered to be deficient.

J. S. A.

**Nitrogen, calcium, magnesium, phosphorus, and iron balances in children of 7—8 years.** A. PETRUNKINA (Z. Kinderheilk., 1934, 56, 219—226).—For each of the elements studied the balance rises or falls with the intake (I) of the particular element and in no case is max. retention attained. Reasonably good Ca balances are obtained only with a daily (I) of 30—40 mg. per kg. body-wt., 450—500 c.c. of milk being consumed. The Mg balance is negative with (I)



of < 10 mg. per kg. The daily milk (I), or the absence of milk from the diet, has no marked influence on the P balance, which is good with (I) of 60—70 mg. per kg. The Fe balances are positive. NUTR. ABS. (m)

**Availability of iron in biological materials.** W. C. SHERMAN, C. A. ELVEHJEM, and E. B. HART (J. Biol. Chem., 1934, 107, 383—394).—The availability of the Fe as determined by the 2 : 2'-dipyridyl method (I) is > 60% in ox and pig liver and cardiac muscle and in soya beans, 50% in beef skeletal muscle, and < 25% in oysters (II), spinach (III), lucerne (IV), and blood, agreeing with the vals. obtained by the acid extraction method (V) except in the cases of (II), (III), and (IV), where (V) gives considerably higher vals. Hæmoglobin regeneration in anæmic rats  $\propto$  the amount of available Fe determined by (I).

C. G. A.

**Influence of fruit and vegetable feeding on iron metabolism of the infant.** F. W. SCHLUTZ, M. MORSE, and H. OLDHAM (J. Pediat. St. Louis, 1933, 3, 225).—Vegetable [spinach (I)] or fruit (apricots) in addition to milk has no significant effect on the amount of Fe retained by the infant or on the hæmoglobin (II) level. In an anæmic infant, fed exclusively on milk, no effect was produced by dried (I), but apricots or Fe NH<sub>4</sub> citrate caused a marked increase in the retention of Fe, but scarcely affected (II) and erythrocyte count.

NUTR. ABS. (m)

**Influence of the ingestion of iron caseinogenate on body-weight and carbon and nitrogen content of the urine of the non-anæmic adult dog.** G. FONTÉS and L. THIVOLLE (Compt. rend. Soc. Biol., 1934, 116, 784—787).—Two healthy adult dogs received a diet of milk, rice, and NaCl for 50 days. There was much loss of wt., and the C : N ratio in the urine was 1.0. Early symptoms of vitamin-B deficiency appeared and the animals were given 6 g. of fresh yeast daily. Growth was resumed for a time, but ceased after 25 days. The C : N ratio was now 0.78. The addition of FeCl<sub>3</sub> (40 mg. daily), administered simultaneously with the milk, so that Fe caseinogenate was formed, resulted in rapid growth, an improved N balance, and a urinary C : N ratio of 0.96. CaCO<sub>3</sub> did not have the same effect.

NUTR. ABS. (b)

**Alkali losses after administration of sodium and potassium.** H. GLATZEL (Z. ges. exp. Med., 1934, 93, 666—678).—Oral administration of KCl leads to marked and rapid increase in the alkalinity of the urine and its content of K and Na and a very slight fall in the alkali reserve (I) of the blood : the changes are to some extent dependent on the dose. After NaCl there is a very gradual increase in Na output, little change in K or urinary reaction, and slight rise in (I). The liver plays an important part in these changes, which are in part due to the necessity for maintaining the Na+K concn. of the blood const.

NUTR. ABS. (m)

**Chlorine metabolism.** J. BOTTIN (Rev. belge Sci. méd., 1934, 6, 173—211).—Dogs on a mixed diet maintain a steady level of Cl in whole blood (I) and plasma. Most of the ingested Cl is excreted in the urine. During starvation excretion of Cl ceases, and the Cl in (I) is reduced by about 10%, whilst the level in plasma and corpuscles remains const. The no. of

red blood corpuscles increases and the decrease in Cl in (I) is probably a function of the reduction in plasma-vol. After re-feeding with a mixed diet the excretion of Cl rises rapidly and for a time exceeds the intake. Equilibrium is then reached and maintained, and Cl in (I) and plasma-vol. return to normal. There is no difference between venous (II) and arterial (III) blood as regards Cl level, but in the gastric vessels the Cl is higher in the (III) and varies with the changes taking place in the Cl content of the gastric juice during digestion. In the renal vessels the Cl level is lower in the veins, the difference between (II) and (III) being greatest when digestion is at its height and urinary excretion of Cl at its max. In the superior mesenteric vessels (II) contains more Cl than does (III), the difference reaching a max. when intestinal digestion is fully active.

NUTR. ABS. (m)

**Increasing the chlorine content of young dogs.** G. TÖRÖK and L. NEUFELD (Arch. Kinderheilk., 1934, 102, 35—45).—Administration of NaCl, in addition to the usual food, to very young puppies produces an increased Cl content of liver, muscle, and brain, but not of skin and lungs, whether or not nutritional disturbances occur. "Dry" retention of Cl may occur.

NUTR. ABS. (m)

**Excretion of iodine in the urine after ingestion of inorganic iodine, thyroxine, and di-iodotyrosine.** A. W. ELMER and W. RYCHLIK (Compt. rend. Soc. Biol., 1934, 115, 1719—1722).—About 31% of the I ingested as KI is excreted in 24 hr., 23% appearing in 6 hr. After ingestion of pure cryst. thyroxine, thyroxine in alkaline solution, and di-iodotyrosine, the amounts excreted are 1, 7, and 9%, respectively, in 6 hr., and 6, 14, and 32%, respectively, in 24 hr.

NUTR. ABS. (m)

**Absorption of iodine from baths through the skin and its fate in the organism.** H. ANTHES and F. SALZMANN (Z. ges. exp. Med., 1933, 91, 100—105; Chem. Zentr., 1934, ii, 465).—No connexion has been found under the conditions employed between the blood-I following KI baths and the [I] of the bath, nor has any increased I excretion in the urine been noticed.

R. N. C.

**Rôle of the liver in the regulation of blood-iodine.** A. W. ELMER and Z. LUCZYNSKI (Compt. rend. Soc. Biol., 1934, 115, 1717—1718).—After a meal the amount of I in the bile of rabbits is increased fivefold, whereas the level in the blood is almost unaltered. The liver holds back the I absorbed from the alimentary tract and returns it by way of the bile, thereby establishing a cycle and preventing any large increases in blood-I.

NUTR. ABS. (m)

**Chemical transmission of nerve impulses.** H. H. DALE (Science, 1934, 80, 450).—A correction (A., 1934, 1386).

L. S. T.

**Physico-mathematical aspects of the conduction of nervous impulse.** N. RASHEVSKY (Physical Rev., 1933, [ii], 43, 372).

L. S. T.

**Action of acetylcholine on the brain and its occurrence therein.** B. B. DIKSHIT (J. Physiol., 1934, 80, 409—421).—A substance resembling acetylcholine (I) occurs in brain (principally in basal ganglia) and occasionally in cerebrospinal fluid after vagal



stimulation. (I) may be concerned in transmission of nerve stimulus to the brain. CH. ABS. (p)

Does vagus stimulation cause an increase in the acetylcholine content of heart muscle? A. VARTIAINEN (J. Physiol., 1934, 82, 282—292).—Extracts of heart muscle with  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  show no evidence of increased acetylcholine content as the result of vagus inhibition. R. N. C.

Influence of the vagus nerves on sugar tolerance in dogs. R. C. RANQUIST (Amer. J. Physiol., 1934, 108, 210—214).—The lowered sugar tolerance and fall in blood-sugar following double vagotomy (I) result, not from (I) *per se*, but from the associated operative procedure. NUTR. ABS. (m)

Humoral control of the secretion by the sub-maxillary gland of the cat following sympathetic stimulation. J. SECKER (J. Physiol., 1934, 82, 293—304).—Stimulation of the cervical sympathetic nerve or injection of adrenaline induces a secretion of saliva containing a "cholinergic" substance. Secretion resulting from either stimulus is enhanced by eserine and inhibited by atropine. The active substance is similar to acetylcholine in being inactivated by alkali. R. N. C.

Function of sympathetic nerves in relation to skeletal muscle. Evidence for humoral action. O. W. TIEGS (Proc. Roy. Soc., 1934, B, 116, 351—375).—Stimulation of the sympathetic nerves sets free a substance with adrenaline-like action, which is probably responsible for the Orbeli phenomenon. H. G. R.

Identification of the substance liberated in the nictating membrane of the cat by sympathetic stimulation. Z. M. BACQ and H. FREDERICQ (Bull. Acad. roy. Belg., 1934, [v], 20, 931—947).—*l*-Adrenaline is the only known substance which has an effect similar to stimulation of the sympathetic system. H. G. R.

Anaphylactic metabolic reaction of isolated tissues. G. BOSTROM (Klin. Woch., 1934, 13, 399—403).—The glycolysis and  $\text{O}_2$  uptake of the liver and skin of sensitised animals are increased by very high dilutions of the antigenic protein, whilst rather more conc. solutions cause a decrease. True sensitisation or immunisation occurs. NUTR. ABS. (m)

Colloidal nature of anaphylactic precipitates. A. LUMIERE and P. MEYER (Bull. Soc. Chim. biol., 1934, 16, 1266—1283).—The addition of antigen to the sera of the rabbit and the guinea-pig previously sensitised to horse-serum causes in both cases a ppt. consisting mainly of globulins. The supernatant liquid shows a decrease in osmotic pressure and surface tension, and an increase in viscosity, compared with the corresponding vals. of the sensitised sera. These effects may be due to an increase in size of the globulin aggregates. A. L.

Histamine test-meals on normal students. F. P. L. LANDER and N. F. MACLAGAN (Lancet, 1934, 227, 1210—1213).—Results of 100 test-meals on normal males are recorded, the highest free acidity, the vols. of gastric juice and free acid per hr. being used as characteristics of the test. L. S. T.

Effect of histamine on blood-sugar in adren-alectomised rats. L. C. WYMAN and C. T. SUDEN (Amer. J. Physiol., 1934, 108, 424—427).—Injection of small amounts of histamine caused hyperglycaemia in normal rats and hypoglycaemia in those the adrenals of which had been removed with or without transplanted cortical tissue. CH. ABS. (p)

Effect of the acid secretion of the stomach on blood-sugar after histamine stimulation. S. MARINO and F. ROMEO (Arch. Farm. sperim., 1934, 58, 233—241).—The hyperglycaemia resulting from injection of histamine has no relation to the acidity of gastric secretion in starvation, and is frequently increased by introduction of gastric juice into the stomach. R. N. C.

Histamine and blood-cholesterol. F. GOEBEL (Compt. rend. Soc. Biol., 1934, 117, 535—537).—Intramuscular injection of histamine causes hypercholesterolaemia in the dog lasting for 2 hr. This does not occur if the gastric juice, secreted owing to the injection, does not pass into the duodenum. H. G. R.

Toxicity of some esters of diethylaminoethyl alcohol. H. VINCENT and J. DETRIE (Compt. rend. Soc. Biol., 1934, 117, 597—598).—The ratios of the toxicities of the esters and salts of  $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  with  $\text{AcOH}$ , *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , and *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  are respectively 6, 9, and 13 when injected intravenously in mice, and approx. half these vals. when injected subcutaneously. R. N. C.

Influence of "octinum" on bile excretion. G. BALTĂCEANU, H. ANGELESCU, and C. VASLIU (Arch. exp. Path. Pharm., 1934, 177, 29—33).—Subcutaneous injection of small doses (0.2 g. daily) of "octinum" [octenylamine (?)] into dogs has little influence on the vol., viscosity, and dry wt. of the bile; with larger doses (0.8 g. daily), the vol. is reduced by 30%, whilst viscosity and dry wt. are unchanged. F. O. H.

Influence of cholagogues on the respiration of liver tissue. H. NAKAGAWA (J. Biochem. Japan, 1934, 20, 327—342).—The respiration (I) of mouse liver tissue is inhibited by *in-vitro* application, and increased (max. after 15 min.) by intravenous administration, of atophan. Bile salts *in vitro* inhibit or increase (I) according to their concn., whilst *in vivo* a marked rise (max. after 30 min.) occurs. Diuretics which are also cholagogues (II) generally increase the *in-vivo* (I); avertin and chloral hydrate are exceptions. The relation between (I) and (II) is discussed. F. O. H.

Micro-determination of ethyl alcohol in blood and tissues. M. NICLOUX, E. LE BRETON, and A. DONTCHEFF (Bull. Soc. Chim. biol., 1934, 16, 1314—1332).—A modification of the method of Nicloux (A., 1931, 752) permits the determination of 0.8—10 $\times$  10<sup>-4</sup> g. of EtOH with an error  $\gt$  2%. A. L.

Absorption, distribution, and elimination of ethyl alcohol. I. Determination in air, blood, and urine by iodine pentoxide. II. Excretion in urine and expired air. Distribution between air and water, blood, and urine. III. Rate of oxidation in the body. H. W. HAGGARD and L. A.



GREENBERG (J. Pharm. Exp. Ther., 1934, 52, 137—149, 150—166, 167—178).—I. EtOH vapour [liberated from urine (I) or blood (II) by heat] is passed over  $I_2O_5$  at 150—180°, the liberated HI+I being absorbed successively in  $H_2O$  and aq. KI and determined by titration. The error is approx. 2.5 and 10% for samples of 1.0 and 0.1 c.c., respectively.

II. The ratio of the relative solubilities of EtOH in (I) and (II) (calc. from the air-fluid partition) is 1.144:1. After ingestion of EtOH by dogs, the concns. in (I) and arterial (II) agree with this ratio; hence EtOH passes through the kidneys by simple diffusion. With the exception of that of the peripheral veins (which is markedly < normal), the concn. of EtOH in (II) from different blood vessels after ingestion is approx. the same. During the first 16 hr., 2.1—4.3% of the vol. ingested is excreted in (I), whilst approx. 8% occurs in the expired air; the distribution between alveolar air and arterial (II) gives the same ratio as that of the air-(II) distribution *in vitro*.

III. The rate of oxidation of EtOH intravenously injected into dogs is not const., but  $\propto$  the amount of EtOH in the body; the (II)-EtOH diminishes, however, by an approx. const. % each hr. (cf. Mellanby, M.R.C. Rep., 1919). The solubility of EtOH in (II) is > that in the tissues as a whole (1:0.62). Data for (II)-EtOH after ingestion of EtOH and the derived curve for EtOH absorption from the stomach are discussed. F. O. H.

Alcohol content of the blood of different vessels in the rabbit after its administration. B. FALCONER and H. GLADNIKOFF (Skand. Arch. Physiol., 1934, 68, 245—251; Chem. Zentr., 1934, ii, 267).—No differences were established between the EtOH contents of arterial and venous blood, but portal blood after administration of EtOH contained more EtOH than that of the vena cava. R. N. C.

Experimental alcoholism. Mechanism of alcohol tolerance. J. LÉVY (Compt. rend., 1934, 199, 973—975).—The concns. in the brain, kidney, and liver after a given time of EtOH (I) injected into normal rats and those accustomed to (I) are comparable, as are the rates of oxidation of (I). Normal rats are anaesthetised by smaller doses than the latter, the brain cells of which are probably hyposensitive. J. L. D.

Effect of physical work on the fate of alcohol in the organism. E. NYMAN and A. PALMLÖV (Skand. Arch. Physiol., 1934, 68, 271—294; Chem. Zentr., 1934, ii, 89).—The increase in respiration due to physical exertion has no effect on the removal of EtOH. Similarly the amount of EtOH in urine or sweat is not increased. The immediate augmentation in the blood at the commencement of muscular activity recedes after abs. rest. R. N. C.

Chemistry and pharmacology of campherol and related compounds.—See this vol., 89.

[Pharmacology of] phenanthrene derivatives. III. Disubstitution products. N. B. EDDY (J. Pharm. Exp. Ther., 1934, 52, 275—289).—Disubstituted derivatives are in general less active than monosubstituted containing the same groups, except

when the two substituents are in the 9:10- or 3:4-positions. H. G. R.

Chemical changes accompanying muscle contraction and fever. IV. Changes in composition of muscle, blood, and liver in fever. T. CAHN. V. Muscle metabolism unit and hypotheses on carbohydrate breakdown in muscle. T. CAHN and J. HOUGET (Ann. Physiol. Physicochim. biol., 1933, 9, 393—426, 427—450; Chem. Zentr., 1934, ii, 88).—IV. In hyperthermia (I) in dogs from intravenous injection of 2:4-dinitrophenol, and in "spontaneous" (I), the muscular system was fully atonic, and a considerable disappearance of carbohydrate occurred in the muscles (II) and liver (III), with occasional hyperglycaemia. (II)-lactic acid was only slightly raised, whilst fats and lipins fell in (II), but rose in blood (IV) and (III). Creatinephosphoric acid was extensively broken down in (III), adenylophosphoric acid less extensively; inorg.  $PO_4'''$  in (II) rose. Urea rose more in (II) than in (III). Creatine and creatinine increased in (II), (III), and (IV); Na, K, and Ca were unchanged.

V. Theoretical.

R. N. C.

Pharmacological and chemical studies of the digitalis group. I. *Adonis*, *Apocynum*, and *Convallaria*. J. C. MUNCH and J. C. KRANTZ, jun. (J. Amer. Pharm. Assoc., 1934, 23, 988—996).—Biological assays show that the potencies of *Adonis*, *Apocynum*, and *Convallaria* are, respectively, 1, 2, and 3 times that of *Digitalis*. A. E. O.

Excretion of glucose, creatinine, and urea following phloridzin administration. P. GOVAERTS and P. CAMBIER (Bull. Acad. roy. Méd. Belg., 1934, 14, 226—243).—Excretion of glucose runs parallel with that of creatinine in dogs given phloridzin.

NUTR. ABS. (m)

Grayanotoxin, the active principle of *Leucothoe grayana*.—See A., 1934, 1359.

Toxic material in *Lathyrus* peas. R. STOCKMAN (J. Hygiene, 1934, 34, 145—153).—The material (I) consists of  $H_2O$ -sol. phytic acid salts precipitable by  $Pb(OAc)_2$ ,  $Hg(OAc)_2$ , and conc. EtOH. (I) is toxic to monkeys, rabbits, and frogs and causes lathyrism in man.

NUTR. ABS. (m)

Cardiac activity and toxicity towards rats of red and white squill from Cyprus. F. WOKES and S. G. WILLMOTT (Quart. J. Pharm., 1934, 7, 565—573).—Cultivated and wild red squill and white squill have approx. equal cardiac activity, but red squill is 10—15 times as toxic as the white. C. G. A.

Action of piperidinomethyl-3-benzodioxan on glycaemia in the dog. E. ZUNZ and J. PERLA (Compt. rend. Soc. Biol., 1934, 117, 473—476).—Intravenous injection raises the blood-sugar (I), which later falls below the initial val. Intramuscular injection increases (I) slightly, with a return to normal after 5—6 hr. H. G. R.

Can chlorogenic acid be formed in coffee poisoning? M. KOCHMANN (Med. Welt, 1934, 8, 577—578; Chem. Zentr., 1934, ii, 279).—Free chlorogenic acid (I) is toxic to mice in doses of 70 mg. per 20 g. body-wt. injected intraperitoneally, but not



subcutaneously. Orally, 70—85 mg. per 20 g. has no action in mice, nor 1.0 g. per kg. in rabbits. (I) is effective only in the free state; it ppts. protein, and when injected subcutaneously in 7% solution causes local necrosis and suppuration, which can lead to death. Equiv. quantities of HCl exhibit the same effect as free (I). The neutral Na salt is not toxic even when injected intraperitoneally in 7% solution. The Na caffeine salt has the same effect as the corresponding dose of caffeine, the toxic effect of (I) in coffee indulgence being due to neither its concn. nor its total quantity. R. N. C.

**Relation between chemical constitution and purgative action.**—See this vol., 79.

**Excretion of eucodal.** K. SCHÜBEL (Arch. exp. Path. Pharm., 1934, 177, 34—37).—With dogs, subcutaneously injected eucodal (I) (B., 1931, 945) appears (up to 12%) in the urine. With animals and men, (I) is excreted in urine and fæces. The detection of (I), depending on the appearance in mice of typical tail and respiratory movements lasting for some hr. and not given by morphine or thebaine (cf. A., 1934, 556), is described. F. O. H.

**Detection of barbituric acid derivatives in blood.** P. CHÉRAMY and R. LOBO (J. Pharm. Chim., 1934, 20, [viii], 461—462).—The blood after treatment with COMe<sub>2</sub> is acidified with tartaric acid, boiled for 20—30 min., and filtered. The filtrate is concn., treated with aq. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate extracted with Et<sub>2</sub>O. The extract is examined for barbituric acid. E. H. S.

**Characterisation of barbituric derivatives in urine.** FOUCHET (J. Pharm. Chim., 1934, [viii], 20, 403—406).—A modification of Zwickler's reaction (A., 1931, 1328) is described. Barbiturates (I) give a violet ppt. with a 3% aq. solution of CuSO<sub>4</sub> containing sufficient C<sub>5</sub>H<sub>5</sub>N to redissolve the hydroxide first pptd. The (I) may be recovered by sublimation of the ppt. Derivatives containing N-Me (prominal, evipan) do not react. C. G. A.

**Extraction of barbituric derivatives from viscera by acetone.** P. CHÉRAMY and R. LOBO (J. Pharm. Chim., 1934, [viii], 20, 400—403).—COMe<sub>2</sub> is preferable to EtOH for the extraction of barbiturates in toxicological work. C. G. A.

**Detection of barbital in human viscera.** C. STRZYZOWSKI (Ann. Méd. lég. Criminol., 1933, 13, 49—53).—Crude barbital from liver, kidneys, etc. is dissolved in H<sub>2</sub>O, made alkaline with NaOH, and filtered. The Et<sub>2</sub>O extract of the filtrate is decolorised with C, and crystallised from HCl solution. The product is examined by micro-sublimation, by the cryst. form of the Ag salt, and by colour reactions of the Cu and Hg salts. A. G. P.

[Pharmacology of] barbiturates. VIII. Distribution in the brain. T. KOPPANYI, J. M. DILLE, and S. KRÖP. IX. Effect on the embryo and on pregnancy. J. M. DILLE. X. Acute barbital poisoning in dehydration and diuresis. T. KOPPANYI, W. S. MURPHY, and S. KRÖP (J. Pharm. Exp. Ther., 1934, 52, 121—128, 129—136, 223—230).—VIII. Various barbiturates (I), intravenously adminis-

tered in anæsthetising doses to dogs, are recoverable from every part of the central nervous system in approx. equal concn. and from the organs and tissue fluids. The classification of (I) as thalamic hypnotics must therefore be rejected. Lecithin interferes with the determination of (I) in nerve tissue and must first be removed.

IX. With pregnant rabbits, cats, and guinea-pigs, intravenously injected (I) are detectable in the embryo (II) 15 min. after injection; after some time (II) is freed from (I) by maternal elimination. Whilst small single doses of (I) are not harmful, repeated dosage produces abortion or absorption of (II).

X. With dogs poisoned by (I), treatment with diuretics (Na<sub>2</sub>SO<sub>4</sub>, glucose, CaCl<sub>2</sub>, or 0.9% aq. NaCl) does not increase their excretion. Intravenously injected NH<sub>4</sub>Cl increases the urinary excretion of barbital, but recovery from the narcosis is not hastened. F. O. H.

**Metabolic processes during growth. I. Metabolism of isobarbituric acid in the growing dog.** L. R. CERECEDO and J. A. STEKOL (J. Biol. Chem., 1934, 107, 425—428).—In contrast with adult dogs, puppies do not metabolise isobarbituric acid (I) to urea. The fall in inorg. S and corresponding rise in ester-S indicate partial excretion of (I) in conjunction with SO<sub>4</sub>". No change in the neutral S fraction is observed after feeding small amounts of (I). C. G. A.

**Comparative effects of anæsthetics on the isolated nervous system of the frog (*Rana esculenta*).** A. RABBENO and V. RUFFINI (Arch. int. Pharmacodyn. Théor., 1933, 46, 425—445; Chem. Zentr., 1934, i, 3879).—The reflex excitability of the Herlitzka prep. can be used to compare anæsthetics and other depressors; it is sensitive to concn. differences between 10<sup>-15</sup> and 10<sup>-5</sup>. The effect is dependent on the chemical nature of the drug; the strongest effects being given by sandoptal (Na isobutylallylmalonylurea) and CCl<sub>3</sub>-CHO, and the weakest by Et urethane and Na veronal. R. N. C.

**Relative anæsthetic effects.** (a) Urea derivatives. E. J. DEBEER and A. M. HJORT. (b) Aliphatic ureas. E. J. DEBEER, J. S. BUCK, and A. M. HJORT (J. Pharm. Exp. Ther., 1934, 52, 211—215, 216—222).—(a) The toxicity (I) and anæsthetic action (II) in mice were determined for a series of alkylaryl derivatives of urea and barbituric acid. The position of MeO has no consistent influence on (I) or (II), whilst (II) with low (I) occurs with relatively simple urea derivatives.

(b) The (I) and (II) in mice of a series of *n*- and *iso*-alkylureas [including *n*-amylurea, m.p. 100° (corr.)] increase with increasing mol. wt., the rise in (II) being > that in (I). F. O. H.

**Tobacco smoking in relation to blood-sugar, blood-lactic acid, and metabolism.** D. B. DILL, H. T. EDWARDS, and W. H. FORBES (Amer. J. Physiol., 1934, 109, 118—122).—The smoking of one cigarette produced no change in blood-sugar or -lactic acid or R.Q., but increased the metabolic rate in some cases. CH. ABS. (p)

**Nicotine content of milk from women who smoke.** L. NAGY (Pharm. Zentr., 1934, 75, 737—



740).—100—150 c.c. of milk are coagulated by warming for 20 min. with a few c.c. of 1% HCl, 4 c.c. of 20% CaCl<sub>2</sub>, and 10 c.c. of 25% CCl<sub>3</sub>·CO<sub>2</sub>H solutions. The ppt. of caseinogen is extracted thrice with 40 c.c. of boiling 0.5% HCl and the extracts are combined with the whey. The combined liquids are evaporated to 20—25 c.c. and the nicotine (I) is separated by distillation in presence of MgO into 10 c.c. of 0.1N-H<sub>2</sub>SO<sub>4</sub>, which is then evaporated to 1 c.c. and treated with 1% silicotungstic acid solution. The results are accurate within  $\pm 2 \times 10^{-6}$  g. of (I). Human milk from patients smoking 50—60 cigarettes per day contained a negligible amount of (I) ( $13-15 \times 10^{-6}$  g. per litre). S. C.

**Pharmacological assay of nicotine with rats and mice.** F. J. NIEUWENHUYZEN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 575—578).—Nicotine (I) produces catatonic symptoms accompanied by tremor in mice (II) and rats. The action on (II) may be used for the determination of (I).

W. O. K.

**Absorptive action of aconitine ointments. Biological detection and determination of aconitine.** P. PULEWKA and H. GREVENER (Arch. exp. Path. Pharm., 1934, 177, 74—84).—Methods of assay of aconitine (I) and veratrine, based on characteristic changes in the respiration and body movement and on their toxicity in mice, are described. Inunction of mice with 50 mg. of ointment containing 3—5% of (I) produces the same effect as, but much more slowly than, subcutaneous injection of 0.0012 mg. of (I) nitrate. F. O. H.

**Experimental catatonia by means of derivatives of mescaline and adrenaline.** L. NOTEBOOM (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 562—574).—Of various compounds allied to mescaline,  $\beta$ -3 : 4-dimethoxyphenylethylamine gave the most strongly marked symptoms of catatonia in cats. A no. of sympathomimetic bases including ephedrine, sympathol, and norsympathol produced superficial catatonic reactions. W. O. K.

**Atropine tolerance in infants and children. Negative action of serum of tolerant subjects.** J. D. PILCHER (J. Pharm. Exp. Ther., 1934, 52, 196—205).—The serum of atropine-tolerant children does not neutralise the action of atropine as indicated by dialysis and subsequent testing of the cutaneous reaction or by the cat's pupil response (cf. A., 1926, 1267). Phenomena associated with atropine tolerance are described. F. O. H.

**Comparative actions of atropine and *l*- and *d*-hyoscyamine in infants and very young children.** J. D. PILCHER (J. Pharm. Exp. Ther., 1934, 52, 206—210).—The relative activities (as indicated by both central and peripheral action) of atropine and *l*- and *d*-hyoscyamine are approx. 20 : 40 : 1—2, respectively. F. O. H.

**Fate of azo-dyes in the organism.** G. HECHT (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 167—176; Chem. Zentr., 1934, i, 3877).—In the cat and rabbit, acid mono- and bis-azo dyes containing  $\geq 3$  SO<sub>3</sub>H are taken up in the gall-bladder. R. N. C.

**Effect of insulin and other factors on iodoacetate hyperglycaemia.** J. T. IRVING (J. Physiol., 1934, 80, 360—368).—CH<sub>2</sub>I·CO<sub>2</sub>H causes hyperglycaemia by mobilising liver-glycogen and interfering with the disappearance of sugar in the tissues.

CH. ABS. (p)

**Kinetics of penetration. IX. Models of mature cells.**—See this vol., 42.

**Asphyxial arrest of the isolated frog's ventricle.** A. J. CLARK, R. GADDIE, and C. P. STEWART (J. Physiol., 1934, 82, 265—277).—Total lactic acid (I) of the ventricle (II) rises sharply on asphyxiation (III); the (I) of the ventricular fluid rises more steadily, is relatively higher, and on aëration falls less rapidly than that of (II) itself. (I) production and mechanical response (IV) fall together in (III); (I) production appears to be the only source of energy available in (III), and the amounts produced are adequate for the maintenance of the (IV) observed. Failure of (IV) is not due solely to (I) accumulation, since it occurs prior to this. Fall of  $p_H$  increases rate of fall of (IV) in (II), and inhibits aërobic recovery. Most of the (I) excreted by a fresh heart in the first 10 min. of (II) is in neutral form, so that the (I) excretion cannot be calc. from the  $p_H$ .

R. N. C.

**Effect of cyanide and other substances on the oxygen uptake of rat tissue.** E. MUNTWYLER and D. BINNS (Amer. J. Physiol., 1934, 108, 80—90).—The O<sub>2</sub> uptake (I) of tissues and the degree of inhibition of (I) by KCN are unrelated to the indophenol-oxidase colour. KCN and pyrophosphate decrease O<sub>2</sub> consumption and inhibit the ability of the tissue to take up O<sub>2</sub> in presence of *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (II). Urethane and AsO<sub>3</sub>''' decrease (I), but do not inhibit the absorption of additional O<sub>2</sub> in the presence of (II).

CH. ABS. (p)

**Urinary elimination of bismuth after injection of bismuth preparations.** J. POUZERGUES (Ann. Inst. Pasteur, 1934, 53, 535—553).—The absorption of Bi after intramuscular injection of insol. compounds in guinea-pigs is very low. Bi metal is the least, and Na tartrobismuthate the most, readily absorbed; Bi camphorcarboxylate is intermediate between the two. Death follows in < 8 days after injection of lethal doses of sol. compounds which give rise to acute uræmia, whilst insol. compounds lead to diarrhœa with ultimate death. P. G. M.

**Toxicity and fixation in the organism of magnesium thiosulphate.** R. E. CARRATALÁ and C. L. CARBONESCHI (Semana méd., 1934, II, 25—29).—The protective action of MgS<sub>2</sub>O<sub>3</sub> (I) in HCN intoxication is much < that of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Toxicity of (I) is examined. The normal Mg of the organism is increased by repeated narcosis with (I). CH. ABS. (p)

**Rôle of copper in the setting, metamorphosis, and distribution of the American oyster, *Ostrea virginica*.** H. F. PRYTHORCH (Ecol. Monographs, 1934, 4, 47—107).—The duration of the setting process varied with the salt concn. (optimum 1.60—1.86%). Setting was most pronounced at the stage of tide when Cu content was max. (0.05—0.60 mg. per litre) and in this range  $\propto$  the amount of Cu present. The oyster larva is stimulated through ingestion of Cu as



a colloidal ppt., and its further development depends on further ingestion of Cu. Distribution of oysters is examined in relation to concns. of salt and Cu.

CH. ABS. (p)

**Biologically electronegative nature of potassium.** R. KELLER (Arch. Phys. Biol. Chim.-Phys. Corps organisés, 1933, 11, 31—39; Chem. Zentr., 1934, ii, 257).—The significance of the nature of the electric charge on the intake, transport, and accumulation of substances in plant and animal organisms is examined.

A. G. P.

**Investigations on lipins in view of a theory of the pharmacodynamic effect of alkalis and alkaline earths.** J. WAJZER (Compt. rend. Soc. Biol., 1934, 115, 830—833).—The min. concn. of  $\text{CaCl}_2$  to ppt. a 1% soap solution is 0.003—0.006*N*, that of  $\text{NaCl}$  is 0.125—0.25*N*, whilst  $\text{KCl}$  does not ppt. soap. Mixed solutions of the salts show simple additive effects. The surface tension of 0.001*N*- $\text{NaOH}$  is lowered by 0.001*N*- $\text{Na}$  oleate to the same extent as the corresponding  $\text{KOH}$  solution is by  $\text{K}$  oleate.

R. N. C.

**Microchemical examination of blood-serum for the detection of industrial poisoning.** E. A. PRIBRAM (Arch. Gewerbepath. Gewerbehyg., 1934, 5, 345—354).—The fixation of simultaneously injected sugar, urca, and  $\text{PO}_4'''$  by blood-serum is normally controlled by definite equilibrium relationships, but is decreased by injections of  $\text{As}$ ,  $\text{Hg}$ , or  $\text{Pb}$  chlorides and increased by  $\text{FeCl}_3$ . Use is made of this phenomenon in detecting incipient industrial poisoning by heavy metals.

A. G. P.

**Behaviour of residual nitrogen in blood following administration of arsenic, phosphorus, and sodium chlorate and in oxygen deficiency.** H. E. BÜTTNER (Z. ges. exp. Med., 1934, 93, 391—401; Chem. Zentr., 1934, ii, 1323).—Small dosages of  $\text{As}$ ,  $\text{P}$ , and  $\text{NaClO}_3$  or slight reduction in atm.  $\text{O}_2$  reduce, and large dosages or great reduction in  $\text{O}_2$  increase, residual  $\text{N}$ .

A. G. P.

**Avidity determination of new arsenobenzene preparations (mysalvarsan, solusalvarsan).** R. SCHNITZER (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 253—262; Chem. Zentr., 1934, i, 3764).—The avidity index is defined as the ratio  $N/F$  of the chemotherapeutic indices of preps. towards normal strains of trypanosomes ( $N$ ) and towards strains resistant to salvarsan ( $F$ ). The therapeutic vals. of compounds are high as  $N/F$  approaches 1. Vals. obtained are arsenophenylglycine 1/3, solusalvarsan 1/4—1/10, mysalvarsan 1/23, neosalvarsan 1/62, salvarsan 1/80. J. S. A.

**Colloidal chemical properties of chemotherapeutically active substances and their relationship to constitution.** R. LABES and F. BILLMANN (Biochem. Z., 1934, 274, 75—86).—Of a no. of acid and basic dyes, those substances which are most active chemotherapeutically (germanin, a trypan dye) exert the greatest colloidal chemical action on caseinogen, their effect being still apparent at dilutions which correspond with the chemotherapeutically active dose.

F. W. C.

**Significance of amines in chemotherapy.** I. K. KINDLER (Arch. Pharm., 1934, 272, 811—817).—A lecture. The "toxic val.," T.V., of a substance against *Paramecia* (I) is defined as  $x/t$ , where  $x$  is the no. of mg. of solution containing 1 mg. of the substance and  $t$  is the time in sec. required for death of at least 90% of (I). The "relative toxic val.," R.T.V., of a substance is defined as its T.V. compared with that of quinine (II) taken as 1000.  $x$  must be chosen so that  $t$  is 1—10 min., since otherwise irregular results for T.V. are obtained; thus T.V. for (II) is 3000 if  $x=1000$ , 1300—1100 if  $x=2000$ —10,000 ( $t=1.5$ —16 min.), and approx. 25 if  $x=30,000$ . Aliphatic amines have a low R.T.V., e.g.,  $\text{NH}_3$  1—2 <  $\text{NH}_2\text{R}$  ( $\text{R}=\text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}$ , or *iso*amyl),  $\text{NHMe}_2$ ,  $\text{NH}_2\text{Et}_2$ ,  $\text{NHPr}_2$ ,  $\text{NMe}_3$ , piperidine, and *dl*-2-methylpiperidine (all 1—2), scopolamine and coniine < 1, atropine 3. Introduction of aryl groups increases R.T.V. greatly, e.g., R.T.V. for  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$  is 10—20,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$  50—100, and  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{NH}_2$  100—200, although  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  has R.T.V. only slightly > 2. Introduction of two or more aryl groups increases R.T.V. still further, and substituents, such as  $\text{OH}$  and  $\text{OR}$ , often have a profound influence. Similarly, 1-aryl-*iso*quinolines, -di- and -tetra-hydro-*iso*quinolines are much more toxic than their 1-Me analogues. Numerous examples are given. The most potent substance recorded is 1-*p*-methoxycinnamyl-3:4-dihydro-*iso*quinoline (R.T.V. 10,000).  $\beta$ - $\text{C}_{10}\text{H}_7$  and  $\alpha$ -thienyl groups have effects similar to those of  $\text{Ph}$ . There is no relation between toxicity to mammals and to (I) (cf. coniine etc.), but probably between toxicity to the latter and to protozoa in general. R. S. C.

**Physical basis of the biological effects of high-voltage radiations.** W. V. MAYNEORD (Proc. Roy. Soc., 1934, A, 146, 867—879).—The importance of the range of the secondary electrons produced in living materials by high-voltage X- and  $\gamma$ -rays is discussed.

L. L. B.

**Susceptibility of infusoria to ultra-violet rays as related to the colloidal properties of their protoplasm changed by different physico-chemical methods.** V. V. ALPATOV and O. K. NASTUKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 595—600).—The resistance of *Paramecium caudatum* to the destructive action of ultra-violet light (I) was increased by colloid-condensing electrolytes ( $\text{Na}_2\text{SO}_4$ ).  $\text{KCNS}$  produced the opposite effect. Narcosis renders the infusoria less resistant to (I). Increase in the viscosity of the protoplasm produced by an electric current increases the resistance to (I). H. J. E.

**Relation of substances of the cell nucleus to the lethal action of ultra-violet light.** F. F. HEY-ROTH and J. R. LOOFBOUROW (Bull. Basic Sci. Res., 1933, 5, 13—22).—Ultra-violet irradiation (I) in the range 295—200  $\text{m}\mu$  destroys pyrimidines (II) and purines. Curves showing absorption by (II) and lethal action on micro-organisms rise abruptly at 295  $\text{m}\mu$  and show max. at 260  $\text{m}\mu$ . In bacteria, action of (I) on nuclear substances is more important than its effect on proteins. Stimulative effects in the range 320—295  $\text{m}\mu$  correspond with increased absorption of thymus-nucleic acid and may produce growth-promoting substance.

CH. ABS. (p)



**Effect of ultra-violet light on carbohydrate metabolism.** P. KALLÓS and L. KALLÓS-DEFFNER (*Strahlenther.*, 1934, 50, 191—192).—In rabbits the rise in blood-sugar after intravenous injection of glucose is less when the animals are irradiated than when they are kept in the dark. Prolonged irradiation increases sugar tolerance, which remains high for 8—10 days. NUTR. ABS. (m)

**Enzymes, vitamins, and the zone of maximum colloidal stability.** J. B. SUMNER (*Science*, 1934, 80, 429).—A criticism (A., 1934, 1136). L. S. T.

**Enzymic oxidation and reduction systems.** H. VON EULER (*Ergebn. Enzymforsch.*, 1934, 3, 135—162; *Chem. Zentr.*, 1934, ii, 258).—A discussion. A. G. P.

**Biological oxidations. III. Oxidation-reduction potential of the system lactate-enzyme-pyruvate.** E. S. G. BARRON and A. B. HASTINGS. **IV. Mechanism of the catalytic effect of reversible dyes on cellular respiration.** R. H. DE MEIO, M. KISSIN, and E. S. G. BARRON (*J. Biol. Chem.*, 1934, 107, 567—578, 579—590).—III. When  $\alpha$ -hydroxymethylase from gonococci is added to lactate+pyruvate in presence of a dye only partly reduced by this system, a stable, reproducible potential is reached in 1—2 hr. For the above system at 35°, the normal potential is  $+0.248 \pm 0.002$  volt, the free energy change  $\Delta F$  is 11,440 g.-cal., and the heat of reaction  $\Delta H$  is 21,639 g.-cal.

**IV. Reversible dyes (I) influence the O<sub>2</sub> consumption of cells containing no hæmoglobin (II) only when respiration has been inhibited by HCN or CO. (I) evidently act as catalysts for the oxidation of lactic acid. In the case of cells containing (II), (I), if sufficiently positive, also oxidise (II) to methæmoglobin, which then oxidises, irreversibly and stoichiometrically, a portion of the substrate.** A. E. O.

**Acceleration of an enzymic dehydrogenation by irradiation.** H. VON EULER and E. KLUSMANN (*Naturwiss.*, 1934, 22, 777).—The reduction of methylene-blue at 30° in presence of yeast extract with EtOH as H donor is accelerated by exposure to Hg light. With liver succinodehydrogenase as enzyme and Na succinate as H donor, a similar acceleration is not produced by irradiation. W. O. K.

**Thermodynamics of the fumarase system.** K. P. JACOBSON, F. B. PEREIRA, and J. TAPADINHAS (*Biochem. Z.*, 1934, 274, 167—180).—The dependence of the fumaric-malic acid equilibrium in presence of fumarase on the temp. is investigated, similar results being obtained by both gravimetric and polarimetric methods. P. W. C.

**Co-enzymes.** O. WARBURG and W. CHRISTIAN (*Biochem. Z.*, 1934, 274, 112—116).—1 g. of a substance (I) has been isolated (no details) from the erythrocytes of 250 litres of horse blood, 0.0001 mg. of which added to a system in which hexose monophosphate is being oxidised by O<sub>2</sub> causes an increased absorption of O<sub>2</sub> by 1 c.c. per min. Useful characterisation of (I) is obtained in terms of the velocity coeff. of destruction by acids and alkalis. (I) fluoresces blue in acid and yellow-green in alkaline solution and contains 10% of organically bound PO<sub>4</sub>'''

and 11% of N. It is similar in elementary composition to the co-enzyme of yeast, but cannot replace the latter in its action on fermentation either with or without PO<sub>4</sub>'''. (I) is a mixture of phosphoric esters and on hydrolysis yields 70% of its N as adenine. After removal of adenine, two other bases have been isolated, one of which is contained in larger amounts in the more active preps. P. W. C.

**Enzymes of *Bombyx mori*, L. VII and VIII. Catalase of the eggs. IX. Blood-protease and -amylase.** K. YAMAFUJI (*Bull. Agric. Chem. Soc. Japan*, 1934, 10, 112—116, 116—118, 119—127; cf. A., 1934, 559, 1032).—VII. Treatment of aq. extracts of silkworm eggs with EtOH and CHCl<sub>3</sub>, adsorption on Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> followed by elution, and dialysis yields a catalase (I) prep. the unimol. reaction coeff. of which gradually diminishes. (I), with optimum temp. and  $p_H$  of 25° and 6.8, respectively, is inactivated at > 55°. Max. thermostability, which increases with increasing concn., occurs at  $p_H$  6.8. Data for the affinity const. and temp. coeffs. are given.

VIII. The action of (I), purified by adsorption on Al(OH)<sub>3</sub> and elution with Na<sub>2</sub>HPO<sub>4</sub>, is inhibited by the following anions in increasing order of activity: butyrate, SO<sub>4</sub>, PO<sub>4</sub>, Cl, lactate, OAc, NO<sub>3</sub>, F, oleate, SH, S, CN.

IX. The blood-protease activity of the male larva is somewhat > that of the female; the level is also influenced by health, starvation, and type. The content of protease-a ( $p_H$  optimum 2.3) increases during the five larval stages, decreases after cocoon-spinning, and increases again to a max. at the end of the pupal stage; that of protease-b ( $p_H$  optimum 8.8), which is less evident than -a, follows an almost opposite course. The blood-amylase in the male larva is < that in the female, is independent of growth, and increases with starvation. Its level during development follows a course approx. parallel with that of protease-a. F. O. H.

**Action of trypsin and amylokinase on the amylase content of grains.** T. CHRZĄSZCZ and J. JANICKI (*Biochem. Z.*, 1934, 274, 274—284; cf. A., 1934, 1258).—Different grains [barley (I), wheat (II), rye, oats, buckwheat, maize, millet (III)] exhibit great differences as regards the extent to which their power to convert starch into dextrin and sugar is increased by trypsin (IV). The starch-liquefying powers remain weak. As regards saccharifying effect (V), (IV) acts in virtue of its proteolytic power, its effect being great with (I), less with rye and (II), and quite weak with the other grains. The increase in dextrin-forming power (VI) is due to the amylokinase (VII) (produced during germination) in (IV). Variations in (VI) with const. (V) are due to variations in the amount of (VII). The activity of the amylase of (III) is not reduced by (IV). Inactive (IV) may act like an eleuto-substance. The assumptions of Ohlsson (A., 1932, 303) and Oparin (A., 1934, 1258) are not justified. W. McC.

**Absorption-spectrographic examination of invertase preparations.** H. ALBERS and I. MEYER (*Z. physiol. Chem.*, 1934, 228, 122—140).—Highly purified invertase preps. were obtained from yeast autolysates by adsorption with Al(OH)<sub>3</sub> C<sub>2</sub>. Trypto-



phan (I) was detected in the preps. by the ultra-violet adsorption spectrographic method even when not shown by the colorimetric method of von Fürth and Lieben. The (I)-peptide concn.  $\propto$  the difference between the absorption max. and min. Higher absorption coeffs. are shown as the preps. become inactive (by ageing), owing to aggregation of the high-mol. carrier, accompanied by a masking of the active group. J. H. B.

**Autolysis of placental glycogen.** A. DAVY and A. ST. G. HUGGETT (J. Physiol., 1934, 81, 183—193).—In minced rabbit placenta no change in total carbohydrate occurred on autolysis for 24 hr. in Ringer's solution, at 37°, in presence of air, O<sub>2</sub>, or N<sub>2</sub>. As with liver, lactic acid remained unchanged, and of the glycogen (I) which disappeared, one third was accounted for as dextrin, the remainder as glucose. Change in  $p_H$  did not affect the disappearance of (I) but an acid reaction inhibited glucose formation. The enzymes concerned were in the placental cells, not in the blood, and were unaffected by F' or PO<sub>4</sub>'''. NUTR. ABS. (b)

**Antiglyoxalase.** J. O. GIRŠAVIČIUS, P. H. EFENDI, and A. P. RYZHOVA (Biochem. Z., 1934, 274, 87—94).—Glyoxalase (I) is inhibited both by histidine and pancreatin (II) and the inhibition is reversed in both cases by addition of glutathione, whilst the inhibition by (II) is dependent on the presence of sufficient protein. These facts support the view of Ochoa and Dudley, according to whom antiglyoxalase is the protease of (II) under the action of which NH<sub>2</sub>-acids arise, of which especially histidine has a powerful inhibitory action on (I). P. W. C.

**Relation between the synthesis of adenosinetriphosphoric acid and the oxido-reductive transformation of dihydroxyacetonephosphoric ester during glycolysis.** Z. DISCHE (Naturwiss., 1934, 22, 776—777).—The disappearance of hexose diphosphate in presence of hæmolysed washed human erythrocytes and phosphate at 40° which takes place without production of triose phosphate is accelerated by adenylic acid. Addition of phosphoglyceric acid causes a similar acceleration, in this case with an increased formation of AcCO<sub>2</sub>H. The acceleration is accompanied by increased formation of lactic acid and formation of easily split phosphoric esters. The increased esterification is associated with an increased oxido-reductive activity of the intermediate triose esters. Erythrocytes with glucose at 0° synthesise the Harden-Young hexose diphosphate, for which the P appears to come from adenosinetriphosphoric acid and a relatively stable ester. W. O. K.

**Enzymic decomposition of adenosinetriphosphoric acid (adenyl pyrophosphate) in heart muscle.** A. N. PARSCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 626—630).—Adenyl pyrophosphate (extraction described) from the heart muscle of a frog or white rat is hydrolysed nearly completely in 0.5 hr. at 20° in 0.9% KCl. 0.5—0.05*N*-NaF partly inhibits the hydrolysis, whereas 0.005*N* is without action. 0.004*N*-CH<sub>2</sub>I-CO<sub>2</sub>H accelerates hydrolysis, but 0.02*N* has no effect. Analogous results are obtained with skeletal muscle. KCN results in immediate hydrolysis. J. L. D.

**Influence of the hydrogen-ion concentration of the medium on the hydrolysis of  $\alpha$ - and  $\beta$ -glycerophosphoric acids by grain phosphatases.** J. COURTOIS (Compt. rend., 1934, 199, 1252—1254; cf. A., 1934, 927).—The phosphatase (I) of white or black mustard hydrolyses both isomerides (II) at any  $p_H$ , but the rates of hydrolysis are different. The (I) of sweet almonds hydrolyses the (II) (as an emulsion) at equal rates (max. at  $p_H$  5.8), although the affinity of the (I) for the substrate diminishes with increase in  $p_H$ . Contrary to taka-diestase, these (I) hydrolyse both (II) in mixtures. J. L. D.

**Enzymic activity of the phosphatase of cobra venom.** E. ROUSSEAU (Compt. rend. Soc. Biol., 1934, 117, 565—566).—The activity is not destroyed by heating at 70° for 30 min. R. N. C.

**Specificity of phosphatase.** R. HOTTA (J. Biochem. Japan, 1934, 20, 343—360).—The following new substrates were prepared: NH<sub>4</sub> sec.-Bu phosphate and its Ph ester (as K salt); NH<sub>4</sub> cyclohexyl phosphate, its 1:2- and 1:3-Me<sub>2</sub> derivatives (as Ba salts), and the Ph ester of the former (as K salt); bis-sec.-Bu phosphate (as K salt); biscyclohexyl phosphate (as K salt). The action of various mono- and di-phosphatase preps. (from dialysed kidney autolysate, taka-phosphatase, pig's liver, rice bran, snake venom, etc.) on these and other substrates indicates that the specificity of phosphatases depends not only on linking of H<sub>3</sub>PO<sub>4</sub>, but also on the nature of the ester-forming alcohol (cf. A., 1932, 650; 1933, 426). F. O. H.

**Determination of plasma-phosphatase.** A. BODANSKY (Proc. Soc. Exp. Biol. Med., 1934, 28, 760—762; Chem. Zentr., 1934, i, 3604).—Errors in Kay's method are corr. by addition of Na diethylbarbiturate (0.1*M*). To 1 c.c. of centrifuged plasma are added 7 c.c. of H<sub>2</sub>O, 2 c.c. of veronal solution, and 1 c.c. of glycerophosphate solution. After 2 hr. at 37° the liquid is rapidly cooled, and 5 c.c. of 10% solution of CCl<sub>3</sub>-CO<sub>2</sub>H are added. Total inorg. PO<sub>4</sub>''' is determined in the filtrate. Phosphatase activity is expressed as mg. inorg. PO<sub>4</sub> formed per 100 c.c. of plasma per hr. A. G. P.

**Crystalline proteins: hormones and enzymes.** E. GORTER (Chem. Weekblad, 1934, 31, 682—685).—An account is given of measurements on unimol. films of ovalbumin, insulin (I), trypsin (II), and pepsin (III) at various  $p_H$  vals. (I), (II), and (III) are protein complexes, the protein in (II) being combined with a strong base and that in (III) with a strong acid. S. C.

**Proteolytic enzymes in plants.** R. SCHAEDE (Ber. Deut. bot. Ges., 1934, 52, 378—383).—The distribution of gelatin-liquefying enzymes in the roots, rhizomes, and leaves of a no. of plants is recorded. A. G. P.

**Activation of plant proteinases.** E. MASCHMANN (Z. physiol. Chem., 1934, 228, 141—186).—The activation of papain (I) on gelatin substrate by Fe''' [for which ascorbic acid (II) is not necessary] is due to the activation of a concomitant (III) (not present in all preps.) which is removed by pptn. of (I) with 90% EtOH. (III) is apparently not a SH-compound,



since it is more quickly activated, neither is it a flavin. In the hydrolysis of peptone with (I) the specificity range is broadened by  $Fe^{++}$ . Peptone is almost unattacked by (I), but after treatment with  $Fe^{++}$  it becomes susceptible to hydrolysis. (III) immediately accelerates the hydrolysis in presence of  $Fe^{++}$ , no pre-treatment being necessary. (II) promotes hydrolysis only after long "incubation" with (I), treatment of the substrate with (II) produces immediate fission. The favourable effect of HCN is probably due to reduction of  $\cdot S \cdot S \cdot$  groups. The effect of Pd-C in inactivating gelatin hydrolysis is incompletely removed by  $H_2$ . Bromelin behaves similarly to and is probably identical with (I). The proteinase activity of a yeast autolysate towards gelatin is not affected by (II) or  $Fe^{++}$  either singly or together. (III) treated with  $Fe^{++}$  has no effect on this reaction.

J. H. B.

**Activation of papain, applied to the determination of physiologically active substances in blood.** A. PURR and M. RUSSEL (Z. physiol. Chem., 1934, 228, 198—206).—Cysteine hydrochloride and glutathione solutions of equal  $\cdot SH$  content show the same power of activation of papain. This is the basis of a method for determination of active or potential  $\cdot SH$  groups in blood (I). Carcinomatous (I) shows a lower activating power than normal (I). The activator in (I) occurs exclusively in the (I)-cells. Cathepsin is also activated by (I)-cells, an important fact in considering intracellular proteolysis.

J. H. B.

**Enzymic components of the proteinase from pancreas.** E. WALDSCHMIDT-LEITZ and S. AKABORI (Z. physiol. Chem., 1934, 228, 224—234).—The activity of cryst. trypsin (I) towards caseinogen (II) is < that of pancreas-proteinase (III), towards sturin and clupein about the same, towards clupean markedly greater. (I) together with chymotrypsin (IV) has about the same effect as (III). Hence (III) contains (IV), which may also be inferred from the milk-coagulating properties of (III); the  $Ca^{++}$  required to produce clotting gives a measure of (IV). In a purified (III) prep. the ratio of "trypsin" to (IV) was about 9:1 calc. on this basis. (IV) in (III) was separated by adsorption on  $Al(OH)_3$ . A. J. H. B.

**Activation of pancreas extract by acidification.** LISBONNE, R. SEIGNEURIN, and A. FRANK (Bull. Soc. Chim. biol., 1934, 16, 1306—1313).—The pancreas excretion of rabbits and dogs, having no proteolytic activity, when brought within the  $pH$  range 4.2—3.8 by addition of 0.125N-HCl and kept at 42° for 12 hr., develops tryptic activity. The activation may be connected with the pptn. of the protein carrier of the enzyme, since within the active range considerable pptn. takes place.

A. L.

**Activation of the pancreatic juice of the rabbit by enterokinase. Rapid diminution at 30° of curdling power.** M. GUILLAUME (Compt. rend. Soc. Biol., 1934, 117, 604—607).—The curdling power (I) of rabbits' pancreatic juice (II) activated by enterokinase (III) at 30° rises to its max. after a time lag, which decreases as the amount of (III) increases. (I) reaches its max. before the proteolytic activity (IV), and then falls rapidly to a low val.;

(IV) on reaching its max. falls only slowly. Further addition of (III) to a mixture comparatively poor in it after its (I) has begun to fall increases (I) only slightly, but (IV) considerably. These results suggest that (I) and (IV) are due to separate enzymes. The (II) of the dog has (I) three times as high as that of the rabbit, for quantities with equal (IV).

R. N. C.

**Biochemical micro-methods. V. Nephelometric micro-determination of trypsin and cathepsin.** B. J. KRIJGSMAN (Z. physiol. Chem., 1934, 228, 256—266).—Trypsin is determined on a caseinogen (I) substrate, cathepsin best on (I), but also on edestin or by means of the protein in the enzyme extract.

J. H. B.

**Ground Congo-red-fibrin for testing rates of action of enzymes.** H. HARTRIDGE (Proc. Physiol. Soc., J. Physiol., 1934, 81, 11 p).—Fibrin is treated with Congo-red, washed, dried, and powdered. Enzyme activity is indicated by the rate of liberation of colour from the dry powder added to the test solution.

CH. ABS. (p)

**Properties of uricase.** H. KLEINMANN (Bull. Soc. Chim. biol., 1934, 16, 1252—1265).—Uricase (I) preps. made from powdered pigs' liver (II) by the author's method (A., 1933, 864) decompose uric acid in blood even in the absence of air. Evaporation in vac. of the preps. destroys the activity. Whilst (I) may be extracted from (II) by aq.  $NH_3$ ,  $Na_2B_4O_7$ , NaOH, and NaCl, the ppt. obtained from such extracts by addition of acids, EtOH, or  $COMe_2$  is inactive.  $NH_4$  salts catalyse the decomp. of uric acid in aq. solution, but not in human blood.

A. L.

**Biochemical hydrogenations. I. Hydrogenation of unsaturated  $\alpha$ -keto-acids, aldehydes, and alcohols by fermenting yeast.** F. G. FISCHER and O. WIEDEMANN (Annalen, 1934, 513, 260—280).—An actively fermenting mixture of brewer's bottom yeast (I), sucrose, and aq.  $NaH_2PO_4$  reduces  $CHMe:CH:CHO$  (concn. about 1%) to  $Bu^cOH$  and a little  $CHMe:CH:CH_2:OH$  (also similarly reduced to  $Bu^cOH$ ); repeated additions of (I) are necessary to maintain fermentation.  $CHPh:CH:CHO$  similarly gives  $CH_2Ph:CH_2:CH_2:OH$  (II) and a little  $CHPh:CH:CH_2:OH$  [also similarly reduced to (II)];  $\Delta^{\alpha\gamma}$ -hexadienal (concn.  $\approx$  0.5%) affords  $\Delta^{\beta\delta}$ -hexadien- $\alpha$ -ol (which undergoes slow reduction) and a mixture of  $\Delta^{\gamma\epsilon}$ - and  $\Delta^{\delta}$ -hexen- $\alpha$ -ol;  $\Delta^{\alpha\gamma\epsilon}$ -octatrienal (concn.  $\approx$  0.5%) yields  $\Delta^{\beta\delta\epsilon}$ -octatrien- $\alpha$ -ol (III) [the action of impoverished yeast (IV) gives this as the main product] and octadienol (V).  $\zeta$ -Methyl- $\Delta^{\epsilon}$ -hepten- $\beta$ -ol is similarly unaffected.  $CHPh:CH:CO:CO_2H$  (as Na salt) undergoes decarboxylation and reduction to (II); little or no change occurs with (IV).  $\alpha$ -Keto- $\Delta^{\beta\delta\epsilon}$ -nonatrienoic acid and (I) give (III) and then (V); (III) and  $\Delta^{\alpha\gamma\epsilon}$ -octatrienoic acid are formed using (IV). The main type of reduction appears to be  $\alpha\beta$ .

H. B.

**Ion antagonism and activation in alcoholic fermentation.** V. KULIKOV and A. POPOVA (Mikrobiologiya, 1933, 2, 51—56).—In 25—30% sugar solutions, 10% of  $K_2SO_4$  retarded fermentation. Subsequent addition of  $CaSO_4$  accelerated the process.

CH. ABS. (p)



**Reduction of hyposulphite by yeasts.** M. P. KORSAKOVA (*Mikrobiologiya*, 1933, 2, 251—259).—Reduction of hyposulphites is unrelated to the fermentative process. A substance resembling glutathione is the causative agent. CH. ABS. (p)

**Death of a yeast culture as registered by electrical resistance.** B. J. LUYET (*Proc. Soc. Exp. Biol. Med.*, 1934, 31, 800—801).—Resistance-temp. effects in yeast cultures were reversible between 15° and 62°. An irreversible fall in resistance occurs at > 62°. CH. ABS. (p)

**Resistance of individual cells of micro-organisms of the same species to the action of ultra-violet rays.** J. BEAUVÉRIE (*Compt. rend.*, 1934, 199, 881—883).—Resistance is associated with the thickness of the glycogen layer in yeast cells. A. G. P.

**Effects of inositol, crystalline vitamin-B<sub>1</sub>, and "pantothenic acid" on the growth of different strains of yeast.** R. J. WILLIAMS and D. H. SAUNDERS (*Biochem. J.*, 1934, 28, 1887—1893).—The addition of 0.000008 mg. of a highly conc. prep. of "pantothenic acid" (A., 1933, 982; 1934, 254) to each ml. of a synthetic medium containing sucrose, asparagine, and all essential inorg. constituents results in a striking increase of growth with 5 out of 6 strains of *Saccharomyces cerevisiae* tested, and a slight but definite increase with "old process" yeast (I). The effect was usually enhanced by inositol (II) (in relatively large amount), by vitamin-B<sub>1</sub> (III) (in extremely minute amount), or both. (II) has little effect alone, and (III) alone produces a striking effect only with (I) and one other strain of yeast tested. An unknown basic factor, not (III), promotes the growth of Wildier's yeast. "Pantothenic acid" is the most important constituent of "bios." A. E. O.

**Yeast as an indicator for growth-promoting substance.** E. ALMOSLECHNER (*Planta*, 1934, 22, 515—542).—By means of single-cell drop cultures of yeast the presence of growth-promoting substance is established in *Boletus edulis*, *Rhizopus suinus*, and in urine. The active agent is insol. in Et<sub>2</sub>O, sol. in H<sub>2</sub>O and EtOH, and resistant to heat and oxidation, but has no action on the growth of *Avena* coleoptiles. It is probably of the group of growth-substances-B of Nielsen. A. G. P.

**Influence of antiseptics on yeast autolysis.** H. HAEHN and H. LEOPOLD (*Woch. Brau.*, 1934, 51, 353—356).—Autolysis was carried out by heat-treatment (I) (50—52°), with PhMe, CHCl<sub>3</sub>, or with EtOAc. With (I), *p<sub>H</sub>* fell from 5.9 to 5.3 in 21 days; with PhMe or CHCl<sub>3</sub>, *p<sub>H</sub>* changes were smaller, due to the presence of buffer substances, despite considerable development of titratable acidity. EtOAc gave abnormal results, due to its own hydrolysis. Volatile acids are formed chiefly during the first 12 hr. of autolysis, but there is considerable prolonged liberation of inorg. PO<sub>4</sub><sup>'''</sup>. Proteolysis is hindered by CHCl<sub>3</sub> and EtOAc, as compared with (I) and PhMe. At the close of autolysis, all the yeast-P appears to be in solution, although not necessarily in the inorg. form. Alkaline autolysis gave reduced liberation of inorg. PO<sub>4</sub><sup>'''</sup> as compared with (I). I. A. P.

**α- and β-Glucosidase.**—See this vol., 69.

**Soil protozoa.** F. S. BODENHEIMER and K. REICH (*Soil Sci.*, 1934, 38, 259—265).—The annual cycle of protozoa in soil and the heat-tolerance of various cysts is examined. A. G. P.

**Micro-moving pictures showing the lethal effects of ultra-violet radiation on certain living protozoa.** R. FRANKLIN, A. J. ALLEN, and E. McDONALD (*Physical Rev.*, 1933, [ii], 43, 1041).—Ultra-violet radiation below 2900 Å. causes immediate cessation of all motion of *Entosiphon*, *Euglena*, *Colpoda*, and *Paramecia*. Some light is thrown on the mechanism of death caused by the photochemical changes which occur. L. S. T.

**Microphotography and some radiation effects on living organisms with various wave-lengths of monochromatic ultra-violet light.** A. J. ALLEN, R. FRANKLIN, and E. McDONALD (*Physical Rev.*, 1933, [ii], 43, 1041; cf. preceding abstract).—Absorption of wave-lengths below 2900 Å. by nuclei of the cells of different kinds of tissue produces an effect similar to staining. Photomicrographs of cancer tissue taken 5 min. and 3 hr. after the death of an animal show a marked change in the micro-absorption spectra of the cells. L. S. T.

**Soluble enzymes secreted by *Hymenomyces*. Cytolysis of cellulose.** L. LUTZ (*Compt. rend.*, 1934, 199, 893—894).—Decomp. of cellulose (cotton) by *Stereum purpureum* involves the successive stages, cellulose, hydrocellulose, erythrocellulose, xanthocellulose, insol. gums, sol. gums, intermediate products, cellobiose, monoses. A. G. P.

**Occurrence of tyrosine in the protein of *Aspergillus niger*.** M. VORBRÖDT (*Bull. Acad. Polonaise*, 1934, B, 85—88).—0.3% of tyrosine has been isolated from the protein, containing 9% N, of the mycelium. H. G. R.

**Chemistry and enzyme chemistry of acid formation and degradation by moulds. XI. Formation of oxalic acid from formic, glycollic, succinic, and other acids by *Aspergillus niger*.** K. BERNHAUER and F. SLANINA (*Biochem. Z.*, 1934, 274, 97—111).—Using dil. solutions of HCO<sub>2</sub>Na (I) a yield of > 60% of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (II) was obtained [calc. on amount of (I) disappearing], whilst with more conc. solutions the yield of (II) was halved, the chief reaction being the degradation of (I) to CO<sub>2</sub>+H<sub>2</sub>O. Under parallel conditions AcOH, succinic, fumaric, glycollic, aconitic, and citric acids gave 77.6, 68, 67.2, 65.6, 60, 61.1% yields, respectively, of (II). The bearing of these results on the mechanism of the degradation of sugar is discussed. The views of Butkewitsch (A., 1934, 1139) on the mechanism of the formation of citric acid from AcOH and EtOH are critically examined and repudiated. P. W. C.

**Citric acid fermentation.** W. P. DOELGER and S. C. PRESCOTT (*Ind. Eng. Chem.*, 1934, 26, 1142—1149).—A standard mineral salt-acid-sucrose medium is used for citric acid (I) fermentation by a selected variety of *Aspergillus niger*, care being taken to limit the hydrolysis of sucrose during the preliminary sterilisation. Adjustment of the initial *p<sub>H</sub>* to 1.6—



2.2 gives improved yields of (I), HCl being best used for this purpose. The optimum temp. for (I) production is 26–28°. Titratable acidity (II) increases rapidly from the 6th to the 12th day of fermentation, and thereafter increases more slowly, (I) being converted into other products. Repeated transference of spores to new fermentations gives increasing (II), and spore-formation decreases as ability to produce (I) increases. The efficiency of the process increases with the ratio surface area/depth of medium. For a 9–12-day fermentation, 14% of sucrose in the medium gives the most satisfactory yield of (I); addition of other sugars gives a decreased yield. Shallow containers of 99.8–99.98% Al with Cu covers and min. air circulation may be used; the use of open containers necessitates a high R.H. I. A. P.

**Glucose metabolism of *Trypanosoma equiperdum* in vitro.** L. REINER and C. V. SMYTHE (Proc. Soc. Exp. Biol. Med., 1934, 31, 1086–1088).—Glucose is converted by suspensions of *T. equiperdum* into 1 mol. each of glycerol and  $\text{AcCO}_2\text{H}$  (I) anaerobically and into 2 mols. of (I) aerobically. Aerobically glycerol gives 1 mol. of (I) and utilises 1 of  $\text{O}_2$ . Neither  $\text{CO}_2$  nor lactic acid is produced. C. G. A.

**Action of arsenopyridine derivatives on resistant strains of trypanosomes.** H. SCHLOSSBERGER and R. SCHÜFFNER (Angew. Chem., 1934, 47, 768–771).—The action of various arsenopyridine derivatives on strains of *T. brucei* resistant to trypanamide or to the Na salt of 2-pyridone-5-arsinic acid was determined in mice (cf. A., 1930, 1213). The data are compared with those from corresponding arsenophenyl derivatives. F. O. H.

**Malarial pigment (hemozoin). III. Action of solvents and of oxidising and reducing agents on optical properties and on crystallisation.** J. A. SINTON and B. N. GHOSH (Rec. Malaria Survey, India, 1934, 4, 205–221).—The pigment was obtained from the centrifuged  $\text{Na}_2\text{CO}_3$  extract of the parasites by pptn. with  $\text{H}_2\text{C}_2\text{O}_4$ . Chemical and physical properties were identical with those of hæmatin. CH. ABS. (p)

**Cytochrome and the respiratory systems of bacteria.** W. FREI, L. RIEDMÜLLER, and F. ALMASY (Biochem. Z., 1934, 274, 253–267).—Bacteria (I) may be divided into 4 groups on the basis of the presence or absence of respiratory catalysts. (I) of the first group contain hæmochromogen (II) (cytochrome) and indophenol-oxidase (III); (I) of the second, (II) but no (III); (I) of the third, (III) but no (II); and (I) of the fourth, neither (II) nor (III). Cytochrome scarcely ever occurs unless (III) is also present. With increase of age or for other reasons some (I) may pass from one group to another. (I) of the first three groups always, and (I) of the fourth group which can act anaerobically usually, contain peroxidase and catalase. Not all aerobically grown (I) contain detectable amounts of hæmatin. In special cases pigments (IV) other than those mentioned are encountered. (IV) are probably respiratory. W. McC.

**Fermentation of cellulose.** V. PERVOSVANSKI and Y. CHELTZOVA (Brodilnaya Prom., 1933, 3, 3–6).

—With Langwell's process, thermophilic organisms isolated from horse manure increased their capacity for cellulose decomp. on repeated subculturing, and produced max. yields of 25% of EtOH in 3 days.  $\text{HCO}_2\text{H}$  and  $\text{PrCO}_2\text{H}$  are also formed.

CH. ABS. (p)

**Rôle of a cellulolytic bacterium of the stomach in the conversion of cellulose into glucose in the alimentary canal of ruminants.** J. ROCHON (Compt. rend., 1934, 199, 983–985).—Fermentation of cellulose *in vitro* by *Plectridium cellulolyticum* in a neutral medium (cf. A., 1934, 812) gives (80%) mainly  $\text{HCO}_2\text{H}$ ,  $\text{AcOH}$ , and some  $\text{PrOH}$ , but by Pringsheim's method affords glucose (I) (10%), which indicates the presence of a cellulase. (I) is formed in small amounts when the fermentation liquor becomes gradually acid, and in optimum concn. at  $p_{\text{H}}$  4.8. A symbiosis of bacteria is unnecessary to account for cellulose digestion.

J. L. D.

**Fermentation product of galactose by acetic acid bacteria. Production of galactonic and comenic acids.** T. TAKAHASHI and T. ASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 604–607).—Bacteria isolated from "sanbokan" (citrus) fruit, grown in yeast extract containing 5% of galactose, produced galactonic and comenic acids.

CH. ABS. (p)

**Restriction of butyric acid fermentation by carbon monoxide.** F. KUBOWITZ (Biochem. Z., 1934, 274, 285–298; cf. A., 1934, 113).—The degradation of glucose (I) by *Clostridium butyricum* (II) is unaffected by  $\text{CO}$ , which, however, affects some degradation product (III) in such a way that  $\text{PrCO}_2\text{H}$  fermentation (IV) is replaced by lactic acid fermentation (V). The consumption of (I) is decreased only about 25%. The degree of restriction of (IV) by  $\text{CO}$  depends on  $[\text{H}^+]$ , increasing from 23.5% at  $p_{\text{H}}$  5.6 to 71% at 7.15. 0.01M-HCN acts like  $\text{CO}$ , but higher concns. also restrict (V).  $\text{H}_2$  reversibly restricts (IV), but does not affect consumption of (I).  $\text{CO}$  reversibly restricts (53% at  $p_{\text{H}}$  4.5, 25% at 6.64) fermentation (VI) of  $\text{AcCO}_2\text{H}$  by (II).  $\text{H}_2$  also acts thus. Restriction by  $\text{CO}$  of (VI) by (II) is counteracted by irradiation. The enzyme in (II) which attacks  $\text{AcCO}_2\text{H}$  seems to be identical with that which produces  $\text{PrCO}_2\text{H}$  from (I). W. McC.

**Action of sodium salicylate on the fermentation of salicin and glucose by streptococci.** E. VALENTINE and L. REINER (Proc. Soc. Exp. Biol. Med., 1934, 31, 926–929).—Na salicylate inhibits the fermentation of salicin and glucose by streptococci, but has little or no effect on the viable count, although the chains of organisms are shorter.

C. G. A.

**Chemistry and pharmacology of fermented foodstuffs. II.** W. KEIL and E. KUNZ (Arch. exp. Path. Pharm., 1934, 177, 25–28; cf. A., 1934, 1134).—The juice of salted cucumbers contained putrescine, choline, and acetylcholine (0.002%), but not histamine. F. O. H.

**Sulphur bacteria. II. Cyanophyces accompanying sulphur bacteria. III. Cell structure in sulphur bacteria.** I. TUROWSKA (Bull. Acad.



Polonaise, 1933, B, 135—138, 139—148).—Organisms from various sources are examined in relation to  $H_2S$  assimilation. A. G. P.

**Cultivation of organisms concerned in the oxidation of thiosulphate.** R. L. STARKEY (J. Bact., 1934, 28, 365—386).—Development of *Th. thio-parus* (I) and *Th. novellus* (II) is favoured by initial alkalinity in media. The latter become increasingly acid with the growth of the bacteria. Strong buffering increases the oxidation of  $S_2O_3''$  by (II). Association of organisms producing acidity with those producing alkalinity in media frequently effects more rapid oxidation of  $S_2O_3''$  than either species alone. Growth of (II) was improved by org. matter, but the rate of its action on  $S_2O_3''$  was not increased. (II) utilises various forms of org. N, whereas (I) uses only  $NH_3$ ,  $NO_2'$ , and  $NO_3'$ . Forms of S other than  $S_2O_3''$  are oxidised very slowly or not at all. A. G. P.

**Production of polythionates from thiosulphate by micro-organisms.** R. L. STARKEY (J. Bact., 1934, 28, 387—400).—Organisms producing dithionates from  $S_2O_3''$  were more active in media containing org. matter. Heterotrophic species alone are concerned. A. G. P.

**Neutralising power of anti-tuberculosis sera with respect to tuberculin.** W. SCHAEFER and C. ZOBOLI (Compt. rend. Soc. Biol., 1934, 117, 404—405).—Anti-tuberculosis sera cannot neutralise tuberculin. H. G. R.

**Chemical composition of virulent, avirulent, and weakened bovine and human tubercle bacilli.** E. REMY (Z. Immunität., 1932, 75, 527—536).—Cultures of BCG and weakened bovine (I) and human (II) strains of tubercle bacillus were compared with a virulent (I) as regards chemical composition (III). The composition of the medium affected (III), particularly in the case of egg medium (IV). (I) always had a higher fat content than (II), the use of (IV) increasing it still further; (II) contained more unsaturated fat than (I). The  $KMnO_4$  val. for (I) was < for (II). From (II) was isolated a glucoprotein containing 10.75% N, which gave on hydrolysis a reduction val. corresponding with 13% of glucose. R. N. C.

**Specific polysaccharide of the anthrax bacillus.** J. TOMCSIK and H. SZONGOTT (Z. Immunität., 1932, 76, 214—233).—A polysaccharide (I) is extracted from both capsulated and capsuleless strains of anthrax bacillus (II) by the following method. The EtOH-pptd. bacilli are boiled with 1% KOH, nucleoproteins pptd. with AcOH, the neutralised solution is filtered through a Seitz filter, and the (I) extracted with EtOH and purified by repeated pptn. with EtOH and  $COMe_2$ . (I) contains 0.8% N, and on hydrolysis gives 60% of glucose. It is a hapten, and gives a precipitin reaction. There is no relation between virulence and hapten activity. No carbohydrates can be extracted from (II) capsules, but only a  $CuSO_4$ -precipitable protein (I) exhibits no "agressin" reaction in anthrax. R. N. C.

**Specificity changes in immune sera after chemical pre-treatment.** F. BREINL and F. HAUROWITZ (Z. Immunität., 1932, 77, 176—186).—

Coupling of agglutinating horse-serum (I) with diazotised atoxyl,  $NH_2Ph$ , or metanilic acid reduces agglutinins (II) and type-specificity (III). Introduction of I into the protein mol. lowers (II) > (III).  $CH_2O$  in suitable concn. destroys selectively secondary (II) and the fine-flocculating primary (II) of dysentery, but (III) is unaltered. Strong alkalis destroy the antibodies and (III) completely. Diphtheria antitoxin and typhus vaccine behave similarly to (I). R. N. C.

**Analysis of pyocyanase.** L. BIRCH-HIRSCHFELD (Z. Hyg., 1934, 116, 304—314).—The bactericidal action of pyocyanase (I) is dependent on its content of high-mol. fatty acids. These occur largely as sol. salts and only to a small extent as free acids. The activity of (I) is a function of its surface tension effects and can be determined by means of its action in increasing the drop no. at appropriate dilution. A. G. P.

**Ionic effects [on micro-organisms], especially anion phenomena.** F. BOAS (Planta, 1934, 22, 445—461).—The selective action of  $SCN'$  on micro-organisms results from its inhibitory effect on the catalase system of the cell. The reverse effect is shown by  $SO_4''$ . In both cases the anions are active in hypo- and in hyper-tonic concns. Purple bacteria are relatively resistant to the action of  $SCN'$  and  $SO_4''$ . A. G. P.

**Silver picrate.** J. C. BIRD and A. BAROL (J. Amer. Pharm. Assoc., 1934, 23, 996—1000).—Ag picrate is readily sol. in certain glycol ethers, and, as an antiseptic, combines the effects of Ag and of picric acid. A. E. O.

**Antiseptic and growth-inhibiting power of benzene and its halogen derivatives.** A. MOREL, A. ROCHAIX, and Y. DUMAS (Compt. rend. Soc. Biol., 1934, 117, 445—447).—The antiseptic power of  $C_6H_6$  is insignificant, but is increased by halogen substitution ( $Cl > Br$  and I) and depends on the no. of halogen atoms present. H. G. R.

**Preparation and germicidal properties of 4-hydroxy-2-methylphenyl alkyl sulphides.**—See this vol., 79.

**Preparation and germicidal properties of some derivatives of 4-n-butylresorcinol.**—See this vol., 79.

**Apparatus for purification of air.** P. HAUDUROY (Compt. rend. Soc. Biol., 1934, 117, 431—433).—An apparatus for the sterilisation of air is described. H. G. R.

**Counting bacteria in suspension by means of a photo-cell.** E. S. AVTONOMOVA and T. A. STESSEL (Biochem. Z., 1934, 274, 220—230; cf. Andreev, A., 1930, 1115).—Suspended micro-organisms (I) are counted with the help of a modification of Andreev's apparatus, using a formula applicable to other than spherical particles. If the shape and dimensions of (I) do not vary beyond certain limits results more accurate than those obtained by other methods are obtained within a few sec. W. McC.

**Melanophoric hormone in colostrum.** S. KONSULOFF (Endokrinol., 1934, 13, 323—324; Chem. Zentr., 1934, i, 3759).—The presence of melanophoric



hormone in colostrum (I) was shown by darkening of the skin of frogs on subcutaneous injection of (I), and of fish placed in H<sub>2</sub>O containing (I). J. S. A.

**Adrenaline oxidation and stabilisation.** A. D. WELCH (Amer. J. Physiol., 1934, 108, 360—372).—At physiological  $p_{\text{H}}$  and temp. glutathione or cysteine protects adrenaline (I) from irreversible oxidation. In autoxidation of (I) the O<sub>2</sub> consumption is 8—9 atoms of O per mol. CO<sub>2</sub> is produced in the later stages.

CH. ABS. (p)

**Relation between blood-pressure, blood-urea-nitrogen, and fluid balance in the adrenalectomised dog.** W. W. SWINGLE, J. J. PEIFFNER, H. M. VARS, and W. M. PARKINS (Amer. J. Physiol., 1934, 108, 428—437).—Blood pressure and blood-urea-N (I) are inversely related during the cycle of insufficiency and recovery after hormone treatment. High (I) is related to dehydration following disturbance of the mechanism for blood dilution with fluid, and salt mobilisation.

CH. ABS. (p)

**Effect of diverting adrenal-vein blood into the portal vein on the blood-sugar of dogs.** L. R. DRAGSTEDT (Amer. J. Physiol., 1934, 108, 42—45).—A persistent increase in blood-sugar is recorded without glycosuria or increased tolerance to insulin.

CH. ABS. (p)

**Influence of adrenaline on the exchange of sugar between blood and muscle.** S. SOSKIN, W. S. PRIEST, and W. J. SCHUTZ (Amer. J. Physiol., 1934, 108, 107—117).—In amygalised dogs, arterio-venous blood-sugar differences have no quant. significance as regards sugar utilisation (I) by the muscles unless measurement is also made of blood flow and H<sub>2</sub>O retention. When allowance is made for these, constantly injected adrenaline does not decrease (I) by the muscles.

NUTR. ABS. (b)

**Action of insulin on the respiratory quotient, oxygen utilisation, carbon dioxide production, and sugar utilisation in the mammalian diabetic heart.** E. W. H. CRUICKSHANK and C. W. STARTUP (J. Physiol., 1934, 81, 153—161).—Insulin administration increases CO<sub>2</sub> production and sugar oxidation, but does not affect O<sub>2</sub> consumption. The glycogen of the heart is not markedly altered.

CH. ABS. (p)

**Effect of crystalline insulin on substances of the residual carbon group.** BÜRGER (Zentr. inn. Med., 1934, 55, 487—490).—An improved method for determining the non-protein-C of the serum is described. Injection of insulin into the mesenteric vein of dogs anaesthetised by somnifen caused a reduction in serum-C which was not accounted for by the fall in blood-sugar, so that the reduction in carbohydrate is not accompanied by the production of lipid substances. Subcutaneous injections of insulin into diabetic patients caused a reduction of C in the serum fraction sol. in light petroleum; the reduction was less marked in patients with the more severe types of diabetes, although none of the subjects had acidosis.

NUTR. ABS. (b)

**Effect of insulin on amino-acid metabolism.** A. LACQUET, P. DE NAYER, and J. P. BOUCKAERT (Arch. internat. Pharmacodyn., 1934, 47, 318—348).—The effects of massive and slow continuous injections

of glycine on the NH<sub>2</sub>-acid (I) content of the blood of depancreatised and normal dogs and rabbits receiving insulin indicate that insulin inhibits N metabolism directly or indirectly, most probably by affecting the catalysis of reactions which take place at a stage more complex than that of (I).

NUTR. ABS. (m)

**Physiological variations in the internal secretion of the pancreas. XIII. Internal pancreatic secretion during experimental hyperamino-acidaemia.** J. LA BARRE (Arch. internat. Physiol., 1934, 38, 37—51).—Intravenous injection of glycine (150—500 mg. per kg.) resulted, in the dog, in hyperglycaemia sometimes followed by hypoglycaemia (I). The latter is more marked when the dose is large. After removal of the adrenals, glycine no longer caused appreciable changes in blood-sugar, although (I) might still occur about 5 hr. after the injection. Cross-circulation experiments showed that the (I) could be attributed largely to an increased output of insulin from the pancreas.

NUTR. ABS. (b)

**Absorption of insulin.** K. THIEL, A. RUHNAU, and A. UNGER (Deut. med. Woch., 1934, 60, 975—978).—The absorption of insulin is considerably delayed if it is injected admixed with gelatin. By this means large doses of insulin could be given without the risk of hypoglycaemic symptoms.

NUTR. ABS. (b)

**Standardisation of parathormone and its antagonistic effect on oxalic acid poisoning.** M. KOCHMANN (Deut. med. Woch., 1934, 60, 406; Chem. Zentr., 1934, ii, 267).—The toxic effect of oxalate can be wholly or partly annulled by introduction of Ca into the blood, and also by injection of parathormone, which increases serum-Ca.

R. N. C.

**Action of thyroxine on carbohydrates and proteins in the liver.** R. STERNHEIMER (Compt. rend. Soc. Biol., 1934, 117, 422—424).—Glycogen (I) disappears from the liver without an increase in free sugar (II) or in the blood-(II) or in basal metabolism. During the lowering of (I) an increase in protein was observed, and this was followed by a second phase in which the phenomena were reversed.

H. G. R.

**Action of thyroxine and thyroïdin on lipin and fat metabolism.** L. PASTERNAK and I. H. PAGE (Biochem. Z., 1934, 274, 122—145).—The following changes are detected in the blood and organs after subcutaneous administration of thyroxine (I) or after feeding thyroïdin (II) to rabbits and rats. In muscle, the phosphatide (III) content was increased in rats after (II) by 96%, in rabbits after (I) by 100%, and in rats after (I) by 70%, the I val. was increased, the total fat and fatty acid content decreased, the dry wt. increased, and after (II) but not after (I) there was a considerable increase of cholesterol (IV). In heart muscle the same changes occur with the exception of the increase in (III). In liver there is a fall of dry wt. The (IV) content increases in rabbits after (I), in rats only after (II), whilst the effect on the (III) content is variable. In brain the changes are small, whilst in blood the chief alteration is in respect to the (III) and (IV) contents. Adminis-



tration of bromiodotyrosine reverses the (III) increase after (II). P. W. C.

**Adenotropic hormones of the pituitary.** C. L. LAUTENSCHLAGER (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 19—38; Chem. Zentr., 1934, i, 3608).—The general term "adenotropic" (I) is used for hormones influencing other internal secretions. The (I) hormones of the pituitary are reviewed. R. N. C.

**Diuretic effect of posterior pituitary extract in the anaesthetised animal.** E. E. NELSON (J. Pharm. Exp. Ther., 1934, 52, 184—195).—With rabbits anaesthetised by morphine-urethane and rendered diuretic by rapid intravenous administration of aq. sucrose or, after phloridzin, of aq. glucose, injection of posterior pituitary extract produces a transient diuresis due to an increased rate of filtration. The increase in relative and abs. [Cl'] of the urine indicates an increased flow through the tubules. F. O. H.

**Changes in blood-lactic acid after injection of posterior pituitary extract.** A. D. MARENZI (Compt. rend. Soc. Biol., 1934, 117, 457—458).—Subcutaneous or intravenous injection raises the blood-lactic acid. H. G. R.

**Effect of anterior pituitary extract on blood-lactic acid.** A. D. MARENZI (Compt. rend. Soc. Biol., 1934, 117, 464—465).—An alkaline extract which produces hyperglycaemia in the dog raises the blood-lactic acid. H. G. R.

**Effect of anterior pituitary extracts on ketone excretion in the rat.** P. T. BLACK, J. B. COLLIP, and D. L. THOMSON (J. Physiol., 1934, 82, 385—391).—Injection of anterior pituitary extracts in rats, either fasting or on a filtered butter diet, increases ketonuria (I). The effect is obtained with growth hormone (II) fractions free from thyrotropic hormone (III), or (II)-free (III) fractions, but not with adrenotropic fractions. (I) occurs also with thyroidectomised animals, and is not produced by thyroxine in normal animals. Prolonged pretreatment of rats with the Anderson-Collip (III) extracts containing the ketogenic principle (IV) renders them insensitive to (IV), due to the formation in the serum of an inhibitory principle which can also be produced in horse-serum. R. N. C.

**Gonadotropic anterior-pituitary hormone (prolan).** F. LAQUER, K. DÖTTL, and H. FRIEDRICH (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 117—122; Chem. Zentr., 1934, i, 3608).—Rats are as suitable as mice for repeated assay of prolan (I). Vals. with 13 different preps. of (I) during a year vary  $\pm$  15—20%. (I) in small doses appears to ripen the follicle, and in larger doses to influence the corpus luteum; there is no definite proof that it contains two active substances. R. N. C.

**Gonadotropic hormone in the pregnant mare (pituitary or placental origin).** C. HAMBURGER (Endokrinol., 1934, 13, 305—311; Chem. Zentr., 1934, i, 3608—3609).—Injection of the serum of pregnant mares (I) has a strong stimulating effect on the testis and comb growth of young cocks; the ovaries of young mice increase in wt.; the increase  $\propto$  the amount

of serum injected, up to a high dose. These changes are not produced at all, or only imperfectly, by the gonadotropic hormone (II) of the urine of pregnancy, and hence must be due to a (II) of pituitary origin in (I). R. N. C.

**Preparation of gonadotropic extracts of urine of pregnancy by tungstic acid precipitation.** P. A. KATZMAN and E. A. DOISY (J. Biol. Chem., 1934, 107, 513—518).—The ppt. (I) formed on addition of Na tungstate to acidified urine is decomposed by brucine in aq. suspension to yield all the active material in aq. solution, from which it is then pptd. by COMe<sub>2</sub>. Theelin and theelol may be recovered from the filtrate from (I). A. E. O.

**Influence of gonads on metabolism. I. Change in metabolism due to castration.** T. INABA (Aichi Igakkai Zasshi, 1930, 40, 119, 423).—Ovariectomy in dogs caused a decrease in total urinary N and S. The subsequent increase in body-wt. is due to decreased general and N metabolism. CH. ABS. (p)

**Absorption and excretion of folliculin in man. II. Excretion in urine and faeces.** H. ENG (Biochem. Z., 1934, 274, 208—211; cf. A., 1934, 1039).—Since the amount of folliculin (I) excreted becomes very low when the diet is free from (I) support is given to the view that, in men, excreted (I) is derived chiefly from the diet. W. McC.

**Development of tolerance by the ovary to the prolonged action of folliculin.** C. J. CALATRONI (Compt. rend. Soc. Biol., 1934, 117, 452—453).—After 30 days' treatment the ovaries are atrophied, but become normal if the treatment is continued for 90 days. H. G. R.

**Specific action of oestrin.** P. G. 'ESPINASSE (Nature, 1934, 134, 738).—A sp. effect of oestrin on the Müllerian duct of the mouse (cf. A., 1934, 1412) is described. L. S. T.

**Synthesis of the corpus luteum hormone.** E. FERNHOLZ (Ber., 1934, 67, [B], 1855).—Stigmasterol is converted into 3-acetoxybisnorcholelic acid and thence into the OH-ketone, C<sub>12</sub>H<sub>32</sub>O<sub>2</sub>. The latter substance is transformed into the dibromide, which is oxidised by KMnO<sub>4</sub> to the diketone, m.p. 129° [dioxime, m.p. 246—248° (decomp.)], probably identical with luteosterone-C. H. W.

**Preparation of homogeneous hormones from the corpus luteum. III. Constitution of luteosterone-C and -D.** K. H. SLOTTA, H. RUSCHIG, and E. BLANKE [with, in part, A. NEUHAUS] (Ber., 1934, 67, [B], 1947—1954; cf. A., 1934, 1268).—Luteosterone-D (I) or its mixture with luteosterone-C (II) absorbs 3H<sub>2</sub>, giving a mixture of several diols also obtained by saturation of the double linking and reduction of CO of the OH-ketone, m.p. 190°, derived from stigmasterol. The mixture from either source is converted by gentle oxidation into the same diketone, m.p. 188° (corr.). The corpus luteum hormones have therefore the tetracyclic ring system of the sterols and the CO and Ac groups are at 3 and 17, respectively. The double linking is in conjugation with CO. The possibility is discussed that (I) is a monohydrate of (II). H. W.



**Corpus luteum hormone.** I, II. K. H. SLOTTA and H. RUSCHIG (Z. physiol. Chem., 1934, 228, 207—223).—Fresh pig's corpora lutea are minced and extracted with EtOH. The extract, after removal of EtOH, is extracted with Et<sub>2</sub>O and treated with COMe<sub>2</sub> to ppt. phosphatides. This yields a "crude oil" (dose, 300 mg. per unit), which is then dissolved in MeOH containing 10—12% of glycerol. The solution is extracted with petroleum (benzine), which removes lipoid substances. The hormone is transferred to 70% aq. EtOH, and the solution is again extracted with benzine. An "intermediate oil" (I) (dose, 40—50 mg.) is thus obtained. (I) is further purified by dissolution in glycerol (impurities insol.) and transferred to C<sub>6</sub>H<sub>6</sub>, followed by adsorption of impurities with Al(OH)<sub>3</sub>, which yields the "pure oil" (dose, 4 mg.). J. H. B.

**Mechanism of the action of the male hormone.** R. FUSSGANGER (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 194—204; Chem. Zentr., 1934, i, 3607).—The method of inunction is recommended for the standardisation of commercial preps. of the hormone. R. N. C.

**Vitamin-A content of various foodstuffs.** K. WALTNER (Z. Vitaminforsch., 1934, 3, 245—247).—The contents of 40 common foodstuffs are tabulated. F. O. H.

**Sterols as a source of vitamin-A.** N. K. BASU (Biochem. Z., 1934, 274, 4—6).—The author claims that from liver-oil, egg-yolk, and fish-oil, sterol fractions (I) can be isolated, m.p. 62—67°, which are precipitable with digitonin (II), give a faint Salkowski and a negative SbCl<sub>3</sub> reaction, but after irradiation for 30 min. ( $\lambda$  275—300 m $\mu$ ) gave products no longer precipitable with (II) and showing an ultra-violet absorption band 328 m $\mu$ , a negative Salkowski and a strongly positive SbCl<sub>3</sub> reaction (absorption bands 620, 572 m $\mu$ ). No details are given of the prep. of (I), but the activity of the irradiated (I) is confirmed by feeding to rats. (I) therefore as well as carotene may act as the precursor of vitamin-A. P. W. C.

**Fluorescence of some substances containing vitamin-A.**—See this vol., 12.

**Difference in the vitamin-A content of cow- and bull-liver.** F. ENDER (Z. Vitaminforsch., 1934, 3, 247—253).—With full-grown cattle, the livers of cows have a vitamin-A (or carotene) content approx. 5 times that of the livers of bulls. Both sexes, however, show individual variations. F. O. H.

**Vitamin-A of serum following administration of halibut-liver oil in normal children and in chronic steatorrhea.** J. CHESNEY and A. B. McCOORD (Proc. Soc. Exp. Biol. Med., 1934, 31, 887—888).—Administration of halibut-liver oil to fasting children, subsequently given low-vitamin diet, increased the vitamin-A of the serum to a max. val. after 4 hr. CH. ABS. (p)

**Local vitamin action with cod-liver oil bandages.** W. VON DRIGALSKI (Z. Vitaminforsch., 1934, 3, 260—268).—Experimental skin-wounds in guinea-pigs heal more satisfactorily with application of an ointment containing cod-liver oil than with that of

a control ointment. The effect is attributed to vitamin-A. F. O. H.

**Unit of vitamin-D.** O. SCHULTZ (Z. Vitaminforsch., 1934, 3, 257—260).—Curative treatment of rats in the assay of vitamin-D must be started after the 12th and before the 21st day of feeding the rachitogenic diet. During this period the healing tendency is not influenced by the no. of days during which the diet has been fed. Sub-curative doses have no effect even with continued administration. F. O. H.

**Absorption of vitamin-D through the skin.** M. E. FODOR (Z. Vitaminforsch., 1934, 3, 241—244).—Rickets in rats can be cured by inunction with irradiated ergosterol (10 times the oral curative dose) in olive oil solution. F. O. H.

**Effect of vitamin-D on the oxygen consumption of growing rats.** E. LANDELIUS and G. LJUNGKVIST (Skand. Arch. Physiol., 1934, 68, 252—270; Chem. Zentr., 1934, ii, 464).—The O<sub>2</sub> consumption (I) of normal growing rats per sq. m. body-surface is reduced about 9% between the 6th and 11th weeks of life, but in vitamin-D deficiency the reduction is 20%. R. N. C.

**Experimental production of hypercalcemia in man by means of irradiated ergosterol.** T. D. SPIES and R. F. HANZAL (Proc. Soc. Exp. Biol. Med., 1934, 31, 747—750).—Administration of large doses of irradiated ergosterol, together with NaH<sub>2</sub>PO<sub>4</sub> and Ca lactate, to four hopelessly diseased young adult patients, during 9—25-day periods preceding death caused a rise in blood-Ca, unaccompanied by tissue calcification. NUTR. ABS. (b)

**Convulsions due to excessive dosage of biosterol.** M. MATSUOKA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1267—1283).—Subcutaneous or intraperitoneal injection of 0.5 c.c. of a 25% solution of biosterol (A., 1925, i, 1365) in olive oil into rats produces clonic convulsions (I) within 20—30 min. Removal of vitamin-A (II) by hydrogenation or oxidation has no effect on the occurrence of (I), whilst the (II) fraction obtained by distillation is inactive. Injection of large doses of camphor, but not of cholesterol, ergosterol, carotene, squalene, etc., produces a similar effect. F. O. H.

**Vitamin-E. II. Stability of concentrates towards oxidising and reducing reagents.** H. S. OLCOTT (J. Biol. Chem., 1934, 107, 471—474).—Vitamin-E (I) is destroyed by O<sub>3</sub>, BzO<sub>2</sub>H, KNH<sub>2</sub>, KOEt, and Cl<sub>2</sub>. Chlorinated and brominated concentrates may be reactivated by boiling with Zn and HCl in MeOH. HBr does not attack (I). Cottonseed oil is as satisfactory as wheat-germ oil for the prep. of active concentrates. (I) concentrates exhibit an absorption band at 2940 Å. not apparently connected with the vitamin activity. C. G. A.

**Vitamin-E.** F. C. GELLER and C. SCHUSTER (Arch. Gynäkol., 1934, 155, 363—380; Chem. Zentr., 1934, ii, 87).—Rats on a diet containing yeast or "vitox" and cod-liver oil, vitamin-A, or "vigantol," undergo degeneration of the testes (I) after 6 months, and loss of fertility (II) earlier. Addition of 8% of butter (III) retards (I) and prevents (II). (I) does



not occur with a diet of barley germ (IV) with vitamin-*A* and -*D*, but it occurs in animals fed with vitamin-*E* adsorbate (V). Female rats produce no young with yeast or "vitox" as the sole vitamin source, or with vitamin-*A* and -*D* in addition, but the oestrous cycle is normal. Addition of (III) has no effect, but with (IV) or wheat-germ oil, young are produced. (V) has no inhibitory effect. The ovaries are normal in all cases except in the animals fed on the diet containing yeast only. R. N. C.

**Possible relation of vitamin-*E* to unrestricted cell division.** F. B. ADAMSTONE (Science, 1934, 80, 450).—Evidence which indicates that vitamin-*E* is intimately associated with, and probably exerts an indirect controlling influence over, the cell nucleus during division has been obtained. L. S. T.

**Association of fat-soluble vitamins and antioxidants in plant tissues.** E. M. BRADWAY and H. A. MATTILL (J. Amer. Chem. Soc., 1934, 56, 2405—2408; cf. A., 1931, 773, 776).—The unsaponifiable matter of the material extracted by hot 90% MeOH from dried (vac. at 100°), canned tomatoes is freed [essentially as previously described (*ibid.*, 1341)] from carotenoid pigments and sterols, and then separated by diphasic distribution between 92% MeOH and light petroleum (I) into vitamin-*E* (II) and antioxidant (III) fractions. Distillation of the (III) (MeOH-sol.) gives a fraction, b.p. 90—115°/0.1—0.2 mm., possessing high (III)-activity. The (III) in carrots [which contain little (II)] is similarly separated. The (III) present in wheat-germ oil is sol. in (I) and could not be separated from (II) by fractional distillation. The various specimens of (III) obtained are probably all different. Lycopene, like carotene, shortens the induction period of autoxidation (of fat) (cf. Franke, A., 1933, 49). H. B.

**Pyruvic acid and the avitaminotic brain.** R. A. PETERS and R. H. S. THOMPSON (J. Physiol., 1934, 81, 22P).—AcCO<sub>2</sub>H occurs in avitaminotic (but not in normal) pigeon brain during respiration in lactate solutions, but disappears on addition of vitamin-*B*.

CH. ABS. (p)

**Biological reduction. VI. Oxidation of sugar by striated and cardiac muscle in *B*-avitaminosis. Effect of adrenal cortex. VII. Oxidation of lactic acid in *B*-avitaminosis.** T. SAKAI (J. Biochem. Japan, 1934, 20, 193—203, 205—209).—VI. With fowls suffering from *B*-avitaminosis (I) induced by a diet of polished rice and H<sub>2</sub>O, the contents of H donator [probably hexose phosphate (A., 1932, 1062)] in leg- and heart-muscle and of dehydrogenase co-enzyme in the hypertrophied adrenal cortex (II) are reduced. Administration of vitamin-*B*<sub>1</sub> (III) produces a rapid return to normal vals., whilst the onset of (I) is delayed by administration of extracts of (II) but not of liver, kidney, or brain. The rôle of (II) and (III) in carbohydrate metabolism is discussed.

VII. Determinations of methylene-blue reduction and of reduction-oxidation potentials indicate that (I) in fowls produces a marked diminution in the content of lactic acid dehydrogenase in the cardiac muscle. F. O. H.

**Sparing action of fat on vitamin-*B*<sub>1</sub>. VI. Influence of the levels of protein and vitamin-*B*<sub>2</sub>. VII. Effectiveness of natural fats in sparing vitamin-*B*<sub>1</sub>.** H. M. EVANS, S. LEPKOVSKY, and E. A. MURPHY (J. Biol. Chem., 1934, 107, 429—437, 439—442).—VI. For fat to exert optimal sparing action on vitamin-*B*<sub>1</sub> both protein and vitamin-*B*<sub>2</sub> must be high. The relationship of the three factors is discussed.

VII. The order of effectiveness of the fats is coconut oil, lard, hydrogenated cottonseed oil, butter-fat, synthetic lard, hydrogenated coconut oil, maize oil, olive oil, hydrogenated sesamé oil (I), sesamé oil. Solid fats are more effective than liquid fats with the exception of (I). C. G. A.

**Sparing action of fat on vitamin-*B*<sub>2</sub>.** H. M. EVANS, S. LEPKOVSKY, and E. A. MURPHY (J. Biol. Chem., 1934, 107, 443—447).—Although variable the results seem not to indicate a beneficial effect of fat on diets low in vitamin-*B*<sub>2</sub>, but otherwise adequate. C. G. A.

**Concentration and chemical nature of vitamin-*B*<sub>2</sub>.** L. E. BOOHER (J. Biol. Chem., 1934, 107, 591—597).—A 200—300-fold concn. of vitamin-*B*<sub>2</sub> (I) from whey is accomplished by adsorption of the 50-fold concentrate (A., 1933, 1213) on Lloyd's reagent followed by extraction with dil. C<sub>5</sub>H<sub>5</sub>N and elimination of H<sub>2</sub>O-insol. material. The orange-red powder so obtained contains 3000—3500 (I) units per g. The H<sub>2</sub>O-sol., yellow, fluorescent pigment of whey is either (I) or an integral part of (I). A. E. O.

**Mode of action of vitamin-*B*<sub>2</sub> and the participation of flavoproteins in enzymic dehydrogenations.** T. WAGNER-JAUREGG, H. RAUEN, and E. F. MÖLLER (Z. physiol. Chem., 1934, 228, 273—276).—Dehydrogenation of *l*-malic acid in presence of frog-muscle extract, the co-enzyme from horse-erythrocytes, and methylene-blue is greatly accelerated by lactoflavin. J. H. B.

**Growth-promoting properties of vitamin-*B*<sub>2</sub> concentrates.** L. E. BOOHER, H. M. BLODGETT, and J. W. PAGE (J. Biol. Chem., 1934, 107, 599—605).—Vitamin-*B*<sub>1</sub> and -*B*<sub>2</sub> together do not constitute the whole of the vitamin-*B* complex and, in order to promote continuous growth in rats, the addition of a supplementary factor (I), occurring in an 80% EtOH extract of whole wheat and probably also in autoclaved yeast, is necessary. (I) is Et<sub>2</sub>O-insol., and is only partly destroyed when autoclaved at 120° for 5 hr. in alkaline solution. A. E. O.

**Ascorbic acid and its determination.** J. P. SPRUYT and W. F. DONATH (Med. Dienst Volksgezond. Ned.-Indië, 1934 No. 2—3, 117—128).—Aq. ascorbic acid (I) is unstable; the stability is greater in 0.25% CCl<sub>3</sub>·CO<sub>2</sub>H, especially when kept under H<sub>2</sub>S. Oxidised (I) in orange juice [content of normal (I)=0.056—0.071%] is reduced by H<sub>2</sub>S. The titration of (I) with 2:6-dichlorophenol-indophenol is independent of p<sub>H</sub> and is not influenced by the presence of 0—20% of CCl<sub>3</sub>·CO<sub>2</sub>H. F. O. H.

**Identification reactions for *l*-ascorbic acid (vitamin-*C*).** R. FISCHER (Pharm. Ztg., 1934, 79, 1207—1208, 1263).—In the presence of ascorbic acid



(I),  $\text{NHPh}\cdot\text{NH}_2$  (II) in 20% EtOH gives dibenzoylhydrazine. (I) after oxidation (by air, methylene-blue, or I solution) gives crystals, m.p. 192—194°, with (II) in aq. solution. Conditions for the use of these reactions for the micro-detection of (I) are described. The tests can be used for vitamin-C in botanical preps. H. G. M.

**Synthesis of ascorbic acid (vitamin-C) by means of tissues *in vitro*.** B. C. GUHA and A. R. GHOSH (Nature, 1934, 134, 739).—The production of ascorbic acid (I) by means of the liver, kidney, and spleen tissues of the rat from glucose, fructose, galactose, mannose (II), arabinose, and xylose at 37° in phosphate buffer (III) ( $p_H$  7.4) or in a mixture of (III) and Ringer-Locke solution has been investigated. Only (II) is converted into (I) by all these tissues; significant amounts of (I) are formed. L. S. T.

**Vitamin-C and plasma-proteins.** A. BÖGER and H. SCHRÖDER (Klin. Woch., 1934, 13, 842—843).—In mild hæmophilia prolonged treatment with "Nateina" (I), a prep. of plant origin containing vitamin-A, -B, -C, and -D with added  $\text{Ca}_3(\text{PO}_4)_2$  and lactose, causes a decrease in the coagulation time of the blood to below normal, accompanied by increase in plasma-protein (II) (chiefly albumin). Daily intravenous injections of 100 mg. of ascorbic acid cause a rise in (II) after 3—4 days' treatment, in selected cases of *peliosis rheumatica*, pseudohæmophilia, and simple jaundice. In severe focal nephritis with hæmaturia (I) (8 tablets daily) stops the bleeding and causes (II) to rise in 14 days from 2.9 to 5.1 g. per 100 c.c. The styptic effect of vitamin-C is due to its power of raising the plasma-albumin.

NUTR. ABS. (m)

**Urinary excretion of vitamin-C.** A. F. HESS and H. R. BENJAMIN (Proc. Soc. Exp. Biol. Med., 1934, 31, 866—868).—Under normal conditions vitamin-C (I) is not excreted in appreciable amounts in human urine and occurs only in small amounts in that of guinea-pigs, rabbits, and rats. Children receiving large amounts of (I) excrete only the surplus after complete saturation of body tissues.

CH. ABS. (p)

**Parallelism between vitamin-C and chlorophyll.** A. GIROUD, R. RATSIMAMANGA, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1934, 117, 612—614).—The ascorbic acid (I) contents of plant leaves and tissues vary with their chlorophyll (II) contents. (I) is absent from plants grown in darkness, and diminishes in leaves in the autumn as (II) disappears. R. N. C.

**Significance of the reduction of silver salts at the surface of chloroplasts.** A. GIROUD, C. P. LEBLOND, and R. RATSIMAMANGA (Compt. rend. Soc. Biol., 1934, 117, 614—615).—Chloroplasts (I) reduce a  $\text{AgNO}_3$  solution at  $p_H$  4 in a similar manner to that of animal tissues containing ascorbic acid, indicating that it is contained in (I). R. N. C.

**Sunlight and the action of vitamins.** N. K. BASU (Z. Vitaminforsch., 1934, 3, 254—256).—With rats and guinea-pigs, sunlight enhances the efficacy of vitamin-C and the conversion of carotene into vitamin-A. F. O. H.

**Pea test method for auxin, the plant growth-hormone.** F. W. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 547—555).—Pea shoots split medially constitute suitable test objects for the detection and determination of auxin (I); the rate of curvature of the split portions approx.  $\propto$  the logarithm of the (I) concn. The method is simple and sp. and less sensitive to the effect of light and temp. variations than is the *Avena* coleoptile reaction. W. O. K.

**Effect of ionised air on respiration of green plants.** G. B. PORTSMOUTH (Ann. Bot., 1934, 48, 1013—1027).—In ionised air respiration of barley seedlings increased by approx. 2%. A. G. P.

**Characteristics of green plants which develop in air enriched with carbon dioxide.** M. MOLLARD and A. CRÉPIN (Compt. rend., 1934, 199, 1077—1080).—As the proportion of  $\text{CO}_2$  increases in the ratio 1, 5, 25, 100, and 50 the yield of dry substance increases as 1, 2.4, 4.7, 6.5, and 8.8. Sucrose and  $\text{CO}_2$  are simultaneously utilised, but the former diminishes the effect of the latter, the ratio being 1, 1.8, 2.6, 3.6, and 3.2. The  $\text{H}_2\text{O}$  content of plants diminishes gradually with increasing  $\text{CO}_2$  content of the atm. H. W.

**Physiology of apples. XV. Relation of carbon dioxide output to loss of sugar and acid in Bramley's Seedling apples during storage.** H. K. ARCHBOLD and A. M. BARTER (Ann. Bot., 1934, 48, 957—966).—Sugar concn. in apples is higher on the "blushed" than on the "unblushed" side, and increases from stalk to calyx and from inside to outside. The decline in sugars and acids of stored apples was > could be accounted for by  $\text{CO}_2$  production. A. G. P.

**Development of sugar-beet in the first year of growth.** A. I. SMIRNOV (Trans. Centr. Sci. Res. Inst. Sugar Ind. U.S.S.R., 1932, No. 8, 120—125).—The dry matter content of immature leaves varies irregularly, but that of mature leaves increases steadily. The  $\text{H}_2\text{O}$ -absorbing capacity of young leaves is > that of mature ones. Osmotic pressure,  $d$ , and viscosity of juice from leaves and roots increase with growth to a max. (in roots) at the ripe stage. Leaves have low starch but high sol. carbohydrate contents. Monosaccharides decrease and disaccharides (I) increase with leaf-growth. Of (I) only sucrose occurs in roots. CH. ABS. (p)

**Nutritional physiology of sugar-cane.** T. H. VAN DER HONERT (Arch. Suikerind. Nederl.-Ind., 1932, No. 23, 1539—1608; Bied. Zentr., 1934, A, 4, 485—486).—The effects of variation in concn. of the nutrient media and of deficiency of essential nutrients on the growth of sugar-cane are examined in sand and  $\text{H}_2\text{O}$  cultures. A. G. P.

**Nutrient intake of plants (maize and mustard) from undisturbed and from flowing nutrients.** E. UNGERER (Z. Pflanz. Düng., 1934, A, 36, 15—26).—Plants grown in dil. flowing media produced less dry matter, and absorbed more Ca and P but less K and N, than those in conc. but stationary media. A. G. P.

**Influence of temperature during germination on the subsequent development of certain winter**



cereals and its relation to the effect of length of day. O. N. PURVIS (Ann. Bot., 1934, 48, 919—955).—Reduction of the N supply checked vegetative growth but did not affect flowering (I) at any day-length examined. (I) was not affected by limitation of K supply after germination at 1°, but was retarded after germination at 18°. Variation in N and sugar contents of leaves is an effect rather than a contributory cause of flower formation. A. G. P.

Germination of cereal seed in media of different hydrogen-ion concentration and the resultant changes in reaction. F. AICHELE (Diss., Tübingen, 1931; Bied. Zentr., 1934, A, 4, 513).—The influence of the reaction of the medium on germination depends not only on [H<sup>+</sup>], but also on the degree of dissociation of other ions involved. In very acid solutions PO<sub>4</sub><sup>'''</sup> is more injurious to germination than other anions in media of the same p<sub>H</sub>. In all cases germinating seeds tend to change the reaction of the medium towards neutrality. A. G. P.

Influence of plants on the concentration of hydrogen ions in the medium. A. KOSLOWSKA (J. Ecol., 1934, 22, 396—419).—Plant species of sp. associations occurring in soils having a relatively narrow range of p<sub>H</sub> are able to change the p<sub>H</sub> of more alkaline or more acid media towards a mean val. Curves showing the p<sub>H</sub> changes by any individual species are of similar character irrespective of the reaction of the soil from which the plants were taken. Species having a wide range of occurrence and not attached to sp. associations produce curves intermediate in type between those of definitely "alkalising" and those of "acidifying" species. Seeds of individual species taken from soils of widely different p<sub>H</sub> produce, in garden soils of given p<sub>H</sub>, the same curve. Saps from strongly alkalising plants have high buffer power, especially in the acid range. Those of plants widely distributed are but weakly buffered. A. G. P.

Influence of sodium chloride content in the nutrient medium on the development of *Salicornia herbacea* and on the composition of the cell salts of these plants. M. VAN ELJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 556—561).—As [NaCl] in the nutrient medium increased from 0 to 3%, the concn. in the cells of both Na and Cl<sup>-</sup> increased, but Na/Cl, which was < 1 with 0% NaCl, became > 1 with the higher concns. of NaCl. The [Ca] in the cells decreased with increasing [NaCl], although [Ca] of the medium remained const. W. O. K.

Relation between the hydrogen-ion concentration of soil and plant distribution. H. E. G. EMMETT and E. ASHBY (Ann. Bot., 1934, 46, 869—876).—In soils having p<sub>H</sub> 4.7—6.2, the occurrence of *Pteridium aquilinum* and *Vaccinium myrtillus* is unrelated to p<sub>H</sub>. A. G. P.

Introduction of heavy hydrogen into the growing organism. O. REITZ and K. F. BONHOEFFER (Naturwiss., 1934, 22, 744).—Algae (*Chlamydomonas*) could assimilate H<sup>2</sup> from H<sub>2</sub>O containing H<sub>2</sub><sup>18</sup>O, although the rate of assimilation was about one fifth of that of H<sub>2</sub>. The H<sup>2</sup> after assimilation were directly

linked to C, and could not be exchanged for H<sup>1</sup> by continued washing with H<sub>2</sub>O. A. J. M.

Ecological and physiological action of ammonium salts on the clover content of turf. G. E. BLACKMAN (Ann. Bot., 1934, 48, 975—1001).—Reduction in the proportion of clover (I) in frequently cut turf following treatment with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is attributed to the toxicity of NH<sub>4</sub><sup>+</sup>. Simultaneous treatment with sucrose delayed the disappearance of (I). Differences between the amount of N applied as NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> and that recovered in grass are > the residual NH<sub>4</sub><sup>+</sup>- or NO<sub>3</sub><sup>-</sup>-N of soil. Utilisation by bacteria is indicated. A. G. P.

Bursting of cells by polarised sunlight. E. S. SEMMENS (Nature, 1934, 134, 813).—When a hyacinth leaf is exposed to polarised direct sunlight the rapidly-increased turgor due to hydrolysis ruptures the cell wall and the guard-cells burst. Starch disappears. L. S. T.

Effect of elliptically-polarised light on the formation of carbohydrates in leaves. R. H. DASTUR and L. K. GUNJIKAR (Ann. Bot., 1934, 48, 1003—1012).—Carbohydrate in leaves exposed to elliptically polarised light was < that in leaves in non-polarised light. A. G. P.

Avitaminosis in plants and its elimination by vitamin additions. H. BURGEFF (Ber. Deut. bot. Ges., 1934, 52, 384—390).—The transmission of vitamin between host and symbiont is examined. A. G. P.

Evolutionary status of plant families in relation to some chemical properties. J. B. MCNAIR (Amer. J. Bot., 1934, 21, 427—452; cf. A., 1932, 99, 663).—Relationships between the distribution and nature of the alkaloids, fats, and volatile acids in plant families, their habitat, and stage of botanical evolution are examined. A. G. P.

Chemical investigation of Indian medicinal plants. IV. *Teramus labialis*. S. N. CHAKRAVARTI and K. GANAPATI (J. Annamalai Univ., 1934, 3, 216—222).—From the light petroleum (b.p. 30—50°) extract (0.88%) of dry powdered *T. labialis* are isolated a substance, C<sub>27</sub>H<sub>46</sub>O<sub>2</sub> (I), m.p. 83—84°, and a cryst. substance, C<sub>27</sub>H<sub>40</sub>O<sub>2</sub> (II), m.p. 129° (reduces Fehling's solution after hydrolysis); the Et<sub>2</sub>O extract (0.79%) contains (I) and acidic material; the CHCl<sub>3</sub> extract (0.49%) contains an acid and a substance, m.p. 92—93°, and the EtOH extract (2.39%) affords a substance, m.p. 123°, a crude acid, m.p. 169—175°, and (?) a Ca salt; the extract (4.61%) with 70% aq. EtOH also contains protein, carbohydrate, K and Ca salts. An attempt to isolate the glucoside by extraction with CaCO<sub>3</sub>-boiling 70% or 95% EtOH afforded a cryst. substance, m.p. > 300°, a substance, m.p. 83°, and a mixture, m.p. 85—101°, the presence of glucose being indicated by the formation of an osazone, m.p. 209°. (I) with warm HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> gives a (?) NO<sub>2</sub>-derivative, m.p. 102°, and with boiling Ac<sub>2</sub>O-1 drop H<sub>2</sub>SO<sub>4</sub>, a crude product, m.p. 167°. With material collected at a different period of the year (II) could not be detected, but a substance, m.p. 143° (C 82.55; H 17.6%), was obtained, other variations also being observed. J. W. B.



[Constituents of] *Canchalagua Panamena*. R. A. BENEDETTI (J. Amer. Pharm. Assoc., 1934, 23, 1012—1013).—Extraction of the dried plant (therapeutically important as a febrifuge) by  $\text{Et}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{H}_2\text{O}$  yields a bitter glucoside, free acids, sugar, wax, gum, tannin, and green pigment. Alkaloids are absent.

A. E. O.

**Chemical constituents of Irish lichens.**  
*Buellia canescens*. I. T. J. NOLAN (Sci. Proc. Roy. Dublin Soc., 1934, 21, 67—72).—The dried lichen (300 g.) gave 9.0 g. of  $\text{Et}_2\text{O}$  extract. The portion insol. in light petroleum after washing with  $\text{Et}_2\text{O}$  and crystallisation from  $\text{C}_6\text{H}_6$  and  $\text{EtOH}$  gave a yellow cryst. product, m.p. 205—206°, and *diploicin* (colourless needles from  $\text{C}_6\text{H}_6$ ),  $\text{C}_{16}\text{H}_{10}\text{O}_5\text{Cl}_4$  (?), m.p. 232° (*Ac* derivative, m.p. 234—235°). A compound, m.p. >250°, was obtained by further  $\text{EtOH}$  extraction of the  $\text{Et}_2\text{O}$ -extracted residue.

P. G. M.

**Chemical composition of maize kernels.** N. V. VOITCHISHIN (Trans. Centr. Sci. Res. Inst. Sugar Ind. U.S.S.R., 1932, No. 9, 26—33).—Vals. for protein, starch, and fats in grain with and without embryo are recorded for 3 successive year's crops. CH. ABS. (p)

**Chemical examination of the liana "Efiri."**  
I. Localisation in the plant of a substance showing reactions of alkaloids. II. Presence of *cyclohexanepentaol* in "Efiri" stems. E. CASTAGNE (Congo, 1934, 41—48, 341—347; Chem. Zentr., 1934, ii, 76).—I. Stems and leaves of this antipyretic plant contain materials giving alkaloid reaction with I in KI.

II. *d*-Quercitol was obtained by extraction of leaves with boiling 95%  $\text{EtOH}$ .

A. G. P.

**Variations in the alkaloid content of lupins.**  
N. IVANOV and M. LAVROVA (Trudy prikl. Bot., 1931, 25, 291—303; Bied. Zentr., 1934, A, 4, 488).—The N content of blue lupins ranged between 3.9 and 6.1%, and of yellow lupins, 5.3—7.2%. The alkaloid (I) contents showed parallel variations. Plants from northern areas contained less N and (I). The latter is probably a by-product of increased N nutrition.

A. G. P.

**Alkaloids accompanying nicotine and methods for determining them.** A. SCHMUCK (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 63—66).—Various methods for determining nicotine indicate the presence of other alkaloids in *N. americana*.

CH. ABS. (p)

**Decomposition of nicotine in the tobacco plant.** G. S. ILJIN (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1933, No. 104, 141—145).—Treatment of etiolated leaves and seedlings with  $\text{PhMe}$  vapour caused decomp. of nicotine which was taken up by the metabolic activities of the plant.

CH. ABS. (p)

**Conductivity determinations of nicotine and ammonia in tobacco.** A. N. KHARIN (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 31—45).—The conductivity method of titrating nicotine and  $\text{NH}_3$  in aq. distillates from tobacco is rapid, but results may be 10% > those of the pptn. method.

CH. ABS. (p)

**Determination of nicotine in tobacco by measuring surface tension.** G. A. KORZHENIOV-

SKI (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 47—61).—Tobacco distillates are examined by the capillary manometric titration method. Results were > those of the gravimetric method.

CH. ABS. (p)

**Fractionation of resins of tobacco and makhorka.** A. SCHMUCK and V. SHIROKAYA (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 77—87).—The residue from citric acid extraction of makhorka resin contains melanin 11.5, hydrocarbons 9.1, varnish-like substances 10.5,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -tabacenic acids 1.2, 9.0, 5.9, phenols 3.3, complex  $\text{Et}_2\text{O}$  fraction 39.2%.

CH. ABS. (p)

**Determination of citric acid in tobacco.** M. P. PIATNITZKI (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 67—70).—In the pentabromoacetone (I) method the formula used should be, wt. citric acid =  $0.424 \times \text{wt. of (I)} + 7$ .

CH. ABS. (p)

**Determination of citric and malic acids in tobacco and makhorka.** A. SCHMUCK (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 71—75).—Piatnitzki's method is modified by use of  $\text{HCl}$  for  $\text{H}_2\text{SO}_4$  and of  $\text{CO}_2$  for  $\text{Et}_2\text{O}$ . The solution containing citric (I) and malic (II) acids is divided. Total acidity is determined in one portion and (I) in the second. (II) is calc. by difference.

CH. ABS. (p)

**Carbohydrates of tobacco.** A. SCHMUCK (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 3—14).—In dry and fermented tobaccos fructose is the primary sugar. Amounts of glucose, mannose, galactose, and other sugars present are negligible.

CH. ABS. (p)

**Carbohydrates and carbohydrate metabolism in leaves.** III. Determination of glucose and fructose in mixed solutions; application to extracts of plant organs. H. SCHROEDER and F. HERMANN (Planta, 1934, 22, 468—489).—A no. of analytical methods are compared. The distribution of hexoses and sucrose in *Tropaeolum majus* is examined.

A. G. P.

**Intracellular processes during formation of mucilage in the seeds of *Linum usitatissimum*, L., and in the roots of *Althaea officinalis*, L.** R. JARETZKY and H. ULBRICH (Arch. Pharm., 1934, 272, 796—811).—By examination of stained sections mucilage is shown to be formed at the expense of starch in the materials named in the title, but an intermediate, "pre-mucilage" stage intervenes. The nuclei, however, also play some part in the process, possibly by providing activating substances.

R. S. C.

**Crystalline erythrodextrin.** L. KÖHLER-HOLLANDER (Z. physiol. Chem., 1934, 228, 249—255).—Hydrolysis of amyloamylose by salivary amylase to a "maltose val." of 16% yields a cryst. *erythrodextrin*, chars at 220—250°,  $[\alpha]_D^{25} +170^\circ$  in  $\text{H}_2\text{O}$ , giving a reddish-violet I colour and comprising 18 glucose units (from reduction val.). Other non-cryst. fractions contain 24 and probably 12 glucose units, respectively.

J. H. B.

**Starch of the *Floridaea*.** H. COLIN (Compt. rend., 1934, 199, 968—970).—Starch grains (I) of



*Lithothamnion calcareum* are birefringent and give a brownish-red colour with I, but not after treatment with pancreatic enzyme at 40° during some min. (I) closely resembles glycogen. J. L. D.

**Rubber resins.** A. J. ULTÉE (Rec. trav. chim., 1934, 53, 953—960).—In addition to substances already isolated, the latex of *Plumiera acutifolia*, Poir, contains ceretyl- and acetyl-lupeol,  $\beta$ -amyirin, and lupeol (I); of *Ficus Benjaminia*, Linn.,  $\alpha$ -acetyl-amyirin (II); of *F. glomerata*, Roxb., principally (II), some  $\beta$ -acetyl-amyirin (III) and (I); of *F. superba*, Miq., an alcoholate of cinnamic acid; and of *F. toxicaria*, Linn., and *F. fulva*, Reinw., compounds of stearic acid and (III). F. R. S.

**Occurrence of furan derivatives in volatile oils.** B. S. RAO and K. S. SUBRAMANIAN (Proc. Indian Acad. Sci., 1934, 1, A, 189—200).—Oil from leaves of *Clausena willdenovii* consists principally of 3 furan derivatives,  $\alpha$ -clausenan (I)  $C_{10}H_{12}O$ , di- $\alpha$ -clausenan  $C_{20}H_{24}O_2$ , and  $\beta$ -clausenan  $C_{10}H_{14}O$ . Reactions and properties are described. (I) is determined as the ferro- or ferri-cyanic additive compound. A. G. P.

**Acids of croton oil.**—See this vol., 64.

**Fat of *Cortinellus Shiitake*, P. Henn.** M. SUMI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1257—1264).— $Et_2O$ -extraction of the dried material yielded 1.6% of fat [30% unsaponifiable, the saponifiable fraction yielding palmitic (16%), cerotic (2%), linoleic (64%), and oleic acid (8%)]. Small amounts of fungi-, neo-, and ergo-sterol, and ceryl alcohol (?), but not of stearic or linolic acid, were isolated. F. O. H.

**Fat in barley and its malting products.** G. GAMPERL (Diss., Munich, 1931; Bied. Zentr., 1934, A, 4, 485).—From the fat of barley, malt, and spent grains are isolated sitosterol, palmitic acid, trilinolein, and a monoaminomonophosphatide. A. G. P.

**Identity of globulins from the seeds of some *Cucurbitaceae*.** H. LEONTJEV (Biochem. Z., 1934, 274, 163—166).—The similarity in vals. for viscosity, refraction, surface tension, tyrosine and tryptophan contents, and of the racemisation curves of globulin (I) solutions prepared from water-melons, melons, and gourds indicates that the (I) of the various types of *Cucurbitaceae* are probably identical. P. W. C.

**Glutamine in the tomato plant.** H. B. VICKERY, G. W. PUCHER, and H. E. CLARK (Science, 1934, 80, 459—461).—Glutamine (I) is formed in considerable amount in tomato plants grown in media which provide  $NH_3$  as the sole source of N. (I) accumulates in the stems and more is formed in  $NH_3$  than in  $NO_3$  cultures. L. S. T.

**Solubility of phosphorus compounds of wheat flour and the ability of phytin to combine with protein substances therein.** H. WIĄZOWNICKA (Bull. Acad. Polonaise, 1933, B, 107—122).—The distribution of inorg., phytin-, nuclein-, and lecithin-P and of sol. N in flour is examined by extraction with NaOH and HCl of varying concn. The isoelectric point of extracted gliadin (I) was  $p_H$  6.2—6.4. The

phytin prep. corresponded with a  $Ca_2$  inositoltetraphosphate. Phytin and (I) form insol. compounds. A. G. P.

**Hydrolysis of phytin compounds from seeds of hemp, beans, flax, horse chestnut, and wheat and from rye embryos.** W. JAROSZ (Bull. Acad. Polonaise, 1933, B, 123—133).—Effects of acid and of heating on seed extracts are examined in relation to determinations of org. and inorg. P (I) by the molybdate method. The (I) in aq. extracts is  $>$  that of 0.1%  $HNO_3$  extracts, and increases steadily on boiling (to 70—80% of total P in 64 hr.). Heating at 60° for 5 hr. produces little change. Decomp. of org. P on boiling with  $<$  0.1%  $HNO_3$  was more rapid than with higher concns. In alkaline solutions decomp. was much less rapid than in equiv. acid solutions. A. G. P.

**Radiotropism in plants as shown by seedlings of *Pharbitis hispida*.** V. KILIAN (Planta, 1934, 22, 462—467).—Unilateral exposure to radioactive emanation results initially in a positive and later in a negative curvature of the seedlings. A. G. P.

**Photometric determination of nitrogen.** R. A. CLEGHORN and L. JENDRASSIK (Biochem. Z., 1934, 274, 189—193).—N in org. matter (e.g., urine) is determined by conversion into  $NH_3$  by heating with  $H_2SO_4$  and  $H_2O_2$  as in the Kjeldahl method (complete removal of  $CO_2$  essential) and treatment with Nessler solution containing 8 g. of KI per 100 c.c. The colour is measured with the step photometer. W. McC.

**Determination, with the glass electrode, of the hydrogen-ion concentration of biological fluids.** G. HAUGAARD (Biochem. Z., 1934, 274, 231—252).—If made of suitable glass the electrode (I) gives satisfactory results (II) in determining the  $[H^+]$  of biological fluids. (II) differ by only 0.02—0.03  $p_H$  unit from those obtained with the  $H_2$  electrode (III). (I) may be used in cases where it is difficult or impossible to use (III). W. McC.

**Electrometric determination of chlorides in the ash and sap of plants and in ground waters.**—See this vol., 52.

**Photometric determination of calcium and oxalic acid.**—See this vol., 54.

**Modification of Macallum's method for histochemical detection of potassium.** V. D. MARZA and L. CHIUSA (Compt. rend. Soc. Biol., 1934, 117, 524—526).—After pptn. with  $Na_3Co(NO_2)_6$  the sections are washed with 50% EtOH, treated with  $(NH_4)_2SO_4$ , and mounted in Canada balsam. H. G. R.

**Determination of potassium in body-fluids.** L. JENDRASSIK and F. TAKÁCS (Biochem. Z., 1934, 274, 194—199; cf. A., 1933, 687; 1934, 269).—Improvements in previously described procedure enable the K content of body-fluids to be determined without destruction of org. matter. The ppt. is separated by filtration or by centrifuging and the subsequent determination is volumetric, colorimetric, or photometric (step photometer). W. McC.

**Determination of amino-acids and polypeptides.**—See this vol., 102.

