

抄 録

ABSTRACTS OF THE PHYSICO-CHEMICAL
LITERATURE IN JAPAN

Vol. XVII

March, 1943

No. 2

1—GENERAL

(STRUCTURE—PROPERTIES—REACTIONS)

Characters of the products and their derivatives in the reaction of the system ammonia-sulphur trioxide. I. The crystallographic and optic characters, of ammonium imidosulphonate and ammonium amidosulphonate. S. Utida. *J. Chem. Soc. Japan*, **63**, 504-509 (1942).—Non-aqueous reaction of the system ammonia and sulphur trioxide was studied with the aim to obtain sulphamic acid as a new industrial chemical. The observed crystallographic and optical data are tabulated. *Ammonium imidosulphonate* Crystal system: monoclinic, according to Münzinger. Refractive indices: $\alpha=1.521$, $\beta=1.532$, $\gamma=1.550$ for D light. Optical axial angle: $2V=70^\circ$. Dispersion: very weak. Optical character: positive. Optical orientation: optic axial plane is perpendicular to 010, $b=X$, $cAZ=50^\circ$ (in obtuse angle β). *Ammonium amidosulphonate* Crystal system: ortho-rhombic holohedral class. Lattice const.: $a=7.45\text{\AA}$, $b=14.14\text{\AA}$, $c=7.74\text{\AA}$. Axial ratio: $a:b:c=0.527:1:0.547$. Space group: $V_h^{15} (D_{2h}^{15}) - P_{hca}$. Crystal habit: plates from water soln. Refractive indices: $\alpha=1.528$, $\beta=1.536$, $\gamma=1.543$ for D light. Optical axial angle: $2V=86^\circ$. Dispersion: $\rho > \nu$. Optical character: neg. Optical orientation: optic axial plane is 001, $a=Z$.

Author.

Chemical investigations of deep-sea deposits. VIII. Radium content

of deep-sea deposits. III. H. Hamaguti. *J. Chem. Soc. Japan*, **62**, 9, 836-842 (1941).—The present writer who had already reported on radium content of twenty six deep-sea deposits has now extended his study on thirteen new samples. The results fully agree with the previous ones to the effect that the radium content of shallow-water deposits and deep-sea deposits near the land is not very different from that of continental rocks, but it tends to get considerably higher in the deep-sea deposits farther away from land and less disturbed by the oceanic currents. The chemical analysis shows that radium content and manganese-and-iron content are proportional to each other. About the mech. of radium concn. in deep-sea deposits, several factors are suggested, the most important of which is considered to be the fact that the radium dissolved in the sea water is pptd. by adsorption by colloidal manganese-iron oxides. Author.

Studies on the molecular structure of the high polymers. I. The molecular structure of styrene-methyl methacrylate copolymer as revealed by its dipole moment data. A. Kotera. *J. Chem. Soc. Japan*, **63**, 4, 364-367 (1942).—The electric polarisation of the mixed polymerisation product of styrene-methyl methacrylate is measured in benzene soln. at 20°C . The total specific polarisation p_2 of the product

may be expressed by the following eq. $p_2 = w_{St}p_{St} + w_{Me}p'_{Me}$, where w denotes the wt. fraction of each component in the product, and p_{St} the total specific polarisation of polystyrene in benzene. The mean value of p'_{Me} for the two samples ($w_{Me} = 0.17$ & 0.34) is 0.827 c.c. and P'_{Me} 82.7 c.c., which represents the total molecular polarisation of "one" methyl methacrylate radical in the mixed polarisation product. Since this P'_{Me} value does not coincide with the P_{Me} value of simple polymer of methyl methacrylate, which has been already found to be about 60 c.c. (20°C), the possibility that the present product may be a mixt. of two individual simple polymers, may be excluded. If the product is a "real" copolymer as generally accepted, then the polar methyl methacrylate radicals are separated by non-polar styrene radicals, and the orientation polarisation P_0 of one polar component in the chain molecules will approach that value in the free state, just as in the case of the molecules of $X(\text{CH}_2)_nX$ type. As the sum of the electronic and atomic polarisation of the methyl methacrylate radicals is about 24.7 c.c., then its P_0 is 58.0 c.c., and its dipole moment becomes 1.65 D for two samples, which falls into the range 1.65 – 1.70 D, the estimated moment of tert. fatty acid esters. Therefore it may be said that this copolymer of styrene-methyl methacrylate is a "real" copolymer, in which the two components are distributed fairly at random in one chain molecule.

Author.

Molecular structure and the dielectric constants of gases. III. Dipole moments of fluorobenzene, *o*-difluorobenzene, chlorobenzene, and *o*-dichlorobenzene. I. Watanabe. *Bull. Inst. Phys. Chem. Research*, 21, 5, 468–475 (1942).—The dielectric consts. of fluorobenzene, *o*-difluorobenzene, chlorobenzene, and *o*-dichlorobenzene were measured in the gaseous state. The dipole moments calcd. from these exptl. data are 1.56 D, 2.62 D, 1.73 D, and 2.53 D, resp. From these results, the solvent

effect and the ortho effect are discussed. The moments of monohalogenobenzenes are considered in relation to the double bond character of carbon-halogen bonds.

Author.

The vapour pressure of quartz glass. H. Inuzuka and M. Ueba. *J. J. Ceramic Assoc.*, 50, 105–106 (1942).—When one works with quartz glass, a white powder, seemingly a coagulated quartz vapour, is found deposited a little apart from the white heat part. In connection with this phenomenon, the author heated the Mo or W wire coated with quartz glass and measured the vaporized volume for a unit time, and the vapour press. of quartz glass (P atm. press.) by the Langmuir method. In the case of Mo wire, P is found to be 1.3×10^{-8} ($1,000^\circ$) and 1.1×10^{-7} ($1,200^\circ$); with W wire, it is 5.6×10^{-8} ($1,100^\circ$) and 2.6×10^{-7} ($1,300^\circ$).

J. C. L.

Heat diffusion of a solution. I. Heat diffusion coefficients of several inorganic solutions. K. Hirota. *Bull. C. S. J.*, 16, 475–484 (1941).—The author found that in Clausius-Dickel's heat diffusion app. which is satisfactorily applicable to the detn. of heat diffusion coeffs. of liquid solns. the distance between the walls must be relatively long. Therefore, using a modified app., the separation of aq. solns. of HCl, H_2SO_4 , NaCl, KCl, NH_4Cl , Na_2CO_3 , Na_2SO_4 , CuSO_4 and NaOH was observed. The results obtained agree well with Debye's theory, and they give Soret's consts. as correct as the values hitherto observed. The nature of thermal diffusion is also discussed on the basis of these coeffs.

J. C. L.

On the viscosity of ethers, ketones and esters. O. Kimura. *J. Chem. Soc. Japan*, 63, 423–433 (1942).—The viscosity formula: $\eta = ae^{\theta}$ ($\theta = T_b/T$, T_b = absolute boiling point, T = absolute temp.), which was derived by the author, was applied to aliphatic

ethers, ketones, and esters. The consts. a and b are independent of substances in a homologous series, as was found on paraffinic hydrocarbons. Moreover, the value of b for these homologous series is almost const.

Author.

Note on the partial separation of iso-octane from hydrocarbon mixtures by azeotropic distillation. R. Negishi and C. Isobe, *J. Chem. Soc. Japan*, **63**, 396—398 (1942).—By use of the principle of azeotropic distillation, iso-octane (99.23°C) has been partially separated from its binary solns. with n -heptane (98.41°C) and commercial gasoline (98.3—100.3°C). While by ordinary distillation 75 vol. % of iso-octane in n -heptane has been separated into two extreme fractions, 18.8 vol. % and 23.2 vol. % of the total distillate, contg. 69.97 and 79.64 vol. % iso-octane, resp., by single azeotropic distillation, in the presence of n -propyl alcohol (97–98°C), the same mixt. has been separated into 19.1 vol. % of the total distillate, contg. 65.64 vol. % and 21.9 %, each cont. 92–56 % of iso-octane. In the gasoline iso-octane mixt., contg. originally 47.5 vol. % of the latter, iso-octane has been enriched to 72.07. In these calcns. the additivity of refractive indices has been assumed. The azeotropic mixt. of iso octane and normal propyl alcohol has been found to boil at 84.2°C at 749 mm.Hg, contg. approximately 31 vol. % of alcohol at 25°C; and that of n heptane and n -propyl alcohol, 83.7°C at 752 mm.Hg, contg. approximately 31.5 vol. % of alcohol.

Author.

The theory of the transition in solid ammonium halogenides at low temperatures. I. Ammonium chloride. T. Nagamiya. *Proc. Phys.-Math. Soc. Japan*, **24**, 137–164 (1942).—The λ -transition in NH_4Cl at -30°C is interpreted as the order-disorder transition concerning the orientation of the ammonium radicals. It is assumed, in the first place, that the ammonium radical

can take one of the two possible orientations in the crystal of NH_4Cl (the NH -arms are orientated to chlorine atoms), and a theory analogous to the Weiss theory of ferromagnetism is set up. The transition temp., its press. dependence, the volume change at the transition and the specific heat anomaly are computed on the basis of this theory and of the electrostatic interaction between two ammonium radicals, which are near neighbours (not necessarily the nearest neighbours). The agreement with experiments proves to be in the right order of magnitude. The order at low temps. is, however, much more rapidly attained in actual than in the theory. In the second place, the potential for each ammonium radical is calcd. for any orientation of it. The calcn. is based on those of the electrostatic lattice potential and of the repulsive potential between a chlorine ion and a hydrogen atom, the latter being detd. from the stability of the crystal and the compressibility data. The assumption of the stability of the two orientations initially made is confirmed here. A new theory of order-disorder is worked out, which accounts for the quantum-mech. rotatory oscillations of the ammonium radicals. The transition temp. is once more calcd. The isotope effect (ND_4Cl) is also discussed.

Author.

The absorption of hydrogen sulfide in contact with aqueous solutions. O. Kamiike, S. Kataoka and S. Inaba. *J. Chem. Soc. Japan*, **63**, 1007–1014 (1942).—The absorption of a gas by a liquid kept undisturbed and stationary, is considered from the concept of the double film theory. Under several reasonable assumptions, $i^2 = Akt$ is theoretically derived for a gas, especially of high absorption velocity. Here t is the time, l is the distance, or extent, of absorption from the surface during the time t , k is the diffusion coeff. of the gas in the liquid, and A is a const. The authors have applied the above relation to water— H_2S and NaCl — H_2O — H_2S systems. The absorption velocity

and the diffusion coeff. of H_2S in aqueous sodium chloride solns. of different salt concns. were detd. by means of the indicator method, using bromocresol purple. Authors.

Improvements of the crystallizing process of the Rochelle-salt used as piezoelectric vibrators. Modified forms of Rochelle-salt crystals. Z. Kamayachi and E. Kamiseki. (Research Laboratories, Nippon Electric Co., Ltd.). The manufacturing process of Rochelle-salt crystals presented in this paper, was devised as more economical and convenient than the ordinary process with perfect or half crystals, in the mass production of Rochelle-salt vibrator, and especially the production of special vibrator such as the L-cut advocated by W. G. Cady (*Phys. Soc.*, 49, 646-653, (1937) or α -45° cut (N. C. Stamford, *I. R. E.*, 25, 465-471, (1937)), etc. This process improves upon the ordinary technique used to form half crystal and is based upon the idea that the part becoming useless in the case when Rochelle-salt vibrator is cut off from the natural forms of the crystal, is suppressed in the course of crystallization and made to grow up in the required parts. Thereby it is modified into a form having a higher utilization-rate. This expt. was performed in two ways: one in which the development in the α -axis direction of the half crystal is suppressed, and the other in which it grows long in 45° inclination to both axes b and c . Good results were obtained in both cases. By applying this process to a wider range a crystal having the most useful form is manufactured in cutting vibrators, by growing the required elements and suppressing the others as we want. It is detd. by the optical test that the modified form of the Rochelle-salt crystal obtained by the above process is not different from the ordinary half crystal.

Authors.

On the velocity of reduction of vanadium oxide by hydrogen. K. Sano.

Nippon Kinzoku Gakkai-shi, 6, 339-341 (1942). — From the thermodynamical considerations, it is expected that the reduction of vanadium oxide will proceed like that of manganese oxide and be accelerated by the co-existence with iron or nickel oxide. C. H. Fougner and E. J. Kohlmer, however, investigated the velocity of reduction of vanadium oxide with hydrogen at 1530° and obtained results differing from those above expected. The present author studied, using the absolutely dry hydrogen, the reduction of vanadium oxides at 1000° and 1100°, and has found it to agree with that of the thermodynamical calcns. Author.

Studies on the reactions between oxides in solid state at higher temperatures. VI. Discussion of the reaction mechanism with a special reference to the effect of particle size on the reaction. Y. Tanaka. *Bull. Chem. Soc., Japan*, 17, 229-244 (1942). — The main characteristics of the solid reactions between the oxides, studied in the present series of investigations, are summarized. These reactions can be classified into two types: (1) the reactions of the systems, $MgO-TiO_2$, $CaO-TiO_2$ and $MgO-Al_2O_3$, which have a rapid initial reaction period and a small energy of activation, and (2) those of the systems, $MgO-SnO_2$ and $CaO-SnO_2$, in which no rapid initial reaction and a large energy of activation are observed. The rapid initial reaction is probably due to the existence of a rapid surface diffusion, and when the reaction proceeds chiefly by the inner diffusion no rapid initial part may be observed. The effect of the particle size of the components on these reactions is discussed. In the reaction without distinct surface diffusion, the effect of the particle size of the component, of which total surface area is smaller, should be great, while that of the diffused component becomes remarkable when the surface diffusion takes place rapidly. For the three reactions, $MgO-SnO_2$, $MgO-Al_2O_3$,

and $\text{CaO}-\text{TiO}_2$, the above view was proved exptl. by changing the particle size of each component. Tech. importance of the effect of particle size on solid reactions is pointed. Some further considerations on the diffusion mech. are given, and the difference in the energy of activation is explained. Finally, the phenomenon of sintering due to solid reaction is considered to be brought forth by the reaction in which a rapid surface diffusion takes place.

Author.

Oxidation by the air of the ammonia molecules co-ordinated on metal atoms. S. Kawakubo. *J. Chem. Soc. Japan*, **63**, 9-11, 12-14 (1942).—(1) When cobaltammin compds. are heated to 100-184° with the air, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ evolve part of co-ordinated NH_3 as nitrogen oxides at about 140° and above 125° resp. (2) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ evolves most of NH_3 with no change at 75-78°. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ is thermally decomposed above 135° and at 200° evolves part of NH_3 as an oxide. In the cases of $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, too high a temp. causes the yield of the

oxidation products of NH_3 to decrease.

J. C. L.

Ignition of inflammable gases. Y. Toriyama and S. Saito. *Denki-Gakkai Zasshi*, **62**, 427 (1942).—The min. energy for the ignition of inflammable gases varies with the kind of gases and that of energy sources. The authors detd. the min. energy of spark discharge for the ignition of various mixts. of methane and air by using a new exptl. method. A variable condenser was charged by means of ionized water vapour, and discharged through electrodes arranged in the inflammable gas. The electrostatic energy of the condenser was detd. from the capacity of the condenser and its terminal voltage. By varying the potential difference and the capacity, the min. energy necessary for the ignition of the inflammable gas was measured. In order to ascertain which of the capacitive or the inductive spark was the more effective for ignition, a self-inductance was introduced in the discharge circuit. In the most inflammable mixt. (8.4% of methane), the min. energies were 0.00067 J. and 0.00058 J. for the condensive and the inductive sparks resp.

Authors.

2—SUB-ATOMICS, RADIOCHEMISTRY AND PHOTOCHEMISTRY

Photographic estimation of the mass of the cosmic-ray particle. T. Takeuti. *Bull. Tokyo Univ. Eng.*, **11**, 2, 67-69 (1942).—Direct photographic tracks of cosmic-rays are frequently curved. From these curvatures and ranges of the rays, and also from the angular spread of shower pairs, the mass of the particle can be estimated.

Author.

Study of neutrons in the atmos-

phere. S. Kawata and M. Itô. *Mem. Fac. Sci. Agr. Taihoku Imp. Univ.*, **29**, 175-180 (1941).—Neutrons in the atmosphere were investigated with a boron-coated counter and a linear amplifier put in a light wooden chamber. Firstly, the effect of height on the abundance of C neutrons was examd. by observations at four localities, Taihoku (10 m), Nimandaira (2000 m), Rokurin (2750 m) and Niitakashita (3300 m). A very rapid increase of C neutrons was revealed. Secondly, the effects of

shielding the counter with paraffine (2 cm, 4.5 cm, and 7 cm thick) and lead (3.3 cm thick) were studied at Rokurin. Then, in the case of lead, the decrease of count was seen, and in the case of paraffine, increase was recognised, especially markedly for the layer of 4.5 cm. These effects are discussed in connection with the nature of neutrons in the atmosphere. Authors.

Artificial disintegration of boron and lithium. B. Arakatsu, K. Kimura and Y. Uemura. *Mem. Fac. Sci. Agr., Taihoku Imp. Univ.*, 18, 75-94 (1936).—An exptl. study is made of the artificial disintegration of Li and B caused by the bombardment of these elements with protons having energies between 100 kV and 220 kV. The disintegration particles are observed by means of a valve counter. A study is made of the variation with bombardment energy of the relative yields of particles produced by the two reactions: ${}_3\text{Li}^6 + {}_1\text{H}^2 \rightarrow {}_2\text{He}^4$ and ${}_3\text{Li}^6 + {}_1\text{H}^2 \rightarrow {}_3\text{Li}^7 + {}_1\text{H}^1$. With bombardment voltages of 120 kV the α -particles are about 20-30 times as numerous as the protons; at 200 kV the ratio decreases to about 5:1. By observation of the oscillograph records obtained from the valve counter it was possible, when making these measurements, to distinguish the α -particles from the protons produced by the reaction: ${}_1\text{H}^2 + {}_1\text{H}^2 \rightarrow {}_1\text{H}^3 + {}_1\text{H}^1$, which have a similar range. In the case of B the relative yields of the following two reactions are studied: ${}_5\text{B}^{11} + {}_1\text{H}^1 \rightarrow {}_3\text{He}^4$ and ${}_5\text{B}^{11} + {}_1\text{H}^1 \rightarrow {}_4\text{Be}^8 + {}_1\text{He}^4$. No significant variation in the relative yields is observed as the bombardment voltage is varied between 100 kV and 200 kV. Various speculations as to the heights of the potential barriers in B are given. Authors.

Anomalous absorption of γ -Rays. Possibility of the quantum jump of the rest-mass of an electron. B. Arakatsu. *Mem. Fac. Sci. Agr., Taihoku Imp. Univ.*, 5, 163-168 (1932).—The paper is to

propose the possibility of the existence of heavy electrons. The author assumes that the phenomena of the anomalous absorption of hard γ -rays in heavy elements are due to the quantum jump of the rest mass of an oscillator electron or system of oscillator electrons in the near vicinity of the nucleus. The electrons which surround the nucleus in a radial distance smaller than the half wave length $\frac{\lambda_n}{2}$ of the wave corresponding to the n^{th} harmonics of the characteristic oscillation of the oscillator-electron are assumed to be capable of bearing the mass nm_0 in such a way that

$$\lambda_n = \frac{\lambda_0}{n} = \frac{h}{nm_0C}$$

where

$$\lambda_0 = \frac{C}{\gamma_0} = \frac{h}{m_0C}$$

The theoretical value deduced for the additional absorption coeff. per atom is

$$\mu_A = \frac{8\pi}{3} \frac{e^4}{m^2C^4} \frac{2^{1/2}\pi^{1/2}e^6}{3^4C^3h^3} \cdot Z^3 \sum_n \left[\left(\frac{h^2\nu^2}{(nh\nu_0)^2 - h^2\nu^2} \right) \frac{\varphi^2(\xi_n)}{n^3} \right] \\ \approx 6.75 \times 10^{-30} Z^3$$

which approaches satisfactorily to the exptl. value. For the infinitely high quantum radiation the formula becomes

$$\mu_A \approx 6.07 \times 10^{-30} Z^3. \quad \text{Author.}$$

Electrodeless discharge through hydrogen in a long tube. B. Arakatsu and K. Kimura. *Mem. Fac. Sci. Agr., Taihoku Imp. Univ.*, 5, 15-23 (1932).—Discharges were produced in the hydrogen contained in a tube about 1 m. long. Round the centre of the tube, but not touching it, was a coil of 10 turns, the coil length being 10 cm. Through this coil heavy condenser discharges were passed at the rate of 1 or 2 per sec., the current reaching some thousands of amperes in a period of about 10^{-6} sec. The changes observed in the discharge as the press. of the gas was reduced from about 0.5 mm. are described in detail. In the first stage the glow was pale white, the spectrum

being continuous from the yellow to the limit of the visible spectrum in the violet. At about 0.2 mm. H_{β} was visible in the continuous background, while H_{α} could hardly be detected, and a weak Fulcher band was sometimes observed. At about 0.1 mm. the colour changed abruptly to light pink extending somewhat beyond the ends of the coil, the lines H_{α} , H_{β} and H_{γ} being then seen brilliantly on a weak continuous background. Further evacuation caused the glow to extend, and at about 0.01 to 0.005 mm. its length was about 50 cm. No striations were apparent, but the colour of the glow brilliant pink-white some what tinted with blue-violet at the centre; just beyond the ends of the coil the colour was pink-red, while the ends were deep red. The spectrum of the light from the centre was similar to that of the ordinary Geissler tube discharge. The Balmer lines developed well in the second portion and the spectrum of the end portions was similar except for differences in the intensity distribution among the lines and the sharpness of the assocn. of the continuous spectrum with the last visible line of the Balmer series. The results of the observations are discussed.

Authors.

Activation of air by the electrodeless ring discharge. B. Arakatsu and K. Kimura. *Mem. Fac. Sci. Agr., Taihoku Imp. Univ.*, 5, 143-157 (1932).—The activation of nitrogen and oxygen by means of an electrodeless ring discharge is studied, the technique being similar to that employed earlier for hydrogen, except that in this case a bulb 25 cm. in dia. is employed as container for the gas. Three distinct afterglows are observed; with air at a press. of 1 to 0.07 mm. Hg the afterglow is green; between 0.07 and 0.05 mm. it is blue, whilst below 0.05 mm. the afterglow is orange coloured. These afterglows decay at different rates. Observation of the orange afterglow shows that the α - N_2 bands are the most prominent visual feature. Photographically,

however, the 3rd positive bands (γ -NO) are the strongest feature of the spectrum. The blue afterglow is stated to be due to the β -NO bands. Possible mech. of the discharge are discussed, and it is concluded that the theory of Cario and Kaplan fits the observations best.

Authors.

Electrodeless ring discharge through potassium vapour. B. Arakatsu and Y. Uemura. *Mem. Fac. Sci. Agr., Taihoku Imp. Univ.*, 5, 159-161 (1932).—Previous work on the electrodeless ring discharge through hydrogen in a long tube suggested that the glow in the part of the tube outside the primary coil was due to the positive rays of the neutralising hydrogen atoms expelled from the part of the tube within the coil. The discharge in potassium vapour is now studied and it is found that no trace of the arc lines is to be seen, only spark lines being emitted. The phenomena are considered to support the theory already advanced. The mech. of the process involved is discussed.

Authors.

Total secondary electron emission from solids. T. Matsumoto. *Sci. Repts. Tohoku Imp. Univ.*, 30, 395-415 (1942).—Total secondary electron emission from polycrystalline nickel and evaporated films of sodium chloride, potassium chloride, potassium bromide, sodium bromide, potassium iodide, strontium oxide and barium oxide was studied in a range of low voltage. It was found that several characteristic maxima in the secondary electron emission appear in solid targets, and as to the nature of the phenomenon it was confirmed that the effect was not one of the elastic reflections of incident electrons, but it was related to the inelastic collisions in which the incident electrons lost some energy and were emitted as the secondary electrons. These results were compared with those of Hilsch-Pohl for optical absorption of alkali haloid, and it was found that there was good agreement

between them. For strontium oxide and barium oxide the results were compared with the energy loss spectrum obtained by Rudberg, and found also to be in good agreement. Author.

On the variation of the total secondary electron emission with bombarding potential. T. Matsumoto. *Sci. Repts. Tohoku Imp. Univ.* 30, 416-421 (1942).—Using the same apparatus as in the previous paper, the shape of the total secondary electron curve for polycrystalline nickel and evaporated films of NaCl, KCl, KBr, NaBr, KI, SiO and BaO was studied in the whole range from 24 to 550 volts. For the nickel target it was found that i_s/i_p increases almost linearly from 24 to about 230 volts and it decreases gradually after it attained a broad max. value. For the alkali haloid and the oxide targets, except BaO, it was found that there appears a broad max. below 100 volts and the relation i_s/i_p decreases gradually for higher voltages. These features of the secondary electron emission has been explained from the idea based on the energy levels lying above the Fermi distribution.

Author.

Thermal electron of single crystal barium oxide. T. Arizumi. *Proc. Phys.-Math. Soc. Japan*, III, 23, 1037-1038 (1941).—By means of an electron microscope, it is found, as already expected, that radio-activity of the thermal electron of barium oxide differs on different crystal surfaces.

J. C. L.

On the electron-optical observations of the reversing brightness in the emission-pattern of electrons in the barium-azide coated cathode. T. Hibi. *Sci. Rep.* 30, 3, 372-383, (1942).—Electron-microscopic observations of the electron emission pattern of the barium-azide coated cathode were made, and the reversing brightness in the pattern was found during the

repetition of raising and lowering the temp. of the cathode. This reversing brightness was also observed when the cathode was maintained at a const. temp. for a long time, and also when the temp. of the cathode was raised for several minutes and then lowered to the initial temp. But it was not observed when the cathode temp. was lowered and then raised to the initial temp. The effects of flowing electron current and of sorbing a trace of oxygen or hydrogen on this reversing brightness were studied. It was confirmed that this reversing is due to the decrease and the increase of the brightness in the bright and the dark portions at the initial temp. of the cathode, and not to the relative difference of the brightness between both portions in the pattern. Some considerations of the results obtained are also described.

Author.

On the electron-optical observations of the changes of the emission-pattern of electrons in the barium-azide coated cathode. T. Hibi. *Sci. Rep.* 30, 3, 384-394 (1942).—Here are described the results of the electron-optical observations of the changes of the electron emission pattern of the barium-azide coated cathode due to (1) the heat treatments of repeating the cycles of raising and lowering the temp. of the cathode; (2) the temp. changes of the cathode; and (3) to the sorption of a trace of oxygen and of hydrogen. It is confirmed that the whole course of the change of the pattern due to the heat treatments of the cathode is reproducible in a short duration after the sorption of oxygen by the cathode. The interpretation of the observed results is also given.

Author.

On the behaviour of oxide cathode in the atmosphere of oxygen. H. Kawamura, Y. Tamura and A. Shinohara. *Mazda Kenkyu Jiho*, 17, 189-194 (1942).—As is well known, the active centres of the oxide cathode are the excess barium atoms. In the thermal equilibrium, the density of

these excess barium atoms can be detd. by the press. of oxygen surrounding the oxide cathode. The authors measured the thermionic emission of oxide cathode at different press. of oxygen (10^{-4} – 10^{-7}). The exps. were performed both with flowing oxygen and with sealed-off tube. In the latter case oxygen was introduced by heating the silver wire occluding oxygen and was got rid of by the "batalum getter" at the desired instant. Thus was obtained the relation between activity (measured with the thermionic emission at 970°K) and press. of oxygen (measured with the ionization gauge) as follows: $i = aP - \frac{1}{4}$. This result can be easily understood by considering the thermal equilibrium: $2\text{BaO} = 2\text{Ba} + \text{O}_2$, and also by taking into account the fact that the thermionic emission is proportional to the square root of the density of the excess barium. In this exp. there was employed the electrolytic nickel for the core metal, in order to reject the reducing action due to the impurity in the core.

Authors.

On the emission band spectrum of the OD molecule. Y. Ōta. *Mem. Fac. Sci. Agr., Taihoku Imp. Univ.*, 15, 8, 181–191 (1935).—Passing the electric discharge through water vapour containing deuterium amounting to 65% of the hydrogen isotopes, photographs of the (0,0) band of $^2\Sigma^+ \rightarrow ^2\Pi$ transition were taken by a large quartz prism

spectrograph. From the relative intensity of lines in each of P_1 , P_2 , Q_1 and Q_2 branches, the nature of the abnormal rotation of the excited OD molecule is considered.

Author.

The mechanism of the thermal decomposition and combustion of the monohydric alcohol (In consideration of absorption spectrum). F. Someno. *Sci. Papers Inst. Phys. Chem. Research*, 21, 277–310 (1942).—For the purpose of studying the character of the thermal decompn. and slow combustion of ($\text{C}_1 \sim \text{C}_4$) alcohols, the alcohol (20 mg) and an equimolecular mix. of the alcohol and oxygen were heated to 650°C in about 170 c.c. quartz tube under low press., and then absorption spectra due to the decomposition products at various temps. were determined in the region of ultraviolet to $\lambda 1800\text{Å}$. The first thermal decompn. of the alcohols at $500 \sim 550^{\circ}\text{C}$ was dehydrogenation and dehydration, accompanied by the formation of aldehydes, ketones and olefines. The combustion of the alcohols consisted of a primary oxidation of the CH_3 -radical (end of the chain) into HCHO at $350 \sim 450^{\circ}\text{C}$. The character of thermal decompn. of the alcohol is attributed to the existence of the alcoholic OH - radical. In the combustion, however, the OH -character was secondary and its reaction was similar to that of satd. hydrocarbons.

Author.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY (THERMODYNAMICS)

The Faraday effect of ions in aqueous solutions. A. Okazaki. *Proc. Phys. Math. Soc. Japan*, 24, 357–361 (1942).—The molecular rotation const. $\phi \equiv \frac{M}{S} \frac{n\omega\lambda^2}{(n^2+2)^2}$ (n =refractive index, ω =Verdet's const. for the light of wave-length λ , M =molecular

wt., s =density) of strong electrolytes at infinite dilution is given by the sum of the rotation cons's. of the component ions, i. e. $\phi = \phi_+ + \phi_-$. By assuming that a large ion such as K^+ and Cl^- shows little hydration effect and has the same rotation const. in soln. as in the gaseous state, the rotation

const. of Cl^- for D-lines was calcd. from the Φ -value of KCl in infinite dilution and the values of ionic refraction of K^+ and Cl^- . The rotation const. of several ions were detd. according to the additive law.

Author.

The Faraday effect and refraction of rare gases and rare-gas-like ions. A. Okazaki. *Proc. Phys.-Math. Soc. Japan*, 24, 361-367 (1942).—Assuming that the rotation const. Φ of Cl^- , Br^- , I^- , K^+ , Rb^+ and Cs^+ in the gaseous state have the same values as in soln., as were given in the previous paper (*Proc. Phys.-Math. Soc. Japan*, 24, 357-361 (1942)), the number of dispersion electrons of these atomic ions p were

detd. from the relation $\Phi = \frac{\pi}{2eN} R^2$ (Φ =ionic rotation const., R =ionic refraction, e =the charge of dispersion electron, N =Avogadro's number). The natural frequency ν_0 of these ions was calcd. from the formula $R = \frac{e^2 N}{2\pi m} \frac{P}{\nu_0^2 - \nu}$ (ν =frequency of light, m =mass of electron) using the values of R and p . The values of Φ , R , p and ν_0 for these rare-gas-like ions are compared with those for rare gases.

Author.

On the heat of dilution of strong electrolytes. S. Kaneko. *Bull. Electrotechn. Lab.*, 5, 187 (1942).—To explain the fact that the heat of dilution of strong electrolytes is negative in concd. soln., we must assume with Nernst that the dissocn. of electrolytes is imperfect or the dissocn. is perfect but non-Coulombic force exists between ions.

Author.

The relation between the equivalent conductivity and the viscosity of electrolyte solutions. S. Kaneko. *Bull. Electrotechn. Lab.*, 5, 206 (1942).—According to Johnston there holds the following relation between the equivalent conductivity Λ and the viscosity of the solvent η

$$\Lambda\eta^t = \text{const.}$$

where t is also const. The above relation is verified from the theory of electrolytic conduction previously reported (Researches Electrotechn. Lab. No. 428). Author.

The relation between the Volta effect and temperature. S. Kaneko. *Bull. Electrotechn. Lab.*, 5, 211 (1942).—The temp. coeff. of the Volta effect must be zero according to thermodynamics. Author.

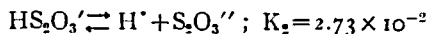
The theory of strong electrolytes. II. S. Kaneko. *Bull. Electrotechn. Lab.*, 6, 323-324 (1942).—Bjerrum's theory of strong electrolytes is somewhat modified and compared with the theory of the author.

Author.

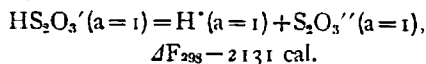
A study on the hydrolysis of bromine by means of a glass electrode. H. Hagiwara. *Se. P.*, 21, 593-596 (1942).—Hydrolysis const. of bromine were detd. at 25° by means of a glass electrode, measuring the pH values of the dilute solns. of various concns. From the result, the mean value of K_h was found to be 4.2×10^{-9} , which is only a little smaller than the previous value.

Author.

Determination of the second dissociation constant of thiosulphuric acid by means of a glass electrode. N. Yui and H. Hagiwara. *Se. P.*, 21, 597-600 (1942).—The pH values of solns. containing sodium thiosulphate and hydrochloric acid were measured at 25° by means of a glass electrode. On the basis of these values the second dissocn. const. was calcd. as follows:



Hence,



Authors.

Determination of the dissociation constant of thiocyanic acid by means of a glass electrode. T. Suzuki

and H. Hagiwara. *Se. P.*, 21, 6, 601-604 (1942).—The dissocn. const. of thiocyanic acid was detd. at 25°C by means of a glass electrode, measuring the pH value at each stage of titration of a dilute potassium thiocyanate soln. with hydrochloric acid. From the result of these titrations, the dissocn. consts. were found to be 0.137, 0.140, and 0.150, and the mean value 0.142 was obtained. Therefore, this acid is not so weak as shown by Latimer's calcn.

Authors.

The activity coefficients of 2-1 and 2-2 salts. S. Kaneko. *Bull. Electro-techn. Lab.* 6, 350 & 437 (1942).—The activity coeffs. of 2-1 and 2-2 salts are calcd. by the theory previously reported (Researches Electrotechn. Lab. No. 403 and 449) and compared with the observed values.

Author.

Ion pair and equivalent conductivity. S. Kaneko. *Bull. Electro-techn. Lab.* 6, 453 (1942).—The fact is verified that the ion pair in the electrolyte soln. does not conduct electricity.

Author.

Calculations of pH and ionic diameter in buffer solutions by the theory of Grownwall, La Mer, Sandved and Greiff. H. Nukada. *J. Chem. Soc. Japan*, 63, 703-710 (1942).—Grownwall, La Mer, Sandved and Greiff extended the Debye-Hückel theory to the symmetrical, and La Mer, Grownwall and Greiff to the unsymmetrical type of valence of salt, and they obtained the eqs. of ionic activity coeff. in the electrolytes. The author applying these eqs. to the acetate and phosphate buffer solns., calculates pH and ionic diameter:

$$\begin{aligned} \text{ionic diameter in acetate buffer} \\ = 3.924 \times 10^{-8} \text{ cm.} \end{aligned}$$

$$\begin{aligned} \text{ionic diameter in phosphate buffer} \\ = 5.025 \times 10^{-8} \text{ cm.} \end{aligned}$$

These values are fully in concordance with the values obtained from the Debye-Hückel eq.

Author.

Studies on concentrating the hydrogen isotope H^2 by the electrolysis of water. I, II. Y. Ōta. *Mem. Fac. Sci. Agr., Taihoku Imp. Univ.*, 15, 3, 71-79 (1934).—I. We started the production of heavy water with ordinary water. The abundance ratio of H^2 to H^1 in the water obtained by distilling the treated electrolyte was detd. by comparing the intensities of the H_2 lines of H^2 and H^1 . After several trials the electrolytic cell was devised which was used conveniently throughout this work, and a large amount of distilled water was obtained, the relative abundance being $H^2:H^1=1:400$. The construction of this electrolytic cell and the procedure of electrolysis are given in details. II. *ibid.*, 15, 6, 165-170 (1935).—With five sets of 40 cells described in the previous report, the preliminary work for producing heavy water was carried out. When the concn. of H^2 in water became high, the hydrogen evolved during electrolysis contained an appreciable amount of H^2 and a device to recover it became necessary and so the heavy water of 90% H^2 was obtained. In the present expt. the relative abundance was detd. by the density measurement and the refractive index measurement.

Author.

Vapour pressure analysis. I. Determination of activities and lattice constants in the KCl-KBr solid solution. Z. Shibata and M. Yoshiyama. *J. Chem. Soc. Japan*, 63, 570-573 (1942).—The authors have proposed a new method of vapour press. analysis by which the study of the solid or liquid phase of binary system can be performed. The vapour press. of binary system and also the compn. of the vapour are detd. by the apparatus (*J. Fac. Sci. Hokkaido Imp. Univ.*, 3, 53 (1940).), using a torsion- and thermo-balance, which was applied in the authors' laboratory to the accurate molecular weight-detn. of vapour. They applied the new method to the study of KCl-KBr solid soln. at 590°C, and then confirmed the ap-

plicability of Lewis' eq. to the activity of each salt. And the deviation from Rault's law is parallel with that from the linear relation between compn. and lattice const. exactly measured by the authors.

Authors.

The vapour pressure of nickel carbonyl. B. Suginuma and K. Tonosaki. *Bull. Inst. Phys. Chem. Research*, **21**, 431-436 (1942).—The vapour press. of $\text{Ni}(\text{CO})_4$ were detd. by a statical method using a glass spring manometer in the temp. range $0^\circ \sim 25^\circ\text{C}$. The relation between the vapour press. p (mm) and the reciprocal of the absolute temp. $T^\circ\text{K}$ may be expressed by the following eq. $\log p = 7.878 - 1574.49/T$. The boiling point 42.1°C calcd. from this eq. agrees with the expl. value $42.1 \sim 42.3^\circ\text{C}$ at 760 mm. The following values are calcd. from these results. The molecular heat of vaporization 7.202 cal/mol, Trouton's const. 22.8 and the critical temp. ca. 200°C .

Authors.

Relation between activation energy of recrystallization and that of self-diffusion in a metal. R. Hasiguti. *Proc. Phys.-Math. Soc. Japan*, **24**, 270 (1942); *Nippon Kinzoku Gakkai-Si*, **6**, 282-284 (1942).—The recrystallization velocity v of a cold-worked metal is expressed by the following equation: $v = Ce^{-\frac{A_r}{RT}}$, where C is a const. and A_r is the activation energy of recrystallization. As the process of recrystallization can be regarded as a sort of so-called "Platzwechselvorgang", A_r should have the same order of magnitude as the activation energy of self-diffusion A_s . Plotting A_r of pure Cu against the degree of cold-working, the present author has found that A_r tends to approach to the value of A_s at the zero of cold-working degree. The numerical data are as follows: the activation energy of recrystallization of a sample elongated at room temp. about 16% of the original length is about 22,000 cal per mol, and that of a sample elongated about 5% is about 55,000

cal per mol. The activation energy of self-diffusion of Cu is about 60,000 cal per mol. It is interesting to see how this fact will serve to the development of the theory of recrystallization. The state of things is very disadvantageous to one of the current theories, which postulates the spontaneous melting at the locations where recrystallization takes place, for A_r is about ten times larger than the heat of fusion, which is about 3,000 cal per mol in the case of Cu. A curve showing the detailed relation is given.

Author.

Studies on calcium carbide. IV. Heat of formation of calcium carbide. N. Kameyama and Y. Inoue. *J. Soc. Chem. Ind. Japan*, **45**, 656-658 (1942).—Pure carbide of calcium was prepd. by the method reported in the previous paper (*J. Soc. Chem. Ind. Japan*, **44**, 825 (1941); *Abst.* **44**, 360B). It was in the form of a cake and its purity was 97.93%. In order to keep this cake from the atmospheric moisture during handling, it was covered by the film of naphthalene or benzoic acid, by being dipped in the molten naphthalene or benzoic acid. Using these cakes, the heat of combustion was measured in a calorimeter bomb in the usual way. Heat of combustion, cal per gram of pure calcium carbide, Measured values: (5161.3, 5154.4, 5131.9, 5153.4, 5152.2, 5157.1, 5155.1), Average value: 5151.9. It was found by the analysis that the products of combustion were CaO and CO_2 , there being practically no CaCO_3 , nor free carbon. Therefore, the above value corresponds to the following: $\text{CaC}_2 + \frac{5}{2}\text{O}_2 = \text{CaO} + 2\text{CO}_2 + 330.1$ kcal. From this, the heat of formation of calcium carbide is calcd. as follows, using $(\text{Ca}, \text{O}) = 152.1$ kcal, $(\text{C}\beta, \text{graphite}, \text{O}_2) = 94.3$ kcal., $\text{Ca}_s \text{ form} + 2\text{C}(\beta, \text{graphite}) = \text{CaO}_2 + 10.6$ kcal. Heat of a few important reactions in which calcium carbide partakes are calcd. as follows: $\text{CaO} + 3\text{C}(\beta, \text{graphite}) = \text{CaC}_2 + \text{CO} + 1114.8$ kcal, $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}(\beta, \text{graphite}) + 74.6$ kcal, $[\text{Ca}, \text{C graphite}, \text{N}_2]$ being

85.2 kcal according to the author (cf. *ibid.*, 30, 5, (1927)).

Authors.

On the equilibrium between iron, sulphur and hydrogen at high temperatures. S. Matoba and T. Unotoro. *Tetsu to Hagane*, 28, 6, 45-55 (1941).—The authors detd. the equil. consts. $K = P_{H_2S}/P_{H_2}$ of the reaction, $FeS + H_2 \rightleftharpoons Fe + H_2S$, at 700°, 800°, 856°, 900° and 1000° by the dynamic method. The results obtained are shown by the eq.; $\log K = 3910.288/T + 0.817$. Applying the dissocn. const. of the hydrogen sulphide, the authors calcd. the dissocn. press. of ferrous sulphide as follows; $2 FeS \rightleftharpoons 2 Fe + S_2$, $\log 1/PS_2 = 16916.4/T - 6.64$. A mix. of hydrogen and its sulphide, prepared by passing hydrogen through the heated bismuth sulphide layer, was led above the molten iron, and after the reaction was completed, the outlet gas and the sulphur content of the iron were analysed. The equil. consts. $K = P_{H_2S}/P_{H_2} [FeS]$ of the reaction, $FeS [in Fe] + H_2S \rightleftharpoons Fe (liq) + H_2S$ were calcd. for 1535°, 1580° and 1620° and found to be $\log K = -4427/T - 0.326$. By means of these results the desulphurization limits of molten iron by carbon, ferrous oxide and lime were also calcd.

Authors.

Thermodynamic properties of ethylene as low temperature refrigerant. S. Sugawara and Y. Suezawa. *The Refrigeration*, 16, 1-14 (1941).—While the appropriateness of ethylene to low temp. refrigeration has been already recognized, its thermodynamic properties have not yet completely been studied. The authors have now calcd. the values of

the important thermodynamic properties of ethylene, using the known exptl. data. The formulae, tables and diagrams thus constructed are given in this paper; the formulae are as follows:—

1. Relation between saturation press. and the temp.,

$$\log_{10} p_s = 11.5909 - 950.13/T - 1.5722 \times 10^{-2}T + 0.242 + 10^{-4}T^2$$

2. Characteristic eq.,

$$v = 30.24T/p - 0.09650/(T/100)^{2.7} - 8 \times 10^{-12}p^{3.2}/(T/100)^{8.7}$$

3. Heat of evaporation,

$$r = 20.45(282.7 - T)^{0.363}$$

4. Specific heat at const. press.,

$$C_p = 0.1400 + 0.0735(T/100)0.2258 \times 10^{-4} p/(T/100)^{3.7} + 0.4941 \times 10^{-14} p^{3.2}/(T/100)^{9.7}$$

5. Enthalpy,

$$i = 112.94 + 0.1400T + 3.675(T/100)^2 - 8.363 \times 10^{-4}p/(T/100)^{2.7} - 5.679 \times 10^{-14}p^{3.2}/(T/100)^{8.7}$$

6. Entropy,

$$s = 1.1923 + 0.3224 \log_{10} T + 0.0735(T/100) - 0.1631 \log_{10} p - 0.06102 \times 10^{-4} p/(T/100)^{3.7} - 0.05094 \times 10^{-14} p^{3.2}/(T/100)^{9.7}$$

where p_s = saturation press. in kg/m²

p = press. in kg/m²

T = absolute temp. in °K

v = specific volume in m³/kg

r = heat of evaporation in kcal/kg

C_p = specific heat at const. press. in

kcal/kg°C

i = enthalpy in kcal/kg

s = entropy in kcal/kg°C

Authors.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY (CONTACT CATALYSIS)

Stability of the liquid film. J. Samehima, M. Nakamuda and R. Terada. *J. Chem. Soc. Japan*, 63, 691-696 (1942).—

Stability of the liquid film was measured by a method devised by the authors. A triangular frame of platinum is dipped in the

liquid, and then it is pulled up slowly from liquid with a film formed over it. The film collapses at a certain height above the surface of the liquid, and this height gives the measure of its stability. The expts. were made on the systems of water—ethyl alcohol, water—methyl alcohol, and water—*n*-butyl alcohol. Very remarkable difference was found between the stabilities of films measured in the open vessel and in the closed vessel. It is more stable in the open vessel exposed to the outer air than that in the closed vessel. In the former there appears max. film stability in a certain compn. of liquid, while no such max. is observed in the latter case. These results were compared with the surface tension and viscosity, but no definite relation was found among them. These phenomena may be explained by the fact that the molecules in the liquid state are somewhat like those in the solid crystal. The film stability will be increased when the molecules have better mobility in the liquid. The life of the foam on the surface of a liquid, especially pure liquid, was remarkably prolonged by blowing the surface with dry air. Evaporation and cooling effect may be the chief cause of this phenomenon. Authors.

A simple model for the adsorption of the surface active electrolyte. Y. Mutō. *Proc. Phys.-Math. Soc. Japan*, 16, 104-107 (1942).—A well known fact that the surface tension of solns. containing organic ions with hydrophobic groups, such as alkyl sulfates or sulfonates, is greatly lowered by the addition of inorganic salts is explained with the use of a simple model. As the main factor that hinders these ions from clustering at the surface is the electrostatic force, which is diminished by the ionic atmosphere produced beneath the surface layer, we can treat the phenomena theoretically on the following assumptions: (1) An active adsorbed surface ion is supposed to have the potential energy excess $E_0(x) + w(x)$, where the first term is due to its electric

charge and the second to its hydrophobic groups, x being the distance between the center of charge and the surface. (2) All ions are confined to the place $x \geq a$. (3) We can replace the function $w(x)$ by a const. w when $a \leq x < a+t$ and zero when $x \geq a+t$, t being the thickness of the surface layer. (4) Electrically, each layer of the soln. can be considered as a thin uniformly charged body. (5) No interaction occurs between the hydrophobic groups of adsorbed ions. Poisson-Boltzmann eq. is derived and solved approximately in the case of 1-1 electrolytes and the depression of surface tension is given as a function of concn., $t \exp(-w/kT)$, and T . As an example, the quantity $t \exp(-w/kT)$ is calcd. to be about 3×10^{-3} for octyl sulfate from its data on surface tension lowering. The formula can not be used when colloidal particles appear appreciably. Author.

On the catalytic action of the Japanese acid earth. XII. The relation between the catalytic activity and adsorption. II. The adsorption isotherms of water and acetonitrile for the earth. K. Ishimura. *Bull. C. S. J.*, 16, 349-356 (1941).—Adsorption isotherms of water and acetonitrile for the Japanese acid earth have been studied by using McBain's sorption balance. A marked hysteresis phenomenon has been observed in both cases. It has been found that as the processes of adsorption and desorption are repeated, the lower region of the hysteresis area tends to be reversible in the case of water, while in the case of acetonitrile hysteresis covers the whole range of the isotherms even after the fourth series of adsorption and desorption. In both cases the upper region of the hysteresis area remains unchanged. The first type of the hysteresis, which tends to disappear, has been explained as due to the existence of the adsorbed foreign substances on the surface of the earth, while the second type is associated with capillary condensation process. The difference

between the behaviours of water and acetonitrile can be attributed to that of the affinity of the two substances to the earth. The total volume of pores of the earth has been calcd. from the adsorbed amts. of the two substances and found to be about 40 c.c. for 100 g. earth.

Catalytic properties of manganese oxides. II-III. W. Sakai, D. Hukuyama, and T. Okuno. *J. Soc. Chem. Japan*, 45, 25-33 (1942).—(II). Adsorption equil. of carbon dioxide by manganese oxides: Adsorption equil. (temp. 25°, 50°; equil. press. 50-250 mm.) of CO₂ was statically observed by using 10 kinds of manganese oxides as adsorbents, each differing in its degree of oxidation. The samples were heated for 4 hours under 10⁻³ mm. press., washed with CO₂ 2 or 3 times and activated. Without this treatment no adsorption occurred. Adsorption equil. obeys Freundlich's formula of isotherm. The constant differential adsorption heat of one sample does not agree with that of another and the value is large leading us to the conclusion that an activated adsorption is taking place. The adsorption consists of two stages. Generally, in the earlier stage the adsorption proceeds rapidly. In the case of the sample obtained by the reaction, $\text{KMnO}_4 + \text{CH}_3\text{OH} \rightarrow \text{Mn}_2\text{O}_3$, the adsorption is considerably rapid even in the later stage. The adsorbed amt. is not exactly proportional to the MnO contained in the sample although it tends to be so. (III) Adsorption velocity of manganese oxide: The CO₂ adsorption velocity of the sample produced according to $\text{KMnO}_4 + \text{CH}_3\text{OH} \rightarrow \text{Mn}_2\text{O}_3$ is measured and its mech. considered under the exptl. conditions: temp. 25 and 50°, the initial press. 47-25 cm. and time, about 500 min. The Langmuir adsorption velocity formula, a revised Langmuir formula and Bangham's exptl. formula could roughly express the observed value. Sameshima's adsorption velocity formula: $p_0 - p = k' \log t + c$, derived from the assumption that soln. is made

not only on the surface but mostly in the gaps between the internal molecules, holds good. In the formula p_0 and p are the initial press. and the press. at a time t resp.; k' and c are consts. The activation energy was measured.

J. C. L.

The contact oxidation of carbon monoxide by deuterium on the surface of copper oxide. I. A. Sikame, and T. Titani. *J. Chem. Soc. Japan*, 63, 36-40 (1942).—The contact oxidation of CO with the copper oxide used as a catalyst is studied by the aid of deuterium. The reaction takes place actively at about 150°C. and is completed at about 400°. Above 400°C, the reaction $\text{CuO} + \text{CO}_2 \rightleftharpoons \text{CuCO}_3$ occurs; above 550°C., $2\text{CuCO}_3 \rightarrow \text{Cu}_2\text{O} + 2\text{CO}_2 + \frac{1}{2}\text{O}_2$, and $\text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO}$ occur simultaneously.

J. C. L.

High pressure hydrogenation of octyl alcohol. On the hydrogenation about dehydroxyl group and its disruption. K. Tanaka, S. Yabuki, and M. Sato. *Bull. Inst. Phys. Chem. Reserch*, 21, 537-544 (1942).—The authors studied the high press. hydrogenation of octanol-(1) and octanol-(2) by Ni₃O₄ or Ni₃O₄-Al₂O₃ (1:5) catalysts at 250 to 400°C. (1) The case of Ni₃O₄: octanol-(1) has a disruptive bond of the C₁-C₂ and *n*-heptane is chiefly produced. Octanol-(2) presents almost no action with hydrogen at 250°C. It has separated hydroxyl and gives a disruptive bond of the C₂-C₃ at 400°C. (2) The case of NiO₃-Al₂O₃: octanol-(1) has no action with hydrogen at 300°C. *n*-octanol was produced at 350° or 400°C. and *n*-Heptane was produced at 400°C. too. Octanol-(2) produces *n*-octanol at 400°C. and no *n*-heptane is produced. Such is the case with Ni₃O₄ catalyst.

Authors.

The high pressure hydrogenation of phenol and naphthalene. II. N.

Tanaka. *J. Chem. Soc. Japan*, **63**, 4, 307-314 (1942).—When the mixt. of phenol and naphthalene is hydrogenated under the high press. of hydrogen with Ni as catalyst, at first naphthalene is reduced to tetralin, phenol is then reduced to cyclohexanol, and finally begins the reduction of tetralin to decalin. The velocity of the reduction of phenol is

retarded by the presence of naphthalene, and the reduction of naphthalene is somewhat accelerated by the presence of phenol, but it is difficult to reduce naphthalene to decalin by the reduction of the mixt. This is very much different from the reduction of naphthalene alone, which is easily reduced to decalin.
Author.