

ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

Vol. XV

December, 1941

No. 3

1—GENERAL CHEMISTRY

On an ion microscope. N. Sasaki and K. Mitani. *Proc. Imp. Acad.*, **17**, 36-37 (1941).—Many substances when heated can emit positive or negative ions with which an ion microscope may be constructed in the same way as with electrons. Such a microscope can reveal many new aspects of the sord surface. A simple ion microscope of Johnson and Shockly type [*Phys. Rev.* **49**, 436 (1936)] was tried at first. It consists of a glass tube coated internally with a fluorescent substance as cathode, and a wire stretched along its axis as anode. The ions emitted from the hot anode are drawn radially to the cathode wall where the image of the emitting spots is formed. It is magnified only in the direction of the circumference by the ratio of the wire radius to the tube radius. (176 times in the present case). A fine tungsten wire thickly coated with alumina, gave some diffuse bands as ion image. On reversing the potential the electron image was obtained at once, which consisted of many oblong spots distributed irregularly and independently of the ion image. Authors.

An electron diffraction study on the corroded state of the alkali and the alkaline earth metals, Li, Na, K, and Ca, on exposure to air. S. Yamaguchi. *Sc. P.*, **37**, 424-434 (1940).—A fresh clean surface of Li was allowed to stand in air for about 5 minutes. The diffraction pattern obtained from such a surface showed the formation of Li_2O mixed with a small amt.

of LiOH . The pattern obtained from the surface of Na similarly treated showed the formation of sodium bicarbonate. On the K metal also its bicarbonate was formed in similar circumstances. Similarly, a moderate quantity of CaO was found to be formed on the surface of Ca. Author.

The electric resistance of liquid sodium. S. Harasima. *Proc. Phys.-Math. Soc. Japan*, **22**, 183-188 (1940).—The elect. resistance of liquid Na measured according to the theory of electrons in the solid metal using the model of Wall (1938) is found to agree fairly well with the observed values. The temp. coeffs. of the resistance are calcd, and the elect. specific resistances of solid and liquid Na at the boiling point are found to be 4.1 and 6.0 microhm-cm. resp. J.C.L.

Solvent effect on the dipole moment of disubstituted benzenes. K. Higasi. *Bull. Inst. Phys. Chem. Research*, **20**, 218-224 (1941).—Dipole moments of *o*- and *m*-dichlorobenzene and of *m*-dinitrobenzene are slightly smaller in dil. soln. in org. solvents than in vacuo. The higher the dielec. const. of the solvent, the greater the effect on the dipole moment of the solute. Dipole moments in the Debye units are: *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ in Et_2O at 20° , 2.00; *m*- $\text{C}_6\text{H}_4\text{Cl}_2$ in Et_2O at 20° , 1.33; *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$ in hexane at 25° , 4.07, in benzene at 25° , 3.96, in Et_2O at 25° , 3.32. The effect of solvent on dipole moment is nearly the same for disubstituted

derivs. as for the corresponding monosubstituted derivs. An explanation of it is found in the author's theory on solvent effect (*Sec. P.*, 28, 284 (1936)). Author.

Determination of the thermo-molecular pressure in hydrogen gas at relatively high temperatures. H. Kitagawa and T. Murai. *J. Chem. Soc. Japan*, 62, 220-226 (1941).—The thermo-molecular press. caused by keeping one end of each of the capillary tubes, 0.2611, 0.6183 and 0.8716 mm. in diameter resp., at room temp. and the other end at 200, 300, 400 and 475°, is measured by means of an improved Rayleigh differential manometer. The larger the temp. difference is, and the smaller the diameter is, the higher the thermo-molecular press. becomes, and it reaches a max. at pressures of 1–2 mm. In the case of one tube and the temp. difference, the $(dP/dT)/(dP/dT)_{max}$ $\log(P/P_{max})$ curve is symmetric and P_{max} approximately proportional to $T^{(1+n)}/R$, where n is const; the value of P_{cold}/P_{hot} increases from $\sqrt{T_{cold}/T_{hot}}$ to 1. In comparison with M. Knudsen's and S. Weber's empirical formulae, it is found that the disparity from those formulae becomes larger when both the temp. and the press. differences are large. And this may be ascribed to "Gleitungs-koeffizient", and the fault of expressing simply such a complicated phenomenon is pointed out. J. C. L.

Studies on glycerin as the standard liquid of high viscosity. J. Tsukamoto and S. Kuriyama. *J. Soc. Chem. Ind. Japan*, 44, 41-43 (1941).—Examination has been made on the relation of viscosity with concn. and specific gravity of glycerin as the standard liquid of high viscosity. The absolute viscosity of concd. glycerin was carefully detd. by means of the Ostwald viscosimeters of different bores. Viscosimeters of larger bores were calibrated with glycerin of known viscosities which had previously been examd. with viscosimeters of finer bores, calibrated with water as standard liquid. The exptl. value

7.815g. cm⁻¹. sec⁻¹. agrees well with 7.82g. cm⁻¹. sec⁻¹. the value obtained by means of the falling sphere viscosimeter by W. H. Gibson and L. M. Jacobs (*Trans. Chem. Soc.* 117, 473 (1920)). From the comparison of the results obtained with the data in literature, it is concluded that, for the detn. of concn. of a sample of glycerin, the oxidation method gives more correct results than the triacetin method. The concn. of a glycerin sample can be measured simply by detg. its specific gravity, so long as it contains no impurity. Authors.

Studies on phenol-formaldehyde resins. X. Relation between the increase in viscosity and density of the phenol-formaldehyde system. S. Tsuruta. *J. Soc. Chem. Ind. Japan*, 44, 139-142B (1940).—When the mixt. of phenol and formaldehyde is heated, its density S and viscosity η_{sp} increase gradually as the resinification proceeds (*ibid.*, 39, 156B, 449B (1936); 44, 57B (1941)). Between η_{sp} and S there exists a linear relation, $S=S_0+(m/k)\eta_{sp}$, where S_0 , m and k are consts. resp. This relation is supposed to be derived from the fact that both formulae, $S=S_0+mC$ and $\eta_{sp}=kC$ co-exist in the reaction system, where C represents the concn. of the resin nucleus formed. It is very interesting that both relations are applicable to the resinsoln., C being the concn. of the dissolved resin (Cf. Tsuruta, *ibid.*, 42, 327B (1939); Houwink, *physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, (1934). Author.

The boiling point of Na₂SO₃ solution under decreased pressure. G. Matui and K. Yamaguti. *Bull. Tokyo Univ. Eng.*, 9, 297-310 (1940).—The boiling points of aq. solns. whose concns. are Na₂SO₃ 2.3–38.1g./H₂O 100g. are detd. under press. of 100–760 mm. by means of an improved Cottrell method. Comparing the boiling points thus observed with those of water under the same press. it is found that the Dühring formula is valid in that case. The thermometer used

was calibrated from the boiling points of water under various press. J. C. L.

Statistical theory of binary alloys.

I. Y. Takagi. *Proc. Phys.-Math. Soc. Japan*, III, 23, 44-65 (1941).—The number of arrangements of atoms A and B on the lattice points, which have a given number of pairs of nearest neighbours of type AA, is given by the idea of probability. In consequence, the free energy formulae are written down explicitly. (1) The superlattice problems of various lattice types and at arbitrary concns. can be treated by the application of one simple and general method. (2) The relation assumed as the basis of the "Quasichemical method" (1) can be obtained as the result of a purely mathematical process. (3) The results of Bethe, Bragg-Williams, and several other investigators can be derived from the author's free energy formulae. Author.

Silicon monoxide. II. The change of silicon monoxide by heating. H. Inuzuka. *Mazda Kenkyu Jiho*, 15, 199-210 (1940).—The sample is heated to 50-1450° and cooled. It is then mixed with a colloidal soln., allowed to attach to silk-thread and dried. The change of the sample thus treated is examd. by X-ray diffraction. Electron diffraction patterns of the samples heated to 50-1000° are also examd. It was found that the interior of the sample heated above 600° turns into cristobalite and its surface is like amorphous silica. J. C. L.

Studies on explosion reaction. The reaction between carbon monoxide and oxygen. I. W. Jono. *This Journal*, 15, 17-30 (1941).

Studies on fluorine at low temperatures. XI. Reaction of fluorine and oxygen by a glow discharge at low temperatures. S. Aoyama and S. Sakuraba. *J. Chem. Soc. Japan*, 62, 208-213 (1941).—Preliminary expts. Photochemical reactions between liquid OF_2 and O_2 ($OF_{2(l)}$)

$+O_{2(l)}=O_3F_{2(s)}$, or $2CF_{2(l)}+O_{2(l)}=2O_2F_{2(s)}$ slightly change the colour of the mixed liquid. Main expts.—According to Ruff's expts., only O_2F_2 (solid) was produced by the reaction of fluorine and oxygen by a glow discharge at low temps.; while in the present case the same expts. yielded besides O_2F_2 (solid) a new oxygen fluoride O_3F_2 (solid) formed by photochemical reaction of liquid fluorine and oxygen. The relative yield of O_2F_2 and O_3F_2 depends upon the conditions of the reaction vessel used, the temp. of vessel, the discharge voltage, the gas press. as well as the duration of the discharge. The mixt. of $O_2F_{2(s)}$ and $O_3F_{2(s)}$ which has been prepared by the above mentioned expts. decomposes into $O_2F_{2(s)}$ and $O_{2(g)}$ by the irradiation of ultra-violet ray at the temp. of liquid nitrogen. Authors.

Studies on the organic molecular compounds. I, II. The influence of nitro radicals and second substitution radicals on the formation of the aromatic-nitroaromatic molecular compounds. C. Shinomiya. *Bull. Chem. Soc. Japan*, 15, 92-103, 137-147 (1940).—Organic molecular compd.-formation is discussed by means of solid-liquid phase diagrams. The compd.-formation and its stability generally decreases in the order: congruent type > incongruent type > simple eutectic type. As to the first type, the sequence of compd.-formation is conveniently discussed with the value of "melting point elevation". Binary systems of naphthalene, naphthols and naphthylamines with various aromatic nitro compds. are treated, and the predominant tendency to compd.-formation seems to be affected by the structure of both components. The compd. ratio is mostly 1:1. α -Compd. has a greater tendency to form mol. compd. than the corresponding β -isomer, while naphthalene shows an intermediate value. The reactivity of nitro compds. is in the decreasing order: trinitro, dinitro, mononitro compds. The decreasing effectiveness of second substitution radicals in symtrinitro compds. is in the order: (H), OH,

NH_2 , CH_3 , Cl , OCH_3 , OC_2H_5 ; in 2, 4-dinitro compds. it is in the order: CO_2H , Cl , OH , Br , CH_3 , (H) , OCH_3 , NH_2 ; and in mononitro compds.: CO_2H , CHO , Cl , Br . The tendency of isomeric nitro compds. to form mol. compds. is compared. The sequences are for trinitro-benzenes: sym- \rightarrow asym- or vic-compd.; for dinitrobenzenes: p- or m- \rightarrow o- compds.; for dinitrophenols or -toluenes: 2,4-, 2,5-, or 3,5- \rightarrow 2,6- \rightarrow 2,3- or 3,4-compd. The comparison indicates that ortho-substitution somewhat hinders the mol. compd.-formation. The aromatic-nitroaromatic combinations show halochromism. The latter is affected by substituents in the order: NH_2 \rightarrow OH \rightarrow (H), OCH_3 , CH_3 ; α - \rightarrow β -position; o- or p- \rightarrow m-position. The mol. ratio, melting point and colour of the isolated compds. are noted together with the phase diagrams.

Author.

Antioxygenic effects of some nitroso compounds. An interpretation of the effects from the view point of resonance. Y. Tsuzuki and Y. Kimura. *Bull. C. S. J.*, 15, 484 (1940).—It was found that aromatic nitroso compds. show more or less strong antioxygenic activity on the autoxydation of benzaldehyde exposed to atmospheric oxygen. The comparative studies of the antioxygenic activities of several p-substituted nitrosobenzenes show that the order of the effects of the substituents is I \rightarrow Br \rightarrow Cl \rightarrow CH_3 \rightarrow H , which coincides with the sequence of the o, p-directive forces of groups in aromatic substitution. Hence it is suggested that the antioxygenic activity depends on the resonance of the nitroso compds.

Authors.

Behaviour of cellulose fibre in alkali solutions. XVIII—XX. G. Saito. *J. Soc. Chem. Ind. Japan*, 43, 466-471 (1940).—XVIII. **Inhomogeneity of cellulose fibre.** The swelling property of single fiber of natural ramie is examd. The different parts of the same single fibre differ in the swelling property, indifferent of the

thickness, as in all the natural cellulose fibres. Comparison between the swelling curve of benberg silk and that of ramie leads to the conclusion that the type of the max. indicates the inhomogeneity of the single fibre. Similar inhomogeneity is expected in the quantity of alkali taken up, the heat evolved, and the X-ray diagram. XIX. **The disintegration degree of cellulose and the relation between the internal structure and the quantity of alkali taken up or the swelling degree.** The quantity of alkali taken up by cellulose is different according to the species of the fibre and its polymerisation degree. This fact is explained by the degree of its resistance against swelling. Namely, cellulose has an affinity for alkali and at the same time is resistant to it. XX. **The reaction between cellulose and alkali.** In the reaction between cellulose and alkali, the linear part of the curve showing the quantity of NaOH taken up and the max. point at the curve of the swelling degree are observed. The quantity of alkali (A) is taken to be a function of the concn. of alkali (C), temperature (T) and the swelling resistance (K) of the fibre, etc. The relation in the case when one or two of the variables are const. is explained with the expt. data and the graphs. As A is in a causal relation to the swelling degree Q , the relation between K , C , T and Q can be obtained.

J. C. L.

On dissolving velocity of glass in basic or acidic solution and water. S. Nagaeia. *J. J. Ceramic Assoc.*, 49, 139-143 (1941).—On this subject the author has deduced a theoretical conception regarding the process as a case of solid-liquid reaction and has tried a few expts. The relation between the quantity of the dissolved matter (x) in unit area of glass (mainly soluble alkaline substances extracted from the glass surface) and the time (t) at const. temp. is expressed by the following formulae under the assumption of the growth of hydrosilica gel layer on the glass surface: $t = k + \frac{1}{k}$

$\ln\left(1 + \frac{x}{C_0}\right)$ in alkali soln.; $t = \frac{1}{k} \left[C_0 \ln\left(\frac{C_0}{C_0 - x}\right) - x \right]$ in acidic soln.; $t = \frac{1}{k} \cdot x^2$ in water, where k is zero or const.; K is const. in relation to the glass composition and dissolving process; C_0 is the initial concn. of the soln. Author.

The velocity of reduction of silver chloride by hydrogen and deuterium.

F. Ishikawa and K. Yoshimura. *Bull. Inst. Phys. Chem. Research*, 20, 201-208 (1941).—The velocity of reduction is studied at 370-440° by measuring the press. incr. at const. volume, using a large excess of AgCl. The reaction occurs between AgCl and the adsorbed hydrogen (or deuterium), and is retarded by the strongly adsorbed HCl. The velocity may be expressed by the following equation: $-dp_{N_2}/dt = k \frac{p_{H_2}}{1 + Bp_{HCl}}$, in which p is the press. and B is the const. By integrating the above expression, $k = 2.303 (1 + p_0 C) k_m - Cv$ where $k_m = \frac{1}{t} \log \frac{p_0}{2p_0 - p}$, $v = \frac{p - p_0}{t}$, and p_0 is the initial press. of H₂ or D₂. The exptl. results show a linear relation between k_m and v . From the inclination of these straight lines the const. C may be evaluated and the velocity const. k calcd. From the values of k , the heat of activation is calcd. and discussed. Authors.

Studies on the reactions in solid state at higher temperatures. VI. The reaction between calcium oxide and stannic oxide in solid state. Y. Tanaka.

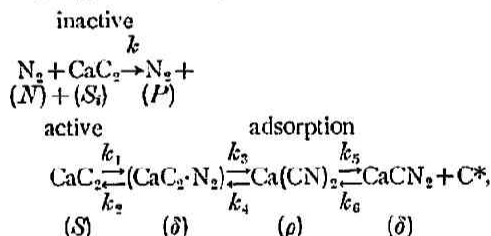
J. Chem. Soc. Japan, 62, 199-203 (1941).—It is confirmed that there exist two addn. compds, CaO·SnO₂ and 2CaO·SnO₂, between calcium oxide and stannic oxide. The crystal structure of CaO·SnO₂, which has been considered as cubic, should correctly be assigned as rhombic with a unit cell size of $a = 3.93\text{Å}$, $b = 3.99\text{Å}$ and $c = 3.87\text{Å}$.

At the early stage of the solid reaction of this system, the product is a solid soln. between CaO·SnO₂ and an excess of SnO₂,

and as the reaction proceeds the compn. of the solid soln. tends gradually to CaO·SnO₂. When an excess of CaO is present, 2CaO·SnO₂ is formed by a further reaction between CaO·SnO₂ and CaO. It is concluded that the reaction is controlled by the diffusion of the two components through the reaction product. The energy of activation of the diffusion process of CaO·SnO₂ formation 950-1100° is estimated to be 85.0 Kcals. per mole. Author.

Studies on reactions between gas and solid. VII. Nitrogenation of calcium carbide and the kinetic discussion. T. Aono.

Bull. C. S. J., 16, 91-98 (1941).—In explaining exptl. results of the nitrogenation of calcium carbide, the author proposes the following scheme: activation of carbide, adsorption of N₂ on its active surface, formation of adsorption compd. and then of Ca(CN)₂ temporarily, and final change of Ca(CN)₂ into CaCN₂ and C.



where $N, S, P, \delta, \rho,$ and δ denote individual concns., and k, k_1, \dots, k_6 , the reaction velocities. For const. temp. and press. S becomes

$$S = \frac{S_{t_0}}{k_1 P - k} \cdot e^{-kt} - \left(\frac{S_{t_0}}{k_1 P - k} - S_0 \right) \cdot e^{-k_1 P t}$$

and the velocity of nitrogen fixation

$$\frac{dN}{dt} = \frac{k_1 (k_3 - k) P S_0'}{K - k} \cdot e^{-kt} - \frac{k_1 P (k_3 - k_1 P) (S_0' - S_0)}{k_2 + k_3} \cdot e^{-k_1 P t} - (k_1 P + k_2) \left\{ \delta_0 - k_1 P \left(\frac{S_0'}{K - k} - \frac{S_0' - S_0}{k_2 + k_3} \right) \right\} e^{-kt}$$

where S_{t_0} and S_0 denote the values of S_t and S at $t=0$, and $S_0' \equiv S_{t_0}/(k_1 P - k)$. After a sufficient time $-\frac{dN}{dt} = \frac{k_1 k_2 P S}{k_1 P + k_2 + k_3}$, and for changing press. at const. volum v ,

$$\frac{dP}{dt} = \frac{P}{\left(\frac{v}{k_3 S}\right)P + \left(\frac{k_2 + k_3}{k_1 k_3 S}\right)v} = \frac{P}{aP + b}$$

The agreement of these eqs. with the exptl. results is discussed and the heat of activation for the adsorbed N to react on CaC_2 to form $\text{Ca}(\text{CN})_2$ is also calcd. Author.

Reactions in solid state between calcium oxide and different preparations of titanium dioxide. J. Arvid Hedvall and Karl Andersson. *Se. P.*, 38.

210-217 (1941).—The reactions in the solid state between different modifications of TiO_2 (anatase and rutile) and CaO were carried out. It was found out that the anatase modification is more reactive than rutile, especially at temps. at which anatase is transformed into rutile. Impure rutile mineral will react still better, if reactive Fe_2O_3 is present as the impurity. The reaction product consists of CaTiO_3 . Comparative expts. carried out in air, N_2 and H_2 , show no difference in the reaction yield. Authors.

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

On the interaction of mesons with radiation fields. M. Kobayasi and R. Utiyama. *Proc. Phys.-Math. Soc. Japan*, III, 22, 882-898 (1940).—In the present paper the transition probabilities of two elemental processes: the scattering of a photon by a meson and the creation of a pair of positively and negatively charged mesons by two photons are examined. From the results obtained, the cross section for the 'Bremsstrahlung' of mesons and the creation of meson pairs by γ -rays in the static field of a nucleus according to the method of impact parameters are estimated. J. C. L.

γ -Ray emitted from Rn and MsTh-I and their daughter elements. J. Itoh and Y. Watase. *Proc. Phys.-Math. Soc. Japan*, III, 23, 142-159 (1941).— γ -ray emitted from radioactive elements of Th and Ra series is investigated by means of a magnetic spectrometer. The relative intensities of several strong γ -rays whose existence has been already confirmed by internal conversion β -rays are detd. directly. From these values and the absolute intensities of conversion β -rays the internal conversion coeffs. are calcd. By comparing them with the theoretical values obtained by Hulme the nature

of radiations, whether of dipole or of quadrupole, is deduced. In the case of Th series, improved level schemes for ThC and ThC' and ThD are proposed in connection with β - and α -transformations. Authors.

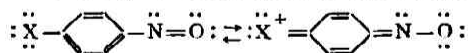
Optical energy-levels of Cu^+ . Y. Yamamoto. *Proc. Phys.-Math. Soc. Japan*, III, 22, 1048-1052 (1940).—The numerical values of the intervals between optical levels are computed for the configurations $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^9$, $4s$, $5s$, $6s$ and $7s$ of Cu^+ , according to the general expression of energy-levels derived by Araki and Yamamoto in the previous paper. The self-consistent field radial functions computed by Hartree and Hartree are used for $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$. Those of $4s$, $5s$, $6s$ and $7s$ are calcd. from Hartree and Hartree's core-functions by the numerical integrations. The agreement with expt. is satisfactory. Author.

Studies on the absorption spectrum of squalene. Z. Nakamiya and K. Koisumi. *Bull. Inst. Phys. Chem. Research*, 20, 141-149 (1941).—1. Squalene has no special selective absorption max. This fact coincides well with the fact that the structure of squalene is a chain, having no conjugated double

bond in it. The absorption bands of crude samples are caused by some impurities, which are removed by chromatographic treatment, using acid clay as an adsorbent. 2. When squalene is fractionally distilled under high vacuum, the earlier distillate has three well defined absorption bands, having absorption max. at 273, 283 and 296 $m\mu$. It has faintly lemon yellow colour and pleasant aroma and has oxygen in its composition. 3. The later fraction may be an isomer or polymer of squalene, having three absorption max. at 265, 276, 287 (heavy), 296 $m\mu$ (weak), quite different from the earlier fraction. 4. The earlier distillate of pristan has also three absorption max., but these are narrow and quite different from the above two.

Authors.

The absorption spectra of substituted nitrosobenzenes. II. The relation between the resonance effect of the substituent and its directive force in aromatic substitution. Y. Tuzaki, T. Uemura, and N. Hirasawa. *J. Chem. Soc. Japan*, 62, 85-87 (1941).—It was found that the absorption spectra of the ultra-violet range (about 3500-2500 \AA) of *p*-halogen-nitrosobenzenes (alcohol soln.) are deeper in colour than those of nitrosobenzene (in the order of $I > Br > Cl$) and that the *p*-substituent is greater in colouring effect than the *o*-substituent. That *p*-halogen-nitrosobenzene is deeper in colour than nitrosobenzene is probably due to the strong resonance effect of the former.



There holds a parallel relation between the *o*- and *p*-directive forces of the substituents and the colouring influence on nitrosobenzene; hence it is concluded that the intensity of the resonance effect is also in the order of $I > Br > Cl$.

J. C. L.

Fluorescent substances. VIII. Fluorescence spectrum of the substances of ZnO·SiO system. Y. Uehara and U. Ume-kawa. *Mazda Kenkyu Jihō*, 15, 199-210

(1940).—The energy distribution of the fluorescence spectra of zinc silicate contg. W, Mo, Pb, U, Sb, Ta, Ti, Mn, Al, Sn and Bi as activators is accurately examd. It is ascertained that the fluorescence spectra are not affected by any element contd. and their mech. are theoretically interpreted. When As, Cr, Zr, Th, Co, or Ge is used as activators, faint fluorescence appears and its spectrum is similar to that of the above mentioned case. In the case of V, fluorescence is not observed. It is also shown that the constitution of a fluorescence substance markedly affects the intensity of fluorescence.

J. C. L.

The photoelectric emission from oxide coated cathode and the exact determination of its workfunction. E.

Nishibori, H. Kawamura, and K. Hirano. *Proc. Phys.-Math. Soc. Japan*, 23, 37-43 (1941).—The photoelectric workfunction of BaO, SrO and their 50% solid soln. activated by the usual way was detd. by measuring the spectral sensibility curves. The spectral sensibility curves do not intersect with the frequency axis, but approach it exponentially. These exponential part incr. with the temp. of the cathode, and it seems to disappear at 0°K. The authors detd. the threshold value extrapolating to 0°K, to be 1.63, 2.58 and 1.66 eV for BaO, SrO and their solid soln. (BaSrO) resp. From the stand point of modern theory of solid the thermo-ionic workfunction ψ_T and the photoelectric workfunction ψ_P of semi-conductor are different and there are relations $\psi_T = \frac{E}{2} + \phi$

$$\psi_P = E + \phi$$

where E is the energy required to excite the electron in impurity level to conduction band and ϕ is the workfunction detd. previously by the authors for BaO and SrO. Hence ψ_T 's are found as follows: BaO 0.97, SrO 1.44, BaSrO 0.98, which appear to be reasonable. It is very interesting that the workfunction of BaO and solid soln. of BaO and SrO are almost equal.

Authors.

Studies on the photoconductivity of semi-conducting layers composed of some heavy-metal sulphide or selenide.

III. The relation between the structure and the photoconductivity of some layer composed of bismuth sulphide.

C. Asai. *Bull. Inst. Phys. Chem. Research*, 19, 1403-1418 (1940).—Among several kinds of artificially made thin layers of bismuth sulphide, which are different in microscopic structure and photoconductive properties, the one composed of Bi_2S_3 crystal contg. excess metallic bismuth as impurity shows the largest photoconducting effect. When a composite layer is made by suitable superposition of the thin layers mentioned above, semi-conductor (the resistance of the sample was $10^7 - 10^{10}$ of the order) with excellent photoconductive properties is obtained which is suited to the amplification of the photocurrent by a vacuum-tube amplifier. The sensitivity of the composite layer is further improved by heat treatment and other after-treatments, and the cause is ascribed to the incr. of the concn. of the excess bismuth atoms in the Bi_2S_3 crystal. Thus the photoconductivity is considered to be due to the impurity of bismuth atoms in the crystal. The composite layer, when suitably treated, shows an enormous current sensitivity, with spectral selectivity maxima in the extreme red (7100-7600Å) and the near infra-red (9100-10100Å) regions.

Author.

Studies on the metallic complexes coordinating hydroxy-compounds. V.

Rotatory dispersion of tartaric acid-copper-alkali complexes.

M. Kubota. *J. Chem. Soc. Japan*, 62, 90-92 (1941).—When the optical activity of d-tartaric acid-copper-alkali complex in soln. is dextro rotatory, the activity in the rotatory dispersion rapidly increases as the wave length approaches to the end-absorption band. On the contrary, when the activity of the complex is leavo rotatory,

as when the compn. of the soln. is d-tartaric acid 0.01, copper sulphate 0.01, caustic soda 0.037 mol/l. the rotatory power scarcely changes as the wave length approaches to the end-absorption. These facts show that there are fundamental differences between the rotatory powers of the two solns. In the former case the rotatory power is surely due to the activity of d-tartaric acid mol. and in the latter case it is due to the activity of asymmetric structure of the complex radical. In this way the author's explanation in the fourth report of this study is proved. **VI. Optical activities of mannitol-copper-alkali complexes.** *ibid.*, 93-95 (1941).—The relation between rotatory power and compn. of various mannitol-copper-alkali complex solns. is observed. Also the rotatory dispersion of mannitol and mannitol-copper-alkali complex is measured. From the results upon d-tartaric acid and mannitol, it was found that in the optically active substance whose rotatory power increases in leavo rotation as the wave length approaches to its absorption band it increases in dextro rotation as the wave length approaches to the special absorption band of the complex, and vice versa. **VII. Formation of complex salts having alkali metals as central ion.** *ibid.*, 214-219 (1941).—Light absorption of aq. solns. of mannitol and glycerin with caustic alkali in high concn. was measured, and two absorption bands, frequency $85 \times 10^{13} \text{ sec}^{-1}$ and $112 \times 10^{13} \text{ sec}^{-1}$, are found. The former absorption band is the so-called second absorption band of metallic complex, due to the coordination centering alkali ion, and the latter is the absorption band due to the combination of oxygen atom of -OH group. In the case of glucose and caustic soda, two absorption bands are clearly observed. It is also observed that ethylacetate, acetylacetone, or acetanilide with sodium ethylate in absolute alcohol form alkali metal complexes.

Author.

3-ELECTROCHEMISTRY AND THERMOCHEMISTRY

Electrolysis and diffusion. S. Kaneko. *Bull. Electrotech. Lab.*, 5, 86-87 (1941).—The change of concn. on the electrode surface by electrolysis when the electrolyte is stirred is considered from Fick's law. Author.

Calculation of pH in buffer solution on the basis of Debye-Hückel's theory. H. Nukuda. *J. Pharmaceutical Soc. Japan*, 60, 605-613 (1940).—Since the buffer soln. is in general a weak acid and its salt, the ionization in uni-valent acid is $HA \rightleftharpoons aH^+ + aA'$, $K = \frac{[aH^+][aA']}{[aHA]}$ or $P_{aH} = P_K - \log \frac{[aHA]}{[aA']}$
 $= P_K - \log \frac{[HA]}{[A']}$ — $\log \frac{f_{(HA)}}{f_{(A)'}}$. In bi-valent acid it is $H_2A \rightleftharpoons aH^+ + aHA'$, $aHA' \rightleftharpoons aH^+ + aA''$, $K_1 = \frac{[aH^+][aA'']}{[aHA']}$ or $P_{aH} = P_{K_1} - \log \frac{[aHA']}{[aA'']}$
 $= P_{K_1} - \log \frac{[HA']}{[A'']}$ — $\log \frac{f_{(HA')}}{f_{(A'')}}$. The term of $\log f$ denotes activity coeff. of ion and was derived by Debye-Hückel from the thermodynamic standpoint as follows: $RT \ln f = -\frac{N_{av}\epsilon^2 Z_i^2}{2D} \cdot \frac{x}{1+ax}$ or $\log f = -\frac{1}{2.303} \cdot \frac{\epsilon^2 Z_i^2}{2DKT} \cdot \frac{x}{1+ax} = -h \frac{Z_i^2 \sqrt{\mu}}{1+g\sqrt{\mu}}$, where $\frac{R}{N_{av}} = K$, $h = \frac{1}{2.303} \cdot \frac{\epsilon^2 g}{2DKT}$, Z_i = valence of ion. a = average ionic diameter, μ = the total ionic strength $\frac{1}{2} \sum c_i Z_i^2$. As the value of a Cohn gives 5×10^{-8} cm, and Kolthoff $(4-6) \times 10^{-8}$ cm, although a varies with the kinds and concns. of ions. The author used $a = 5 \times 10^{-8}$ cm. applying the term of $\log f$ of Debye-Hückel's eq. to the P_{aH} eq., he calcd. the P_{aH} in buffer soln. of $\frac{m}{15} KH_2PO_4$; $\frac{m}{15} K_2HPO_4$; $\frac{m}{10} CH_3COOH$; $\frac{m}{10} CH_3COONa$ and $\frac{m}{10} NaOH$; $\frac{m}{10} KH$ -Phthalate in each of various mixts. These results were in good agreement with those of Sørensen, Kolthoff, Clark-Lubs and Michaelis. By dilution of a buffer soln. its P_{aH} varies with the change of the ionic strength; ΔP_{aH}

$= P_{aH_2} - P_{aH_1} = \log \frac{f_1(HA)}{f_1(A')} - \log \frac{f_2(HA)}{f_2(A')}$ for uni-valent soln., $\Delta P_{aH} = P_{aH_2} - P_{aH_1} = \log \frac{f_1(HA')}{f_1(A'')} - \log \frac{f_2(HA')}{f_2(A'')}$ for uni-bivalent soln. From these considerations, calcs. are carried out for buffers of $\times 5$, $\times 10$ and $\times 50$ dilutions. Author.

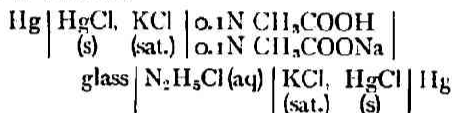
The degree of dissociation of xanthate solutions. S. Komagata. *Bull. Electrotech. Lab.*, 5, 240-241 (1941).—The conductivities of potassium ethylxanthate and potassium amylxanthate, which are collectors in the flotation method, are measured in the concn. range from 0.05 to 5.0 g./L.; hence, the degree of dissocn. Both the diluted solns. dissociate almost 100%, but as the concn. increases, the degree of dissocn. falls; 86% and 46% are the const. values for potassium ethylxanthate and potassium methylxanthate resp. J. C. L.

On the dissociation constant of hydroxylamine. H. Hagiwara. *Bull. Inst. Phys. Chem. Research*, 20, 251-255 (1941).—Hydrolysis const. of hydroxylamine hydrochloride is detd. at 25° by means of a glass electrode, measuring the pH values of the solns. of various concns. The results may be expressed by $pH = \frac{1}{2} pK_a - \frac{1}{2} \log (Cf_H - a_H) f_{NH_4O}$ in which K_a is the hydrolysis const., C is the analytical concn. of hydroxylamine, a_H is the activity of hydrogen ion, and f_H and f_{NH_4O} are the activity coeffs. of hydrogen and hydroxylamine ions. The mean value of K_a is found to be 1.04×10^{-6} . Hence the dissocn. const. of hydroxylamine based on activity units is $K_a = 0.97 \times 10^{-6}$. On the other hand, the distribution equilibrium of HCl between ammonia and hydroxylamine is studied at 25° by the same method. From the results the dissocn. const. of hydroxylamine is found to be $K_a = 0.87 \times 10^{-6}$, using a value

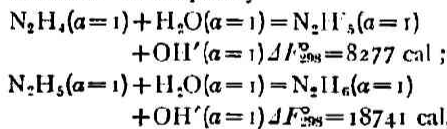
$K=1.8 \times 10^{-6}$ as the dissocn. const. of ammonia. The mean value $K_a=0.92 \times 10^{-6}$ may be taken as the dissocn. const. of hydroxylamine.

Author.

On the dissociation constants of hydrazine. N. Yui. *Bull. Inst. Phys. Chem. Research*, 20, 256-263 (1941).—The dissocn. const. of hydrazine are detd. by means of a glass electrode at 25°C, measuring the pH value at each stage of titration of hydrazine monohydrochloride solns. with sodium hydroxide and hydrochloric acid. The cell used is as follows:



From the result of titration with sodium hydroxide the first dissocn. const. is computed as 7.96×10^{-7} , 8.94×10^{-7} and 8.99×10^{-7} resp. and the mean value 8.63×10^{-7} is adopted. On the basis of the result of titration with hydrochloric acid the second dissocn. const. is found to be 1.80×10^{-14} and 1.91×10^{-14} and the mean value 1.86×10^{-14} is obtained. Consequently



Author.

The specific heat and dissociation heat of ammonium phosphate and the

atomic heat of nitrogen. S. Sato and T. Sogabe. *Bull. Inst. Phys. Chem. Research*, 19, 861-867 (1940).—The mean specific heat of $\text{PO}_4\text{H}_2(\text{NH}_4)$, $\text{PO}_4\text{H}(\text{NH}_4)_2$, and $\text{P}_2\text{O}_5\text{H}_3(\text{NH}_4)_3$ detd. by an ice calorimeter at 0–99.6° are 0.3089, 0.3408 and 0.3309 resp. The disparity of the former two gives the molecular heat of NH_3 ; when the atomic heat (2.4) of hydrogen is subtracted from it, the value of 2.27 is obtained as the atomic heat of nitrogen. This value is smaller than the mean value (3–4) which the authors have obtained by various methods. This can be explained by the general relation that the atomic heat is small in case the atomic weight of the other element taking part in the reaction is small. From the said values of the specific heat and the value of the dissocn. press. of $\text{PO}_4\text{H}(\text{NH}_4)_2$, the dissocn. heat at 25° are thermodynamically calcd. as follows: $\text{PO}_4\text{H}(\text{NH}_4)_2 = \text{PO}_4\text{H}_2(\text{NH}_4) + \text{NH}_3$, –18.5 Cal.

J. C. I.

On the change in specific heat on melting. I. Osida. *Proc. Phys.-Math. S.c. Japan*, III, 23, 205-207 (1941).—Using Mott's formula for the change in interatomic frequency on melting (*Proc. Roy. Soc.*, 146, 465 (1934)) the author calcd. the difference of specific heats in the liquid and the solid phases at the melting temp. The values for A, Hg, K, Na, H_2 and H_2O were found to have the right order of magnitude.

Author.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

Preparation of gold sol. T. Kanai and I. Inoue. *Juzen*, 45, 1982-1986 (1940).—Gold sol was prepared by a compromise between Lange's method and Miller's improved one. 200 c.c. of distilled water is heated to 60°, to which 2.0 c.c. of a gold chloride soln. and 1.5 c.c. of 2.0% potassium carbonate soln. are added. It is heated to 90° and then about 2.0 c.c. of 1.0% formalin

soln. is rapidly added and shaken. The sol thus obtained is transparent and the transmitted light shows crimson colour, which is fluorescent and appears slightly brownish crimson by reflected light.

J. C. L.

Study on rhythmic precipitates.
II. Theory of its formation. A. Yanagihara. *Bull. Inst. Phys. Chem. Research*,

19. 1432-1439 (1940).—The formation of rhythmic ppts., and qualitative relations between periodical intervals, and the reaction product or concs. of inner and outer electrolytes are discussed mathematically. Generally, pptn. occurs periodically in a gel, when it is supersatd., but it does not take place when only very slightly supersatd., excepting such a case as satisfies the formula (11) in the original report. Rhythmic intervals depend upon the value of H/u_0v_0 , where H is the reaction product ($H \geq L$, L is the solubility product.) and v_0 , u_0 , concs. of inner and outer electrolytes resp. Author.

On the critical condition for the drop formation and the capillary condensation. I. Higuti. *Bull. Inst. Phys. Chem. Research*, 20, 130-136 (1941).—From the thermodynamical consideration there could be derived a formula, $\pm a\sigma = kT \ln P/P_0$, which would give a possible range and the critical limit of drop formation and capillary condensation. In the above expression a is the surface tension, a the surface area occupied by a single molecule, k the Boltzmann const., P_0 the vapour press. at temp. T , P the vapour press. under which the considered phenomena can occur. Volmer and Flood (1934) have detd. exptly. the critical relative press. under which supersatd. vapour began to form drop nucleus. Their exptl. values are 0.421, 3, 2.34, 3.05, 2.80, 4.60, 6.05, and 8.6-12.3 for H_2O , CH_3OH , C_2H_5OH , $n-C_3H_7OH$, $i-C_3H_7OH$, $n-C_4H_9OH$, CH_3NO_2 , and $CH_3COO-C_2H_5$ resp. The above formula gives 3.77, 2.11, 2.62, 3.41, 3.17, 4.08, 4.94 ad 7.02 resp. Again, the capillary condensation has been found by Volmer and Flood to commence at relative press. 0.171, 0.142, 0.141, 0.484, 0.375, 0.347, 0.325, 0.232, 0.176, 0.221, 0.145, 0.184, 0.231, 0.320, 0.231, 0.301, 0.412, and 0.263 for C_6H_6 , C_6H_5Cl , $C_6H_5CH_3$, CH_3OH , C_2H_5OH , $n-C_3H_7OH$, $i-C_3H_7OH$, $n-C_6H_{14}$, $n-C_7H_{16}$, $CH_3COOH-C_2H_5$, CCl_4 , $CHCl_3$, CH_2Cl_2 , $(C_2H_5)_2O$, CS_2 , H_2O , NH_3 , and SO_2 . These results are in fairly good agreement with the

authors exptl. values: 0.138, 0.089, 0.115, 0.506, 0.375, 0.298, 0.300, 0.203, 0.185, 0.177, 0.146, 0.203, 0.240, 0.282, 0.198, 0.295, 0.375, and 0.276. Author.

Studies on the oiliness of liquids.

X. The friction coefficients of mono- and multi-molecular layers. T. Isemura. *Bull. C. S. J.*, 15, 467-474 (1940).—The static friction coeffs. of the glass surfaces covered with mono- and multi-molecular layers of some long chain acids are measured. The friction coeffs. of the glass covered with monomolecular films of acids are about one tenth of clean glass. The friction coeffs. of alcohols and esters are somewhat larger, but fluctuate considerably. The friction coeffs. of multimolecular layers are decreased by the increase of their thickness until it becomes 5-7 molecular layers, beyond which there is no further reduction. The effect of compression during the deposition of the film is also investigated. The film deposited in high compression state shows low friction coeff. The force area relations of stearic acid monolayer are studied with freshly distilled water, tap water, and the tap water added with ammonium oxalate, in relation to the transference of the film on a glass plate.

J. C. L.

Orientation of Mo crystals deposited on NaCl crystal. S. Shirai. *Proc. Phys.-Math. Soc. Japan*, III, 23, 12-18 (1941).—The orientation of Mo crystals in a thin film deposited on the NaCl cleavage plane by evaporation *in vacuo* was investigated by the method of cathode ray transmission. NaCl crystals used as the substrate were heated to $T^\circ C$ and then cooled slowly to $t^\circ C$ and at this temp. Mo films were prepd. In all the orientations which Mo crystals could take under these conditions, a face diagonal of the Mo cube was always parallel to an edge of the NaCl cube. The min. temp. t_0 , at which strong patterns due to oriented Mo crystals were obtained, incred. as T incred. up to $520^\circ C$ and then decred.

for a further incred. T . At a temp. higher than 520°C , white sublimates were deposited on the cooler part of the evaporation tube. Among the diffraction patterns obtained, the C-type $\{(001)_{\text{Mo}} \parallel (001)_{\text{NaCl}} \text{ and } [100]_{\text{Mo}} \parallel [110]_{\text{NaCl}}\}$, the D-type $\{(110)_{\text{Mo}} \parallel (001)_{\text{NaCl}} \text{ and } [001]_{\text{Mo}} \parallel [100]_{\text{NaCl}} \text{ or } [010]_{\text{NaCl}}\}$ and the G-type $\{(331)_{\text{Mo}} \parallel (001)_{\text{NaCl}} \text{ and } [110]_{\text{Mo}} \parallel [100]_{\text{NaCl}} \text{ or } [010]_{\text{NaCl}}\}$ patterns were strong in intensity. The strong C-type orientation was obtained when the temp. T was lower than 520°C and the strong C-type, D-type and G-type orientations were obtained when T was higher than 520°C . In the latter case, the strong D-type and G-type orientations occurred in a range of lower temp. of t and this range became broader as T got higher. The arc lengths of the spots of C-type pattern were longer than those of the D-type and the G-type patterns and the arc length of the spot of each type pattern became longer when t was lower. A qualitative explanation for a part of these exptl. results is also given. Author.

On the sorption of phosgene by active charcoal. I. The sorption isotherm. K. Arai and S. Fujita. *Bull. Inst. Phys. Chem. Research*, **20**, 209-217 (1941).—The sorption of phosgene by sugar charcoal activated by heating at 900° for two hrs. is detd. by a static method. The instrument used for the measurement was an all-glass app. which contained Jackson's glass spring manometer and McBain's quartz spring balance. 1. The sorption isotherms are detd. at 20° , 30° , and 40° over a range of press. of 50 mm—1 atm. The results obtained are in good agreement with Langmuir's eq. The following eqs. are derived from the exptl. data by the method of least squares:

$$a_{200} = \frac{12.529p}{1+0.0483p}, \quad a_{300} = \frac{10.349p}{1+0.0409p},$$

$$a_{400} = \frac{8.440p}{1+0.0345p}.$$

In the eqs., a is the sorption amt. expressed in mg per 1 g charcoal, and p is the equilibrium press. in mm Hg. 2. The empirical

eqs. for the isostere (relation between the equilibrium press. and absolute temp. at the const. amt. sorbed) are calcd. as follows:

$$\log p_{200} = 6.01035 - \frac{1222.82}{T},$$

$$\log p_{210} = 6.59460 - \frac{1364.71}{T},$$

$$\log p_{220} = 7.44610 - \frac{1580.87}{T},$$

$$\log p_{230} = 9.06035 - \frac{2011.08}{T}.$$

3. The following empirical eqs. hold for isobar (relation between the amt. sorbed and the temp. at const. equilibrium press.), $a_p = a_0 - Kt$, where a_0 is the amt. sorbed at 0° and K is the const. The values of a_0 can also be represented by Langmuir's eq., $a_0 = \frac{19.5496p}{1+0.071387p}$. The following relation between K and p is obtained, $K = \frac{k}{p^n}$, where $k = 2.9525$ and $n = 0.19514$; thus the general eq. for the system can be expressed as follows: $a = a_0 - kt/p^n$. 4. The differential isosteric heats of sorption are calcd. Author.

Studies on mixed gas of low hydrocarbons. V. Adsorption of a mixed gas. H. Uehara. *J. Chem. Soc. Japan*, **61**, 1149-1158 (1939).—The amount of a mixed gas, $\text{CH}_4 + \text{C}_2\text{H}_6$, $\text{CH}_4 + \text{C}_3\text{H}_8$, and $\text{CH}_4 + \text{C}_4\text{H}_{10}$, adsorbed by active charcoal made from sugar candy was measured by means of a spring balance and the ratio of the components in the remaining gas was detd. by means of an interferometer. It was found that the relation between the total press. of the mixed gas and the total adsorbed amt. obeys Freundlich's formula and that the ratio of the components is proportional to the ratio of partial pressures of the gaseous phase.

J. C. L.

Thermal analysis of the catalytic action of colloids. II. The effect of temperature and heat treatment of platinum sol upon the catalytic decomposition of hydrogen peroxides by

colloidal platinum. E. Suito. This Journal, 15, 1-16 (1941).

Cuprene. I—III. T. Aono. *J. Electrochem. Assoc. Japan*, 9, 108-115 (1941).— I. Heats of combustion, formation and polymerization of cuprene. From the exptl. observations, the following chem. eq. is proposed for the catalytic polymerization of acetylene of normal compn.: $6n\text{C}_2\text{H}_2 = (\text{C}_{12}\text{H}_{10})_n + n\text{H}_2$. The heats of combustion of cuprene of various compns. are measured, from which the heats of formation and condensation are calcd.: $12\text{C} + 5\text{H}_2 = (\text{C}_{12}\text{H}_{10}) + 36.6$ kcal., and $6\text{C}_2\text{H}_2 = (\text{C}_{12}\text{H}_{10}) + \text{H}_2 + 369.7 \pm 0.2$ kcal. II. On the poisoning effect of impurities in acetylene upon its polymerization to cuprene. The impurities in raw acetylene, such as PH_3 , NH_3 , N_2 , and air have no appreciable effect on the copper catalyst, while SH_2 is very injurious. III. The activity of copper catalyst and the mechn. of polymerization of acetylene to cuprene. The activity of copper catalyst of various form and origin is discussed, and from X-ray studies the mechn. of the cuprene formation is explained by the chem. adsorption of C_2H_2 on copper metal and polymerization to cuprene. With copper oxides, Cu_2O or CuO , the first stage is the reduction of the oxides by acetylene to Cu and not the formation of a compl. $\text{Cu}_2\text{O} \cdot \text{C}_2\text{H}_2$, as was formerly believed. Author.

On the catalytic decomposition of neutral salts with Japanese acid clay and other minerals. I. On the action of Japanese acid clay. K. Kobayashi and

H. Ishikawa. *J. Soc. Chem. Ind. Japan*, 44, 222-225 (1941).—Ten years ago, K. Kobayashi showed that HCl is evolved at relatively low temps., when the mixt. of Japanese acid clay and common salt are heated, but the yield of HCl was only 18% of the theoretical value. Recently, the authors have confirmed that the formation of HCl from NaCl is catalytically promoted on the surface of Japanese acid clay when the said reaction is carried out in the presence of steam and that the yield becomes approximately theoretical. It may be supposed that the residue consists of certain substances in which Na atom exists in the form of chemical combination with the mol. of the chief mineral constituent of the clay. The authors carried out the expt. with the natural and artificial colloidal clays and other minerals acting upon the chlorides of alkali and copper group metals. The reaction of NaCl -Japanese acid clay system and the imported decolorizing clay- H_2O system were studied in the const. stream of steam at the temps. from 300°C to 700°C , and the decompn. degrees were detd. by the titration of HCl evolved. It was found that the reaction takes place at such a low temp. as 300°C in this system, and above 500°C it is promoted remarkably. The reaction is completed at 700°C and the decompn. degree reaches almost 100 percent. The reactions below and above 500°C are very different from each other. It may be presumed that, at the lower temp., the catalytic decompn. of Na ion predominates, while at the higher temp. the reaction is mainly due to the chemical combination. Authors.