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The Self-diffusion of Chloride Ions in Nickel Dichoride Crystallites and an Isotopic Exchange Reaction between Chlorine Gas and the Crystallites

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The self-diffusion of chloride ions in the bulk of nickel dichloride crystallites was studied in the temperature range of 180—340°C in a carefully-evacuated vacuum system; the isotopic exchange reaction between gaseous chlorine and the crystallites was also studied. The activation energy for the migration of chloride ions was determined to be 1.01 eV (=23.3 kcal/mol). The exchange reaction proceeded with activation energies of 3.6 and 9 kcal/mol for the active and the less-active part of the surface first layer, 13 and 16 kcal/mol for the active and the less-active one of the second layer, and 21 kcal/mol for the third layer. (These activation energies converge to the value of the self-diffusion in the bulk.) The Θ-rule nearly holds good in the present case.1)

The correlation between the surface reactivities of solids and the surface-structures is a very interesting theme in the field of surface science. Verwey2) proposed that on the surface of ionic crystals, ions within the surface first layer change the degree of polarization and are displaced from the normal lattice position, in this way reducing their surface energies. Benson *et al.*3) and Anderson and Scholz4) extended this model by taking into consideration the relaxation of the first five layers in the crystal of alkali halides. The results of their calculation show that the several surface layers should be distorted.

The isotopic exchange reaction between crystal and gaseous molecules is one of the simplest surface reactions, and the method of this exchange reaction is very useful in the investigation of the self-diffusion of ions in crystals. Such reactions have been studied in the systems of NaCl/Cl$_2$,5,6,10,12) KCl/Cl$_2$,7,10) RbCl/Cl$_2$,8) and KBr/Br$_2$.9) Harrison and his co-workers5) have investigated mainly the surface-exchange reaction. Barr *et al.*9—11) and Laurent and Benard12) have studied mainly the self-diffusion in the bulk of the crystals, while Takaishi and the present author6—8) have studied that of chloride ions, along with the surface-exchange reaction, which shows, successively, the expected correlation between the surface structure and its reactivities of NaCl,6) KCl,7) and RbCl.8) However, there have been few studies of higher valent metal halide crystals, except for the self-diffusion study of the MnCl$_2$/Cl$_2$ system by the present author13) and

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1) G. M. Schwab, *Advan. Catal.* **20**, 251 (1950).

2) E. J. Verwey, *Rec. Trav. Chim.*, **65**, 521 (1946).

3) G. C. Benson, P. I. Freeman, and E. Dempsey, *Advan. Chem. Ser.*, **33**, 26 (1961); *J. Chem. Phys.*, **39**, 302 (1963). G. C. Benson and T. A. Claxton, *ibid.*, **48**, 1356 (1968).

4) P. J. Anderson and A. Scholz, *Trans. Faraday Soc.*, **64**, 2973 (1968).

5) L. G. Harrison, J. A. Morrison, and G. S. Rose, "Solid/Gas-Interface" Butterworths, London (1957), p. 287. L. G. Harrison, J. A. Morrison, and G. S. Rose, *J. Phys. Chem.*, **61**, 1314 (1957). L. G. Harrison, I. M. Hoodless, and J. A. Morrison, *Discuss. Faraday Soc.*, **28**, 103 (1959). R. J. Adams and L. G. Harrison, *Trans. Faraday Soc.*, **60**, 1792 (1964).

6) T. Takaishi and Y. Sensui, *Surface Sci.*, **19**, 339 (1970).

7) T. Takaishi and Y. Sensui, *Trans. Faraday Soc.*, **63**, 1007 (1967).

8) T. Takaishi and Y. Sensui, *ibid.*, **65**, 131 (1969).

9) L. W. Barr and D. K. Dawson, "Phyiscs and Chemistry of Ceramic Surfaces, Proceeding 5 (British Ceramic Soc.)," (1965), p. 77.

10) L. W. Barr, I. M. Hoodless, J. A. Morrison, and R. Rudham, *Trans. Faraday Soc.*, **56**, 697 (1960).

11) L. W. Barr, J. A. Morrison, and P. A. Schroeder, *J. Appl. Phys.*, **32**, 624 (1965).

12) J. F. Laurent and J. Benard, *J. Phys. Chem. Solids.*, **3**, 7 (1957).

13) Y. Sensui, This Bulleitn, **45**, 359 (1972).

the qualitative studies by Willard and his co-workers.[14]

In this paper, results of a study of the exchange reaction between chlorine gas and nickel dichloride crystallites will be presented as well as the results concerning the self-diffusion of chloride ions in the crystallites. This material was chosen for a reason similar to that in the case of manganese dichloride; that is, it is relatively easy to handle because of its layer structure, its relatively low volatility, and its surface homogeneity, presumed from the results of the krypton adsorption study by Larher[15] and from the electron-microscopic data (Fig. 1).

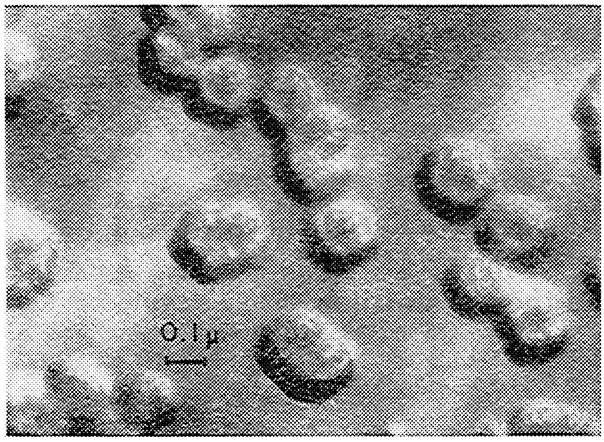

Fig. 1. The external shape of nickel dichloride crystallites used in the present experiment.

Experimental

Procedure. The apparatus used was the same as that described in the previous papers.[6-8] The system was all made of glass, except for two pieces of Teflon stopper in the circulation pump. The sample was dehydrated by baking at 60°C for about 10 hr in a vacuum. Then, the temperature was gradually raised to 200°C over 3 hr and kept at that temperature for about 7 hr. After this pre-baking, the system was sealed off from the main pumping line and thus made grease-free. Baking out at a temperature higher than 200°C was carried out with a Vac-Ion pump, which was isolated when the residual pressure was below 5×10^{-7} torr during the baking of the sample at 340°C.

Chlorine gas of a purity of 99.8%, contained in a glass cylinder (supplied from Takachiho Chemical Co.), was distilled and dehydrated by means of Linde-3A Molecular Sieves. The latter had been baked out prior to use in a vacuum of 5×10^{-7} torr at 400°C. This is a necessary procedure.[7] In the sealed-off vacuum system, purified chlorine gas was introduced, through a breakable seal, into a system containing carefully baked-out radioactive nickel dichloride crystallites. The reaction was followed by measuring the radioactivity of ^{36}Cl in gaseous chlorine, which was circulated by means of a circulation pump made of glass.[15] A thin-wall G.M. counter in a part of the system had a counting efficiency of 3% against 0.714 MeV γ-ray from ^{36}Cl.

Materials. Radioactive nickel dichloride was obtained by the isotopic-dilution method from radioactive hydrochloric acid which had been distilled in a vacuum and from nickel dichloride which had been prepared by a reaction between nickel sponge (Johnson-Matthey's spectrographically-standardised reagent, catalog No. J.M. 891) and distilled hydrochloric acid. The specific radioactivity of the resultant radioactive nickel dichloride was 5.2 μc/g. The precipitates of the radioactive dichloride were prepared by modifing Marshall's method[17] *i.e.*, by adding about 100 parts of distilled ethyl ether to one part of a saturated alcoholic solution of the dichloride. After the supernatant solution had been replaced with ethyl ether, the precipitates were transferred into the vacuum system. The crystallites were obtained by baking them out carefully by means of the procedure described above. The crystallites thus obtained have an even-grained external shape, as is shown in Fig. 1 and by the BET surface area of 26 m^2/g, which agrees with the geometric area calculated from the electron-microscopic data. This means that the crystallites are non-porous and that the roughness-factor of the surface is approximately unity.

Results and Discussion

Self-diffusion of Chloride Ions in the Bulk of the Crystallites. In the crystal of nickel dichloride with a $CdCl_2$ structure, chlorine atoms are arranged in cubic closest-packing, and a nickel atom occupies an octahedral hole made up of chlorine atoms, forming a sandwich-like layer of Cl–Ni–Cl, consisting of two adjacent layers of chlorine atoms with a layer of nickel atoms between them. Since the primary valencies of the nickel and chlorine atoms are satisfied within the sandwich-like layer, there being only van der Waals forces between adjacent layers, this may be regarded as a semi-infinite two-dimensional molecule in a first approximation.[18] However it should be mentioned that there may be some influences of nickel atoms on the configuration of adjacent chlorine layers, because of the cubic close-packed arrangement taking place in nickel dichloride crystals. Therefore, only on the basis of the structure of the crystal, we cannot predict that an anion vacancy migrates predominantly in either direction, either along or beyond the sandwich-like layer in the bulk of the crystal, by exchanging its site with the chlorine atom's. In the following paragraph, the experimental results on the self-diffusion of ^{36}Cl in the bulk of nickel dichloride crystallites will be described in some detail.

The mean length of the shorter sides of the crystallites used was estimated to be 0.06 μ from the electron-microscopic data (*cf.* Fig. 1); this corresponds to a few hundred layers in the direction along the *c*-axis of the crystal. In the present experiments, only the ^{36}Cl in the bulk of the near-surface region diffuses out into the gaseous phase and was measured; the region corresponds to less than 30 layers. Therefore, the diffusion data obtained may be analyzed on the basis of the model of semi-infinite media as a first approximation. For this model, the diffusion equation has the solution;[19]

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[14] M. Blau, W. T. Carnall, and J. E. Willard, *J. Amer. Chem. Soc.*, **74**, 5762 (1952). R. A. Howald and J. E. Willard, *ibid.*, **77**, 2046 (1955). J. R. Wilson and J. E. Willard, *J. Phys. Chem.*, **70**, 1665 (1966).

[15] Y. Larher, *ibid.*, **72**, 1847 (1968).

[16] T. Takaishi, *Shokubai (Catalyst)*, **9**, 127 (1967).

[17] F. G. Marshall, *Phys. Rev.*, **58**, 642 (1940).

[18] A. F. Wells, "Structural Inorganic Chemistry" Oxford University Press, Third Edition (1962).

[19] A. B. Lidiard and K. Thermaligam, *Discuss. Faraday Soc.*, **28**, 64 (1959).

$$X_g = X_s + 2\alpha(Dt/\pi)^{1/2}$$

where X_g designates the amount of ^{36}Cl diffused out into the gaseous phase after time t; X_s that of ^{36}Cl in the surface region which diffused out into the gaseous phase at the initial stage of the reaction; D, the bulk diffusion constant, and α, the product of the surface area and the initial concentration of ^{36}Cl. Denoting the measured counting rate by C, we obtain;

$$C = K\cdot X_g \text{ and } C_s = K\cdot X_s,$$

where K is the conversion factor. Thus we obtain;

$$C = C_s + \frac{2\alpha}{K}(Dt/\pi)^{1/2}$$

in which the value for C_s cannot be obtained directly from the experiments. The exchange process, it is expected, may be rate-controlled by the bulk-diffusion, and the curve of C against $\sqrt{t}$ may be linear, except in the initial stage. However, there are some ambiguities with regard to the start of the reaction. The measured time t must be corrected; namely, it is replaced by $(t+\delta)$, where the value for δ is determined empirically so as to give a linear curve. The results are given in Fig. 2, which the intersection of the straight line with the ordinate gives the value for C_s.

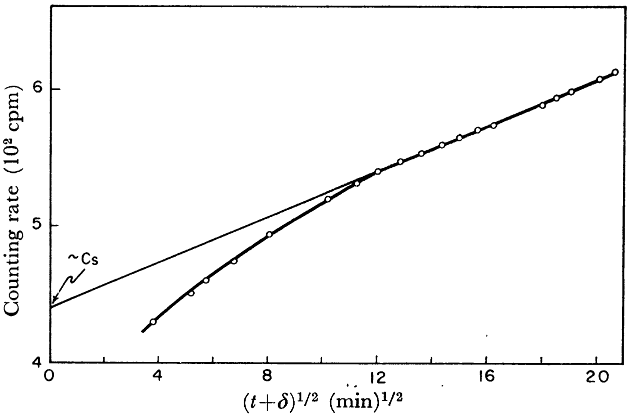


Fig. 2. The plots of C against the square-root of $(t+\delta)$. The data obtained from the specimen II at 180°C.

Next, we suppose that a first diffusion run is carried out at a temperature, T_1, for time t_1, in which the diffusion constant is D_1. If a second run is made at another temperature, T_2, for time t_2, in which the constant is D_2, the total counting rate, C, may be shown by;[19]

$$C = C_s + \frac{2\alpha}{K\sqrt{\pi}}(D_1t_1+D_2t_2)^{1/2}.$$

This may be extended to further runs and be rewritten as follows;

$$(C-C_s)^2 = \left(\frac{4\alpha^2}{\pi K^2}\right)(D_1t_1+D_2t_2+\cdots).$$

The values of $(C-C_s)^2$ thus obtained are plotted against the time in Fig. 3.

The measured points fit well on the straight lines. If the crystallites had a large number of dislocations along which diffusion proceeded much faster, or it concomitant diffusions with different rate constants proceeded, complex curves would be obtained; that is, the plots of $(C-C_s)^2$ against the time would not fit on a straight line when the temperature was changed. This is not observed in the present case, and so it may be concluded that the model used is adequately supported experimentally. When the self-diffusion of chloride ions or anion vacancies takes place uniformly both parallel with and perpendicular to the sandwich-like layers in the bulk of the crystallites, the values of C_s correspond to the amount of ^{36}Cl within about five layers which diffused out into the gaseous phase. Moreover if the diffusion has proceeded predominantly in either direction, the value of C_s agrees with the one which corresponds to nine layers. In the case of alkali chlorides, in which the surfaces are distorted remarkably by electrostatic forces,[3] the value of C_s corresponds to five layers or so.[6-8] Since it may generally be regarded that the degree of distortion in the surface region of covalent crystals is smaller than that of the distortion of ionic crystals, the value of C_s which correlates with the surface distortion may not be larger in the former than in the latter. Therefore, it may be concluded that the diffusion in the bulk of nickel dichloride crystallites proceeds uniformly in both of the directions in the temperature range used in the present experiment, 180—340°C. This presumption is consitent with the analytical results of the exchange reaction in the surface region, which will be presented below. From the slopes in Fig. 3, the values of $(4\alpha^2/\pi K^2)D$ can be obtained. The Arrhenius plots of these values are shown in Fig. 4.

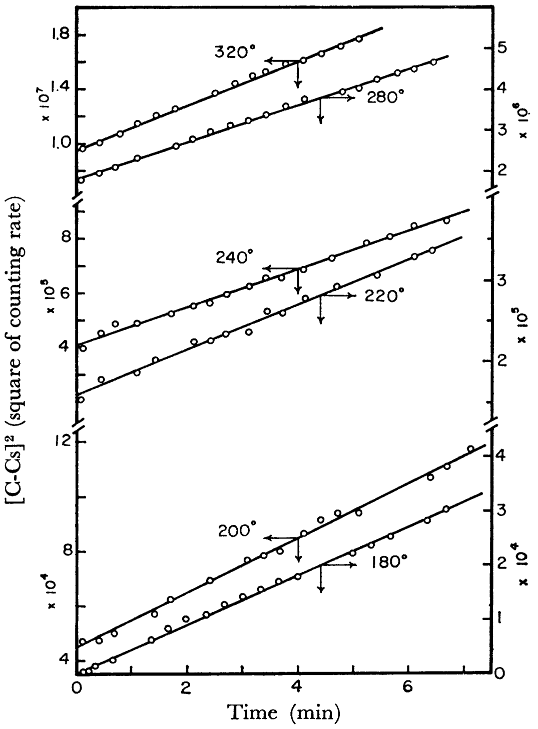


Fig. 3. The plots of $(C\text{–}C_S)^2$ against time. All of data in this figure are obtained from the specimen II.

The slope in this figure gives the activation energy for the migration of ^{36}Cl, ΔE_d, in the bulk of nickel dichloride crystallites. From this experimental results, we obtain;

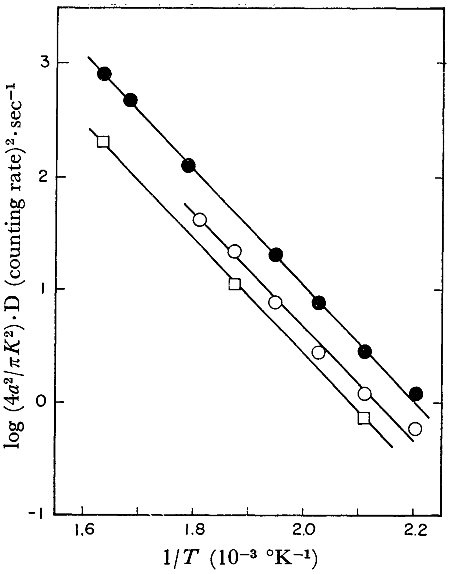


Fig. 4. The Arrhenius plots of apparent self-diffusion rates. ○, ●, and □ refer to different specimens, I, II, and III, respectively.

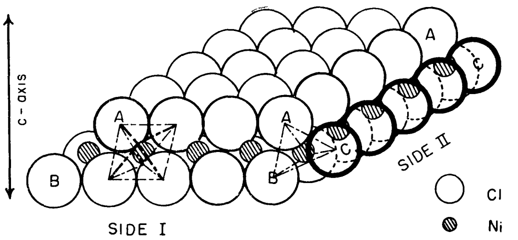
$$D = D_0 \exp(-\Delta E_d/kT),$$

$$\Delta E_d = 1.01 \text{ eV and } D_0 = \sim 3\times10^{-8} \text{ cm}^2\cdot\text{sec}^{-1}.$$

Both of these values are slightly large in comparison with the corresponding values in the crystallites of manganese dichloride[13)] with the same $CdCl_2$-structure, in which ΔE_d=0.95 eV and $D_0=1\times10^{-8}$ cm$^2\cdot$sec^{-1}.

The diffusion experiments in the present work were carried out in the temperature range of 180—340°C. Since ^{36}Cl in the region deeper than the near-surface region diffused out into the gaseous phase within an hour or so at temperatures higher than 340°C, the data obtained in the condition could not be analyzed on the basis of the model of semi-infinite media. No break in the Arrhenius curve was found in the present case, while one appeared obviously at about 330°C in the case of the manganese dichloride crystallites. This discrepancy may be ascribed to the narrow temperature range in which the present experiment was carried out. Hence, the present work was limited to determining the activation energy and the frequency factor of the migration of ^{36}Cl or an anion vacancy; these values for the formation of an anion vacancy or a pair of an anion and a cation vacancies were excluded.

Exchange Reaction in the Surface Region of the Crystallites. In the bulk of nickel dichloride crystallites, a stoichiometric configuration is satisfied by the octahedral coordination of chlorine atoms around a nickel atom, but on the surface the configuration can not always be satisfied. The electron-micrography of the crystallite shows that the surface of the crystal may be approximately regarded as consisting of two kinds of external planes, which are parallel with and perpendicular to the sandwich-like layers. The configuration of the chlorine atoms in the latter planes can not be satisfied by the octahedral configuration for a reason to be explained below. As a help to explanation, a bird's-eye view of the external side model of the sandwich-like layer[18)] is shown in Fig. 5. Side I in this figure shows a section of the octahedral configuration, in which a nickel atom is co-ordinated with three one-third-effectively-valent chlorine atoms (A) and two half-valent chlorine atoms (B).



Fif. 5. A bird's-eye view of the side-model of the sandwich-like layer in nickel dichloride crystal. Chlorine atoms at the position of A, B, and C take the effective valencies of 1/3, 1/2, and unity, respectively.

On this side, there are no chlorine atoms at the apex positions of the octahedral structures. On the other hand, in the crystal side structure shown on Side II of Fig. 5, a nickel atom occupies a tetrahedral hole made up of an effectively uni-valent chlorine atom (C) and three one-third-valent chlorine atoms (A). It may thus be self-evident that the tetrahedral configuration shown on Side II of Fig. 5 is more stable thermodynamically than the vacant octahedral structure on Side I. Therefore, we may predict that, in the external plane perpendicular to the sandwich-like layer, chlorine atoms are arranged in a distorted tetrahedral configuration. Hence, it may be presumed that there are two kinds of domains in the first layer of the crystal surface. The ratio of these two domain areas can be estimated from the electronmicroscopic data as follows;

$$\frac{\text{(Domain I, perpendicular to the sandwich-layer)}}{\text{(Domain II, parallel with the sandwich-layer)}} = \frac{0.8}{1}.$$

The distortion appearing in the first layer of the surface may influence the configuration of the second layer. Hence, it should be considered that there are two kinds of parts in the second layer of the surface, much as in the first layer.

Below, the exchange reactions in the surface region will be analyzed kinetically on the basis of the conditions described above. The surface of nickel dichloride crystallites is highly reactive for chlorine gas; this situation is similar to that with the crystallites of alkali chlorides—that is, gaseous chlorine exchanges with chlorine atoms in the first layer of the surface, even at −21.2°C, and the exchange reaction between the first and the second layers at room temperature takes place rather gradually, as shown in Fig. 6.

Let C and $2C(s)$ be the counting rate at time t and at saturation respectively. Then, we can calculate the value of $C(s)$ from the surface area of the crystallites and the specific radioactivity of the chlorine atoms, if we assume that all of the ^{36}Cl atoms in the first and second layers are transferred into the gaseous phase. [This assumption is valid, since the chlorine atoms in the gaseous phase are about 500 times more than those in the surface monolayer of the crystallites, and the reverse reaction from the phase to the crystal may be neglected.] The calculated values of $C(s)$ are in

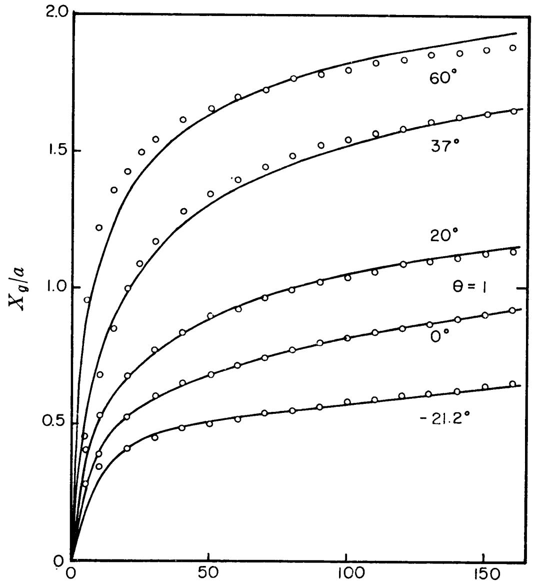


Fig. 6. Counting rates against time curve for the first and the second layer reaction. The line $\theta=1$, designates the monolayer capacity: Solid curves show the values calculated from Eq. (2).

good agreement with those from the measurement of the exchange reaction.

The initial portion of the curve at low temperatures can be analyzed tentatively without taking the second layer into consideration. Now, let us assume that there is a considerable difference between the reactivities of the two domains in the crystal surface. The plots of $\log[1-C/C(s)]$ against the time are shown in Fig. 7. These curves are graphically analyzed in a manner similar to the treatment of the decay of a mixture of radio-isotopes.

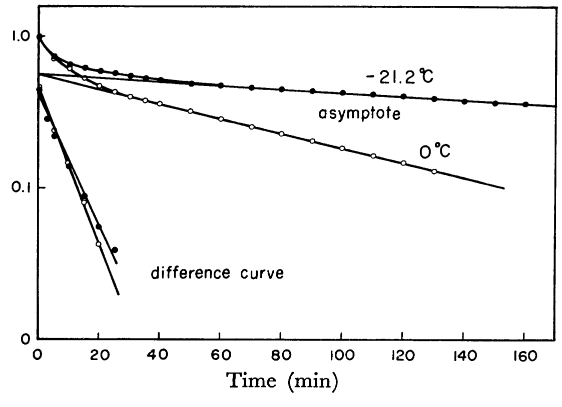


Fig. 7. The plots of log $[1-C/C(s)]$ against time for the reaction in the first and the second layer. The points in the difference curves are calculated from the smoothed experimental curves and the asymptote.

The asymptotes to the tail of the experimental curves give the curves of the relative counting rate against the time referred to the least relative part of the first layer. The difference between the experimental curve and the asymptote is shown as a difference curve, which is approximately linear. The intercepts of the asymptote and the difference curve with the ordinate give the relative values of the two kinds of domain area; the ratio of the active area to the less-active one has the value of 0.78—0.82, in agreement with the ratio estimated from the electron-microscopic data. The best-fitting values of the rate constants for the respective domains, $k_1(1)$ and $k_1(2)$, can be determined from the slopes of the difference curve and the asymptote. The above results indicate that the two-domains model is a good approximation. After the exchange reaction in the first and the second layers were completed at 60°C, the temperature was raised to 80°C, at which point the third-layer exchange reaction proceeded at a slow rate as shown in Fig. 9. The influence of ^{36}Cl in the third layer must be taken into consideration even in the first- and the second-layer exchange reactions at temperatures near 60°C, while the third-layer reaction may proceed at a very slow rate at that temperature.

The approximate reaction scheme is given by;

$$\begin{tikzcd}
 & \begin{array}{c}\text{domain(1) of 1st layer}\\ \text{area} \propto a(1)\end{array} \arrow[dl, "k_1(1)"'] \arrow[r, shift left, "k_2(1)"] & \begin{array}{c}\text{2nd layer}\\ \text{area} \propto a(1)\end{array} \arrow[l, shift left] \arrow[r, shift left, "k_3"] & \begin{array}{c}\text{3rd layer}\\ \text{area} \propto a(1)\end{array} \arrow[l, shift left] \\
\text{gas} & & & \\
 & \begin{array}{c}\text{domain(2) of 1st layer}\\ \text{area} \propto a(2)\end{array} \arrow[ul, "k_1(2)"] \arrow[r, shift left, "k_2(2)"] & \begin{array}{c}\text{2nd layer}\\ \text{area} \propto a(2)\end{array} \arrow[l, shift left] \arrow[r, shift left, "k_3"] & \begin{array}{c}\text{3rd layer}\\ \text{area} \propto a(2)\end{array} \arrow[l, shift left]
\end{tikzcd}$$

In this scheme, the reverse reaction from the gaseous phase to the solid is ignored for the reason mentioned above, and it is assumed that the rate constants for the (1) and (2) domains, $k_3(1)$ and $k_3(2)$, have the same value, k_3. The kinetic analysis, then, is given by;

$$\begin{aligned}
\mathrm{d}X_g(j)/\mathrm{d}t &= k_1(j)x_1(j)\\
\mathrm{d}x_1(j)/\mathrm{d}t &= -k_1(j)x_1(j)-k_2(j)x_1(j)+k_2(j)x_2(j)\\
\mathrm{d}x_2(j)/\mathrm{d}t &= -k_2(j)x_2(j)+k_2(j)x_1(j)-k_3x_2(j)+k_3x_3(j)\\
X_g+x_1(j)+x_2(j)+x_3(j) &= 3a(j),
\end{aligned} \tag{1}$$

and

$$X_g=\sum_{j=1}^{2}X_g(j),\ x_1=\sum_{j=1}^{2}x_1(j),\ x_2=\sum_{j=1}^{2}x_2(j),\ x_3=\sum_{j=1}^{2}x_3(j),$$

$$a=\sum_{j=1}^{2}a(j),$$

where x_n designates the number of ^{36}Cl in the nth layer at time t; a, the number of ^{36}Cl contained in each layer at $t=0$; k_n, the apparent rate constant of the exchange reaction between the $(n-1)$th and the nth layers; the subscript g, the gaseous phase; and (j), the jth kind of domain.

To obtain a solution, an approximation is made;

$$x_3=a\cdot\exp(-\lambda t),$$

where λ is the effective rate constant for the decrease in x_3. Then, using the boundary condition;

$$X_g(j)=0,\ \text{and}\ x_1(j)=x_2(j)=x_3(j)=a(j),\ \text{at}\ t=0,$$

we obtain the solution;

$$\begin{aligned}
\frac{X_g(j)}{a(j)} = {} & \frac{k_1(j)}{\rho_+(j)\rho_-(j)}\left\{\frac{k_2(j)k_3}{\lambda}-\rho_+(j)-\rho_-(j)-k_1(j)\right\}\\
& -\frac{k_1(j)k_2(j)k_3}{\lambda[\lambda+\rho_+(j)][\lambda+\rho_-(j)]}\exp(-\lambda t)\\
& -\frac{k_1(j)}{\rho_+(j)[\rho_+(j)-\rho_-(j)]}\left\{\rho_-(j)+k_1(j)\right.
\end{aligned}$$

$$\left. -\frac{k_2(j)k_3}{\lambda+\rho_+(j)}\right\}\exp\,[\rho_+(j)t]$$
$$-\frac{k_1(j)}{\rho_-(j)[\rho_-(j)-\rho_+(j)]}\left\{\rho_+(j)+k_1(j)\right.$$
$$\left. -\frac{k_2(j)k_3}{\lambda+\rho_-(j)}\right\}\exp\,[\rho_-(j)t]$$

with;

$$2\rho_\pm = -\{[k_1(j)+2k_2(j)+k_3] \pm[k_1(j)^2+4k_2(j)^2+k_3^2-2k_1(j)k_3]^{1/2}\}. \tag{2}$$

By a comparison of Eq. (2) with the experimental curves, the best-fitting values for $k_1(j)$, $k_2(j)$, and k_3 are determined with the aid of an electronic computer. The experimental results are well described by the theory, as is shown in Fig. 6. The Arrhenius plots of $k_1(j)$ and $k_2(j)$ are given in Fig. 8; from them, the activation energies for the exchange reaction can be obtained: 3.6 kcal/mol (=0.16 eV) for the active part of the first layer, 9 kcal/mol (=0.39 eV) for the less-active one, 13 kcal/mol (=0.57 eV) for the active part of the second layer, and 16 kcal/mol (=0.68 eV) for the less-active one.

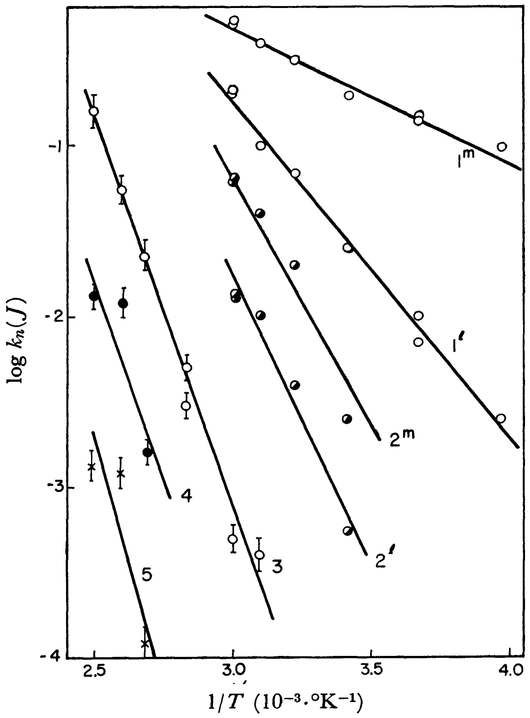


Fig. 8. The Arrhenius plots of the rate constants. The rate constants are given in units of min^{-1}; the numbers in this figure designate the layer's number; the superscripts for number 1 and 2, *m* and *l*, mean the active and the less-active domain, respectively.

In the second-layer exchange reaction, the values of the activation energies are close to each other between the active and less-active parts, and those of the rate constants for the respective parts approach one another with an increase in the temperature. From these results, we may assume that the exchange reaction in the inward layers deeper than the second layer proceeds at rates approximately equal between the two domains. From this point of view, the results of the exchange reaction in these layer may be analyzed as follows.

Since the rate of reaction in the third layer is much lower than that in the second, in analyzing the reaction in the inner layers exceeding the second, it may be assumed that the distribution of ^{36}Cl is in equilibrium between the gaseous phase and the first and second layers. The rates of the reaction in the fourth and fifth layers are similar to the rate in the third; hence, the successive reaction in these layers must be considered. A preliminary analysis of the initial stage of reaction in the third layer showed that the third layer behaves as a uniform one; that is, no remarkable difference in the reactions in the two domains is observed. Thus, the kinetic equation can be given by;

$$\begin{aligned} \mathrm{d}X_g/\mathrm{d}t &= k_3x_3 \\ \mathrm{d}x_3/\mathrm{d}t &= -\,k_3x_3 - k_4x_3 + k_4x_4 \\ \mathrm{d}x_4/\mathrm{d}t &= k_4x_3 - k_4x_4 - k_5x_4 + k_5x_5, \end{aligned} \tag{3}$$

and so on. To obtain a solution, an approximation is made;

$$x_5 = a\cdot\exp\,(-\gamma t),$$

where γ is an effective rate constant for the decrease in x_5. Then, using the boundary conditions;

$$X_g = 0,\ \text{and}\ x_3 = x_4 = x_5 = a,\ \text{at}\ t = 0,$$

we obtain a solution analogous with Eq. (2);

$$\begin{aligned} \frac{X_g}{a} = {} & \frac{k_3}{\eta_+-\eta_-}\left\{\frac{k_4k_5}{\gamma}-\eta_+-\eta_--k_3\right\} \\ & -\frac{k_3k_4k_5}{\gamma(\gamma+\eta_+)(\gamma+\eta_-)}\exp\,(-\gamma t) \\ & -\frac{k_3}{\eta_+(\eta_+-\eta_-)}\left\{\eta_-+k_3-\frac{k_4k_5}{\gamma+\eta_+}\right\}\exp\,(\eta_+t) \\ & -\frac{k_3}{\eta_-(\eta_--\eta_+)}\left\{\eta_++k_3-\frac{k_4k_5}{\gamma+\eta_-}\right\}\exp\,(\eta_-t), \end{aligned} \tag{4}$$

with;

$$2\eta_\pm = -\{(k_3+2k_4+k_5)\pm(k_3^2+4k_4^2+k_5^2-2k_3k_5)^{1/2}\}.$$

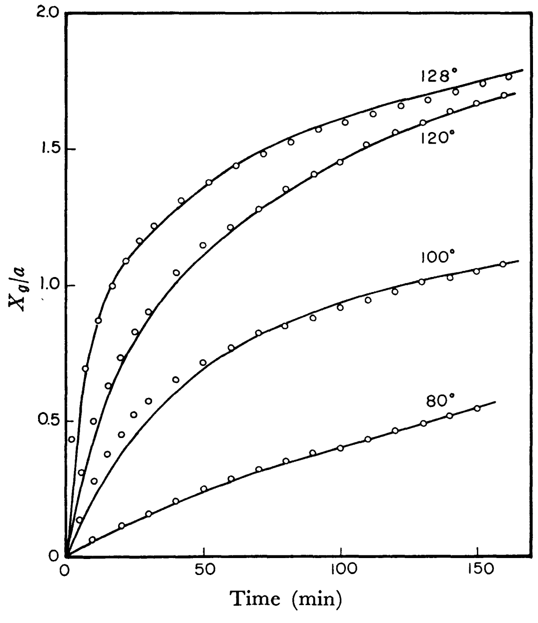


Fig. 9. Counting rates against time curve for the reaction in the third, fourth and fifth layers. Solid curves show the values calculated from Eq. (4).

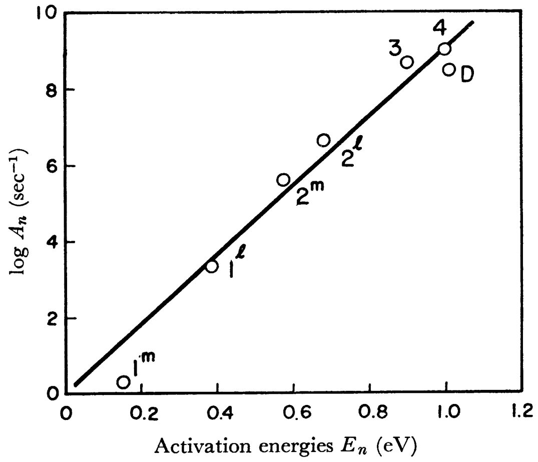


Fig. 10. Linear relationship between log A_n and ΔE_n. A_n is given in the unit of sec^{-1}.

By a comparison of Eq. (4) with the experimental curves obtained, the best-fitting values for k_3, k_4, and k_5 are determined with the aid of a computer. Most of the experimental results are well described by the theory, as is shown in Fig. 9. The Arrhenius plots of k_3, k_4, and k_5 are given in Fig. 8, from which the activation energies for the exchange reaction are obtained: 21 kcal/mol (=0.9 eV) for the third layer and about 23 kcal/mol (=1 eV) for the fourth layer, with some ambiguity.

The actifation energies of the exchange reaction in the surface region converge with that of the self-diffusion in the bulk of nickel dichloride crystallites. This is similar to the previous results on alkali chlorides,[6-8] while the properties of the crystal are remarkably different between nickel dichloride and alkali chlorides.

The relation between the diffusion coefficient, D, and the rate constant, k_d, is given by $D=\frac{1}{2}k_d l^2$, where k_d is the number of jumps per unit time, and l, the distance of a jump. Experssing k_d and k_n in the form $k=A\cdot\exp(-\Delta E/\boldsymbol{k}T)$, we obtain a linear relationship between log A_n and ΔE_n, as is shown in Fig. 10; that is, the Θ-rule holds nearly entirely good in the present case, as in many rate processes.[1]

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