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On the Order of Isotopic Exchange Reactions

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The conditions for the applicability of the McKay law were studied. It was concluded that the first order kinetics no longer holds when the concentrations of intermediates cannot be disregarded when compared with those of reactants and products and when the rate determining step cannot be specified. Some reactions were illustrated in which McKay's law cannot be applied.

In 1938, studying the kinetics of isotopic exchange reaction, McKay[1] arrived at the following conclusion. The exchange reaction is expressed by as,

$$AX^* + BX = AX + BX^*, \tag{1}$$

where X^* represents a tagged X atom, and the reaction (1) is in equilibrium apart from the isotopic distribution. Let the concentration be denoted by

$$\begin{aligned} [AX] + [AX^*] &= a, \qquad [AX^*] = x, \\ [BX] + [BX^*] &= b, \qquad [BX^*] = y, \end{aligned} \tag{2}$$

and the rate of total exchange reaction by R. Then, whatever the reaction mechanism might be, the relation,

$$\frac{dx}{dt} = -\frac{dy}{dt} = R\frac{a-x}{a}\frac{y}{b} - R\frac{x}{a}\frac{b-y}{b} = -\frac{x}{a}R + \frac{y}{b}R \tag{3}$$

holds and we have

$$-\ln\left(\frac{x_\infty - x}{x_\infty}\right) = R\left(\frac{a+b}{ab}\right)t \tag{4}$$

under the condition $x+y=$const., where x_∞ designates the value for x in equilibrium. Equation (4) may be referred to as McKay's law hereafter.

Since then, many workers[2-8] have discussed the validity of McKay's law. Though some modifications must be introduced in such a case where two or more atoms in a molecule are tagged,[7,8] the main features of the law are accepted to be true. Recently, Kawaguchi[9] raised some questions as to its validity. The present author[10] briefly commented on his note, mentioning limitations to the validity of McKay's law. In the present paper, the problem is discussed in more detail and practical problems in kinetic analysis are considered, since kinetic studies today frequently involve special conditions that could not be considered in earlier days.

Conditions for the Applicability of McKay's Law

Elementary Reaction. We adopt, in what follows, the fundamental simplifying assumption that the isotopic mass effects can be ignored not only in rate processes but also in equilibrium properties. This may be appropriate to the study of the fundamental nature of McKay's law. Moreover, we assume that only an atom in a specified position in the molecule is tagged. The case where two or more atoms in some positions in the molecule with different reactivities are tagged[7,8] can be treated as an extension of the presetnt study.

Strictly speaking, McKay's law is only applicable to an elementary reaction or step. The proof of this is very simple. Let the reaction (1) be an elementary reaction. According to the theory of the absolute reaction rate, the rate in the elementary process is given by $\nu\ [Z^{\ddagger}]$, where $Z^{\ddagger}$ denotes the activated complex and ν the frequency of vibration of the activated complexes in the degree of freedom corresponding to their decomposition. Furthermore, there exists a thermodynamic equilibrium between

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[1] H. A. C. McKay, *Nature*, **142**, 997 (1938).

[2] N. Morita, This Bulletin, **15**, 166 (1940).

[3] R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946).

[4] T. H. Norris, *J. Phys. Chem.*, **54**, 777 (1950).

[5] O. E. Meyers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, Ed., John Wiley and Sons, Inc., New York (1951), p. 7.

[6] C. P. Luehr, G. E. Challenger and B. J. Masters, *J. Am. Chem. Soc.*, **78**, 1314 (1956).

[7] S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York (1960), p. 84.

[8] T. Kitayama and K. Hirota, Preprints for The 21st Annual Meeting of the Chemical Society of Japan (April, 1968), No. 23405.

[9] S. Kawaguchi, *Kagaku-no-Ryoiki* (*J. Japan. Chem.*), **21**, 762 (1967), in Japanese.

[10] T. Takaishi, *ibid.*, **22**, 268 (1968), in Japanese.

$Z^{\ne}$ and the reactants. Here we consider that X-atoms at two specified positions in the activated complex are interchanged with each other in the course of the decomposition of activated complex, and that one of the exchangeable X-atoms comes from an AX-molecule and is transfered to a BX-molecule while another from a BX to an AX. These exchangeable atoms may be designated by A-site atom and B-site one, respectively. Let us consider the activated complex, $Z^{\ne *}$, whose A-site atom is tagged and B-site atom untagged. The ratio of the number of such tagged activated complexes to the total number of activated complexes becomes equal to $[AX^*][BX]/\{([AX]+[AX^*])([BX]+[BX^*])\}$. Consequently, for the forward reaction of (1), we have

$$\frac{\text{(rate of reaction of tagged molecules)}}{\text{(total reaction rate)}} = \frac{\nu[Z^{\ne *}]}{\nu([Z^{\ne}]+[Z^{\ne *}])} = \frac{x(b-y)}{ab},$$

irrespective of the molecularity of the reaction. Similarly, for the backward reaction of (1), we get

$$\frac{\text{(rate of reaction of tagged molecules)}}{\text{(total reaction rate)}} = \frac{y(a-x)}{ab}.$$

Thus, the net increase of AX* is given by the difference of the two, *i. e.*, by Eq. (3).

Complex Reaction. When the reaction (1) is a complex reaction, the validity of Eq. (4) must carefully be examined. Even when applicable for appropirate conditions, Eq. (4) may be only approximate. As there are numerous reaction mechanisms, we cannot arrive at the necessary and sufficient conditions for general applicability of Eq. (4). Some typical cases, however, may be discussed.

Consecutive Reactions. If the reaction kinetics can well be described by assuming the existence of a rate determing step, the reaction scheme may be expressed as

$$AX+BX^* \rightleftarrows CX+DX^* \overset{R}{\not\rightleftarrows} CX^*+DX \rightleftarrows AX^*+BX,$$

where R designates the over-all rate and consequently that of rate determining step.

Using the notation (2), and further denoting

$$[CX]+[CX^*]=\alpha,\ [CX^*]=\xi$$

and $$[DX]+[DX^*]=\beta,\ [DX^*]=\eta,$$

we have, irrespective of the molecularity of the reaction,

$$\frac{d(x+\xi)}{dt} = -R\frac{\xi}{\alpha}+R\frac{\eta}{\beta} = -\frac{d(y+\eta)}{dt}, \qquad (6)$$

and $x+y+\xi+\eta=\text{const.}$

Since the reaction $AX+BX \rightleftarrows CX+DX$, is very rapid and in equilibrium, it becomes,

$$\frac{\xi}{\alpha}=\frac{x}{a},\ \frac{\eta}{\beta}=\frac{y}{b}.$$

Introducing these into Eq. (6), we get

$$\frac{d(x+\xi)}{dt} = R\left(\frac{y}{b}-\frac{x}{a}\right).$$

As far as the relations

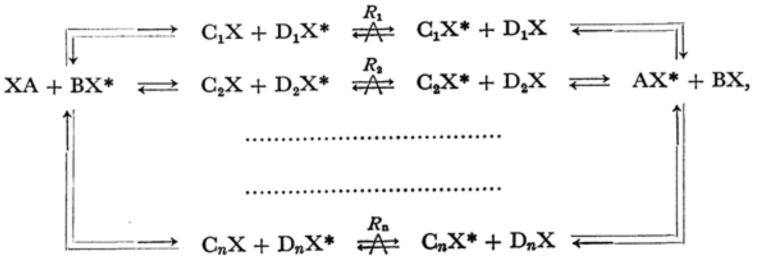
$$\frac{dx}{dt} \gg \frac{d\xi}{dt} \text{ and } x, y, \gg \xi, \eta \qquad (7)$$

hold the above relation reduces to

$$\frac{dx}{dt} = R\left(\frac{y}{b}-\frac{x}{a}\right),$$

i. e., Eq. (3) may be applied.

Concurrent Consecutive Reactions. When there exist parallel reaction paths, the typical reaction scheme may be expressed as



$$\begin{array}{l} C_1X + D_1X^* \overset{R_1}{\not\rightleftarrows} C_1X^* + D_1X \\ XA + BX^* \rightleftarrows C_2X + D_2X^* \overset{R_2}{\not\rightleftarrows} C_2X^* + D_2X \rightleftarrows AX^* + BX, \\ \cdots\cdots\cdots \\ \cdots\cdots\cdots \\ C_nX + D_nX^* \overset{R_n}{\not\rightleftarrows} C_nX^* + D_nX \end{array} \qquad (8)$$

where the existence of rate determining step in the respective path is assumed. Then the rate equation is given by

$$\frac{d(x+\xi_1+\cdots+\xi_n)}{dt} = \sum_{i=1}^{n} R_i\left(\frac{\eta_i}{\beta_i}-\frac{\xi_i}{\alpha_i}\right),$$

where

$$\alpha_i=[C_iX]+[C_iX^*],\quad \xi_i=[C_iX^*],$$

and

$$\beta_i=[D_iX]+[D_iX^*],\quad \eta_i=[D_iX^*].$$

If $x, y \gg \xi_i, \eta_i$, and $dx/dt \gg d\xi_i/dt$, we have, by virture of the relations $x/a=\xi_i/\alpha_i$ and $y/b=\eta_i/\beta_i$,

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\left(\frac{y}{b}-\frac{x}{a}\right)\sum_{i=1}^{n}R_i=R\left(\frac{y}{b}-\frac{x}{a}\right)$$

with
$$R=\sum_{i=1}^{n}R_i.$$

Since R corresponds to the over-all rate, McKay's law holds.

Rate Determining Step cannot be specified. Let us consider a more general case where the rate of reaction is controlled by several steps which occur in series; namely,

$$\left.\begin{matrix}\mathrm{A_1X}\overset{R_1}{\rightleftarrows}\mathrm{A_2X}\overset{R_2}{\rightleftarrows}\cdots\overset{R_{n-1}}{\rightleftarrows}\mathrm{A}_n\mathrm{X}\\ +\\ \mathrm{B_1X^*}\overset{R'_1}{\rightleftarrows}\mathrm{B_2X^*}\rightleftarrows\cdots\overset{R_{m-1}}{\rightleftarrows}\mathrm{B}_m\mathrm{X^*}\end{matrix}\right\}\overset{R_n}{\rightleftarrows}$$

$$\left\{\begin{matrix}\mathrm{A}_n\mathrm{X^*}\overset{R_{n-1}}{\rightleftarrows}\cdots\rightleftarrows\mathrm{A_1X^*}\\ +\\ \mathrm{B}_m\mathrm{X}\overset{R'_{m-1}}{\rightleftarrows}\cdots\rightleftarrows\mathrm{B_1X}.\end{matrix}\right.$$

Then the rate equations are

$$\frac{\mathrm{d}x_1}{\mathrm{d}t}=-R_1\frac{x_1}{a_1}+R_1\frac{x_2}{x_2}\tag{9}$$

$$\left.\begin{aligned}
\frac{\mathrm{d}x_2}{\mathrm{d}t}&=R_1\frac{x_1}{a_1}-R_1\frac{x_2}{a_2}-R_2\frac{x_2}{a_2}+R_2\frac{x_3}{a_3}\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
\frac{\mathrm{d}x_n}{\mathrm{d}t}&=R_{n-1}\frac{x_{n-1}}{a_{n-1}}-R_{n-1}\frac{x_n}{a_n}-R_n\frac{x_n}{a_n}+R_n\frac{y_m}{b_m}\\
\frac{\mathrm{d}y_m}{\mathrm{d}t}&=R_n\frac{x_n}{b_n}-R_n\frac{y_m}{b_m}-R'_{m-1}\frac{y_m}{b_m}+R'_{m-1}\frac{y_{m-1}}{b_{m-1}}\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots
\end{aligned}\right\}\tag{10}$$

$$\frac{\mathrm{d}y_1}{\mathrm{d}t}=-R'_1\frac{y_1}{b_1}+R'_1\frac{y_2}{b_2},\tag{11}$$

where

$$[\mathrm{A}_i\mathrm{X}]+[\mathrm{A}_i\mathrm{X^*}]=a_i,\ \ [\mathrm{A}_i\mathrm{X^*}]=x_i,$$

and

$$[\mathrm{B}_i\mathrm{X}]+[\mathrm{B}_i\mathrm{X^*}]=b_i,\ \ [\mathrm{B}_i\mathrm{X^*}]=y_i.$$

From Eqs. (9)—(11), a $(m+n)$th order differential equation for $x_1(t)$ may be obtained, and its exact solution is to have a different form from Eq. (4). Under appropriate conditions, however, this equation may be reduced approximately to Eq. (3). This is studied in the following.

If the approximation of the steady state reaction[11] is used, *i. e.*, the relations,

$$\frac{\mathrm{d}x_2}{\mathrm{d}t}=\frac{\mathrm{d}x_3}{\mathrm{d}t}=\cdots=\frac{\mathrm{d}x_n}{\mathrm{d}t}=\frac{\mathrm{d}y_m}{\mathrm{d}t}=\cdots=\frac{\mathrm{d}y_2}{\mathrm{d}t}=0,$$

are assumed, then Eq. (10) become

$$\left.\begin{aligned}
&(R_1+R_2)\frac{x_2}{a_2}-R_2\frac{x_3}{a_3}=R_1\frac{x_1}{a_1},\\
&-R_2\frac{x_2}{a_2}+(R_2+R_3)\frac{x_3}{a_3}-R_3\frac{x_4}{a_4}=0,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&-R_{n-1}\frac{x_{n-1}}{a_{n-1}}+(R_{n-1}+R_n)\frac{x_n}{a_n}-R_n\frac{y_m}{b_m}=0,\\
&-R_n\frac{x_n}{a_n}+(R_n+R'_{m-1})\frac{y_m}{b_m}-R'_{m-1}\frac{y_{m-1}}{b_{m-1}}=0,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&-R'_2\frac{y_3}{b_3}+(R'_1+R'_2)\frac{y_2}{b_2}=R'_1\frac{y_1}{b_1}.
\end{aligned}\right\}\tag{10$'$}$$

Solving Eq. (10)′, we can express x_2/a_2 as a function of x_1/a_1 and y_1/b_1,

$$\frac{x_2}{a_2}=\frac{1}{\varDelta}\begin{vmatrix}
\frac{R_1}{a_1}x_1, & -R_2, & \cdots & \cdots & 0\\
0, & R_2+R_3, & -R_3, & & \vdots\\
\vdots & -R_3, & R_3+R_4, & -R_4 & 0\\
\vdots & & \ddots & & \\
\vdots & & -R'_3, & R'_3+R'_2, & -R'_2\\
\frac{R_1}{b_1}y_1, & \cdots\cdots, & 0, & -R'_2, & R'_1+R'_2
\end{vmatrix},\tag{12}$$

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[11] K. J. Laidler, "Reaction Kinetics, Vol. I Homogeneous Gas Reactions," Pergamon Press, Oxford (1963).

where

$$\varDelta = \begin{vmatrix} R_1+R_2, & -R_2, & 0 \cdots\cdots\cdots\cdots\cdots\cdots, & & 0 \\ -R_2, & R_2+R_3, & -R_3 & & \vdots \\ 0, & & \ddots & & \vdots \\ \vdots & & & \ddots & 0 \\ \vdots & & -R'_3, & R'_3+R'_2, & -R'_2 \\ 0 \cdots\cdots\cdots\cdots, & & 0, & -R'_2, & R'_2+R'_1 \end{vmatrix} = Q\cdot\frac{1}{R},$$

with

$$\frac{1}{R} = \frac{1}{R_1} + \cdots + \frac{1}{R_n} + \frac{1}{R'_{m-1}} + \cdots + \frac{1}{R'_1}, \tag{13}$$

and

$$Q = R_1\cdot R_2\cdot \cdots \cdot R_n\cdot R'_{m-1}\cdot \cdots \cdot R'_1.$$

Eq. (12) becomes

$$\frac{x_2}{a_2} = \frac{1}{\varDelta}\,\frac{R_1}{a_1}x_1 \begin{vmatrix} R_2+R_3, & -R_3, & 0 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & & 0 \\ -R_3, & R_3+R_4, & -R_4 & & \vdots \\ 0, & -R_4, & \cdots\cdots\ddots & & \vdots \\ \vdots & & & \ddots & 0 \\ \vdots & , & -R'_3, & R'_3+R'_2, & -R'_2 \\ 0 \cdots\cdots\cdots\cdots, & & 0, & -R'_2, & R'_2+R'_1 \end{vmatrix} +$$

$$(-1)^{m+n-2}\frac{1}{\varDelta}\cdot\frac{R_1}{b_1}y_1 \begin{vmatrix} -R_2, & 0, & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & & & 0 \\ R_2+R_3, & -R_3, & 0, & & & \vdots \\ -R_3, & R_3+R_4, & -R_4, & & & \vdots \\ 0, & & \ddots\cdots\cdots\cdots\cdots & \ddots & & \vdots \\ \vdots & , & -R'_4, & R'_3+R'_4, & -R'_3, & 0 \\ 0 \cdots\cdots, & & 0, & -R'_3, & R'_2+R'_3, & -R'_2 \end{vmatrix}$$

$$= \frac{1}{\varDelta}\,\frac{R_1}{a_1}x_1(R_2\cdot R_2\cdot\ \cdots\ \cdot R'_1)\left(\frac{1}{R_2} + \frac{1}{R_3} + \cdots + \frac{1}{R'_1}\right) + \frac{1}{\varDelta}\,\frac{R'_1}{b_1}y_1\cdot R_2\cdot R_3\cdot\ \cdots\ \cdot R'_2.$$

Introducing this relation into Eq. (9), we get

$$\begin{aligned} \frac{\mathrm{d}x_1}{\mathrm{d}t} &= -\frac{R_1}{a_1}x_1 + \frac{R_1}{\varDelta}\,\frac{x_1}{a_1}(R_1\cdot R_2\cdot\ \cdots\ \cdot R'_1)\left(\frac{1}{R_2} + \frac{1}{R_3} + \cdots + \frac{1}{R'_1}\right) + \frac{Q}{b_1R_1}y_1 \\ &= -R_1\frac{x_1}{a} + R\cdot R_1\frac{x_1}{a_1}\left(\frac{1}{R_2} + \cdots + \frac{1}{R'_1}\right) + \frac{y_1}{b_1}R = R\left(\frac{y_1}{b_1} - \frac{x_1}{a_1}\right). \end{aligned}$$

Thus McKay's law is proved inasmuch as R corresponds, according to Eq. (13), to the rate of the overall reaction.

It may be deduced from these examples, that McKay's law approximately holds, when concentrations of reaction intermediates are negligibly smally as compared to those of reactants and products and consequently changes of concentrations of tagged intermediates are also negligible.

Failure of McKay's Law

Now, two questions may arise: firstly, whether McKay's law necessarily breaks down in the case where concentrations of reaction intermediates cannot be disregarded, and secondly, whether such a case has a practical meaning. In the usual cases, concentrations of reaction intermediates are negligibly small as compared to those of reactants and products, but in some reactions this is not the case. Several such examples are discussed.

Excess Catalysts. The direct observation of reaction intermediates is one of current topics, especially in the field of contact catalysis. Some adsorbed species on solid catalysts constitute reaction intermediates and can be studied by ESR, NMR, IR, isotope techniques and so on. For the convenience of measurements, in some cases, excess amounts of solid catalyst are used as compared to those of the reactants and products in gaseous phase. Such examples were reviewed by Tamaru.[12] Let us discuss one of the simplest cases.

$$\mathrm{AX} \overset{R_1}{\rightleftarrows} \left.\begin{array}{c}(\mathrm{AX})_a\\ +\\ \mathrm{BX}^*\end{array}\right\} \overset{R_2}{\rightleftarrows} \left\{\begin{array}{c}(\mathrm{AX}^*)_a\\ +\\ \mathrm{BX}\end{array}\right. \overset{R_1}{\rightleftarrows} \mathrm{AX}^*,$$

where the subscript a designates adsorbed species. Using the notation (2), and designating

$$[(\mathrm{AX})_a] + [(\mathrm{AX}^*)_a] = \alpha$$

and

$$[(\mathrm{AX}^*)_a] = \xi,$$

we have the rate equations

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -R_1\frac{x}{a} + R_1\frac{\xi}{\alpha},$$

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = R_1\frac{x}{a} - R_1\frac{\xi}{\alpha} - R_2\frac{\xi}{\alpha} + R_2\frac{y}{b},$$

and

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -R_2\frac{y}{b} + R_2\frac{\xi}{\alpha},$$

with $x + y + \xi = \text{const.} = I.$

These equations reduce to

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \left(\frac{R_1+R_2}{\alpha} + \frac{R_1}{a} + \frac{R_2}{b}\right)\frac{\mathrm{d}x}{\mathrm{d}t} + \frac{a+b+\alpha}{ab\alpha}R_1R_2x = \frac{R_1R_2}{b\alpha}I, \tag{14}$$

of which the solution becomes

$$x = x_\infty\left[1 + \frac{\rho_-}{\sqrt{D}}\exp(\rho_+t) - \frac{\rho_+}{\sqrt{D}}\exp(\rho_-t)\right], \tag{15}$$

with

$$\rho_\pm = -\frac{1}{2}\left(\frac{R_1}{a} + \frac{R_2}{b} + \frac{R_1+R_2}{\alpha}\right) \pm \frac{\sqrt{D}}{2},$$

$$D = \left(\frac{R_1}{a} + \frac{R_2}{b} + \frac{R_1+R_2}{\alpha}\right)^2 - \frac{4(a+b+\alpha)}{ab\alpha}R_1R_2,$$

and

$$x_\infty = \frac{a}{a+b+\alpha}I,$$

under the intial condition

$$x = 0,\ \xi = 0 \text{ at } t = 0.$$

Let us consider the case where R_1 is much larger than R_2, *i. e.*, the reaction $\mathrm{AX}\rightleftarrows(\mathrm{AX})_a$ is in equilibrium. Then, Eq. (14) reduces approximately to

$$\left(\frac{R_1}{\alpha} + \frac{R_1}{a}\right)\frac{\mathrm{d}x}{\mathrm{d}t} + \frac{a+b+\alpha}{ab\alpha}R_1R_2x = \frac{R_1R_2}{b\alpha}I,$$

and hence to

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{a+\alpha+b}{b(a+\alpha)}R_2x + \frac{a}{b(a+\alpha)}R_2I,$$

and consequently we have

$$-\ln\frac{x_\infty - x}{x_\infty} = \frac{b+a+\alpha}{b(a+\alpha)}R_2t. \tag{16}$$

This is a slight modification of Eq. (4) obtained by replacing a by $a+\alpha$.

In the case where the step $(\mathrm{AX})_a+\mathrm{BX}^*\rightleftarrows(\mathrm{AX}^*)_a+\mathrm{BX}$ is in equilibrium, the same result is obtained. Thus, it may be concluded that in this reaction scheme McKay's law seriously breaks down only if the intermediate rate determining step cannot be specified and further the amount of intermediates cannot be disregarded in comparison with those of reactants and products.

NaCl/HCl System. Now let us show another example, to which McKay's law cannot be applied, *i. e.*, the exchange reaction between sodium chloride crystallites and hydrogen chloride gas.[13] The exchange of ^{36}Cl in this system proceeds layer by layer, and the activation energy of the reaction becomes progressively higher as the reaction proceeds from the first layer to inner layers, approaching that for self-diffusion. The exchange reaction scheme is expressed as

$$\mathrm{HCl} + \mathrm{Cl}^*(1) \overset{R_1}{\rightleftarrows} \mathrm{HCl}^* + \mathrm{Cl}(1)$$

$$\mathrm{Cl}(1) + \mathrm{Cl}^*(2) \overset{R_2}{\rightleftarrows} \mathrm{Cl}^*(1) + \mathrm{Cl}(2)$$

$$\mathrm{Cl}(2) + \mathrm{Cl}^*(3) \overset{R_3}{\rightleftarrows} \mathrm{Cl}^*(2) + \mathrm{Cl}(3)$$

and so on,

where Cl(i) designates a chloride ion in the ith layer. Thus, the rate equation becomes

$$\begin{aligned}\frac{\mathrm{d}x_g}{\mathrm{d}t} &= -R_1\frac{x_g}{a_g} + R_1\frac{x_1}{a_1},\\ \frac{\mathrm{d}x_1}{\mathrm{d}t} &= R_1\frac{x_g}{a_g} - R_1\frac{x_1}{a_1} - R_2\frac{x_1}{a_1} + R_2\frac{x_2}{a_2},\\ \frac{\mathrm{d}x_2}{\mathrm{d}t} &= R_2\frac{x_1}{a_1} - R_2\frac{x_2}{a_2},\end{aligned} \tag{17}$$

with $x_g + x_1 + x_2 = \text{const.} = I,$

and $a_1 = a_2,$

when the experiments carried out at such temperatures as that the third layer does not participate in the reaction. Solving Eq. (17) with the initial condition, which is a situation really encountered,[13]

$$x_g = 0 \text{ and } x_2 = 0 \text{ at } t = 0,$$

we get a solution quite simmilar to Eq. (15).

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[12] K. Tamaru, "Advances in Catalysis," XV, Academic Press Inc., New York, London (1964), p. 65.

[13] L. G. Harrison, J. A. Morrison and G. S. Rose, *J. Phys. Chem.*, **66**, 1314 (1957).

Concluding Remark

We may conclude, from the above considerations, that an isotopic exchange reaction cannot be described by first order kinetics with respect to the isotopic concentration when:

the concentrations of intermediates are significant compared to those of reactants and products and no intermediate step is rate controlling

Otherwise, first order kinetics may hold. First order kinetics contains such a case as Eq. (16), and has a wider meaning than McKay's law. This conclusion cannot be proved strictly in a mathematical sense, but it may presumably be true as judged from the rather wider considerations given in the preceding sections.

As for cases where two or more atoms in the same molecule are exchanged, their reaction kinetics may have various forms8) and may not be concerned in the present paper.