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Isotope Exchange Kinetics at Heterogeneous Solid Surfaces (Solid—Liquid Interfaces)

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A system of equations describing isotope exchange kinetics at heterogeneous solid surfaces (solid—liquid interfaces) is studied numerically. The theoretical kinetic curves, characterizing the isotope exchange, are calculated for different discrete distributions of the isotope exchange rate constant.

(Keywords: Liquid/solid interface; Heterogeneity effects in isotope exchange kinetics; Heterogeneous isotope exchange; Isotope exchange kinetics)

Isotopenaustauschkinetik an heterogenen Festkörperoberflächen (Fest—flüssig Grenzflächen)

Ein die Kinetik des Isotopenaustausches an heterogenen Festkörperflächen (fest—flüssig Grenzflächen) beschreibendes Gleichungssystem wird einer numerischen Auswertung unterzogen. Die theoretischen kinetischen Kurven des Isotopenaustausches werden für verschiedene diskontinuierliche Verteilungen der Isotopenaustausch-Geschwindigkeitskonstante berechnet.

Introduction

Isotope exchange kinetics in solution/solid systems have been studied in a fragmentary fashion by assuming homogeneity of the solid surface[1–5]. Recently *Kosmulski* et al.[6] summarized and compared different models of the isotope exchange phenomena occurring at liquid/solid interfaces. These models distinguish different steps of the isotope exchange process between bulk solution and solid phase.

In this paper isotope exchange kinetics are discussed assuming heterogeneity of the solid surface. For a discrete distribution of the isotope exchange rate constant, the kinetics of this phenomenon are described by a system of differential equations. The numerical solution of this equation system gives kinetic curves characterizing the isotope exchange at the liquid/solid interface. Kinetic curves are calculated for different types of distributions to study the influence of surface heterogeneity on the isotope exchange process.

Theory

Different models of heterogeneous isotope exchange have been discussed in the previous paper[6]. In one of these models the isotope exchange is represented by the following quasi-chemical reactions:

$$A_b^* + A_i \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} A_b + A_i^* \quad \text{for } i = 1, 2, \ldots, n \tag{1}$$

where A^* and A denote the radioactive and inactive forms of the component A, respectively; the subscript "b" refers to the bulk solution, the subscript "i" to the component A in the i-th surface state. In the further considerations isotope effects are neglected and the concentration of A^* is low. Therefore the equilibrium constant of reaction (1) is unity for the rate constant $k_i = k_{-i}$.

According to reaction (1) isotope exchange occurs only between the bulk solution and certain surface states without any mediating processes. Absence of direct exchange between surface states is assumed. The kinetics of the heterogeneous isotope exchange occurring according to the reactions (1) may be described by the system of the following differential equations:

$$\frac{\partial [A_i^s]^*}{\partial t} = k_i [A_b^*][A_i^s] - k_i [A_i^s]^*[A_b] \quad \text{for } i = 1, 2, \ldots, n \tag{2}$$

where $[A_b]$, $[A_b^*]$ and $[A_i^s]$, $[A_i^s]^*$ denote the concentrations of A and A^* in the bulk solution and in the i-th surface state, respectively. Eq. (2) was solved by assuming:

(a) the concentration of A is considerably greater than that of A^* in the bulk phase and all surface states, i.e.,

$$[A_b] \gg [A_b^*] \text{ and}$$
$$[A_i^s] \gg [A_i^s]^* \quad \text{for } i = 1, 2, \ldots, n \tag{3}$$

(b) initial conditions: at time $t = 0$ the concentrations $[A_i^s]^*$ and $[A_b^*]$ are assumed to be equal to:

$$[A_b^*] = B \tag{4}$$
$$[A_i^s]^* = 0 \quad \text{for } i = 1, 2, \ldots, n \tag{5}$$

and the concentrations $[A_b]$ and $[A_i^s]$ are assumed to be equal to:

$$[A_b] = c_b \text{ and } [A_i^s] = c_i^s \tag{6}$$

For A^* (radioactive form of A) at time t we have:

$$(B-[A_b^*])\,V=\sigma\sum_{i=1}^{n}[\overset{s}{A}_i]^* \tag{7}$$

where V is the volume of the bulk solution and σ is the surface area. The solution of the system of equations (2) with the initial conditions (3)–(7) gives:

$$1-\frac{[A_b^*]}{B}=\frac{\sigma}{V}\sum_{i=1}^{n}\frac{\beta_i}{r_i}\left(1-e^{r_i t}\right)\sum_{j=1}^{n}\alpha_{ji} \tag{8}$$

where r_i are the zeros of the polynomial:

$$\frac{\sigma}{V}\begin{bmatrix} c_b k_1+\frac{\sigma}{V}\overset{s}{c}_1 k_1+r_i & \frac{\sigma}{V}\overset{s}{c}_1 k_1 & \dots & \frac{\sigma}{V}\overset{s}{c}_1 k_1 \\ \overset{s}{c}_2 k_2 & c_b k_2+\frac{\sigma}{V}\overset{s}{c}_2 k_2+r_i & \dots & \frac{\sigma}{V}\overset{s}{c}_2 k_2 \\ \dots & \dots & \dots & \dots \\ \frac{\sigma}{V}\overset{s}{c}_n k_n & \frac{\sigma}{V}\overset{s}{c}_n k_n & \dots & c_b k_n+\frac{\sigma}{V}\overset{s}{c}_n k_n+r_i \end{bmatrix}=0 \tag{9}$$

From eq. (9) we obtain n values of r_i, i.e., $r_1, r_2, \dots, r_n$. For a given value of r_i the parameters α_{ji} for $j=1,2,\dots,n-1$ are obtained by solving the system of linear equations:

$$\begin{gathered}
\alpha_{1i}\left(c_b k_1+\frac{\sigma}{V}\overset{s}{c}_1 k_1+r_i\right)+\alpha_{2i}\frac{\sigma}{V}\overset{s}{c}_1 k_1+\dots+\alpha_{n-1,i}\frac{\sigma}{V}\overset{s}{c}_1 k_1+ \\
+\frac{\sigma}{V}\overset{s}{c}_1 k_1=0 \\
\alpha_{1i}\frac{\sigma}{V}\overset{s}{c}_2 k_2+\alpha_{2i}\left(c_b k_2+\frac{\sigma}{V}\overset{s}{c}_2 k_2+r_i\right)+\dots+\alpha_{n-1,i}\frac{\sigma}{V}\overset{s}{c}_2 k_2+ \\
+\frac{\sigma}{V}\overset{s}{c}_2 k_2=0 \\
\dots\dots\dots\dots\dots\dots\dots\dots \\
\alpha_{1i}\frac{\sigma}{V}\overset{s}{c}_{n-1} k_{n-1}+\alpha_{2i}\frac{\sigma}{V}\overset{s}{c}_{n-1} k_{n-1}+\dots+\alpha_{n-1,i} \\
\left(c_b k_{n-1}+\frac{\sigma}{V}\overset{s}{c}_{n-1} k_{n-1}+r_i\right)+\frac{\sigma}{V}\overset{s}{c}_{n-1} k_{n-1}=0
\end{gathered} \tag{10}$$

and

$$\alpha_{ni}=1 \quad \text{for } i=1,2,\dots,n \tag{11}$$

The parameters β_i are evaluated by solving the following equation system:

$$\sum_{i=1}^{n} \alpha_{ji}\beta_i = \overset{s}{c_j} k_j \quad \text{for } j = 1, 2, \ldots, n \tag{12}$$

Evaluating the parameters r_i, α_{ji} and β_i by means of eqs. (9), (10), and (12) for a given distribution of the isotope exchange rate constants, i.e., $(k_i, \overset{s}{c_i})$ for $i = 1, 2, \ldots, n$, we can calculate the kinetic curve $[A_b^*]$ vs. t, characterizing the isotope exchange process at liquid/solid interface.

Results and Discussion

Equation (2) was solved by means of numerical methods using standard procedures for calculating zeros of polynomial and solving the linear equation system. The numerical results are presented as plots of $\ln\frac{I_0 - I_\infty}{I - I_\infty}$ vs. time, where I denotes the activity of the solution, I_0 and I_∞ denote the initial and equilibrium activities, respectively. The activity I is proportional to the concentration $[A_b^*]$. $\frac{I_0 - I_\infty}{I - I_\infty}$ is reciprocal of $1 - F$, where F is the exchange fraction. Such representation is suitable for comparing isotope exchange kinetic curves over a wide range of time and for different rate constants of this process. For the calculations presented below, the following assumptions were used:

a) $\overset{s}{c_i} = f_i \overset{s}{c}$ for $i = 1, 2, \ldots, n$ and $\sum_{i=1}^{n} f_i = 1$

b) $\overset{s}{c} = 1$

c) $c_b = 1$

d) $\frac{\sigma}{V} = 1$

Under these assumptions, we have $\frac{I_\infty}{I_0} = 0.5$. Table 1 presents the distributions of the isotope exchange rate constants used in the calculations. The distribution function of the exchange rate constants is represented by n pairs of (k_i, f_i). There is no qualitative difference in the shape between kinetic curves for two distribution functions a and b $[(k_{ai}, f_{ai}); (k_{bi}, f_{bi})]$, when $\frac{k_{bi}}{k_{ai}} = \text{const.}$ and $f_{ai} = f_{bi}$ for $i = 1, 2, \ldots, n$. For a homogeneous surface ($n = 1$) the kinetic exchange curve is a straight line (curve a). If the minimum and maximum rate constants are not far removed, the kinetic exchange curve for a heterogeneous surface

Table 1. *Distributions of the isotope exchange rate constants used in model calculations*

Code of distribution	k_1	f_1	k_2	f_2	k_3	f_3
a	3	1				
b	3	0.5	10	0.5		
c	3	0.5	20	0.5		
d	1	0.4	2	0.6		
e	1	0.2	2	0.3	10	0.5
f	1	0.2	2	0.3	100	0.5
g	1.5	0.4	5	0.1	10	0.5
h	1.5	0.1	5	0.4	10	0.5
j	1	0.8	3	0.15	9	0.05
k	1	0.5	3	0.3	9	0.2
l	1	0.05	3	0.15	9	0.8
m	1	0.2	3	0.3	9	0.5
n	1	0.1	3	0.8	9	0.1
o	1	0.25	3	0.5	9	0.25

resembles a straight line (e.g., Fig. 1, curve d). Moreover in Fig. 1 the kinetic exchange curves for the distributions a, b and c are compared. For distribution functions e and f three kinds of surface sites were assumed (cf. Fig. 2). These results are compared with the curve for distribution d (two kinds of sites). No additional effects are expected for more than three kinds of surface sites. The curves b, c (Fig. 1) and e, f (Fig. 2) approach straight lines for long exchange times t. The slopes of the linear segments of b, c and e, f are less than the slopes of a and d, respectively. Extrapolation of linear part of curve f to $t = 0$ gives roughly the exchange fraction corresponding to full isotope exchange for the sites characterized by $k = 100$ and no exchange for the remaining sites. However, for curves b, c and e, extrapolation of the linear parts to $t = 0$ leads to an overestimate of the fraction of the fast exchanging sites.

The slope of the isotope exchange curves at $t = 0$ is given by:

$$\lim_{t \to 0} \frac{\mathrm{d} \ln I}{\mathrm{d} t} = -\frac{\sigma}{V} \sum_{i=1}^{n} c_i^s k_i \tag{13}$$

Eq. (13) makes possible the evaluation of $\sum f_i k_i$ from the experimental data. This possibility may be practically limited by the necessity of measuring activities for very short exchange times. A second basic limitation of interpretation of experimental data is due to the error of sample collection and of activity measurements. Fig. 3 presents the kinetic exchange curves for the distribution functions g and h. The

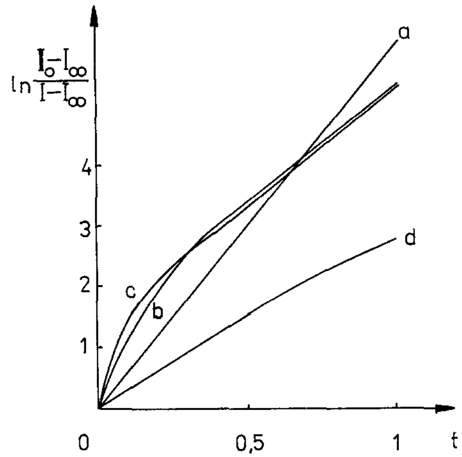

Fig. 1. Kinetic curves of heterogeneous isotope exchange for distributions a, b, c and d (cf. Table 1)

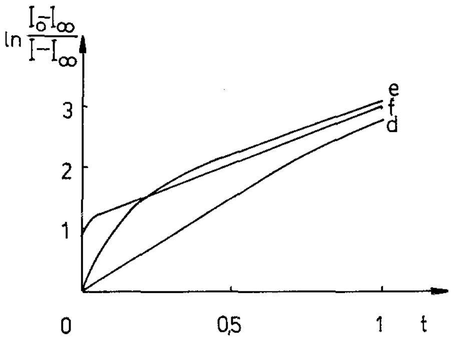

Fig. 2. Kinetic curves of heterogeneous isotope exchange for distributions d, e and f (cf. Table 1)

vertical bars denote the range of $\ln\frac{I_0 - I_\infty}{I - I_\infty}$ for $\ln\frac{I_0 - I_\infty}{I_0 - I_\infty} = 1, 2, 3$ and 4 when the error of measurement of I is $\pm 2\%$. It is seen that the experimental error is larger than the difference between curves g and h, thus preventing an experimental decision between the two distributions. The range of $\ln\frac{I_0 - I_\infty}{I - I_\infty}$ due to the experimental error is decreased when $\frac{I_\infty}{I_0}$ is decreased.

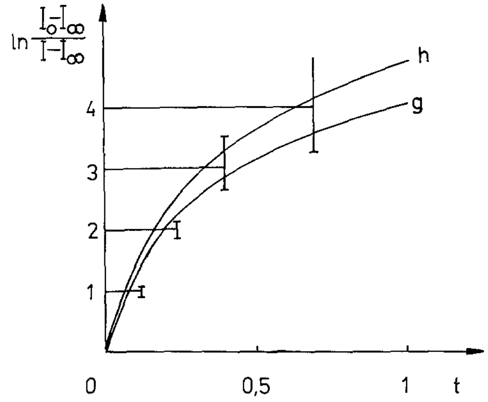

Fig. 3. Kinetic curves of heterogeneous isotope exchange for distributions g and h (cf. Table 1)

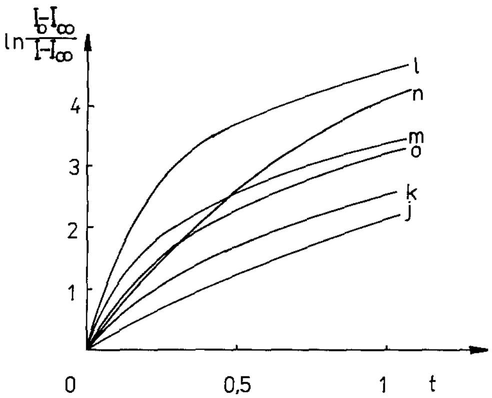

Fig. 4. Kinetic curves of heterogeneous isotope exchange for distributions j, k, l, m, n and o (cf. Table 1)

An unexpected effect is observed by comparison of curves a and b. For sufficiently long exchange time, the exchange fraction for distribution a exceeds that for distribution b. However, this effect has little practical meaning because of the experimental error (cf. Fig. 3).

In the theory of physical adsorption on heterogeneous surfaces three main types of continuous distributions are used[7]: decreasing exponential distribution, increasing exponential distribution and normal distribution. It has been shown by *Czarniecki* and *Jaroniec*[8] that main features of the continuous distributions may be well approximated by discrete distributions with three to five kinds of surface sites. Fig. 4

indicates that for the decreasing exponential distribution, the curve j corresponding to a sharper distribution lies below curve k corresponding to a flattened distribution. For an increasing exponential distribution, curve l corresponding to the sharper distribution, lies above the other one (curve m). Curves n and o present the typical course of isotope exchange for two different normal distributions, where curve n relates to a sharper distribution.

The observed regularities coincide with the courses of the physical adsorption kinetic curves for particular types of the energy distributions[8].

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