Monatshefte für Chemie 116, 305—310 (1985)

Monatshefte für Chemie
Chemical Monthly

A Generalized Equation Describing Isotope Exchange Kinetics at Solid – Liquid Interface

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(Received 28 May 1984. Accepted 14 June 1984)

A generalization of the kinetic equation for the isotope exchange at solid – liquid interface is presented. The generalized equation may be used to describe kinetics of the isotope exchange process limited by surface reactions and diffusion without assumption of spherical symmetry of solid particles.

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

Eine generalisierte Gleichung für die Kinetik des Isotopenaustausches an Fest-Flüssig-Phasengrenzen

Es wird eine generalisierte kinetische Gleichung angegeben, die die Kinetik des Isotopenaustausches an Fest-Flüssig-Phasengrenzen beschreibt, wobei der Austauschprozeß durch Oberflächenreaktionen und Diffusion ohne der Annahme sphärischer Symmetrie für die festen Partikel begrenzt ist.

Introduction

The rate of the isotope exchange process at solid – liquid interface may be governed by surface reactions and diffusion. Different models of isotope exchange at solid – liquid interface were proposed to study the influence of surface reactions and diffusion on the kinetics of this phenomenon. They lead to different expressions describing the exchange fraction F upon time t. When diffusion is one of the rate determining processes, the theoretical equations derived from *Fick*'s law by means of the *Laplace* transform are very complex and their application for describing the experimental data of isotope exchange is difficult[1,2] except for some very simplified models[3]. Moreover, these equations were derived assuming spherical symmetry of solid particles and their homogeneity.

In this paper a generalized equation for describing the isotope exchange kinetics is derived without the above assumptions. It may be applied for interpretation of the kinetic curves F vs. t characterizing the isotope exchange limited by surface reaction and diffusion.

Theory

In the previous paper[4] we presented the kinetic equation of isotope exchange occuring at solid–liquid interface according to the following model. There are n kinds of the surface sites, for which the isotope exchange is represented by the surface reactions

$$A_b^x + A_{s(i)} \xrightarrow{k_i} A_b + A_{s(i)}^x \tag{1 a}$$

$$A_b + A_{s(i)}^x \xrightarrow{k_{-i}} A_b^x + A_{s(i)} \tag{1 b}$$

$$i = 1, 2, \ldots, n$$

where A^x and A denote the radioactive and inactive form of the component A, the subscript "$s(i)$" refers to the i-th surface state and "b" to the bulk solution, respectively.

The concentration of A^x was assumed to be low, the isotope effects were neglected ($k_i = k_{-i}$) and the concentrations of A were assumed to be constant during the isotope exchange process. No immediate exchange between particular surface states was also assumed.

The rate of reversible reaction (1) may be described by the following differential equations

$$\frac{\mathrm{d}c_{A^x}^{s(i)}}{\mathrm{d}t} = k_i c_A^{s(i)} c_{A^x}^b - k_i c_A^b c_{A^x}^{s(i)} \quad i = 1, 2, \ldots, n \tag{2}$$

or

$$\frac{1}{\sigma} \frac{\mathrm{d}q_{A^x}^{s(i)}}{\mathrm{d}t} = \frac{1}{\sigma V} k_i q_A^{s(i)} q_{A^x}^b - \frac{1}{\sigma V} k_i q_A^b q_{A^x}^{s(i)} \quad i = 1, 2, \ldots, n \tag{3}$$

where σ denotes the surface area, V is the volume of the solution, c denotes the concentrations and q the amounts of A and A^x in particular states (solution or the i-th surface state), respectively. Putting together the quantities remaining constant during the isotope exchange process, eq. (3) may be rewritten as follows

$$\frac{\mathrm{d}q_{A^x}^{s(i)}}{\mathrm{d}t} = f_i^s q_{A^x}^b - f_i^b q_{A^x}^{s(i)} \qquad i = 1, 2, \ldots, n \tag{4}$$

where f_i^f represents the fraction of the radiotracer amount in the solution at the time t, which is transfered from the solution to the i-th surface state in a time unit according to reaction (1 a) and f_i^b represents the fraction of radiotracer transfered according to reaction (1 b), respectively. When the reaction (1) is the process causing the radiotracer transfer and diffusion is instant, the coefficients f_i^f and f_i^b may be expressed as follows

$$f_i^f = \frac{k_i q_A^{s(i)}}{V} \quad f_i^b = \frac{k_i q_A^b}{V} \qquad i = 1, 2, \ldots, n \tag{5}$$

so they are constant during the isotope exchange process.

When the rate of diffusion is finite, eq. (4) is also valid, however the coefficients f_i^f and f_i^b are less than calculated from eq. (5). When the system under consideration satisfies the conditions listed before eq. (2), the equations (1) may represent any physical or chemical process of transfer between solution and the i-th surface state or the i-th state in the solid particle. The only problem is to divide the solid into sufficient number of parts, so that f_i^f and f_i^b may be regarded to be constant for the particular parts. The constancy of f_i^f and f_i^b means that division of the i-th part into subparts leads to the same value of f^b and f^f for each subpart.

Equation (4) with the initial values of $q_{A^x}^b$ equal to q and $q_{A^x}^{s(i)} = 0$ for $i = 1, 2, \ldots, n$ gives the following kinetic equation of isotope exchange

$$1 - \frac{q_{A^x}^b}{q} = \sum_{i=1}^{n} \frac{\beta_i}{r_i} [1 - \exp(r_i t)] \sum_{j=1}^{n} \alpha_{ji} \tag{6}$$

where r_i are the zeros of the polynomial

$$\begin{vmatrix} f_1^b + f_1^f + r_i & f_1^f & \ldots & f_1^f \\ f_2^f & f_2^b + f_2^f + r_i & \ldots & f_2^f \\ \multicolumn{4}{c}{\ldots\ldots\ldots\ldots\ldots} \\ f_n^f & f_n^f & \ldots & f_n^b + f_n^f + r_i \end{vmatrix} = 0 \tag{7}$$

For $i = 1, 2, \ldots, n$, one obtains the parameters α_{ji} for $j = 1, 2, \ldots, n\text{-}1$ by solving the following systems of linear equations

$$\begin{gathered} \alpha_{1i}(f_1^b + f_1^f + r_i) + \alpha_{2i} f_1^f + \ldots + \alpha_{n-1,i} f_1^f + f_1^f = 0 \\ \alpha_{1i} f_2^f + \alpha_{2i}(f_2^b + f_2^f + r_i) + \ldots + \alpha_{n-1,i} f_2^f + f_2^f = 0 \\ \ldots\ldots\ldots\ldots\ldots \\ \alpha_{1i} f_{n-1}^f + \alpha_{2i} f_{n-1}^f + \ldots + \alpha_{n-1,i}(f_{n-1}^b + f_{n-1}^f + r_i) + f_{n-1}^f = 0 \end{gathered} \tag{8}$$

and

$$\alpha_{ni} = 1 \qquad \text{for} \qquad i = 1, 2, \ldots, n \tag{9}$$

The parameters β_i are the solutions of the following equation system

$$\sum_{i=1}^{n} \alpha_{ji}\beta_i = f_i^f \qquad \text{for} \qquad j = 1, 2, \ldots, n \tag{10}$$

Results and Discussion

The course of the kinetic curves obtained from the equations (6)–(10) is the same as that of curves analysed in the previous paper[4]. The mathematical shape of these equations is the same but they have different physical meaning.

Considering equation (4) at the equilibrium state ($t \rightarrow \infty$) one has

$$f_i^f q_{A^x}^{b\infty} - f_i^b q_{A^x}^{s(i)\infty} = 0 \tag{11}$$

Neglecting isotope effects, i.e., $q_{A^x}^{b\infty}/q_{A^x}^{s(i)\infty} = q_A^b/q_A^{s(i)}$ and taking into account eq. (11), one has

$$\frac{f_i^b}{f_i^f} = \frac{q_A^b}{q_A^{s(i)}} \tag{12}$$

for any mechanism of radiotracer transfer from the solution into the i-th part of the solid phase. It is also convenient to denote

$$f_i = q_A^{s(i)} / \sum_{j=1}^{n} q_A^{s(j)} \tag{13}$$

where f_i is the fraction of solid phase exchanging according to the i-th of eqs. (4). Taking into account eq. (12) (equilibrium condition), (13) and equations (6)–(10), one can easily fit the parameters f_i and f_i^b to the experimental data using the standard numerical procedures to calculate zeros of polynomial and solve the linear equation systems. Some results are shown in Figs. 1–3 and Table 1. In the majority cases $i = 3$ is enough for a good agreement between theoretical equation and experimental points. For many systems the linear dependence $\ln(1 - F)$ vs. t is obtained i.e., $i = 1$ and eq. (6) reduces to the well known *McKay* law. The factors f_i and f_i^b depend on the conditions of the experiment. When the parameters f_i^b for $i = 1, 2, \ldots, n$ are proportional to the concentration of exchangeable species in the solution eq. (5), one can suppose that isotope exchange is governed by kinetic equation (2). Otherwise, another mechanism of transfer e.g. diffusion should be taken into account.

When diffusion in the solid determines the rate of isotope exchange, the parameters f_i^b increase when the dimensions of the solid particles decrease. The qualitative dependence of the parameters f_i^b and f_i on the factors affecting the rate of isotope exchange may be proposed by comparison of eq. (6) with the formerly derived equations describing the kinetics of isotope exchange.

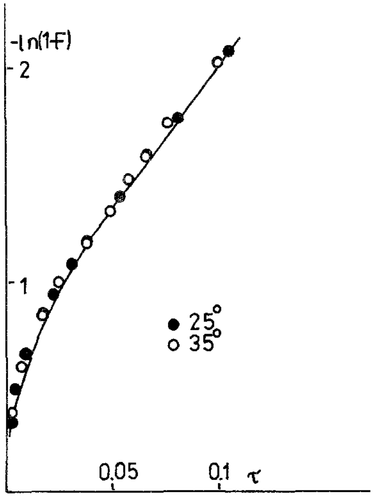

Fig. 1. Comparison of experimental points (Ref.[5], Fig. 5) for Ca^{2+} exchange between aqueous solution and CaC_2O_4 with a model curve. For parameters f_i and f_i^b see Table 1. Dimensionless time $\tau = Dt/a^2$ where D is the diffusion coefficient in solid phase and a is the radius of the solid particles

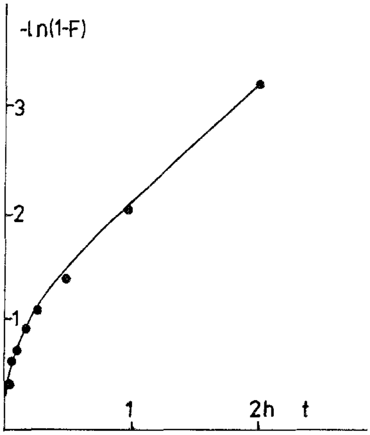

Fig. 2. Comparison of experimental points (Ref.[6], Fig. 3) for Sr^{2+} exchange between aqueous solution and $SrSO_4$ with a model curve. For parameters f_i and f_i^b see Table 1; time in hours

The kinetic equation of isotope exchange derived above leads to experimental values of parameters f_i^b and f_i. It does not give a relation between these parameters and the conditions of the experiment. However, contrary to the formerly derived kinetic equations it does not require the

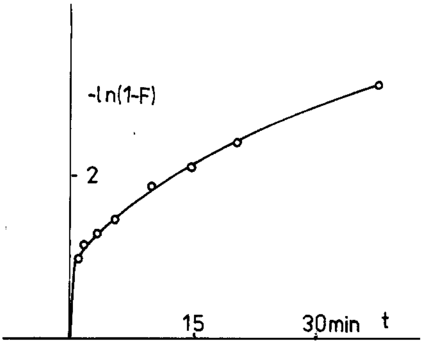

Fig. 3. Comparison of experimental points (Ref.[7], Fig. 2, curve 5) for Fe(III) exchange between an aqueous solution and an adsorption layer formed on alumina with model curve. For parameters f_i and f_i^b see Table 1; time in minutes

Table 1. *Parameters used in model calculations; the parameters f_i^b refer to the time units used in the figures*

Figure	Parameters f			Parameters f^b		
	1	2	3	1	2	3
1	0.3	0.4	0.3	320	16	6.2
2	0.0001	0.0001	0.9998	12	0.072	0.00024
3	0.3	0.4	0.3	1.4	0.06	0.016

assumption of spherical symmetry of solid particles and their homogeneity, when diffusion is one of the processes determining the rate of isotope exchange.

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