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A Review Paper on the Kinetic Study of the Pressure-Jump Method

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ABSTRACT

Kinetic research often is conducted using tradition methods of kinetic study, namely batch and flow methods. Reaction rate constants and reaction mechanisms, however, are difficult to determine using these methods because too many factors, such as mass-transfer, diffusion, adsorption, and desorption, occur simultaneously in a system. In addition, kinetic information from fast reactions cannot be easily detected. This review paper focuses on the pressure-jump technique, which detects any change in an equilibrium system due to a sudden pressure change, and hence, is able to illustrate the reaction mechanisms and calculate the rate constants. Pressure-jump applications in complex formation, hydrolysis, ion exchange, and adsorption/desorption are discussed in this paper.

Key Words: kinetic study, adsorption, pressure-jump

I. Introduction

In a natural aquatic environment, the fate of most reactive elements is controlled by the presence of minerals (Stumm, 1992). Reactions like adsorption/desorption and precipitation occurring at the interface between the aqueous solution and minerals, such as iron and/or aluminum oxides and hydroxides, play an important role in regulating the distribution and partitioning of reactive substances and other environmental pollutants. Adsorption/desorption reactions at the water/solid interface also alter the stability of colloidal particles and subsequently influence the aquatic ecosystem (Stumm, 1992). The surfaces of minerals provide reactive sites for oxidation/reduction as well as surface enhanced dissolution. As a result, reactivities of aqueous species are dramatically modified at the water/mineral interface; thus, many reactions which proceed with difficulty in aqueous condition are able to advance under the comparable situation at the mineral surface (Dzombak and Morel, 1990).

Many studies have been devoted to investigation of chemical phenomena at the oxide/mineral interface. Specifically, studies on the solution/oxide interface can be classified into the following categories: equilibrium, model development, kinetics, spectroscopic, thermochemical, and engineering process. Study on the equilibrium in ion adsorption experiments is important for the development of a thermodynamic data base. Kinetic study can provide an overview of the forward and backward reactions in the system. The kinetic data not only provide reaction rate constants, but also reaction steps.

In this review paper, emphasis is placed on advances in experimental techniques for reaction kinetics in heterogeneous systems. In particular, the pressure-jump method of chemical relaxation is described in detail, as it is the most suitable technique for kinetic study of a heterogeneous system. Its applications in complex formation, hydrolysis, and ion exchange reactions as well as on the solid/water surface are discussed. A summary of complex formation constants and reaction mechanisms as well as rate constants of cations/anions under different adsorption/desorption in different heterogenous systems using the pressure jump technique will certainly be useful for future reference.

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II. Background

1. Methods for Measuring Reaction Kinetics at the Solid/Water Interface

One of the most important tasks in studying reaction kinetics is to find the reaction rate constants and reaction mechanisms. Because there are advantages and disadvantages associated with different methods, there is no perfect technique available for measuring these reaction parameters and elucidating the pathways. Generally speaking, if the half-life of a reaction is faster than one second, then it is called a fast reaction (Strehlow and Knoche, 1977). Such fast reactions require the use of unique techniques to determine the important kinetic constants.

The measurement techniques used in studying solid/liquid reaction kinetics can be classified as batch, flow and relaxation methods.

A. Batch Method

In the batch method, the adsorbent and adsorbate are completely mixed in the same reaction vessel; the change of adsorbent concentration with time is then analyzed after solid/liquid separation. This method is widely applied to the study of metal ion adsorption onto solid surfaces. The adsorption kinetics are affected by the degree of mixing due to mass transfer and diffusion between the adsorbent and adsorbate. The other disadvantages include the following:

(1) A constant pH and temperature is difficult to maintain during the reaction process.
(2) The reversible reaction proceeds simultaneously in the system, and the individual forward and backward reactions cannot be controlled; therefore, the determined reaction rate constant is difficult to interpret (Sparks, 1989).
(3) Species desorbed from the adsorbate cannot be removed and may inhibit the subsequent reaction (Sparks, 1985, 1987), may even promote hysteretic reactions, and may create secondary precipitation during dissolution of soil minerals (Chou and Wollast, 1984).

Some modified batch techniques were developed for measuring reaction kinetics. Van Riemsdijk and Lyklema (1980) and Van Riemsdijk and de Haan (1981) used a batch reactor under pH-stat and phosphorus-stat conditions to study phosphorus retention kinetics in soils under constant metal phosphates supersaturation conditions. Similarly, Phelan and Mattigod (1987) used a pH- and Ca-stat reactor to study the kinetics of phosphorus precipitation from supersaturated solutions. These are examples of specialized adapta-tions of the basic batch reactor to study precipitation kinetics.

Many ion exchange reactions on organic matter and clay minerals are completed within a few minutes, or even seconds. Some reactions involving metal adsorption onto oxides are too rapid to be observed using any batch technique. For these reactions, one has to employ the rapid kinetic techniques, which will be discussed in the Relaxation Methods section.

B. Flow Method

The flow methods are so called because the adsorbent is continuously injected into the system to react with the adsorbate. The change of the adsorbent concentration with time is analyzed to determine the reaction kinetics. Flow methods include the fluidized-bed method, stirred-flow method, and continuous flow method.

The fluidized bed reactor has been used to study various kinetic phenomena (Chou and Wollast, 1984; Holdren and Speyer, 1985, 1987). It is widely used in the chemical industry to study physical and chemical processes involving a solid phase and a gas or liquid phase. The flow is adjusted such that its velocity equals the settling rate of the solid particles in the particular suspension. Because the suspension is often quite dense, the settling rates of different-sized particles are equalized through frequent collisions with other particles. The kinetic coefficients calculated from the fluidized-bed method are affected by the difference of the packing column length and packing density. Incompletely dispersed adsorbate affects solute mass-transfer; the degree of mixing, and hence of mass transfer, is controlled by the flow rate. Because of the nature of the system, the concentration of adsorbent in the reaction tank may not be equilibrated with the effluent concentration. Sparks *et al.* (1980) introduced a continuous flow system, similar in principle to liquid-phase column chromatography, to study potassium adsorption dynamics on soils and clay minerals (Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984; Ogwada and Sparks, 1986), and SO_4^{2-} sorption and desorption on soils (Hodges and Johnson, 1987).

As for continuous stirred-flow methods, they have long been used to obtain kinetic data in homogeneous as well as heterogeneous soil systems (Carski and Sparks, 1985; Randle and Hartmann, 1987; Seyfried *et al.*, 1989). The stirred-flow technique is an improvement over the fluidized method; the former provides a high degree of mixing so that the chamber and effluent concentrations are equal and transport phenomena are minimized. The stirred-flow technique is also attrac-

Table 1. Effect of the Kinetic Method on the Adsorption Rate Coefficient (k_a) and the Energies of Activation for Adsorption (E_{aa}) in the Systems Studied

| | Temp. K | Method | | | | |
		Static	Continuous flow	Batch	Stirred	Vortex batch
		k_a, (min^{-1})				
Kaolinite	283	0.03	0.03	1.30	1.32	1.44
	298	0.03	0.04	2.38	2.84	3.48
		(5.1)[a]	(7.6)	(26.1)	(26.0)	(30.6)
	313	0.04	0.05	3.76	3.78	4.98
Chester loam	283	0.03	0.03	0.18	0.19	0.87
	298	0.03	0.04	0.23	0.25	2.33
		(5.3)	(7.5)	(9.2)	(19.9)	(32.6)
	313	0.03	0.04	0.26	0.29	3.24
Vermiculite	283	0.02	0.01	0.06	0.05	0.42
	298	0.02	0.02	0.08	0.06	0.95
		(6.2)	(10)	(13.2)	(13.4)	(33.6)
	313	0.03	0.02	0.10	0.07	1.65

Source: Ogwada and Sparks (1986)
[a]values inside parentheses are E_{aa} in kJ/mol.

tive because it removes desorbed species at each step of the reaction process and because it makes studying desorption kinetics phenomena easy.

Flow methods are better than batch methods because the desorbed species can be continuously removed from the system, thereby reducing interference from desorbed species.

Ogwada and Sparks (1986) conducted a study investigating the effect of agitation on rate parameters using five different methods: a static technique in which no mixing occurred, a continuous-flow method, a batch method in which the sample was agitated at 180 rpm, a stirred method where the mixture was stirred at 435 rpm, and a vortex batch technique in which the mixture was rapidly mixed at 2240 rpm. Table 1 shows the effect of each method on the adsorption rate coefficients and adsorption activation energies. As mixing intensity increased, both the adsorption rate coefficients and adsorption activation energies increased. The results indicate that the degree of mixing significantly affects the kinetic parameters in a given system.

C. Stopped-Flow Method

This method employs pneumatic pressure to eject two types of reactants into the reaction chamber, thus enabling them to be completely mixed in several milliseconds. The change of concentration with time in the chamber is then measured by a suitable detector. The major advantage of this method is that it requires only a small sample. Unfortunately, this method can only be used to study irreversible reactions. Several investigators (Bridger *et al.*, 1982, 1983; Plankey and Patterson, 1987; Lin *et al.*, 1994) used the stopped-flow method to investigate the complexation of different anions and metal ions. Plankey and Patterson studied the kinetics of aluminum-fulvic acid complexation in acidic water. Lin *et al.* (1994) studied the kinetics of copper complexation with dissolved organic matter. The stopped-flow method and fluorescence techniques were also used to measure the reaction kinetics. The results of these investigations demonstrate that the method is adequate for kinetic studies of irreversible reactions.

D. Relaxation Method

The rates of reactions over a range of 10 to 10^{-10} s can be determined using the relaxation method (Bernasconi, 1976), in which a perturbed equilibrium system is re-equilibrated through the original reaction steps. Data on the progress of relaxation are then used to investigate the reaction kinetics of the system. The main advantage of this method is the absence of mass transfer phenomenon. On the other hand, the relaxation techniques are only applicable to systems that are reversible and are at equilibrium.

The relaxation techniques can be categorized into two types of methods; the transient method and the jump method. The latter includes the temperature-, pressure-, concentration-jump, and electrical field pulse; this method detects changes in the equilibrium system affected by the temperature, pressure, concentration, and electrical field. The other type of relaxation method is known as the stationary method (Strehlow and Knoche, 1977), which includes ultrasonic and dielectric dispersion methods that detect changes in wave energy and capacity, respectively. For each method, there are optimum conditions and an optimum detection time range. For example, the temperature-jump method needs a higher concentration of electrolyte; therefore, electrolysis interferes with the results, and reaction rates slower than 0.2 s are difficult to measure (Strehlow and Knoche, 1977). The reaction rate needs to be faster than 10^{-4} s (Strehlow and Knoche, 1977) for the electrical field pulse and ultrasonic methods to be applicable. The concentration-jump method is not suitable for inorganic and heterogeneous reaction systems as the detector used is a spectrophotometer or spectrofluorophotometer. The pressure-jump method is a more suitable method for detecting the change of conductivity in ion interactions between the solid and liquid phases.

III. Pressure-Jump Technique

1. Theory

The pressure-jump method is based on the fact that chemical equilibrium is dependent on pressure. The relationship between the equilibrium constant (K) and pressure (P) in homogeneous and heterogeneous systems at constant temperature is (Bernasconi, 1976):

$$[\frac{\partial \ln K}{\partial P}]_T = -\frac{\Delta V}{RT}, \tag{1}$$

where ΔV is the standard molar volume change of the reaction, P the pressure, T the temperature, and R the molar gas constant. For a small perturbation, Eq. (1) can be written as:

$$\frac{\Delta K}{K} = -\frac{1}{RT}\int \Delta V dP. \tag{2}$$

Equation 2 indicates that the reaction kinetics of the shift in equilibrium are affected by a change in pressure. For example, the maximum value of dK/K for ion formation or dissociation, which causes the molar volume to change as the reaction proceeds, is about 4.1% over a 10 mPa change in pressure (Bernasconi, 1976). Therefore, the pressure-jump method is suitable for kinetic study of an equilibrium system that is disturbed by pressure changes.

Pressure-jump measurements can be made using optical or conductivity detection methods. However, conductivity detection is preferred for systems involving ion association, since the equilibrium displacement following a pressure-jump is usually small (Bernasconi, 1976). The change of specific conductance (σ) during disturbance to equilibrium can be determined (Bernasconi, 1976):

$$\sigma = \frac{F}{1000}\Sigma |Z_i|u_iC_i = \frac{F}{1000}\rho|Z_i|u_im_i, \tag{3}$$

where F is the Faraday constant, Z_i the valence of ion i, u_i its electrical mobility, C_i the molar concentration and m_i the molal concentration of ion i, and ρ the density of the solution. For small disturbances, Eq. (3) can be written as

$$\Delta\sigma = \frac{F}{1000}(\rho\Sigma |Z_i|u_i\Delta m_i + \rho\Sigma |Z_i|m_i\Delta u_i$$

$$+ \Sigma |Z_i|m_iu_i\Delta\rho). \tag{4}$$
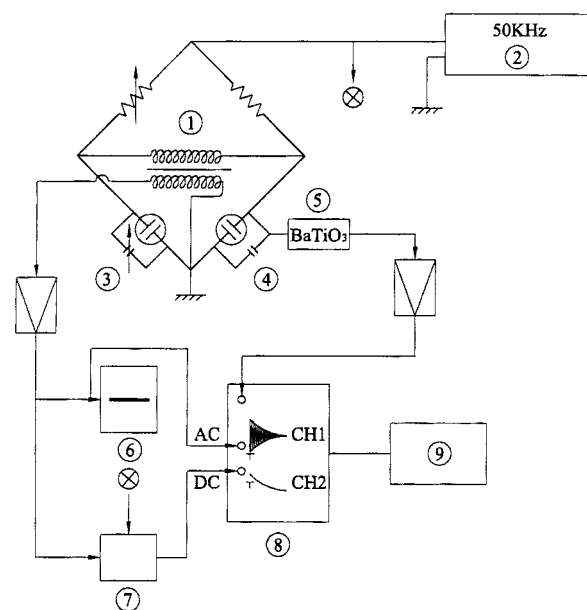
The first term on the right-hand side of Eq. (4)

Fig. 1. Schematic diagram of the pressure-jump apparatus. 1, Wheatstone Bridge; 2, Function Generator; 3, Sample Cell; 4, Reference Cell; 5, Trigger Cell; 6, Analog Oscilloscope; 7, RC Filter; 8, Digital Storage Oscilloscope; 9, Plotter and Computer. [Adapted, by permission, from Chang (1993)]

is the change of species concentration, which is affected by the relaxation reaction. The second and third terms are the change of electrical mobility and the change of density, respectively, resulting from the change of pressure and temperature. The first term represents chemical relaxation whereas the remaining terms represent physical effects. The physical effects can be eliminated by using a reference cell filled with a nonrelaxing solution (e.g., KCl or KNO_3) with the same temperature dependence on conductivity as the sample cell and by maintaining the system under a constant-temperature environment.

2. Apparatus

The primary components of the pressure-jump apparatus consist of a Wheatstone bridge, a function generator, sample and reference cells, and a digital storage oscilloscope. A schematic diagram of the apparatus is shown in Fig. 1. The sample and reference cell are covered with a plastic membrane which effectively transmits the pressure. A piece of brass membrane is clamped on one wall of the autoclave with a bayonet socket. When the pressure in the autoclave is high enough, the brass membrane bursts, and the pressure in the autoclave returns to ambient pressure. After the membrane bursts, a sample suspension having equilibrium at a higher pressure is out of equilibrium

Table 2. Complex Formation Rate Constants Obtained Using the Pressure-Jump Technique at 25 °C

Metal ion	Ligand	k_f (M^{-1}s^{-1})	k_f (s^{-1})	References
Ni	malonate	$(4.2\pm0.4)\times10^5$	42 ± 4	Hoffmann and Stuehr (1966)
Ni	malonate	2.7×10^5	24	Bear and Lin (1968)
Ni	succinate	4.3×10^5	2.7×10^3	Bear and Lin (1968)
Ni	malate	5.6×10^5	17	Harada *et al.* (1972)
Ni	maleate	8.4×10^5	2.1×10^3	Harada and Yasunaga (1973)
Ni	phthalate	6.3×10^5	2.6×10^3	Harada *et al.* (1973a)
Ni	lactate	$(2.6\pm0.3)\times10^4$	$(1.7\pm0.4)\times10^2$	Harada *et al.* (1973b)
Ni	glycolate	2.6×10^4	2.6×10^2	Harada *et al.* (1974)
Mg[a]	BDS^{2-}	$(9\pm3)\times10^4$	12 ± 3	Macri and Petrucci (1970)
Mn[a]	BDS^{2-}	$(11\pm2)\times10^4$	11 ± 2	Macri and Petrucci (1970)
Co[a]	BDS^{2-}	$(12\pm2)\times10^4$	9 ± 2	Macri and Petrucci (1970)
Ni[a]	BDS^{2-}	$(9\pm2)\times10^4$	8 ± 2	Macri and Petrucci (1970)
Cu[a]	BDS^{2-}	$(19\pm2)\times10^4$	11 ± 2	Macri and Petrucci (1970)
Zn[a]	BDS^{2-}	$(13\pm2)\times10^4$	10 ± 2	Macri and Petrucci (1970)

Note: Reaction Mechanisms: $M^{2+}+L^{Z-}\leftrightarrow ML^{(2-Z)+}$

[a] $M_{solv}^{2+}+BDS_{solv}^{2-}\leftrightarrow MBDS$

solv: methanol and BDS: benzenedisulfonate

due to the "instantaneous" pressure jump. The time required to approach equilibrium at ambient pressure is then monitored by a conductivity detector. Water is circulated in the autoclave to maintain a constant temperature.

3. Relaxation Curve and Relaxation Time

The change in concentration (or conductivity/ voltage) data on pressure perturbation is used to graph the relaxation curve with time as shown in Eq. (5):

$$C = C_o\exp\left(\frac{-\Delta t}{\tau}\right), \qquad (5)$$

where C_o and C are the initial and final concentrations (or conductivity/voltage), respectively, two arbitrary points in the curve, Δt is the time interval between these two points, and τ is the relaxation time. The reciprocal of relaxation time (τ^{-1}) is then calculated using Eq. (6) or from the slope of the semi-log plot of t versus C:

$$\tau^{-1} = \frac{\ln C_o - \ln C}{\Delta t}. \qquad (6)$$

IV. Pressure-Jump Applications

1. Complex Formation, Hydrolysis, and Ion Exchange Reaction

A. *Complex Formation Reaction*

Most studies on metal complex formation in the environment have only considered the effects of equi-

librium and have ignored the kinetics. Pankow and Morgan (1981), on the other hand, indicated that a natural system never reaches an equilibrium state, and that kinetic processes are more important. The use of the pressure-jump method is, thus, suitable for calculating the kinetic parameters of forward and backward reactions.

There have been many studies which have used pressure jump techniques to evaluate reaction kinetics of metal complexation. For example, Hoffmann and Stuehr (1966) investigated the complex reaction kinetics of Ni^{2+} reaction with malonate; Bear and Lin (1968) probed the complexation of Ni^{2+} reaction with succinate; Macri and Petrucci (1970) explored Mg^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} complexation with m-benzenedisulfonates in methanol; Dickert *et al.* (1972) investigated Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+} complexation with chloride in methanol; and Kalidas *et al.* (1971) studied Al^{3+} and Ga^{3+} complexation with SO_4^{2-}. The research group of Yasunaga (Harada *et al.*, 1972, 1973a, 1973b, 1974; Harada and Yasunaga, 1973) probed a series of complexation kinetics involving Ni^{2+} complexation with bidentate ligands. Hiraishi *et al.* (1978) and Harada *et al.* (1980) explored the kinetics of Al^{3+} complexation with acetate and monoacetate, respectively. The kinetic constants of the above reactions are summarized in Table 2.
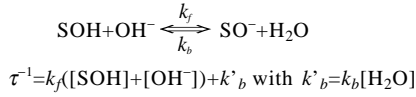
B. *Hydrolysis*

With hydrolysis of the surface hydroxyls, the charge density on the oxide and the dynamic behavior of these hydroxyls will change simultaneously. Therefore, the mechanism of oxide hydrolysis must be

Table 3. Rate Constants of Hydrolysis on the Zeolite 4A, X, and Y Surface at 25 °C

| Zeolite	k_f (M^{-1}s^{-1})	k'_b (s^{-1})	References
Zeolite 4A	1.6×10^2	8.7×10^{-2}	Ikeda *et al.* (1981a)
Zeolite X	2.0×10^2	2.0×10^{-2}	Ikeda *et al.* (1982b)
Zeolite Y	8.1×10^1	7.3×10^{-1}	Ikeda *et al.* (1982b)

Note: Mechanism:

$$SOH + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} SO^- + H_2O$$

$$\tau^{-1} = k_f([SOH] + [OH^-]) + k'_b \text{ with } k'_b = k_b[H_2O]$$

clarified before the mechanism of ionic adsorption and exchange can be well-understood.

Ikeda *et al.* (1981a) observed a single relaxation curve from a solution of zeolite 4A (Na$_2$O•Al$_2$O$_3$•2SiO$_2$•nH$_2$O) above pH 11.5 using the pressure-jump technique. This relaxation phenomenon may have been due to sodium ion entering the zeolite framework, resulting from base-catalyzed adsorption-desorption of the sodium ion. However, in a system to which tetramethylammonium hydroxide was added as the base where the tetramethylammonium could not enter the zeolite framework, the same relaxation phenomenon was also observed. Therefore, it is clear that the relaxation observed was due to interaction between the hydroxide ion and the active sites on the zeolite surface. In other words, hydrolysis on the zeolite 4A surface led to this relaxation phenomenon. Ikeda *et al.* (1982b) further performed a similar study on the suspension of zeolite X (Na$_2$O•Al$_2$O•2.5 SiO$_2$) and zeolite Y (Na$_2$O•Al$_2$O•4.8 SiO$_2$), and obtained similar results. The hydrolysis constants and mechanism of zeolite interaction are summarized in Table 3.

The amphoteric properties of the active surface group on metal oxides play an important role in colloid science and catalytic chemistry. It is well known that the amphoteric surface group adsorbs both anions and cations. Ashida *et al.* (1978, 1980) investigated the adsorption-desorption of H$^+$ and OH$^-$ in the TiO$_2$-H$_2$O system, which was caused by hydrolysis of the TiO$_2$ surface. The reaction mechanisms and kinetic parameters can be represented as follows:

$$SOH + H^+ \underset{k_d}{\overset{k_a}{\rightleftharpoons}} SOH_2^+,$$
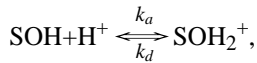
where k_a is the adsorption rate constant (4×10^{-4} dm^3 cm^{-2} s^{-1}) and k_d the desorption rate constant (8×10^{-9} mol cm^{-2} s^{-1});

$$SOH + OH^- \underset{k_d}{\overset{k_a}{\rightleftharpoons}} SO^- + H_2O;$$
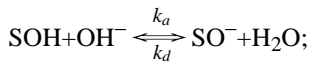
where $k_a = 4.1 \times 10^{-4}$ M^{-1}s^{-1}, and $k_d = 8.5 \times 10^{-3}$ s^{-1}.

Table 4. Ion Exchange Rate Constants and Mechanisms of Different Cations in Zeolite 4A at 25 °C

cation	Volume (nm^3)	k_1 (M^{-1}s^{-1})	k_{-1} (s^{-1})	k_2 (s^{-1})	k_{-2} (s^{-1})
methylamine		1.2×10^4	2.1	2.4	0.24-0.48
NH$_4^+$	0.013	1.8×10^4	2.8	3.7	3.7
CH$_3$NH$_3^+$	0.062	1.2×10^4	1.8	2.3	
C$_2$H$_5$NH$_3^+$	0.090	2.8×10^3	0.4	1.3	
(CH$_3$)$_2$NH$_2^+$	0.086	2.1×10^3	0.7	1.8	
n-C$_3$H$_7$NH$_3^+$	0.111	1.6×10^3	1.3	0.3	0.5

Source: Ikeda *et al.* (1981b, 1983)

Note: Mechanism:

$$S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S.A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} S(A)$$
$$A^+$$
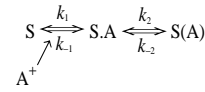
S: the vacant site

S.A: adsorbed state on the surface

S(A): adsorbed site of A$^+$ which diffused into the cage

k_1: forward reaction rate constant of the first step

k_{-1}: backward reaction rate constant of the first step

k_2: forward reaction rate constant of the second step

k_{-2}: backward reaction rate constant of the second step

C. Ion Exchange

Ikeda *et al.* (1981b, 1983) explored the ion exchange kinetics of methylamine, NH$_4^+$, CH$_3$NH$_3^+$, C$_2$H$_5$NH$_3^+$, n-C$_3$H$_7$NH$_3^+$, i-C$_3$H$_7$NH$_3^+$, (CH$_3$)$_2$NH$_2^+$, (CH$_3$)$_3$NH$^+$ and (CH$_3$)$_4$N$^+$ in zeolite 4A suspensions. Their results revealed a double relaxation phenomenon in the methylamine, NH$_4^+$, CH$_3$NH$_3^+$, C$_2$H$_5$NH$_3^+$, n-C$_3$H$_7$NH$_3^+$ and (CH$_3$)$_2$NH$_2^+$ systems. Fast relaxation and slow relaxation are created by the diffusion of these ions across the zeolite surface and adsorption into the zeolite framework, respectively. The rate of adsorption is dependent upon the steric factor, indicating that the rate decreases as the volumes of these ions increase. The ion volumes, kinetic coefficients, and mechanisms of ion exchange are summarized in Table 4. In a similar study, Ikeda *et al.* (1982c) found that L-lysine also displayed a similar reaction to zeolite X. The mechanisms and kinetic parameters can be represented as follows:

$$S(Na) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S(NaA^+) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} S(A),$$
$$A^+ \qquad Na^+$$
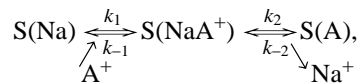
where $k_1 = 2.8 \times 10^2$ M^{-1}s^{-1}, $k_{-1} = 9.1 \times 10^{-1}$ s^{-1}, $k_2 = 5.9 \times 10^{-1}$ s^{-1}, and $k_{-2} = 1.1 \times 10^2$ M^{-1}s^{-1}.

Ikeda *et al.* (1984) further investigated the reaction kinetics of NH$_4^+$ exchange with hydrogen ion in zeolite H-ZSM-5 and observed a single relaxation. The

reaction mechanisms and kinetic constants can be expressed as:

$$S(H) + NH_4^+ \underset{k_b}{\overset{k_f}{\rightleftarrows}} S(NH_4^+) + H^+,$$

$$\tau^{-1} = k_f([S(H)] + [NH_4^+]) + k_b([S(NH_4^+)] + [H^+]),$$

$k_f = 650$ $M^{-1}s^{-1}$, and $k_b = 800$ $M^{-1}s^{-1}$.

2. Solid/Water Interface

A. *Cation Adsorption/Desorption*

Most traditional batch and flow methods are incapable of providing detailed information regarding processes at the interface, owing to an inability to detect changes in the system as rapidly as the adsorption reaction proceeds. Relaxation methods, especially the pressure-jump technique, not only compensate for the disadvantages of traditional methods, but can also describe reaction mechanisms.

Cation adsorption/desorption reactions observed using the pressure-jump technique are classified according to valency.

B. *Monovalent Cations*

Astumian *et al.* (1981) explored the adsorption/ desorption of protons on the iron oxide surface. Single relaxations were observed in aqueous suspensions of γ-Fe$_2$O$_3$ (hematite) and Fe$_3$O$_4$ (magnetite), but no relaxation could be observed in a goethite (FeOOH) suspension. The reciprocal relaxation times obtained for both the hematite and magnetite suspensions showed the same parabolic dependence on pH, with a minimum at pH 3.4. The relaxation can be interpreted in terms of proton adsorption-desorption at the surface of the iron oxide particles with the following kinetic constants:

$$\gamma\text{-}Fe_2O_3 \quad k_a^{int} = 2.4 \times 10^5 \ M^{-1}s^{-1}, \quad k_d^{int} = 1.6 \times 10^{-1} \ s^{-1},$$

$$Fe_3O_4 \quad k_a^{int} = 1.4 \times 10^5 \ M^{-1}s^{-1}, \quad k_d^{int} = 3.4 \times 10^{-1} \ s^{-1},$$

where k_a^{int} is the proton intrinsic adsorption rate constant and k_d^{int} the proton intrinsic desorption rate constant. The "intrinsic" equilibrium (or reaction rate) constants which do not depend on surface charge and these intrinsic constants in this paper are denoted as "int" in superscript.

Astumian *et al.* (1981) further indicated that the pK$_{a1}$ (pK$_a$: acidity quotient) of the oxides plays an important role in obtaining relaxation signals. They also observed that relaxations could be observed only in the approximate range of $2 \leq pK_{a1} \leq 4$ because systems

with very small or very large equilibrium constants were relatively insensitive to perturbation. From this point of view, when comparing different pK$_{a1}$ values of several oxide suspensions (pK$_{a1}$<1 for SiO$_2$, 2.5-3.0 for TiO$_2$, 4.3-5.0 for goethite, and 4.4-6.0 for γ-Al$_2$O$_3$), it is not surprising that no relaxation could be observed in SiO$_2$, goethite, or γ-Al$_2$O$_3$.

Hachiya and Yamaguchi (1994) performed a kinetic study on the adsorption-desorption of alkali metal ions on Carboxymethyl Sephadex C-25 using the pressure-jump technique, and a single relaxation was observed. The relaxation time increased in speed with increasing concentrations of the added alkali metal ions. The relaxation was attributed to the conformational change of the Sephadex particles accompanying the ion-pair formation between alkali metal ions and the dissociated Carboxymethyl groups. The reaction mechanism can be represented as:

$$-COO^- + M^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (-COO^-....M^+)_I$$

$$\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (-COO^-....M^+)_{II},$$
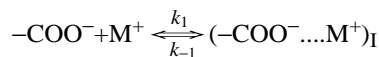
where $(-COO^-....M^+)_I$ and $(-COO^-....M^+)_{II}$ denote the two types of ion pairs. The authors assumed that the speed of step 1 was faster than that of step 2 and determined k_2^{int} (s^{-1}) values for Li$^+$(97), Na$^+$(70), and K$^+$(34). The movement for conformation change follows the atomic weights of the alkali metal ions, or K$^+$> Na$^+$>Li$^+$, resulting in k_2^{int}(Li$^+$)>k_2^{int}(Na$^+$) >k_2^{int}(K$^+$).

C. *Divalent Cations*

Hachiya *et al.* (1979) evaluated the kinetics of Pb^{2+} adsorption-desorption on a γ-Al$_2$O$_3$ surface using the electric field pulse method for a fast reaction and the pressure-jump method for a slow reaction. Double relaxations were found in aqueous γ-Al$_2$O$_3$ suspension containing Pb^{2+}, and the reciprocal fast relaxation decreased while the slow relaxation increased with increasing Pb^{2+} concentration. The fast relaxation measured was attributed to adsorption-desorption of Pb^{2+} on the hydrous oxide surface group Al-OH, and the slow one to the deprotonation-protonation process induced by the adsorbed Pb^{2+}. The forward and backward reaction rates of the first step were 1. 4×10^8 M^{-1}s^{-1} and 1.0×10^4 s^{-1}, respectively, and of the second step, 1.3×10 s^{-1} and 1.5×10^6 M^{-1}s^{-1}, respectively.
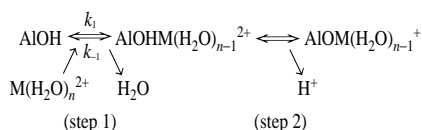
Hachiya *et al.* (1984) further studied the kinetics of adsorption-desorption of Cu^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+} and Pb^{2+} on the γ-Al$_2$O$_3$ surface using the pressure-jump technique, all with double relaxations. The authors

Table 5. Intrinsic Rate Constants and Mechanisms of Adsorption-Desorption of Metal Ions on the γ-Al_2O_3 Surface at 25 °C

metal ion	k_1^{int} ($M^{-1}s^{-1}$)	k_{-1}^{int} ($M^{-1}s^{-1}$)
Pb^{2+}	$(6.4\pm1.6)\times10^4$	$(4.1\pm1.0)\times10^6$
Cu^{2+}	$(7.4\pm2.0)\times10^3$	$(3.1\pm0.9)\times10^5$
Zn^{2+}	$(5.1\pm0.8)\times10^2$	$(1.3\pm0.2)\times10^5$
Mn^{2+}	$(3.2\pm0.5)\times10$	$(1.8\pm0.3)\times10^6$
Co^{2+}	$(1.5\pm0.4)\times10$	$(6.9\pm1.9)\times10^4$

Source: Hachiya *et al.* (1984)
Note: Mechanism:

$$AlOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AlOHM(H_2O)_{n-1}^{2+} \rightleftharpoons AlOM(H_2O)_{n-1}^+$$

$$M(H_2O)_n^{2+} \quad H_2O \qquad\qquad H^+$$

$$\text{(step 1)} \qquad\qquad \text{(step 2)}$$
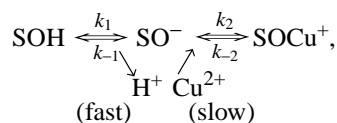
M: divalent metal ion

found that the order of the adsorption rate constants of metal ions corresponded to that of the rate constants for the release of a water molecule from hydrated metal ions in homogeneous metal complex systems. Chang *et al.* (1993) also found a similar relationship in the Cu^{2+}/γ-Al_2O_3 system. For this relationship, Lin *et al.* (1997) provided an overall explanation. This relationship, however, does not exist in the Cr(III)/γ-Al_2O_3 system (Chang *et al.*, 1994), nor in the Ga(III) and In(III)/γ-Al_2O_3 system (Lin *et al.*, 1997). The adsorption/desorption of trivalent cations will be described in detail in the following section. Table 5 shows the reaction mechanisms and kinetic parameters of adsorption-desorption of divalent metal ions onto the γ-Al_2O_3 surface.

Hayes (1987) studied the adsorption-desorption of Pb^{2+} onto α-goethite under experimental conditions similar to those used by Hachiya *et al.* (1984) and found the same fast reaction mechanism. Verification of the slow reaction mechanism, however, failed after several possible reactions were tested. The author inferred that the background electrolyte might have interferred with the kinetic measurements. Because two close background electrolyte concentrations (0.01 M and 0.015 M $NaNO_3$) were used, its effect was not noticeable. Nevertheless, Hayes (1987) assumed that the ion pair formation with NO_3^- was responsible for the slow reaction; this assumption, however, was somewhat different from the experimental results.

Mikami *et al.* (1983b) studied the kinetics of the adsorption-desorption of uranyl ion on the γ-Al_2O_3 surface. A single relaxation was observed, and the reciprocal relaxation time increased with the uranyl ion concentration whereas it decreased and then approached a constant value with increasing pH. The relaxation was attributed to the adsorption-desorption

of $(UO_2)_3(OH)_5^+$ on the surface hydroxyl group of γ-Al_2O_3. The intrinsic values of the adsorption and desorption rate constants were found to be 1.6×10^3 $M^{-1}s^{-1}$ and 1.1×10^5 $M^{-1}s^{-1}$, respectively.

As a reference, a constant concentration of background electrolyte was added to the system for pressure-jump testing. Because the background electrolyte ions could react with the metal oxides, a superfluous signal was produced and interferred with the results of the adsorption-desorption reaction. Chang *et al.* (1993) studied the adsorption kinetics of Cu^{2+} on the γ-Al_2O_3 surface to correct this interference. They added different concentrations of background electrolyte in the adsorption experiment and concluded that the reaction of Cu^{2+} with γ-Al_2O_3 was an inner-adsorption reaction. When no background electrolyte was added for pressure-jump measurements, a double relaxation was observed. The triple-layer model Hayes and Leckie (1987) developed, in conjunction with kinetic experiments using a pressure-jump apparatus, essentially verified the formation of the inner-sphere Cu^{2+} complex at the surface of γ-Al_2O_3. The mechanisms and kinetic constants can represented as follows:

$$SOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SOCu^+,$$

$$H^+ \quad Cu^{2+}$$

$$\text{(fast)} \qquad \text{(slow)}$$

where $k_1^{int}=1.2\times10^{-3}$ s^{-1}, $k_{-1}^{int}=4.7\times10^5$ $M^{-1}s^{-1}$, $k_2^{int}=9.1\times10^6$ $M^{-1}s^{-1}$, and $k_{-2}^{int}=1.8\times10^{-3}$ s^{-1}.

D. Trivalent Cations

Chang *et al.* (1994) and Lin *et al.* (1997) studied the kinetics of adsorption-desorption of Cr(III), Ga(III), and In(III) on the surface of γ-Al_2O_3. The reaction mechanisms for the adsorption of trivalent cations onto the γ-Al_2O_3 surface are listed in Table 6, in which both Mechanisms I and II correspond with the experimental results. The adsorption process occurs with proton release from the surface hydroxyl group, followed by coordination of Me^{3+} and $MeOH^{2+}$ to induce bidentate and monodentate adsorption. The intrinsic rate constants are summarized in Table 7.

Hachiya *et al.* (1984) and Stumm (1992) have found that the intrinsic adsorption rate constants of divalent metal ions are linearly related to the rate constants for the release of water molecules from hydrated metal ions. The relationship was further quantified by Lin *et al.* (1997), who provided a summary of adsorption mechanisms of bivalent and trivalent metal ions.

In summary, sorption of trivalent metal ions

Table 6. Mechanistic Pathways and the Relationship between Reciprocal Relaxation Times and Concentrations of Cr(III), Ga(III), and In(III) Species on the γ-Al$_2$O$_3$ Surface

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Mechanism I

(1) Mechanistic pathway:

$$2SOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2SO^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (SO)_2Me^+.$$
$$\qquad\qquad 2H^+ \quad Me^{3+}$$

(2) Relationship between reciprocal relaxation times and species activities

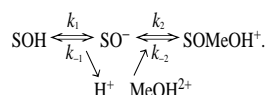$$\tau^{-1}\exp\left(\frac{-3\Psi_0 F}{2RT}\right) = k_2^{int}\{\exp(\frac{-3\Psi_0 F}{RT})([\overline{SO^-}]^2 + \frac{[\overline{SO^-}]\{\overline{Me^{3+}}\}}{G})\}$$

$$+ k_{-2}^{int} = k_2^{int}\{MIII^*\} + k_{-2}^{int}$$

with

$$G = \frac{\{\overline{H^+}\}^2[\overline{SO^-}]}{(K_{a2}^{int})^2\exp(2\Psi_0 F/RT)[\overline{SOH}] + \{\overline{H^+}\}[\overline{SO^-}]^2} + 1.$$

Mechanism II

(1) Mechanistic pathway:

$$SOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SOMeOH^+.$$
$$\qquad\quad H^+ \quad MeOH^{2+}$$

(2) Relationship between reciprocal relaxation times and species activities

$$\tau^{-1}\exp(\frac{-\Psi_0 F}{RT}) = k_2^{int}\{\exp(\frac{-2\Psi_0 F}{RT})([\overline{SO^-}] + \{\overline{MeOH^{2+}}\}$$

$$\frac{(K_1^{int})\exp(\Psi_0 F/RT) + [\overline{SO^-}]}{(K_1^{int})\exp(\Psi_0 F/RT) + \{\overline{H^+}\}[\overline{SO^-}]})\} + k_{-2}^{int}$$

$$= k_2^{int}\{MIV^*\} + k_{-2}^{int}.$$

Source: Lin *et al.* (1997)
Note: *Me denotes Cr or Ga or In.

Table 7. The Intrinsic Rate Constants and Equilibrium Constants in Mechanism I and II at 25 °C

Mechanism	$\log k_2^{int}$ (M^{-1}s^{-1})	$\log k_{-2}^{int}$ (s^{-1})	$\log K_{2, kinetic}^{int}$ (M^{-1})	$\log K_{2, equil}^{int}$ (M^{-1})
Cr(III) I	11.45[a]	−7.08	18.53[b]	18.46[b]
II	7.06	−6.20	13.26	11.85
Ga(III) I	13.22	−8.92	22.13	22.15
II	8.04	−6.39	14.43	13.83
In(III) I	12.83	−8.96	21.34	20.63
II	7.44	−8.06	15.49	13.76

Sources: Chang *et al.* (1994) and Lin *et al.* (1997)
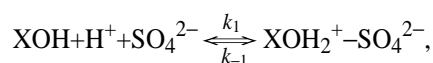[a] unit: M^{-2}s^{-1}
[b] unit: M^{-2}

nonmetal, the valance of the central atom, the number of oxygen molecules which are bonded in anions, and the valance of the ions. It is not possible to elucidate a unfied reaction mechanism of anions to the oxide surface. Therefore, anion adsorption reactions can only be categorized as outer-sphere adsorption and inner-sphere adsorption reactions.

A. Outer-Sphere Adsorption

Ikeda *et al.* (1982a) investigated the adsorption-desorption kinetics of acetic acid on silica-alumina particles in aqueous suspensions, and a double relaxation was observed. The fast relaxation was attributed to protonation-deprotonation reaction on the silica-alumina surface, and the slow relaxation to the adsorption-desorption process of the acetate ion, accompanied by elimination of a water molecule from the surface. The intrinsic values of the protonation and deprotonation rate constants determined were 2.9×10^4 M^{-1}s^{-1} and 46 s^{-1}, respectively, and those of the adsorption and desorption rate constants were 6.5 M^{-1}s^{-1} and 3.8×10^{-3} s^{-1}, respectively.

Zhang and Sparks (1990a) observed the kinetics and mechanisms of sulfate adsorption-desorption onto goethite. The sulfate adsorption isotherm indicated that adsorption decreased with increasing pH in the goethite suspension. The triple-layer model predicted the experimental data well, and sulfate adsorption onto goethite was found to be an outer-sphere adsorption. A single relaxation was observed using the pressure-jump technique. The intrinsic equilibrium constants obtained from the triple-layer model simulation and kinetic measurement were similar. The mechanism and rate constants can be shown as follows:

$$XOH + H^+ + SO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XOH_2^+ - SO_4^{2-},$$

where $k_1^{int} = 2.1 \times 10^8$ M^{-2}s^{-1} and $k_{-1}^{int} = 0.14$ s^{-1}.

onto aluminum oxide is an associative mechanism. Proton(s) is released from surface hydroxyl group(s), followed by the attachment of metal ions to form a surface complex. On the other hand, sorption of divalent metal ions is a dissociative mechanism, where the proton present in the oxide does not have to leave before the surface reaction site coordinates with the metal ion.

3. Anion Adsorption/Desorption

Unlike cation adsorption, where a small variance exists between each cation, there are significant differences among anions. For example, there are differences in the central atoms, which can be metal or

Zhang and Sparks (1990b) further conducted a similar study on the kinetics of selenate adsorption-desorption at the goethite/water interface, and the reaction mechanism was the same as that of sulfate. The adsorption and desorption rate constants were 3.5×10^8 $M^{-2}s^{-1}$ and 3.34 s^{-1}, respectively.

Wu et al. (1998a) explored the sulfate and selenate adsorption/desorption on γ-Al_2O_3 in aqueous suspension. The triple-layer model fit the experimental data well when adsorbed sulfate and selenate were assumed to form outer-sphere complexes (SOH_2^+–$SO_4^{2-}$and SOH_2^+–SeO_4^{2-}). Based on the relaxation theory and combined results of TLM simulations, a single-step process was proposed. The intrinsic rate constants of the adsorption and desorption were determined to be $k_1^{int}=2.7 \times 10^8$ $M^{-2}s^{-1}$ and $k_{-1}^{int}=1.1 \times 10^{-2}$ s^{-1} in the SO_4^{2-}/γ-Al_2O_3 system, and $k_1^{int}=4.3 \times 10^8$ $M^{-2}s^{-1}$ and $k_{-1}^{int}=4.4 \times 10^{-2}$ s^{-1} in the SeO_4^{2-}/γ-Al_2O_3 system.

Mikami et al. (1983a) investigated the kinetics of the adsorption-desorption of phosphate on the γ-Al_2O_3 surface. A double relaxation was observed within the pH range of 5-8.5, and the fast relaxation time decreased while the slow one increased with the pH. The proposed reaction mechanisms and reaction rate constants are
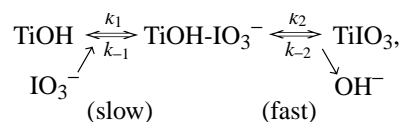
$$AlOH_2^+ + H_2PO_4^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AlOH_2^+ - H_2PO_4^-,$$

$$AlOH_2^+ + HPO_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} AlOH_2^+ - HPO_4^{2-},$$
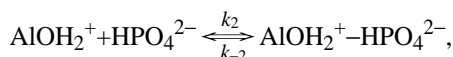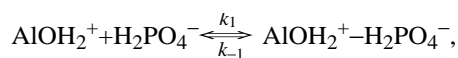
where $k_1^{int}=4.1 \times 10^5$ $M^{-1}s^{-1}$, $k_{-1}^{int}=2.3$ s^{-1}, $k_2^{int}=4.1 \times 10^7$ $M^{-1}s^{-1}$, and $k_{-2}^{int}=2.7$ s^{-1}.

Mikami et al. (1983c) performed a similar study on chromate. The results indicated that both the fast and slow relaxation times decreased with an increasing chromate concentration, and that the fast relaxation time was independent of the pH while the slow time increased with the pH. The chromate reaction mechanisms were the same as those for phosphate. The reaction rate constants were $k_1^{int}=5.3 \times 10^4$ $M^{-1}s^{-1}$, $k_{-1}^{int}=1.9 \times 10$ s^{-1}, $k_2^{int}=9.9 \times 10^4$ $M^{-1}s^{-1}$, and $k_{-2}^{int}=5.2 \times 10$ s^{-1}. A comparison of the values of the adsorption-desorption rate constants for phosphate and chromate shows that k_{-1}^{int} (chromate) $>k_{-1}^{int}$ (phosphate) and k_{-2}^{int} (chromate) $>k_{-2}^{int}$ (phosphate), indicating that the interaction of chromate with $AlOH_2^+$ is weaker than that of phosphate with $AlOH_2^+$.

B. Inner-Sphere Adsorption

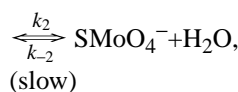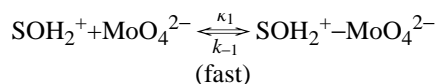Hachiya et al. (1980) investigated the adsorption-desorption of IO_3^- on a TiO_2 surface, and a double relaxation was observed using the electric field pulse and pressure-jump techniques. The reciprocal relaxation times of both methods increased with the concentration of IO_3^-. The reaction mechanisms and kinetic constants can be displayed as follows:

$$TiOH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} TiOH\text{-}IO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} TiIO_3,$$

$$IO_3^- \qquad \qquad \qquad OH^-$$
$$\text{(slow)} \qquad \qquad \text{(fast)}$$

where $k_1=4.3 \times 10^3$ $M^{-1}s^{-1}$, $k_{-1}=2.0 \times 10$ s^{-1}, $k_2=1.9 \times 10^2$ s^{-1}, $k_{-2}=5.8 \times 10^8$ $M^{-1}s^{-1}$, and $TiOH\text{-}IO_3^-$ is a stable complex formed by adsorption of IO_3^-. The kinetic constants indicate that k_{-2} is larger than k_1, due to the higher IO_3^- adsorption activation energy.
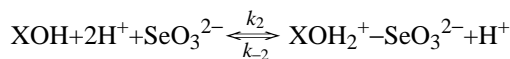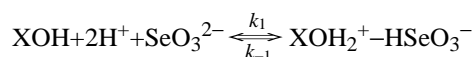
Zhang and Sparks (1989) studied the kinetics and mechanisms of molybdate adsorption-desorption at the goethite/water interface. Both the equilibrium and kinetic data fit the postulated mechanism for the reaction steps and the modified adsorption model well. The reaction mechanisms and rate constants can be represented as:
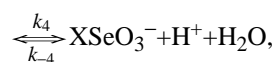
$$SOH_2^+ + MoO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SOH_2^+ - MoO_4^{2-}$$
$$\text{(fast)}$$

$$\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} SMoO_4^- + H_2O,$$
$$\text{(slow)}$$

where $k_1^{int}=4019$ $M^{-1}s^{-1}$, $k_{-1}^{int}=392$ s^{-1}, $k_2^{int}=1.9$ $M^{-1}s^{-1}$, and $k_{-2}^{int}=42.3$ s^{-1}.

Wu et al. (1998b) investigated the kinetics and mechanisms of molybdate adsorption/desorption at the γ-Al_2O_3/water interface. Based on the relaxation theory and combined results of TLM simulation, a two-step process was proposed. The first step (k_1, k_{-1}) is the formation of an ion-pair complex through electrostatic attraction between the reacting surface sites and MoO_4^{2-} and H^+. The second step (k_2, k_{-2}) involves a ligand exchange process, whereby one water molecule is replaced by one adsorbed MoO_4^{2-} from the surface. The values of the adsorption and desorption rate constants in the MoO_4^{2-}/γ-Al_2O_3 system were determined to be $k_1^{int}=5.23 \times 10^6$ $M^{-2}s^{-1}$, $k_{-1}^{int}=2.41 \times 10$ s^{-1}, $k_2^{int}=1.74$ s^{-1} and $k_{-2}^{int}=3.26 \times 10^{-1}$ s^{-1}.

In another study, Zhang and Sparks (1990b) reported on the adsorption mechanisms of selenite on the goethite surface. The first step is the formation of an outer-sphere surface complex through electrostatic attraction. In the second step, the adsorbed selenite ion replaces a H_2O molecule from the protonated surface hydroxyl group and forms an inner-sphere surface complex. The reaction mechanisms and kinetic parameters can be shown as follows:

$$XOH+2H^++SeO_3^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XOH_2^+-HSeO_3^-$$

$$\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} XHSeO_3+H_2O^-,$$

$$XOH+2H^++SeO_3^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} XOH_2^+-SeO_3^{2-}+H^+$$

Step 1 (fast)

$$\underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} XSeO_3^-+H^++H_2O,$$

Step 2 (slow)

where $k_1^{int}=3.82\times10^{14}$ $M^{-3}s^{-1}$, $k_{-1}^{int}=4.07$ s^{-1}, $k_3^{int}=$ 101 s^{-1}, $k_{-3}^{int}=9.7\times10^{-5}$ s^{-1}, $k_2^{int}=2.18\times10^{13}$ $M^{-2}s^{-1}$, $k_{-2}^{int}=3.26\times10^{-3}$ s^{-1}, $k_4^{int}=0.13$ s^{-1}, and $k_{-4}^{int}=0.05$ s^{-1}.

Grossl *et al.* (1997) proposed reaction mechanisms of arsenate and chromate on the goethite surface, assuming that the mechanism was a two-step reaction. The first step, associated with the fast relaxation time, involves an initial ligand exchange reaction of aqueous oxyanion species $H_2AsO_4^-$ or $HCrO_4^-$ with OH^- ligands at the goethite surface, thus forming an inner-sphere monodentate surface complex. The second step of the slow relaxation time involves a second ligand exchange reaction, resulting in the formation of an inner-sphere bidentate surface complex. A comparison of the equilibrium constants obtained from simulation of the constant capacitance model and kinetic measurement of the pressure-jump indicates that the result of the first step fits well while that of the second step does not. This suggests that although the mechanism proposed for step 1 is valid, the step 2 reaction may involve a more elementary reaction than has been imagined, thereby leading to incomplete results. The results from both kinetic and equilibrium batch experiments suggest that arsenate is more likely to form an inner-sphere surface complex with goethite than with chromate. Con-sequently, arsenate may be more readily adsorbed in soil systems, and chromate may be the more mobile of the two oxyanions in natural systems.

V. Summary

From this review, it is clear that the pressure-jump technique, which is different from the traditional batch and flow methods, is an excellent technique for kinetic studies on heterogeneous adsorption/desorption system. It can be used to elucidate the reaction mechanisms and determine kinetic parameters of a complex reaction, hydrolysis, ion-exchange reaction, and cation/anion adsorption on an oxide surface. For cation adsorption, the divalent and trivalent cations exhibite the dissociative and associative processes, respectively. Therefore, the trivalent cations cannot be used to estimate the

sorption rate constant using the LFER, which is appropriate only for divalent cations. For anion adsorption, however, no general conclusion is obtainable. Many researchers cited in this paper have significantly advanced the pressure jump technique in general, and have studied many applications in particular. Undoubtedly, the results summarized in this review paper will enhance our understanding of complicated chemical reactions at the microlevel.

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壓力跳躍法於反應動力研究之回顧

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摘　要

傳統動力學之研究常採用批次式及流動式之實驗法，但因質傳、擴散、吸附、脱附等反應同時發生於一系統中，故難以求得真正之反應速率常數及反應機制。本文介紹之壓力跳躍法基於釋放動力學之理論，偵測已平衡系統中受壓力擾動平衡後之變化，可推求真正之反應速率常數並引證其反應機制。本文將解釋說明壓力跳躍法於錯合反應、水解反應、離子交換反應及吸附、脱附等反應之應用。