

# A Critical Evaluation on the Use of Kinetics for Determining Thermodynamics of Ion Exchange in Soils<sup>1</sup>

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## ABSTRACT

Thermodynamics of K-Ca exchange were compared using equilibrium and kinetic approaches in two Delaware soils. The classical Argersinger theory was employed for the equilibrium approach, while a kinetic approach was studied using miscible displacement, batch, and vigorously mixed batch techniques. These three techniques were used to determine how diffusion affects the comparison between thermodynamic parameters using kinetic and equilibrium approaches. Rate coefficients and energies of activation were profoundly affected by the type of kinetic technique employed and their magnitude was in the order: vigorously mixed batch > batch > miscible displacement. Energies of activation for adsorption ( $E_{ad}$ ) in the two soils ranged from 7.42 kJ mol<sup>-1</sup> using the miscible displacement technique to 32.96 kJ mol<sup>-1</sup> with the vigorously mixed batch, while energies of activation for desorption ( $E_{sd}$ ) ranged from 11.87 to 42.1 kJ mol<sup>-1</sup> for the two methods, respectively. The magnitude of the  $E_{ad}$  and  $E_{sd}$  values indicated pronounced diffusion effects in the miscible displacement and batch techniques, which were greatly reduced with the vigorously mixed batch method. Thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) calculated using the equilibrium and kinetic approaches compared very well in trend, and gave the same inferences of ion behavior for the two soils studied. However, except for the vigorously mixed batch technique, the magnitude of the thermodynamic parameters for the two approaches compared poorly. For example, the  $\Delta G^\circ$  values calculated using the equilibrium approach avg 4.67 kJ mol<sup>-1</sup> for the two soils, while they avg 4.92 kJ mol<sup>-1</sup> with the vigorously mixed batch, 2.12 kJ mol<sup>-1</sup> with the batch, and 2.12 kJ mol<sup>-1</sup> with the miscible displacement. The degree of comparison between the two approaches was directly related to the extent of diffusion controlled exchange. When the influence of diffusion was significantly reduced, as with the vigorously mixed batch technique, our data would indicate that a kinetic approach can be successfully used to gather thermodynamic information about a soil system.

**Additional Index Words:** dynamics of ion exchange, kinetic methods, physical chemistry of K, film diffusion.

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ONE CAN STUDY ion exchange in soils and clay minerals from either a thermodynamic or a kinetic perspective. Most studies on the chemistry of soil K have been of a thermodynamic nature, or were based on the law of mass action (Hutcheon, 1966; Deist and Talibudeen, 1967; Jensen, 1973). However, recently Sparks and his co-workers (Sparks et al., 1980a, b; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984; Carski and Sparks, 1985; Sparks, 1985; 1986) studied soil K exchange from a kinetic viewpoint.

Thermodynamic investigations on K have proved

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valuable, but they do not assist one in understanding the mechanisms and rates of K exchange in clay minerals and soils, nor are they often applicable to field conditions. Agricultural soils are nearly always in a state of nonequilibrium with regard to K reactions. Soils that have been intensively cropped and fertilized with optimal fertilizer additions for many years belong in this group, because equilibrium is precluded by periodic additions of K fertilizers (Sparks, 1985; 1986).

H.C. Thomas (1965) asked whether a relationship existed between the standard enthalpy of exchange for the solid phase ( $\Delta H_s^\circ$ ) and the activation enthalpy,  $\Delta H^\ddagger$ , of an ion exchange reaction, where

$$\Delta H_s^\circ = \Delta H^\ddagger - \Delta H_1^\circ \quad [1]$$

and  $\Delta H_1^\circ$  is the standard enthalpy of exchange for the solution phase (Goulding, 1983). He suggested that the best way to establish such a connection was through self-diffusion studies. Unfortunately, no further publication has appeared clarifying this idea or confirming the relationship.

It has been known for many years that a direct relationship exists between chemical equilibria and completely reversible reactions (e.g., see Glasstone et al., 1941; Laidler, 1965). Keay and Wild (1961) used this approach to calculate the enthalpy and entropy of Na-Mg exchange on vermiculite from measurements of kinetics of Mg-Na and Na-Mg exchange. Sparks and Jardine (1981) first applied the relationship to K<sup>+</sup> exchange studies, and they calculated apparent thermodynamic parameters of K-Ca exchange on a soil from measurements of the kinetics of this reaction. A miscible displacement technique (Sparks et al., 1980b) was used to calculate the kinetic parameters. The magnitude of the apparent thermodynamic parameters determined by Sparks and Jardine (1981) compared well to pseudothermodynamic parameters calculated using Eyring's reaction rate theory. However, the authors did not also calculate thermodynamic parameters from classical exchange isotherm data and compare the results using the two theories.

Such a comparison for soils or clay minerals has not been published. A study of this type would lend credence to both theories. However, Goulding (1983) noted that the apparent thermodynamic parameters calculated by Sparks and Jardine (1981) compared in magnitude to a range of values found by Deist and Talibudeen (1967) for British soils using exchange isotherm data.

Accordingly, we will determine the theoretical and practical implications of using a kinetic approach to calculate thermodynamic parameters for K-Ca exchange in soils. This will be accomplished by comparing both in magnitude and trend the parameters using kinetic and equilibrium theories.

Several methods will be employed for the kinetics approach, while the Argersinger theory (Argersinger et al. 1950) will be used for the equilibrium approach. A

study of this type has not appeared in the soil-chemistry literature.

**MATERIALS AND METHODS**

**Theoretical Considerations**

*Equilibrium Approach*

If one employs the classical theory of Argersinger et al. (1950) to the following exchange reaction,



one finds that the thermodynamic equilibrium constant ( $K_{\text{eq}}$ ) is given by

$$K_{\text{eq}} = \frac{a_{\text{K(ad)}}^2 a_{\text{Ca}}}{a_{\text{Ca(ad)}} a_{\text{K}}^2} \quad [3]$$

where  $a_{\text{(ad)}}$  = activity of the cation on the exchanger phase and  $a$  = activity of the cation in the solution phase.

Treating the exchanger as a nonideal solid solution and assuming the activity of adsorbed water is negligible,

$$a_{\text{K(ad)}}^2 = f_{\text{K}}^2 \bar{N}_{\text{K}}^2 \text{ and } a_{\text{Ca(ad)}} = f_{\text{Ca}} \bar{N}_{\text{Ca}} \quad [4]$$

$$a_{\text{K}}^2 = \delta_{\text{KCl}}^4 m_{\text{K}}^2 \text{ and } a_{\text{Ca}} = \delta_{\text{CaCl}_2}^3 m_{\text{Ca}} \quad [5]$$

where

$f$  = activity coefficient of the cation on the exchanger phase,

$\bar{N}$  = mole fraction of the cation on the exchanger phase,

$\delta$  = mean activity coefficient of the ions in the solution phase, and

$m$  = molality of the cation in the solution phase.

Thus, Eq. [3] assumes the form:

$$\frac{f_{\text{K}}^2 \bar{N}_{\text{K}}^2 \delta_{\text{CaCl}_2}^3 m_{\text{Ca}}}{f_{\text{Ca}} \bar{N}_{\text{Ca}} \delta_{\text{KCl}}^4 m_{\text{K}}^2} = K_{\text{eq}} \quad [6]$$

or

$$K_{\text{eq}} = (f_{\text{K}}^2/f_{\text{Ca}}) k_v \quad [7]$$

where  $k_v$  = Vanselow selectivity coefficient.

Applying the Gibbs-Duhem equation to this binary system and combining with Eq. [6], one may obtain the following using a mole fraction of unity as the standard state for adsorbed ions (Argersinger et al., 1950):

$$\ln K_{\text{eq}} = \int_0^1 \ln k_v d\bar{X}_{\text{K}} \quad [8]$$

where  $\bar{X}_{\text{K}}$  is the equivalent fraction of  $\text{K}^+$  on the colloid. Integrals are then evaluated graphically by plotting  $\ln k_v$  against  $\bar{X}_{\text{K}}$ . The area under the curve that equals  $\ln K_{\text{eq}}$  can be obtained using the trapezoidal rule.

The standard free energy,  $\Delta G^\circ$ ; enthalpy,  $\Delta H^\circ$ ; and entropy,  $\Delta S^\circ$  changes for  $\text{K}^+$  exchange are then calculated from Eq. [9] to [11],

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad [9]$$

where  $R$  = the universal gas constant and  $T$  = absolute temperature in degrees K.

$$\ln \left( \frac{K_{\text{eq1}}}{K_{\text{eq2}}} \right) = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad [10]$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T. \quad [11]$$

*Kinetics Approach*

The general derivation of a kinetics model for cation exchange is based on the rate of the reaction in Eq. [2]. One

assumes at the outset that this rate can be expressed as (Denbigh, 1981; Sposito, 1986):

$$dE/dt = R_f - R_b \quad [12]$$

where  $dE$  = extent of the reaction parameter,  $R_f$  is the rate of the forward, and  $R_b$  is the rate of the backward reaction in Eq. [2], e.g., the same reaction describes both the forward and the backward processes in the K-Ca reaction.

The individual rates  $R_f$  and  $R_b$  each will depend on temperature, pressure, and the concentrations of the species in Eq. [2]. At equilibrium, the left side of Eq. [12] will vanish and  $R_{fe}/R_{be}$ , where  $e$  denotes the equilibrium condition, will be some function of temperature, pressure, and the equilibrium composition of the exchanger and the aqueous solution phase. Since the activity coefficients of the species in Eq. [2] have the same kind of functional dependence, one may infer that  $R_{fe}/R_{be}$  is a function of  $T$ ,  $P$ , and the species activities (Denbigh, 1981). However, this relationship applies also to the quotient of the right and left sides of Eq. [6] and, therefore, one may conclude that, for example,

$$R_{fe}/R_{be} = F [(a_{\text{K(ad)}})_e^2 (a_{\text{Ca}})_e / (a_{\text{Ca(ad)}})_e (a_{\text{K}})_e^2 K_{\text{eq}}] \quad [13]$$

in respect to Eq. [3]. Equation [13] expresses a general relation between reaction rate and thermodynamics, predicated on Eq. [12] and the uniqueness of Eq. [2] as experimental facts of kinetics. If it is assumed further that  $F(x) = x$  on the right side of Eq. [13], then  $R_{fe}/R_{be}$  will equal the quotient of the right and left sides of Eq. [6]:

$$R_{fe}/R_{be} = (a_{\text{K(ad)}})_e^2 (a_{\text{Ca}})_e / (a_{\text{Ca(ad)}})_e (a_{\text{K}})_e^2 K_{\text{eq}} \quad [14]$$

Equation [14] is expected whenever  $R_f$  and  $R_b$  depend on powers of the concentrations of the reactants and products in Eq. [2], and the power exponents are the stoichiometric coefficients of the four species involved (Denbigh, 1981). Even with this simplification of Eq. [12], it is necessary to assume that the mechanism of the cation exchange reaction at equilibrium does not change when  $R_f \neq R_b$  in order that finite rate data can be used in the application of Eq. [14].

For the kinetic phase of this study, we are studying the following exchange reaction (Sposito, 1986):



One could theorize that the applicability of Eq. [12] to [15] depends on the assumption that the rate is not controlled by diffusion processes. Helfferich (1965; 1983) has noted that if the rate-controlling process is diffusion and not the reaction in Eq. [15], then no information about  $K_{\text{eq}}$  can be derived from an analysis of kinetics data. This hypothesis will be tested in our experimental studies. Assuming the influence of diffusion is eliminated or practically so, the rates  $R_f$  and  $R_b$  can be modeled for K-Ca exchange using the equations:

$$R_f = k_a M_s q_{\text{Ca}} m_{\text{K}} \quad R_b = k_d M_s q_{\text{K}} m_{\text{Ca}}^{1/2} \quad [16]$$

where  $k_a$  and  $k_d$  are adsorption and desorption rate coefficients, respectively,  $M_s$  is the mass of the exchanger,  $q_i$  ( $i = \text{Ca}$  or  $\text{K}$ ) is the number of moles of charge of metal  $i$  adsorbed by unit mass of the exchanger, and  $m_i$  is a molality ( $i = \text{Ca}$  or  $\text{K}$ ). The rate of formation of  $\text{K}X(\text{s})$  now can be expressed by the equation:

$$dE/dt = M_s (dq_{\text{K}}/dt) = M_s [k_a q_{\text{Ca}} m_{\text{K}} - k_d q_{\text{K}} m_{\text{Ca}}^{1/2}] \quad [17]$$

If the rate of adsorption of  $\text{K}^+$  is measured by miscible displacement (Sparks and Jardine, 1981) with  $m_{\text{K}}$  maintained constant and  $m_{\text{Ca}} = 0$ , then Eq. [17] reduces to Eq. [18]:

$$dq_{\text{K}}/dt = k_a m_{\text{K}} (q_T - q_{\text{K}}) \quad [18]$$

where  $q_T = q_K + q_{Ca}$  is the cation exchange capacity and  $k_a$  is now an apparent adsorption rate coefficient (Sparks et al., 1980b). Equation [18] is a first-order rate equation with respect to  $K^+(aq)$  and  $KX(s)$ . If the rate of desorption is measured with  $m_{Ca}$  held constant and  $m_K = 0$  as in our experiment, Eq. [17] becomes:

$$dq_K/dt = -k'_d m_{Ca}^{1/2} q_K \quad [19]$$

where  $k'_d$  is an apparent desorption rate coefficient (Sparks et al., 1980b) and which is first-order with respect to  $KX(s)$  but of fractional order in respect to  $Ca^{2+}(aq)$ . Equations [18] and [19] lead to measurement of the coefficients  $k_a$  and  $k'_d$  by standard kinetics analysis (Sparks and Jardine, 1981; Sparks, 1985; 1986; Sparks and Huang, 1985).

Once  $K_{eq}$  is determined through a kinetic approach, e.g.,  $k_a/k'_d = K_{eq}$ ,  $\Delta G^\circ$  can be obtained using Eq. [9].

Using the Arrhenius and van't Hoff equations (Denbigh, 1981), energies of activation for K adsorption and for K desorption ( $E_{aa}$  and  $E_{ad}$ , respectively) can be determined as shown below (Sparks, 1985; 1986):

$$d \ln k_a/dT = E_{aa}/RT^2 \quad [20]$$

and for the desorption kinetic reaction,

$$d \ln k'_d/dT = E_{ad}/RT^2 \quad [21]$$

substituting,

$$d \ln k_a/dT - d \ln k'_d/dT = d \ln K_{eq}/dT \quad [22]$$

and from the van't Hoff equation, the enthalpy for K exchange ( $\Delta H^\circ$ ) can be determined:

$$d \ln K_{eq}/dT = \Delta H^\circ/RT^2, \quad [23]$$

or

$$E_{aa} - E_{ad} = \Delta H^\circ. \quad [24]$$

The  $\Delta S^\circ$  can then be determined using Eq. [11].

### Experimental Procedures

The Ap horizons of a Chester loam (fine-loamy, mixed, mesic Typic Hapludults) and a Downer sandy loam (fine-loamy, mixed, mesic Typic Hapludults) were used in this study. Basic chemical, mineralogical, and physical properties of the soils were determined using standard methods outlined in Jardine and Sparks (1984). The Chester loam contained 15.0, 57.0, and 28.0% sand, silt, and clay; respectively, 3.3% organic matter; had a cation exchange capacity (CEC) of 6.80 cmol kg<sup>-1</sup> and the <2- $\mu$ m clay fraction contained mainly kaolinite and chloritized vermiculite with smaller quantities of quartz, mica, and gibbsite. The Downer sandy loam contained 76.5, 15.0, and 8.5% sand, silt, and clay, respectively; 1.30% organic matter; had a CEC of 4.90 cmol kg<sup>-1</sup>; and the clay fraction contained primarily chloritized vermiculite and kaolinite with smaller quantities of vermiculite and gibbsite.

### Equilibrium Studies

Equilibrium studies were conducted by first saturating the soils with  $Ca^{2+}$  using 0.5 M  $CaCl_2$  and washing with deionized water until a negative test was received using  $AgNO_3$ . Triplicate 1-g dry Ca-saturated soil samples were uniformly applied onto Buchner funnels equipped with 0.45- $\mu$ m filter paper. Eight different solutions of varying KCl and  $CaCl_2$  concentrations, but of a constant ionic strength of 0.01, were prepared. The equivalent fraction of  $K^+$  or  $Ca^{2+}$  in the mixed solution varied from 0 to 1.00. The experiments were performed in a large, temperature controlled incubator at 283, 298, and 308 K. The soil was leached at low pressure suction with about 400 mL of the solution or until the concentration

of  $K^+$  and  $Ca^{2+}$  in the leachate was equal to those concentrations in the original solution. After equilibrium, the entrained salts were removed by washing the soil with 100 mL of deionized water. The free water was removed by suctioning. To determine the extent of adsorbed  $K^+$  and  $Ca^{2+}$  at equilibrium, the soil was leached with 350 mL of a 1.0 M  $NH_4Cl$  solution. The leachate was analyzed for  $K^+$  and  $Ca^{2+}$  using atomic absorption spectrophotometry. Thermodynamic parameters were calculated using Eq. [9] through [11].

### Kinetics Approach

The kinetic approach for determining thermodynamic parameters was investigated using three techniques: a miscible displacement method first proposed by Sparks et al. (1980b), a batch, and a vigorously mixed batch. These three techniques were used to determine how diffusion affects the comparison between thermodynamic parameters calculated using a kinetic approach and an equilibrium method.

The miscible displacement technique was employed by Sparks and Jardine (1981) to investigate the kinetics of K exchange in soil. The apparent kinetic rate coefficients ( $k_a$  and  $k'_d$ ) were then used to calculate apparent thermodynamic parameters. However, the authors clearly referred to the equilibrium constant as an apparent  $K_{eq}$  ( $K'_{eq}$ ). As noted earlier, they did not compare the thermodynamic parameters they calculated with those using exchange isotherm data.

With the miscible displacement (flow) technique, triplicate 1-g dry samples of the Ca-saturated soils were thinly spread onto a 0.45- $\mu$ m nuclepore filter and the filter was securely cupped. The filter was attached to a LKB Ultrarac II 2070 fraction collector and peristaltic pump. The studies were performed at the same temperatures used in the equilibrium studies.

For K adsorption kinetics, the Ca-saturated soils were leached with a 0.01 M KCl solution at a constant flow rate of 1 mL min<sup>-1</sup>. Two-milliliter aliquots were collected at 2-min increments until an apparent equilibrium was attained. Then the sample was leached with 100-mL deionized water to remove any entrained solution and suctioned to remove any excess water. Potassium desorption was subsequently initiated using a 0.01 M  $CaCl_2$  solution. Leaching was continued until no  $K^+$  was detected in the leachates, and  $K^+$  in solution was analyzed as before. Apparent rate parameters ( $k_a$  and  $k'_d$ ) were calculated using first-order kinetic equations for flow techniques outlined by Sparks (1985; 1986) and thermodynamic parameters calculated as given in Eq. [9], [11], and [24].

The batch method consisted of placing triplicate 2-g Ca-saturated soil samples into 50-mL polyethylene centrifuge tubes. Then, 5 mL of a 0.01 M KCl solution was rapidly introduced into the tube and timing was begun. The mixture was then shaken on a reciprocating shaker at 180 rpm for time intervals of 5 s for the 1st min of the reaction, and for 2-min intervals thereafter. This shaking speed was chosen to effect mixing, but to cause minimal abrasion of the soil particles. The mixture was shaken by placing the tube at a 45° angle to the moving plane of the shaker to ensure even mixing and to prevent the soil from adhering to the surfaces of the tube. The latter was observed when the tubes were placed directly on the shaker. After equilibration, the solution was immediately separated from suspension by pouring the mixture into a glass syringe, which was attached to a nuclepore filter holder containing 0.45- $\mu$ m filter paper. The leachate was collected in a plastic test tube [Fig. 1]. The maximum time required for the filtration step was about 5 s.

Desorption studies were conducted by using soils that were equilibrated with 0.01 M KCl. The K was desorbed using 0.01 M  $CaCl_2$  with the procedures and times given above. Adsorption and desorption rate coefficients were determined

using first-order equations given by Sparks (1985; 1986). The batch technique described above was chosen for a number of reasons. First, centrifugation was not necessary and thus, rapid exchange reactions could be observed. It usually takes at least 5 min of centrifugation to separate the solid from the liquid phases. Many exchange reactions are complete by this time or less (Jardine and Sparks, 1984). Second, a narrow soil/solution ratio was employed to minimize the change in reactant concentration with time.

The vigorously mixed batch technique was accomplished using the same procedure as for the batch technique except the soil and solution were rapidly mixed by vortexing rather than by equilibrating on a reciprocating shaker. Rate coefficients were calculated as with the batch technique, and thermodynamic parameters were calculated for both batch methods using Eq. [9], [11], and [24].

The filtrates from the miscible displacement, batch, and vigorously mixed batch studies were analyzed for K<sup>+</sup> using atomic absorption spectrophotometry. All kinetic studies were run at 283, 298, and 308 K.

## RESULTS AND DISCUSSION

### Kinetics Methods

Although not shown, K adsorption and desorption conformed well to first-order kinetics using all three kinetics methods. This has been observed in several previous studies (Sparks et al., 1980a; Sparks and Jardine, 1981; 1984; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984; Carski and Sparks, 1985). The effect of method on  $k_a$ ,  $k_d$ ,  $E_{aa}$ , and  $E_{ad}$  values is shown in Table 1. With all three methods and at all temperatures, the  $k_d$  or  $k'_d$  values are lower than the corresponding  $k_a$  or  $k'_a$  values, indicating that the rate of K desorption was lower than for K adsorption. This observation is further supported by the magnitude of the energy of activation values. Energies of activation vary inversely with the rate of exchange (Sparks, 1985; 1986). With each method, the  $E_{aa}$  values were higher than the  $E_{ad}$  values, indicating that the rate of K desorption was lower than for K adsorption, and that the energy needed to desorb K is greater than that to adsorb K. These results can be explained by the predominance of vermiculitic minerals present in the two soils. In the K adsorption process, a partial collapse of the interlayers occurs due to coulombic attractive forces being greater between the clay surface and the K<sup>+</sup> ions than the hydration forces between the individual K<sup>+</sup> ions. Consequently, K desorption becomes

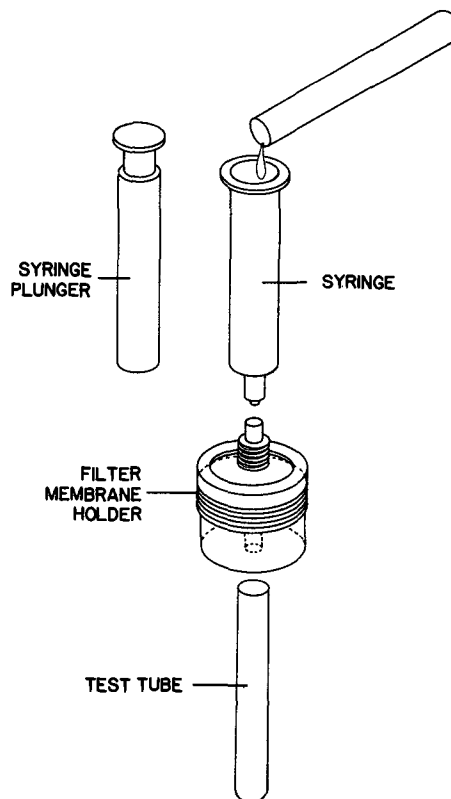


Fig. 1. Schematic diagram depicting various parts of the device used for rapid filtration in the batch and vigorously mixed batch kinetic techniques.

a slower and more difficult exchange process than K adsorption (Kittrick, 1966; Jardine and Sparks, 1984).

The  $E_{aa}$  and  $E_{ad}$  values were quite low, particularly for the miscible displacement and batch techniques (Table 1) which suggests that diffusion controlled exchange is occurring (Boyd et al., 1947; Mortland and Ellis, 1959; Sparks and Jardine, 1981; Sparks, 1985; 1986). The  $E_{aa}$  and  $E_{ad}$  values were considerably higher with the vigorously mixed batch technique, suggesting that the effect of diffusion is being diminished significantly. Mortland and Ellis (1959) found the  $E_{ad}$  for K release from vermiculite, using a leaching technique, was 14.85 kJ mol<sup>-1</sup>. They concluded that film-diffusion was the rate-controlling step. This value is in the range found with the miscible displacement and

Table 1. Effect of kinetic method on adsorption and desorption rate coefficients ( $k_a$  and  $k_d$ ) and energies of activation ( $E_a$  and  $E_{ad}$ ) in soils.

Temperature	Kinetic method											
	Miscible displacement				Batch				Vigorously mixed batch			
	$k'_a$	$k'_d$	$E_{aa}$	$E_{ad}$	$k_a$	$k_d$	$E_{aa}$	$E_{ad}$	$k_a$	$k_d$	$E_a$	$E_{ad}$
K	min <sup>-1</sup>	min <sup>-1</sup>	kJ mol <sup>-1</sup>		min <sup>-1</sup>	min <sup>-1</sup>	kJ mol <sup>-1</sup>		min <sup>-1</sup>	min <sup>-1</sup>	kJ mol <sup>-1</sup>	
	Chester loam											
283	0.031	0.020			0.179	0.061			0.867	0.159		
298	0.036	0.026			0.225	0.086			2.331	0.500		
308	0.040	0.030			0.257	0.113			2.629	0.656		
			7.42	11.87			10.69	18.41			32.96	42.10
	Downer sandy loam											
283	0.054	0.025			0.189	0.076			1.871	0.162		
298	0.061	0.031			0.288	0.097			2.900	0.385		
308	0.069	0.038			0.312	0.211			3.981	0.643		
			7.42	12.47			14.85	30.29			22.39	40.92

Table 2. Comparison of equilibrium and kinetic approaches for determining thermodynamics of K exchange in soils.

Temperature	Equilibrium approach				Kinetic approach											
					Method											
	$K_{eq}$	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$	Miscible displacement				Batch				Vigorously mixed batch			
K	—	— kJ mol <sup>-1</sup>	— J mol <sup>-1</sup> K <sup>-1</sup>	$K_{eq}$	— kJ mol <sup>-1</sup>	— J mol <sup>-1</sup> K <sup>-1</sup>	$K_{eq}$	— kJ mol <sup>-1</sup>	— J mol <sup>-1</sup> K <sup>-1</sup>	$K_{eq}$	— kJ mol <sup>-1</sup>	— J mol <sup>-1</sup> K <sup>-1</sup>	$K_{eq}$	— kJ mol <sup>-1</sup>	— J mol <sup>-1</sup> K <sup>-1</sup>	
				<u>Chester loam</u>												
283	9.59	-5.32	-38.72	1.55	-1.03	-9.14	2.93	-2.53	-16.80	5.45	-3.99	-16.19				
298	6.77	-4.74	-38.69	1.38	-0.80	-9.58	2.62	-2.39	-16.52	4.66	-3.82	-15.96				
308	4.24	-3.70	-40.83	1.33	-0.74	-9.44	2.27	-2.10	-16.83	4.01	-3.57	-16.24				
			-16.28			-4.45			-7.72			-9.14				
				<u>Downer sandy loam</u>												
283	9.81	-5.37	-50.72	2.16	-1.81	-12.09	2.49	-2.15	-36.73	11.55	-5.76	-41.81				
298	6.43	-4.61	-50.72	1.97	-1.68	-12.22	2.76	-2.52	-33.64	7.53	-5.00	-42.24				
308	5.27	-4.26	-50.21	1.82	-1.53	-12.15	1.48	-1.00	-37.45	6.19	-4.67	-42.00				
			-19.73			-5.05			-15.44			-18.53				

batch techniques of our study. Boyd et al. (1947) found that  $E_{aa}$  values for Na<sup>+</sup> adsorption on exchange resins from dilute KCl solutions avg 18.83 kJ mol<sup>-1</sup>, and also concluded film diffusion was rate controlling. Kuo and Lotse (1974) found adsorption of P on gibbsite and hematite was characterized by an  $E_{aa}$  value of 7.95 kJ mol<sup>-1</sup>, again indicating diffusion-controlled exchange.

It is clear from the kinetic data in this study (Table 1) that the rate of K adsorption and desorption is very dependent on the method chosen. The rate follows the order vigorously mixed batch > batch > miscible displacement. This same order is observed in the rate coefficients and energies of activation. For example, the  $k_a$  value for the Downer soil at 283K is ~35 times greater when the vigorously mixed batch technique is used than when miscible displacement is employed.

Most ion exchange reactions are carried out in a batch or column process. In both cases, there is usually some form of agitation of the liquid (stirring, shaking, or flowing) with the object of mixing the liquid and ensuring that its composition remains uniform up to the surface of the particles. Some researchers have assumed that shaking or stirring would eliminate or drastically reduce diffusion (Gonzales et al., 1982). However, for hydrodynamic reasons, there is usually a thin region around each particle in which such mixing is imperfect and the ions can only transverse this region by diffusion. This region may be referred to as the hydrodynamic, or Nernst film (Boyd et al., 1947; Reichenberg, 1957; Sparks, 1985; 1986).

The data in our study clearly show that diffusion is occurring in the miscible displacement and batch techniques, and to a much reduced extent with the vigorously mixed batch technique. It would appear that rapid agitation is required before the effect of diffusion on the rate process is significantly diminished. This kind of agitation is not present in most batch studies. The implications that diffusion have on using kinetics to obtain information about equilibrium processes of ion exchange in soils will be discussed later.

#### Comparison of Equilibrium and Kinetic Approaches

Thermodynamic data obtained from the equilibrium and kinetic approaches are shown in Table 2. In

both soils, the  $\Delta G^\circ$  values for K-Ca exchange were negative indicating an overall selectivity of K<sup>+</sup> over Ca<sup>2+</sup>. The preference for K is probably related to the vermiculitic clay minerals present in the soils that prefer K<sup>+</sup> over Ca<sup>2+</sup> (Jardine and Sparks, 1984). The two soils exhibited similar selectivity, which would be expected due to their similar clay mineralogies and organic matter contents.

In both soils, K preference decreased with increasing temperature for all methods. The observation that  $\Delta G^\circ$  becomes less negative with an increase in temperature has been observed in numerous reports (Udo, 1978; Sparks and Jardine, 1981; Bansal, 1982). Two hypotheses for this seem reasonable. First, the Ca<sup>2+</sup> ion is more hydrated than the K<sup>+</sup> ion. At higher temperatures, the Ca<sup>2+</sup> ion hydration shell is reduced and it can approach the surface more closely than at lower temperatures, which could result in a slightly reduced preference for the K<sup>+</sup> ion. Second, the overall reaction for K-Ca exchange in the soils studied using both the kinetic and equilibrium approaches was exothermic, as evidenced by negative  $\Delta H^\circ$  values (Table 2). Increasing the temperature would therefore result in lowering the preference for the K<sup>+</sup> ion.

The negative  $\Delta H^\circ$  values for K-Ca exchange have been observed by others (Goulding and Talibudeen, 1979; 1980; Sparks and Jardine, 1981), which indicate a stronger binding strength for K<sup>+</sup> than for Ca<sup>2+</sup>. The  $\Delta S^\circ$  values were all negative for both soils with all methods, (Table 2) and indicated an ordered system.

The data in Table 2 show that thermodynamic parameters calculated using the equilibrium and kinetic approaches compare very well in trend, and give the same inferences of ion behavior for the two soils studied. However, except for the vigorously mixed batch technique, the magnitude of the thermodynamic parameters for the two approaches compared poorly. The  $\Delta G^\circ$  values for both soils at all three temperatures calculated using the vigorously mixed batch technique compared well to those calculated using the equilibrium approach. However, with both the batch and the miscible displacement methods, the comparison was poor. The  $\Delta H^\circ$  values using the vigorously mixed kinetic technique and the equilibrium approach compared well, particularly in the Downer soil. The dis-

crepancies are not surprising since Laudelout et al. (1968) even noticed differences in the magnitude of  $\Delta H^\circ$  measured by an equilibrium approach and measured directly by calorimetry.

The large differences in the magnitude of the thermodynamic parameters using the equilibrium and the miscible displacement and batch approaches may be due to assumptions inherent in both theories. However, the more probable explanation for the discrepancies is the pronounced diffusion that exists particularly in the miscible displacement and batch kinetic methods (Table 1).

Helferich (1965; 1983) noted that if the rate-controlling process is diffusion and not the reaction in Eq. [15], then no information about equilibrium can be derived from kinetic analyses. When diffusion is significantly reduced, as with the vigorously mixed batch technique, it appears that a kinetic approach can be successfully used to gather thermodynamic information about a soil system (Tables 1–2). Under the extreme conditions of rapid mass transfer, as found with the vigorously mixed batch system, the influence of diffusion is significantly reduced and the rate coefficients obtained approximate that of the reaction step.

Our findings do not diminish the usefulness of the batch and the miscible displacement techniques for kinetic analyses. In fact, they would be preferred over the vigorously mixed batch technique for such studies, since vigorous mixing may cause abrasion of soil particles, resulting in increased surface area and causing greater adsorption of some ions such as K. However, for equilibrium analyses, these two procedures would not be suitable if one wanted to quantitatively determine  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  values.

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