

# Thermodynamics of Potassium Exchange in Soil Using a Kinetics Approach<sup>1</sup>

D. L. SPARKS AND P. M. JARDINE<sup>2</sup>

## ABSTRACT

Thermodynamics of potassium (K) exchange using a kinetics approach was investigated in Ca-saturated samples from the Ap and B21t horizons of a Matapeake soil from Delaware. Kinetics of adsorption and desorption were determined at temperatures of 0, 25, and 40°C on each soil horizon using a miscible displacement technique. Energies of activation for adsorption and for desorption ( $E_a$  and  $E_d$ , respectively) ranged from 3.83 to 5.52 kcal mol<sup>-1</sup>. The  $E_d$  values were higher than the  $E_a$  values, indicating that more energy was needed to desorb K than to adsorb K. Thermodynamic and pseudothermodynamic parameters were determined using Gibbs' and Eyring's reaction rate theories. The free energy for K exchange ( $\Delta G^\circ$ ) values were negative (ranging from 1,155 to 1,294 cal mol<sup>-1</sup>) and increased with increasing temperature. The free energy of activation values were higher for K desorption ( $\Delta G_d^\ddagger$ ) than for K adsorption ( $\Delta G_a^\ddagger$ ), suggesting a greater free energy requirement to desorb K. The excellent agreement between  $\Delta G^\circ$  calculated from Gibbs' theory and from Eyring's reaction rate theory indicated that pure thermodynamic parameters could be calculated using a chemical kinetics approach. The enthalpy ( $\Delta H^\circ$ ) values were exothermic and indicated stronger binding of K<sup>+</sup> ions in the B21t horizon than in the Ap horizon of the

Matapeake soil. The latter was related to the difference in external surface-to-interlayer surface-charge ratio in the two horizons. The enthalpy of activation ( $\Delta H^\ddagger$ ) values in both horizons were higher for desorption ( $\Delta H_d^\ddagger$ ), than for adsorption ( $\Delta H_a^\ddagger$ ), suggesting the heat energy required to overcome the K desorption barrier was greater than for that of K adsorption.

*Additional Index Words:* enthalpy, entropy, ionic diffusion.

Sparks, D. L., and P. M. Jardine. 1981. Thermodynamics of potassium exchange in soil using a kinetics approach. *Soil Sci. Soc. Am. J.* 45:1094-1099.

---

**T**HERMODYNAMIC PRINCIPLES have been used for many years to characterize exchange equilibria on clay and on soil surfaces (Argersinger et al., 1950; Gaines and Thomas, 1953; Babcock, 1963; Sposito, 1980). These principles have been used to obtain exchange coefficients and thermodynamic parameters for various cation exchange systems (Hutcheon, 1966; Deist and Talibudeen, 1967; Jensen, 1972; Udo, 1978). However, the use of a chemical kinetic approach to determine thermodynamic parameters has received little attention. This is particularly true for potassium (K) exchange in clays and in soils.

Most thermodynamic studies on clays and soils have involved the calculation of the free energy of exchange

<sup>1</sup> Contribution from the Dep. of Plant Science, Univ. of Delaware, Newark, DE 19711. Published with the approval of the Director of the Delaware Agric. Exp. Stn. as Misc. Paper no. 940. Contribution no. 127 of the Dep. of Plant Science. Received 27 Mar. 1981. Approved 20 July 1981.

<sup>2</sup> Assistant Professor of Soil Chemistry and Undergraduate Student, respectively.

( $\Delta G^\circ$ ) from equilibrium constants ( $K$ ) determined through the Gibbs-Duhem equation (Argersinger et al., 1950). Using the latter, negative  $\Delta G^\circ$  values were reported by Hutcheon (1966) for the formation of K-from Ca-montmorillonite. Udo (1978) investigated the thermodynamics of K-Ca and of Mg-Ca exchange on a kaolinitic soil clay. For K-Ca exchange,  $\Delta G^\circ$  values were  $-2,360$  and  $-1,650$  cal mol $^{-1}$  at 10 and 30°C, respectively. Deist and Talibudeen (1967) found  $\Delta G^\circ$  values ranged from  $-1,770$  to  $-3,420$  cal mol $^{-1}$  at 25°C and from  $-1,240$  to  $-3,010$  cal mol $^{-1}$  at 50°C in some British soils. Little can be deduced about the binding strength of cations on negatively charged surfaces from  $\Delta G^\circ$  values alone since these strengths are defined primarily in terms of enthalpy (Moore, 1972; Filep and Khargitan, 1977).

For reactions involving electrostatic or coulombic interactions, such as those for ion exchange, bonding is predominately exothermic (Moreale and Van Bladel, 1979). Deist and Talibudeen (1967) found enthalpy ( $\Delta H^\circ$ ) values of  $-910$  to  $-8,490$  cal mol $^{-1}$  for K-Ca exchange in selected British soils. The negative  $\Delta H^\circ$  values indicated the exchange reactions were not energy consuming (Deist and Talibudeen, 1967; Evans and Jurinak, 1976).

The entropy of a system ( $\Delta S^\circ$ ) is related to probability in that, as the number of ways a system can arrange itself increases,  $\Delta S^\circ$  increases or becomes more positive. Calculated  $\Delta S^\circ$  values include entropies in both the solid and solution phases. Hutcheon (1966) gave the absolute entropies of K $^+$  and Ca $^{2+}$  ions in pure water, each corrected to an ionic strength of 0.01N, as  $+33.4$  and  $-2.9$  e.u., respectively. Thus, K $^+$  ions caused an increase in the entropy of the dissolving water, possibly by altering water's pseudotetrahedral structure. Conversely, Ca $^{2+}$  ions increased the structural order of water.

The objective of this study was to determine thermodynamic parameters for K exchange in a Matapeake soil from Delaware using a kinetics approach. Pseudothermodynamic parameters were also obtained from absolute reaction rate theory.

## MATERIALS AND METHODS

### Theoretical Considerations

In previous studies (Sparks et al., 1980a and b), it was found that K adsorption and desorption in soils conformed to first-order kinetics. Using a miscible displacement technique, the apparent adsorption and desorption rate coefficients ( $k_a'$  and  $k_d'$ , respectively) can be determined from first-order kinetic equations as derived below.

#### APPARENT ADSORPTION RATE COEFFICIENT ( $k_a'$ )

$$d(K_t/K_\infty) = k(K_\infty - K_t) dt, \quad [1]$$

where  $K_t$  = amount of K on the soil at time  $t$ , and  $K_\infty$  = amount of K on the soil at equilibrium.

Separating variables:

$$\frac{d(K_t/K_\infty)}{1 - (K_t/K_\infty)} = k K_\infty dt. \quad [2]$$

Integration of the form  $\int dx/1+x = \ln(1+x)$  yields:

$$\ln(1 - K_t/K_\infty) = -k K_\infty t. \quad [3]$$

Expressed in terms of base 10 logarithms gives:

$$\log(1 - K_t/K_\infty) = -k_a' t, \quad [4]$$

where  $k_a'$  = product of  $k$  and  $K_\infty$  divided by 2.303.

#### APPARENT DESORPTION RATE COEFFICIENT ( $k_d'$ )

For the solid surface phase,

$$d(K_t/K_0)/dt = -k(K_t), \quad [5]$$

where

$K_0$  = amount of K on the exchange sites of the soil at zero time,

$K_t$  = amount of K on the exchange sites of the soil at time  $t$ ,

$t$  = time, and

$k$  = absolute velocity constant.

On integration with boundary conditions,

$t = 0, K_t/K_0 = 1; t = \infty, K_t/K_0 = 0$ , and

$$\log(K_t/K_0) = -k_d' t. \quad [6]$$

#### CALCULATION OF THERMODYNAMIC PARAMETERS FOR K EXCHANGE FROM GIBBS' THEORY

Since 95 to 98% of the adsorbed K was subsequently desorbed in the Matapeake soil, indicating reversibility, the following relationship can be written:

$$K \text{ adsorption } \frac{k_a'}{k_d'} = K \text{ desorption}. \quad [7]$$

From the mass-action law (Denbigh, 1966),

$$\frac{k_a'}{k_d'} = K', \quad [8]$$

where  $K'$  = apparent equilibrium constant.

From classical thermodynamics, the free energy for K exchange ( $\Delta G^\circ$ ) can be obtained,

$$\Delta G^\circ = -RT \ln K', \text{ or} \quad [9]$$

$$\Delta G^\circ = -RT \ln k_a'/k_d'. \quad [10]$$

Using the Arrhenius and van't Hoff equations (Denbigh, 1966), energies of activation for K adsorption and for K desorption ( $E_a$  and  $E_d$ , respectively) can be determined as shown below:

$$d \ln k_a'/dT = E_a/RT^2, \quad [11]$$

and for the desorption kinetic reaction,

$$d \ln k_d'/dT = E_d/RT^2, \quad [12]$$

substituting,

$$d \ln k_a'/dT - d \ln k_d'/dT = d \ln K'/dT, \quad [13]$$

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

$$d \ln K'/dT = \Delta H^\circ/RT^2, \text{ or} \quad [14]$$

$$E_a - E_d = \Delta H^\circ. \quad [15]$$

From the third law of thermodynamics, the entropy for K exchange ( $\Delta S^\circ$ ) can be found,

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T. \quad [16]$$

**Table 1—Selected chemical, mineralogical, and physical properties of Matapeake soil.**

Horizon	Particle size analysis			Organic matter	CEC	Mineral suite of < 2 μm clay fraction†
	Sand	Silt	Clay			
		%			meq/100 g	
Ap	14.5	70	15.5	1.9	8.92	VR <sub>1</sub> ‡, VC <sub>2</sub> , MI <sub>3</sub> , QZ <sub>4</sub>
B21t	7.0	75	18	0.6	10.54	VC <sub>1</sub> , VR <sub>2</sub> , MI <sub>3</sub> , QZ <sub>4</sub>

† VC = chloritized vermiculite; VR = vermiculite; MI = mica; and QZ = quartz.

‡ Subscript 1 = most abundant; 4 = least abundant.

### CALCULATION OF PSEUDOTHERMODYNAMIC PARAMETERS FOR K EXCHANGE USING EYRING'S REACTION RATE THEORY

The transition-state theory for absolute reaction rates (Glasstone et al., 1941) can be used as a model to substantiate the thermodynamic parameters calculated by Gibbs' theory.

In terms of absolute rate theory, pseudothermodynamic parameters can be expressed as (Moore, 1972):

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = -RT \ln K_e^\ddagger, \quad [17]$$

or

$$K_e^\ddagger = \exp(-\Delta G^\ddagger/RT) = \exp(-\Delta H^\ddagger/RT + \Delta S^\ddagger/R), \quad [18]$$

where

$$\begin{aligned} \Delta G^\ddagger &= \text{free energy of activation,} \\ \Delta H^\ddagger &= \text{enthalpy of activation,} \\ \Delta S^\ddagger &= \text{entropy of activation,} \\ R &= \text{universal gas constant,} \\ T &= \text{absolute temperature, and} \\ K_e^\ddagger &= \text{equilibrium constant of activation and where} \\ k'_a &= \frac{k^*T}{h} \exp(\Delta S_a^\ddagger/R) \exp(-\Delta H^\ddagger/RT), \quad [19] \end{aligned}$$

where

$$\begin{aligned} k^* &= \text{Boltzmann's constant,} \\ h &= \text{Planck's constant, and} \\ \text{subscript}(a) &= \text{adsorption reaction.} \end{aligned}$$

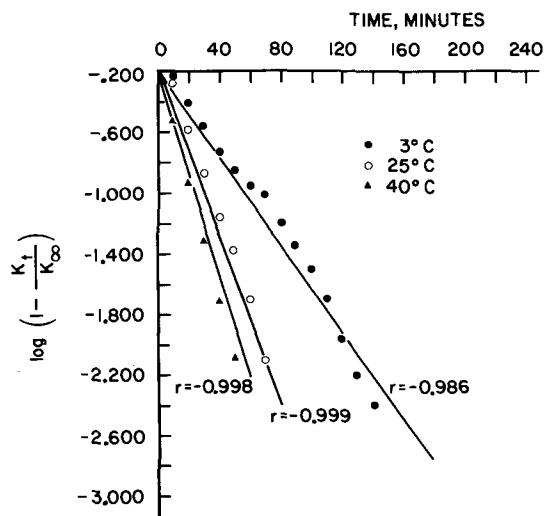


Fig. 1—Log  $(1 - K_t/K_\infty)$  vs. time at 3, 25, and 40°C for the Ap horizon of a Matapeake soil where  $K_t$  represents the quantity of K on soil exchange sites after time  $t$  of adsorption, and  $K_\infty$  denotes the quantity of K on the exchange sites at equilibrium.

Equation [19] would enable the calculation of  $\Delta S_a^\ddagger$ , since  $\Delta H_a^\ddagger$  is found from the following relationship:

$$\Delta H_a^\ddagger = E_a - RT. \quad [20]$$

The  $\Delta G_a^\ddagger$  may be calculated using this expression:

$$\Delta G_a^\ddagger = \Delta H_a^\ddagger - T\Delta S_a^\ddagger. \quad [21]$$

Analogous expressions can be obtained for the reverse reaction through the use of  $k'_d$  and  $E_d$  calculated for the desorption process.

### Experimental Procedures

Bulk samples were taken from the Ap and B21t horizons of a Matapeake silt loam (Typic Hapludults) from New Castle County, Del. The soil was air-dried and ground to pass through a 2-mm sieve in preparation for laboratory analyses. Basic chemical, mineralogical, and physical properties of the soil horizons were determined using techniques outlined earlier (Sparks et al., 1980a and b), and they are reported in Table 1.

### Kinetics of K Adsorption and Desorption

Prior to kinetic measurements, the soil horizons were saturated with  $\text{Ca}^{+2}$  using 1N  $\text{CaCl}_2$ . Excess electrolyte was removed with distilled  $\text{H}_2\text{O}$  and with a 1:1 acetone-to-water mixture until a negative test for  $\text{Cl}^-$  was obtained using  $\text{AgNO}_3$ .

Kinetics of K adsorption was measured using duplicate 1-g samples of the soil horizons. The soil suspension was injected onto a 47-mm nucleopore filter and attached to a Fractomette Alpha no. 200 fraction collector. The soil sample was leached with a 50 μg/ml K solution at a flow velocity of 1.0 ml/min until the concentration of the leachate equalled the concentration of the initial K solution. The tubes connected to the filter were thoroughly rinsed with distilled water, and K desorption was then initiated using 0.01M  $\text{CaCl}_2$ . The latter was passed through the soil until no K appeared in the leachate. The quantity of K in solution for both the adsorption and for the desorption studies was measured by atomic absorption spectrophotometry. The kinetic experiments were conducted at 3, 25, and 40 ± 1.0°C. Apparent adsorption and desorption rate coefficients were determined using the first-order equations elucidated earlier.

Energies of activation for adsorption and for desorption were determined from the Arrhenius and van't Hoff equations. The  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  values for K exchange were determined as outlined previously. The  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  for K exchange were determined from Eyring's absolute reaction rate theory (Laidler, 1965).

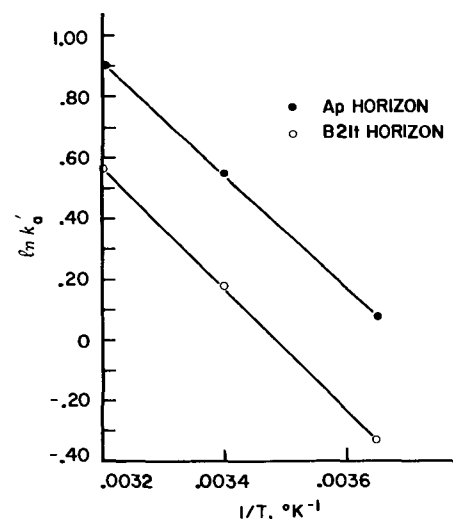


Fig. 2—Arrhenius plot of  $\ln k'_a$  vs.  $1/T$  for Matapeake Ap horizon.

**Table 2—Apparent rate coefficients ( $k_a'$  and  $k_d'$ ) at 3 temperatures, energies of activation ( $E_a$  and  $E_d$ ), and thermodynamic parameters using a kinetics approach for K exchange in Matapeake soil.**

Temperature °C	$k_a'$ † hour <sup>-1</sup>	$k_d'$ hour <sup>-1</sup>	$E_a$ kcal mol <sup>-1</sup>	$E_d$ kcal mol <sup>-1</sup>	$\Delta G^\circ$ cal mol <sup>-1</sup>	$\Delta H^\circ$ cal mol <sup>-1</sup>	$\Delta S^\circ$ cal mol <sup>-1</sup> °K <sup>-1</sup>
<u>Ap Horizon</u>							
3	1.080	0.102			-1,294		-1.430
25	1.860	0.216			-1,274	-1,690	-1.400
40	2.460	0.336			-1,238		-1.440
			3.83	5.52			
<u>B21t Horizon</u>							
3	0.720	0.084			-1,178		-0.587
25	1.351	0.192			-1,155	-1,340	-0.621
40	1.740	0.270			-1,158		-0.581
			4.14	5.48			

† Subscripts *a* and *d* denote adsorption and desorption processes, respectively.

## RESULTS AND DISCUSSION

The kinetics of K adsorption and desorption in the Ap and B21t horizons of the Matapeake soil conformed to first-order kinetics at all three reaction temperatures. The linear relationship for K adsorption in the Ap horizon indicating first-order kinetics is shown in Fig. 1. Although not shown, the data also conformed to the parabolic diffusion law in the Ap and B21t horizons with linear relationships occurring for both the adsorption and desorption processes. The low rate of K exchange is related to the presence of vermiculitic minerals in the Matapeake soil (Table 1) which demonstrate diffusion-controlled exchange (Barshad, 1954; Chute and Quirk, 1967; Sparks et al., 1980b).

### Apparent Adsorption and Desorption Rate Coefficients ( $k_a'$ and $k_d'$ , respectively)

The  $k_a'$  and  $k_d'$  values increased with increasing temperature (Fig. 2, Table 2) as predicted from Bronsted's reaction rate theory (Adamson, 1973) and from the Arrhenius equation. The  $k_d'$  values were lower than the  $k_a'$  values, indicating that the desorption rate was lower than the adsorption rate. Desorption would be slower than adsorption because of the partial collapse of the vermiculitic clay minerals upon K adsorption. The rate coefficients were also lower in the B21t than in the Ap horizon, possibly due to a higher clay content in the former horizon. The larger quantity of clay could promote increased diffusion and intraparticle transport (Sparks et al., 1980a).

### Energies of Activation for Adsorption and for Desorption ( $E_a$ and $E_d$ , respectively) of K

The energy of activation measures the magnitude of the forces to be overcome during the process of ionic exchange (Laidler, 1965; Denbigh, 1966). Energies of activation vary inversely with the rate of exchange (Burns and Barber, 1961). The energies of activation (Table 2) for desorption ( $E_d$ ) were greater than those for adsorption ( $E_a$ ). This indicates that the energy needed to desorb K is greater than that to adsorb K, which is probably due to the partial collapse of the vermiculitic clay minerals upon K adsorption.

The low  $E_a$  and  $E_d$  values (3.83 to 5.52 kcal mol<sup>-1</sup>) suggest diffusion-controlled exchange (Glasstone et al., 1941; Mortland and Ellis, 1959; Kuo and Lotse, 1974) since purely surface-confined reactions have energies of

activation of  $\approx 30$  kcal mol<sup>-1</sup> (Glasstone et al., 1941). This observation correlates well with the finding that the kinetics of K exchange in the Matapeake soil was diffusion controlled. The magnitude of the  $E_d$  values is similar to that found by Mortland and Ellis (1959), who used a film-diffusion experiment to study the kinetics of K release from vermiculite.

### Thermodynamic Parameters of K Exchange Using Gibbs' Theory

The  $\Delta G^\circ$  values for K exchange were negative and increased with increasing temperature (Table 2), and they are comparable to those found by Deist and Talibudeen (1967). The more negative values for  $\Delta G^\circ$  in the Ap than in the B21t horizon would indicate that the driving force for the overall process was greater in the surface horizon (Adamson, 1973). This would be expected since less clay is contained in the Ap horizon (Table 1), causing K reactions to occur more easily with less diffusional resistance.

The  $\Delta H^\circ$  values (Table 2) convey something about the binding strength of K to the soil. The lower negative value of  $\Delta H^\circ$  in the B21t horizon than in the Ap horizon indicates a stronger binding of K in the subsoil compared to the surface soil. The difference in the binding strength of K<sup>+</sup> ions in the two soil horizons may be related to differences in the external surface-to-interlayer surface-charge ratio. The B21t horizon contained 31.6% less organic matter and 86% more clay than the Ap horizon, suggesting a smaller external surface-to-interlayer charge ratio for the former. Adsorption of K<sup>+</sup> ions on organic matter would probably be weaker and less specific than adsorption on interlayer surface sites.

The rate coefficients and energies of activation (Table 2) suggest that in the presence of K<sup>+</sup> ions, a partial collapse of the vermiculitic clay minerals probably occurs in the Matapeake soil. Since the external surface-to-interlayer surface-charge ratio is smaller in the B21t horizon, there should be a stronger binding of K<sup>+</sup> ions. This is evidenced from the less exothermic  $\Delta H^\circ$  value in the B21t horizon. That K exchange is an exothermic process would conform with findings of others (Deist and Talibudeen, 1967; Filep and Khargitan, 1977). Exothermic processes are characteristic of reactions encountered in K exchange where electrostatic attractive forces predominate (Kittrick, 1967; Moreale and Van Bladel, 1979).

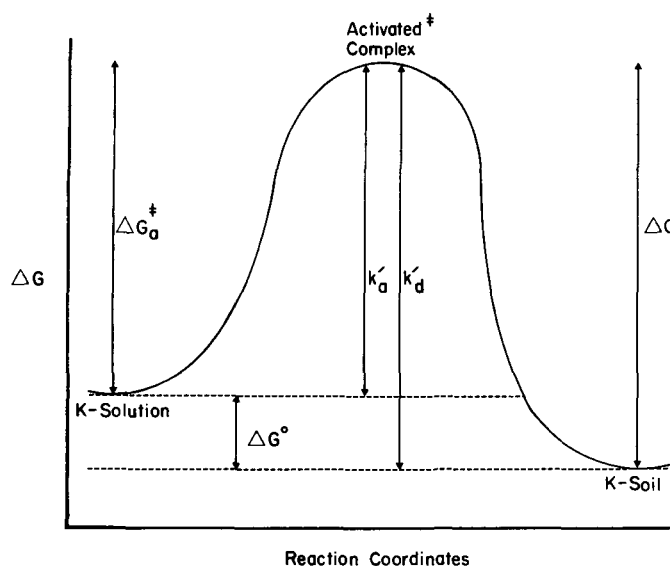


Fig. 3—Schematic diagram of  $\Delta G$  vs. reaction coordinate for K exchange in Matapeake soil.

The  $\Delta S^\circ$  values of the Matapeake soil (Table 2) show a higher (more positive) entropy in the B21t horizon than in the Ap horizon. Since there is more clay in the former horizon, there are more external and internal sites for K reactions to occur. For adsorption, due to more sites for K adsorption in the B21t horizon there would be more ways for  $K^+$  ions to arrange themselves. Thus the solid component of  $\Delta S^\circ$  would increase (Deist and Talibudeen, 1967). In desorption, there would be more desorption of  $K^+$  ions from the solid to solution phases and more  $Ca^{2+}$  ions moving from the solution to the solid phases. This would probably result in a greater increase in the solution component of  $\Delta S^\circ$  in the B21t than in the Ap horizon of the Matapeake soil since  $K^+$  increases the entropy of water (Hutcheon, 1966). Coleman (1952) also noted that replacement of  $K^+$  by  $Ca^{2+}$  on an ion exchange resin produced an increase in  $\Delta S^\circ$ .

#### Pseudothermodynamic Parameters Derived from Eyring's Reaction Rate Theory

The  $\Delta G^\ddagger$  value may be considered as the difference in free energy between the activated complex and the reactants from which it was formed, all substances being in their standard states (Laidler, 1965). It is the  $\Delta G^\ddagger$  value which determines the rate of the reaction (Glasstone et al., 1941.) The  $\Delta G^\ddagger$  values were higher for desorption than for adsorption (Table 3), suggesting a greater free energy requirement for K desorption. This would correlate well with the lower  $k'_d$  and higher  $E_d$  values (Table 2). The  $\Delta G^\ddagger$  values for both adsorption and desorption were also slightly higher in the B21t than in the Ap horizon, suggesting slower reactions due to more binding sites for K in the B21t horizon (Glasstone et al., 1941). Figure 3 illustrates a schematic correlation between the pseudothermodynamic parameters and those established by Gibbs' theory. The  $\Delta G_a^\ddagger$  is the change in free energy required for  $K^+$  to cross the barrier of adsorption at an apparent rate of  $k'_a$ . The  $\Delta G_d^\ddagger$  represents the change in free energy needed by the reverse reaction of desorption at the apparent rate of  $k'_d$ . The difference between these two parameters yields  $\Delta G^\circ$ , the ther-

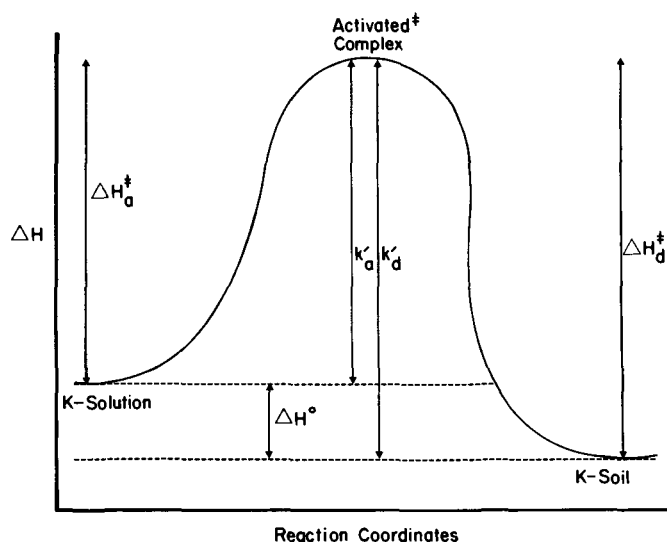


Fig. 4—Schematic diagram of  $\Delta H$  vs. reaction coordinate for K exchange in Matapeake soil.

modynamic parameter established from Gibbs' theory. Comparison of these values to those calculated from Eq. [10] shows excellent agreement (Table 4), indicating that thermodynamic parameters can be calculated using a kinetics approach.

The  $\Delta H^\ddagger$  value is a measure of the energy barrier which must be overcome by reacting molecules (Jencks, 1969). The  $\Delta H^\ddagger$  values in both horizons were higher for desorption than for adsorption (Table 3), suggesting that the heat energy required to overcome the K desorption barrier was greater than that for K adsorption. This was also seen in the magnitude of the  $E_a$  and  $E_d$  values (Table 2). A schematic correlation between  $\Delta H^\circ$  and  $\Delta H^\ddagger$  may be observed from Fig. 4. The  $\Delta H_a^\ddagger$  represents the change in heat energy needed for  $K^+$  to go from the solution phase to the solid phase, whereas  $\Delta H_d^\ddagger$  is the heat energy requirement for the reverse reaction. The difference in these two parameters represents  $\Delta H^\circ$  (Table 4). The adsorption process is an exothermic process whereby heat is liberated, and the desorption process is an endothermic reaction whereby heat is adsorbed. This concurs with findings of others who theorized that solute adsorption was clearly exothermic while desorption was often endothermic (Moreale and Van Bladel, 1979). Since the overall  $\Delta H^\circ$  of the reaction is negative, K exchange is not an energy-consuming process.

Jencks (1969) noted that entropy of activation could be regarded as a measure of the width of the "saddle point of energy" over which reactant molecules must pass as activated complexes. Thus  $\Delta S^\ddagger$  conveys whether a particular reaction proceeds faster or slower than another individual reaction. Recalling that the kinetics of adsorption were faster than the kinetics of desorption, a more highly ordered system would be obtained more rapidly with adsorption than with desorption. This is seen in the slightly larger negative values for  $\Delta S^\ddagger_a$  (Table 3).

These larger negative values would be expected since there is an ionic exchange of Ca from the solid to the solution phase and movement of K from the solution to the solid phase, both of which decrease entropy, due to an alteration of their hydrated radii. Calcium ions,

**Table 3—Kinetic parameters for adsorption and desorption processes at 3 temperatures in Matapeake Ap and B21t horizons using reaction rate theory.**

Temperature °C	$\Delta G^\ddagger$ kcal mol <sup>-1</sup>	$\Delta H^\ddagger$ kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ cal mol <sup>-1</sup> °K <sup>-1</sup>
<b>Ap Horizon</b>			
<u>Adsorption</u>			
3	16.06	3.28	-46.34
25	17.05	3.24	-46.37
40	17.78	3.21	-46.56
<u>Desorption</u>			
3	17.36	4.97	-44.88
25	18.34	4.92	-45.04
40	19.02	4.90	-45.12
<b>B21t Horizon</b>			
<u>Adsorption</u>			
3	16.28	3.89	-44.90
25	17.25	3.55	-45.97
40	18.01	3.52	-46.28
<u>Desorption</u>			
3	17.47	4.93	-45.44
25	18.40	4.89	-45.35
40	19.17	4.86	-45.71

when added to water, cause the viscosity of that water to increase while K<sup>+</sup> ions in the presence of water causes the viscosity to decrease. The greater water viscosity caused by the Ca<sup>2+</sup> ions account for the latter's ability to reinforce the water structure (Kirk and Othmer, 1963). The decrease in water viscosity caused by K<sup>+</sup> ions accounts for the latter's ability to alter the pseudotetrahedral structure of water. Thus, the desorption of Ca<sup>2+</sup> into solution causes a rehydration of the ion—thus an increase in the structural order of water. The adsorption of K<sup>+</sup> onto the solid results in a loss of water (Rich, 1964), thus causing an entropy decrease since less structurally disordered water is associated with the K<sup>+</sup> ions. When one considers desorption of K<sup>+</sup> ions, a less ordered system (more positive  $\Delta S^\ddagger$ ) would be expected since the reverse process is occurring.

### ACKNOWLEDGMENT

The authors appreciate the support for this research from the Potash and Phosphate Institute, and from the University of Delaware Research Foundation.

### LITERATURE CITED

- Adamson, A. W. 1973. A textbook of physical chemistry. Academic Press, New York.
- Argersinger, W. J., A. W. Davidson, and O. D. Bonner. 1950. Thermodynamics and ion exchange phenomena. *Trans. Kan. Acad. Sci.* 53:404-410.
- Babcock, K. L. 1963. Theory of the chemical properties of soil colloidal systems at equilibrium. *Hilgardia* 34(11).
- Barshad, I. 1954. Cation exchange in micaceous minerals: II. Replaceability of ammonium and potassium from vermiculite, biotite, and montmorillonite. *Soil Sci.* 78:57-76.
- Burns, A. F., and S. A. Barber. 1961. The effect of temperature and moisture on exchangeable potassium. *Soil Sci. Soc. Am. Proc.* 25:349-352.
- Chute, J. H., and J. P. Quirk. 1967. Diffusion of potassium from mica-like clay minerals. *Nature* 221:1156-1157.

**Table 4—Comparison of  $\Delta G^\circ$  and  $\Delta H^\circ$  values for K exchange in Matapeake soil using Gibbs' theory and Eyring's reaction rate theory.**

Temperature °C	$\Delta G^\circ$ as established by Eq. [10] cal mol <sup>-1</sup>	$\Delta G^\circ$ as established by difference of $\Delta G_a^\ddagger$ and $\Delta G_d^\ddagger$ cal mol <sup>-1</sup>	$\Delta H^\circ$ as established by Eq. [14] cal mol <sup>-1</sup>	$\Delta H^\circ$ as established by difference of $\Delta H_a^\ddagger$ and $\Delta H_d^\ddagger$ cal mol <sup>-1</sup>
<b>Ap Horizon</b>				
3	-1,294	-1,300		-1,690
25	-1,274	-1,290	-1,690	-1,680
40	-1,238	-1,240		-1,690
<b>B21t Horizon</b>				
3	-1,178	-1,190		-1,040
25	-1,155	-1,150	-1,340	-1,340
40	-1,158	-1,160		-1,340

- Coleman, N. J. 1952. A thermochemical approach to the study of ion exchange. *Soil Sci.* 74:115-125.
- Deist, J., and O. Talibudeen. 1967. Thermodynamics of K-Ca exchange in soils. *J. Soil Sci.* 18:138-148.
- Denbigh, K. G. 1966. The principles of chemical equilibrium with applications in chemistry and chemical engineering. 2nd ed. Cambridge Univ. Press, New York.
- Evans, R. L., and J. J. Jurinak. 1976. Kinetics of phosphate release from a desert soil. *Soil Sci.* 121:205-211.
- Filep, D., and I. Khargitan. 1977. Thermodynamic analysis of cation exchange processes in the soil-solution system. *Sov. Soil Sci.* 9:599-609.
- Gaines, H. L., and H. C. Thomas. 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* 21:714-718.
- Glasstone, S., K. J. Laidler, and H. Eyring. 1941. The theory of rate processes. McGraw-Hill, New York.
- Hutcheon, A. T. 1966. Thermodynamics of cation exchange on clay: Ca-K montmorillonite. *J. Soil Sci.* 17:339-355.
- Jencks, W. P. 1969. Catalysis in chemistry and enzymology. McGraw-Hill, New York.
- Jensen, H. E. 1972. Potassium-calcium exchange equilibria on a montmorillonite and a kaolinite clay. I. A test of Argersinger thermodynamic approach. *Agrochimica* 17:181-190.
- Kirk, A., and T. Othmer. 1963. Encyclopedia of chemical technology. 2nd ed. 21:678-683.
- Kittrick, J. A. 1967. Forces involved in ion fixation by vermiculite. *Soil Sci. Soc. Am. Proc.* 30:801-803.
- Kuo, S., and E. G. Lotse. 1974. Kinetics of phosphate adsorption and desorption by hematite and gibbsite. *Soil Sci.* 116:400-406.
- Laidler, K. J. 1965. Chemical kinetics. 2nd ed. McGraw-Hill, New York.
- Moore, W. J. 1972. Physical chemistry. 2nd ed. Prentice-Hall, Englewood Cliffs, N.J.
- Moreale, A., and R. Van Bladel. 1979. Soil interactions of herbicide-derived aniline residues: a thermodynamic approach. *Soil Sci.* 127:1-9.
- Mortland, M. M., and B. G. Ellis. 1959. Release of fixed potassium as a diffusion controlled process. *Soil Sci. Soc. Am. Proc.* 23:363-364.
- Rich, C. I. 1964. Effect of cation size and pH on potassium exchange in Nason soil. *Soil Sci.* 98:100-106.
- Sparks, D. L., L. W. Zelazny, and D. C. Martens. 1980a. Kinetics of potassium exchange in a Paleudult from the Virginia Coastal Plain. *Soil Sci. Soc. Am. J.* 44:37-40.
- Sparks, D. L., L. W. Zelazny, and D. C. Martens. 1980b. Kinetics of potassium desorption in soil using miscible displacement. *Soil Sci. Soc. Am. J.* 44:1205-1208.
- Spósito, G. 1980. Cation exchange in soils: an historical and theoretical perspective. p. 13-28. *In* R. H. Dowdy et al., (ed.) Chemistry in the soil environment. *Soil Sci. Soc. of Am., Madison, Wis.*
- Udo, E. J. 1978. Thermodynamics of potassium-calcium and magnesium-calcium exchange reactions on kaolinitic soil clay. *Soil Sci. Soc. Am. J.* 42:556-560.