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Application of Chemical Kinetics to Soil Chemical Reactions

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INTRODUCTION

The application of chemical kinetics to even homogeneous solutions is often arduous. When kinetic theories are applied to heterogeneous soil constituents, the problems and difficulties are magnified. With the latter in mind, one must give definitions immediately for two terms—kinetics and

chemical kinetics. *Kinetics* is a general term referring to time-dependent phenomena. *Chemical kinetics* can be defined as the “study of the rate of chemical reactions and of the molecular processes by which reactions occur where transport is not limiting” (Gardiner, 1969). In soil systems, many kinetic processes are a combination of both chemical kinetics or reaction-controlled kinetics, and transport-controlled kinetics. In fact, many of the studies conducted thus far on time-dependent behavior of soils and soil constituents have been involved with transport-controlled kinetics and not chemical kinetics. The reasons for this are discussed later.

There are two salient reasons for studying the rates of soil chemical processes: (1) to predict how quickly reactions approach equilibrium or quasi-state equilibrium, and (2) to investigate reaction mechanisms. There are a number of excellent books on chemical kinetics (Laidler, 1965; Hammes, 1978; Eyring *et al.*, 1980; Moore and Pearson, 1981) and chemical engineering kinetics (Levenspiel, 1972; Froment and Bischoff, 1979) that the reader may want to refer to. The purpose of this chapter is to apply principles of chemical kinetics as discussed in the preceding books to soil chemical processes.

RATE LAWS

Differential Rate Laws

To fully understand the kinetics of soil chemical reactions, a knowledge of the rate equation or rate law explaining the reaction system is required.

By definition, a rate equation or law is a differential equation. In the following reaction (Bunnett, 1986),



the rate is proportional to some power of the concentrations of reactants A and B and/or other species (C, D, etc.) present in the system. The power to which a concentration is raised may equal zero (i.e., the rate may be independent of that concentration), even for reactant A or B.

For reactions occurring in liquid systems at constant volume, reaction rate is expressed as the number of reactant species (molecules or ions) changed into product species per unit of time and per unit of volume of the reaction system. Rates are expressed as a decrease in reactant concentration or an increase in product concentration per unit time. Therefore, if the substance chosen is reactant A, which has a concentration $[A]$ at any time t , the rate is $(-d[A])/dt$, while the rate with regard to a product Y having a concentration $[Y]$ at time t is $(d[Y])/dt$.

However, the stoichiometric coefficients in Eq. (2.1), a , b , y , and z , must also be considered. One can write

$$\frac{d[Y]/dt}{y} = \frac{-d[A]/dt}{a} = k[A]^\alpha [B]^\beta \dots \quad (2.2)$$

where k is the rate constant and α is the order of the reaction with respect to reactant A and can be referred to as a partial order. Similarly, the partial order β is the order with respect to B. These orders are experimental quantities and are not necessarily integral. The sum of all the partial orders, α , β , ... is referred to as the overall order (n) and may be expressed as,

$$n = \alpha + \beta + \dots \quad (2.3)$$

Once the values of α , β , etc. are determined, the rate law is defined. Reaction order is an experimental quantity and conveys only information about the manner in which rate depends on concentration. One should not use order to mean the same as "molecularity," which concerns the number of reactant particles (atoms, molecules, free radicals, or ions) entering into an elementary reaction. An elementary reaction is one in which no reaction intermediates have been detected, or need to be postulated to describe the chemical reaction on a molecular scale. Until other evidence is found, an elementary reaction is assumed to occur in a single step and to pass through a single transition state (Bunnett, 1986). The stoichiometric coefficients in the denominators of the differentials of Eq. (2.2) guarantee that the equation represents the rate of reaction regardless of whether rate of consumption of a reactant or of formation of a product is considered.

Rate laws are determined by experimentation and cannot be inferred only by examining the overall chemical reaction equation (Sparks, 1986). Rate laws serve three primary purposes: (1) they permit the prediction of the rate, given the composition of the mixture and the experimental value of the rate constant or coefficient; (2) they enable one to propose a mechanism for the reaction; and (3) they provide a means for classifying reactions into various orders.

Kinetic phenomena in soil or on soil constituents can be described by employing mechanistic rate laws, apparent rate laws, apparent rate laws including transport processes, or mechanistic rate laws including transport (Skopp, 1986).

Mechanistic Rate Laws

Definition and Verification. The use of mechanistic rate laws to study soil chemical reactions assumes that only *chemical kinetics* phenomena are

being studied. Transport-controlled kinetics which involve physical aspects of soils are ignored. Thus, with mechanistic rate laws, mixing and/or flow rates do not influence the reaction rate (Skopp, 1986).

The objective of a mechanistic rate law is to ascertain the correct fundamental rate law. The reaction sequence for determination of mechanistic rate laws may represent several reaction paths and steps either purely in solution or on the soil surface of a well-stirred dilute soil suspension. All processes represent fundamental steps of a chemical rather than a physical nature (Skopp, 1986).

Given the following elementary reaction between species A, B, and Y, the chemical equation is



A forward reaction rate law can be written as

$$d[A]/dt = -k_1[A][B]^2 \quad (2.5)$$

where k_1 is the forward rate constant.

The reverse reaction rate law for Eq. (2.4) can be expressed as

$$d[A]/dt = +k_{-1}[Y] \quad (2.6)$$

where k_{-1} is the reverse rate constant.

For *chemical kinetics* to be operational and thus Eqs. (2.5) and (2.6) to be valid, Eq. (2.4) must be an elementary reaction. To definitively determine this, one must prove experimentally that Eq. (2.4) and the rate law are valid.

To verify that Eq. (2.4) is indeed elementary, one can employ experimental conditions that are dissimilar from those used to ascertain the rate law. For example, if the k values change with flow rate, one is determining nonmechanistic or apparent rate coefficients. This was the case in a study by Sparks *et al.* (1980b), who studied the rate of potassium desorption from soils using a continuous flow method (Chapter 3). They found the apparent desorption rate coefficients (k'_d) increased in magnitude with flow rate (Table 2.1). Apparent rate laws are still useful to the experimentalist and can provide useful time-dependent information.

The determination of mechanistic rate laws for soil chemical processes is very difficult since microscopic heterogeneity is pronounced in soils and even for most soil constituents such as clay minerals, humic substances, and oxides. Heterogeneity can be enhanced due to different particle sizes, types of surface sites, etc. As will be discussed more completely in Chapter 3, the determination of mechanistic rate laws is also complicated by the type of kinetic methodology one uses. With some methods used by soil and environmental scientists, transport-controlled reactions are occurring and thus mechanistic rate laws cannot be determined.

TABLE 2.1 Effect of Flow Velocity on the Magnitude of the k'_d of the Ap and B22t Soil Horizons from Nottoway County^a

Horizon	Flow velocity (ml min ⁻¹)	k'_d (h ⁻¹)	
		Al-saturated	Ca-saturated
Ap	0.0	0.83	1.11
	0.5	0.85	1.18
	1.0	0.87	1.23
	1.5	0.91	1.32
B22t	0.0	0.33	0.26
	0.5	0.37	0.28
	1.0	0.41	0.30
	1.5	0.48	0.34

^aThese k'_d values were obtained by plotting a regression line of the triplicate k'_d values (determined in triplicate experiments) versus flow velocity. The r values were 0.970 and 0.973 for the Ap and B22t horizons, respectively, which were significant at the 1% level of probability. From Sparks *et al.* (1980b), with permission.

Skopp (1986) has noted that Eq. (2.5) or (2.6) alone, are only applicable far from equilibrium. For example, if one is studying adsorption reactions near equilibrium, back or reverse reactions are occurring as well. The complete expression for the time dependence must combine Eqs. (2.5) and (2.6) such that,

$$d[A]/dt = -k_1[A][B]^2 + k_{-1}[Y] \quad (2.7)$$

Equation (2.7) applies the principle that the net reaction rate is the difference between the sum of all reverse reaction rates and the sum of all forward reaction rates.

Determination of Mechanistic Rate Laws and Rate Constants. One can determine mechanistic rate laws and rate constants by analyzing data in several ways (Bunnett, 1986; Skopp, 1986). These include ascertaining initial rates, using integrated rate equations such as Eqs. (2.5)–(2.7) directly and graphing the data, and employing nonlinear least-square techniques to determine rate constants.

Graphical Assessment Using Integrated Equations Directly. Another way to ascertain mechanistic rate laws is to use an integrated form of Eq. (2.7). One way to solve Eq. (2.7) is to conduct a laboratory study and assume that one species is in excess (i.e., B) and therefore, constant. Mass balance relations are also useful. For example $[A] + [Y] = A_0 + Y_0$ where Y_0 is the initial concentration of product. One must also specify an initial

condition to solve rate equations. For example, Eq. (2.7) can be solved by assuming that $[B]$ is constant and $Y_0 = 0$ and letting the initial condition be specified by $A = A_0$ at $t = 0$. Dropping the brackets from Eq. (2.7) for the sake of simplicity one obtains (Skopp, 1986):

$$A/A_0 = \{k_{-1} + k_c \exp[-t(k_c + k_{-1})]\}/(k_c + k_{-1}) \quad (2.8)$$

where $k_c = k_1 B^2$.

Equation (2.5) can also be integrated using the same initial conditions and one obtains a first-order equation (Skopp, 1986):

$$A/A_0 = \exp(-k_c t) \quad (2.9)$$

If Eq. (2.9) is appropriate, a graph of $\log(A/A_0)$ vs. t should yield a straight line with a slope equal to $-k_c$. However, based on this result alone, it is tenuous to conclude that Eq. (2.5) is the *only* possible interpretation of the data and that a straight-line graph indicates a first-order reaction. One can make these conclusions only if *no* other reaction mechanisms result in such a graphical relationship.

Similar arguments hold for the integrated form of Eq. (2.6) when $Y = Y_0$ at $t = 0$ and $A = Y_0 - Y$ such that

$$A/Y_0 = 1 - \exp(k_{-1} t) \quad (2.10)$$

The solution to Eq. (2.7) assuming $[B]$ is constant and $A_0 = 0$ is (Skopp, 1986),

$$A/Y_0 = [k_{-1}/(k_c + k_{-1})]\{1 - \exp[-t(k_c + k_{-1})]\} \quad (2.11)$$

Graphs of $\log(1 - A/Y_0)$ vs. t are commonly used to test the validity of Eq. (2.10). However, Eq. (2.11), like Eq. (2.8), shows more complex behavior than simple graphical methods reveal. Thus, one should be cautious about making definitive statements concerning rate constants and particularly mechanisms, based solely on data according to integrated equations like those in Eqs. (2.9) and (2.10) unless other reaction mechanisms have been ruled out.

Often when time-dependent data are plotted using an equation for a particular reaction order, curvature results. There are several explanations for this. It can be caused by an incorrect assumption of reaction order. For example, if first-order kinetics is assumed but the reaction is second-order, downward curvature is observed (Bunnett, 1986). If second-order kinetics is assumed but the reaction is really first-order, upward curvature results. Curvature could also be due to fractional, third, or higher reaction orders or to mixed reaction orders.

If a reaction progresses to a state of equilibrium that is short of completion, a kinetic plot based on the assumption that the reaction went

to completion shows downward curvature with an eventual zero slope. Curvature can also be caused by temperature changes during an experiment. Decreasing temperature causes downward curvature, and increasing temperature results in upward curvature (Bunnett, 1986). These changes can result if temperature is not held constant during an experiment, or if the temperature of the sorptive solution is not the same as that used in the kinetic run.

Curvature can also be caused by side reactions. However, these reactions do not always cause deviations from linearity (Bunnett, 1986). This is another reason one should not make definitive conclusions about a linear kinetic plot.

The graphical method of determining k values from integrated equations works well if the points closely approximate a straight line or if they scatter randomly. Sometimes one can draw a straight line through every point; thus, the slope of the line is adequate for evaluation of k (Bunnett, 1986).

Initial Rate Method. Using integrated equations like Eqs. (2.5), (2.6), or (2.7) to directly determine a rate law and rate constants is risky. This is particularly true if secondary or reverse reactions are important in equations like (2.5) and (2.6). One sound option is to establish these equations directly using initial rates (Skopp, 1986).

With this method, the concentration of a reactant or product is plotted versus time for a very short initial period of the reaction during which the concentrations of the reactants change so little that the instantaneous rate is hardly affected (Bunnett, 1986).

The initial rate is the limit of the reaction rate as time reaches zero. Using the initial rate method, one could ascertain Eqs. (2.5) and (2.6) by finding out how the initial rates ($\lim d[A]/dt$) depend on the initial concentrations (A, B, Y). Experiments are conducted such that initial concentrations of each reactant are altered while the other concentrations are constant. It is desirable with this method to have one reactant in much higher concentration than the other reactant(s).

With the initial rate method, one must use an extremely sensitive analytical method to determine product concentrations (Bunnett, 1986). Titration methods may not be suitable, particularly if low levels of product concentration are present. Therefore, physical techniques such as spectrophotometry or conductivity are utilized.

Least-Squares Techniques. The value of k can also be obtained using least-squares techniques. This statistical method fits the best straight line to a set of points that are supposed to be linearly related. The formula for a straight line is

$$y = mx + b \quad (2.12)$$

The most tractable form of least-squares analysis assumes that values of the independent variable x are known without error and that experimental error is manifested only in values of the dependent variable y . Most kinetic data approximate this situation, since the times of observation are more accurately measurable than the chemical or physical quantities related to reactant concentrations (Bunnett, 1986). The straight line selected by least-squares analysis is that which minimizes the sum of the squares of the deviations of the y variable from the line.

The slope m and intercept b can be calculated by least-squares analysis using Eqs. (2.13) and (2.14), respectively.

$$\text{Slope} = m = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2} \quad (2.13)$$

$$\text{Intercept} = b = \frac{\sum y \sum x^2 - \sum x \sum xy}{n \sum x^2 - (\sum x)^2} \quad (2.14)$$

where n is the number of data points and the summations are for all data points in the sets. For further information on least-squares analysis, one can consult any number of textbooks including those of Draper and Smith (1981) and Montgomery and Peck (1982).

Apparent Rate Laws

Apparent rate laws include both chemical kinetics and transport-controlled processes. One can ascertain rate laws and rate constants using the previous techniques. However, one does not need to prove that *only* elementary reactions are being studied (Skopp, 1986). Apparent rate laws indicate that diffusion or other microscopic transport phenomena affect the rate law (Fokin and Chistova, 1967). Soil structure, stirring, mixing, and flow rate all affect the kinetic behavior when apparent rate laws are operational.

Transport with Apparent Rate Law

A fourth type of rate law, transport with apparent rate law, is a form of apparent rate law that includes transport processes. This type of rate-law determination is ubiquitous in the modeling literature (Cho, 1971; Rao *et al.*, 1976; Selim *et al.*, 1976a; Lin *et al.*, 1983). Kinetic-based transport models are more fully described in Chapter 9. With these rate laws, transport-controlled kinetics are emphasized more and chemical kinetics

less. The apparent rate can often depend on water flux (Skopp and Warwick, 1974; Overman *et al.*, 1980) or other physical processes. One also usually assumes either first- or zero-order kinetics is operational.

Transport with Mechanistic Rate Laws

Here one makes an effort to describe simultaneously transport-controlled and chemical kinetics processes (Skopp, 1986). Thus, an attempt is made to describe both the chemistry and physics accurately. For example, outflow curves from miscible displacement experiments on soil columns are matched to solutions of the conservation of mass equation. The matching process introduces a potential ambiguity such that experimental uncertainties are translated into model uncertainties. Often, an error in the description of the physical process is compensated for by an error in the chemical process and vice-versa (i.e., Nkedi-Kizza *et al.*, 1984).

EQUATIONS TO DESCRIBE KINETICS OF REACTIONS ON SOIL CONSTITUENTS

Introduction

A number of equations have been used to describe the kinetics of soil chemical processes (see, e.g., Sparks, 1985, 1986). Many of these equations offer a means of calculating rate coefficients, which then can be used to determine energies of activation (E), which reveal information concerning rate-limiting steps. Energies of activation measure the magnitude of forces that must be overcome during a reaction process, and they vary inversely with reaction rate.

However, as noted earlier, conformity of kinetic data to a particular equation does not necessarily mean it is the best model, nor can one propose mechanisms based on this alone.

First-Order Reactions

Derivations. According to the usual convention, one lets a represent the initial concentration $[A]_0$, of species A, b the initial concentration $[B]_0$, of species B, and y the concentration of product Y or Z [see Eq. (2.1)] at

any time (Bunnett, 1986). For a first-order reaction,

$$\frac{dy}{dt} = k[A] = k(a - y) \quad (2.15)$$

Rearranging,

$$\frac{dy}{a - y} = k dt \quad (2.16)$$

Integrating,

$$-\ln(a - y) + \ln a = kt \quad (2.17)$$

Or, using base 10 logarithms,

$$-\log(a - y) + \log a = \frac{k}{2.30} t \quad (2.18)$$

Eq. (2.17) can also be written as,

$$-\ln[A] + \ln[A]_0 = kt \quad (2.19)$$

Equation (2.17), (2.18), or (2.19) indicates that a plot of the negative of the logarithm of $[A]$ or of $(a - y)$ versus time should be a straight line with slope k or $k/2.30$. As noted earlier (Section IIB, 2b), obtaining such a linear plot from experimental data is a necessary but not sufficient condition for one to conclude that the reaction is kinetically first-order. Even if the kinetic plot using a first-order equation is linear over 90% of the reaction, deviations from the assumed rate expression may be hidden (Bunnett, 1986). When other tests confirm that it is first-order, the rate constant k , is either the negative of the slope [Eq. (2.17) or (2.19)] or 2.30 times the negative of the slope [Eq. (2.18)].

One way to test for first-order behavior is to carry out the rate determination at another initial concentration of reactant A, such as double or half the original, but preferably 10-fold or smaller (Bunnett, 1986). If the reaction is first-order, the slope according to Eq. (2.17) or (2.18) should be unchanged. It is also necessary to show that reaction rate is not affected by a species whose concentrations do not change considerably during a reaction run; these may be substances not consumed in the reaction (i.e., catalysts) or present in large excess (Bunnett, 1986).

The half-life ($t_{1/2}$) of a reaction is the time required for half of the original reactant to be consumed. A first-order reaction has a half-life that is related only to k and is independent of the concentration of the reacting species. After one half-life, $(a - y)$ equals $a/2$, and Eq. (2.17) can be

rewritten as,

$$-\ln \frac{a}{2} + \ln a = kt_{1/2}$$

Consolidating and rearranging,

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (2.20)$$

The half-life depends on reactant concentration and becomes longer the less concentrated the reactant. Thus, it can take a long time to reach a satisfactory infinity value for a second-order reaction.

Application of First-Order Reactions to Soil Constituents. Many investigations on soil chemical processes have shown that first-order kinetics describe the reaction(s) well. Single or multiple first-order reactions have been observed for ionic reactions involving: As(III) (Oscarson *et al.*, 1983), potassium (Mortland and Ellis, 1959; Burns and Barber, 1961; Reed and Scott, 1962; Huang *et al.*, 1968; Sivasubramaniam and Talibudeen, 1972; Jardine and Sparks, 1984; Ogwada and Sparks, 1986b), nitrogen (Stanford *et al.*, 1975; Kohl *et al.*, 1976; Carski and Sparks, 1987), phosphorus (Amer *et al.*, 1955; Griffin and Jurinak, 1974; Li *et al.*, 1972; Vig *et al.*, 1979), copper (Jopony and Young, 1987), lead (Salim and Cooksey, 1980), cesium (Sawhney, 1966), boron (Griffin and Burau, 1974; Carski and Sparks, 1985), sulfur (Hodges and Johnson, 1987), aluminum (Jardine and Zelazny, 1986), and chlorine (Thomas, 1963). First-order equations have also been used to describe molecular reactions on soils and soil constituents, including pesticide interactions (Walker, 1976a,b; Rao and Davidson, 1982; McCall and Agin, 1985). Data from these studies have been fitted to first-order equations by methods described earlier.

Sparks and Jardine (1984) studied the kinetics of potassium adsorption on kaolinite, montmorillonite, and vermiculite (Fig. 2.1) and found that a single first-order reaction described the data well for kaolinite and smectite while two first-order reactions described adsorption on vermiculite. One will note deviations from first-order kinetics at longer time periods, particularly for montmorillonite and vermiculite, because a quasi-equilibrium state is reached. These deviations result because first-order equations are only applicable far from equilibrium (Skopp, 1986); back reactions could be occurring at longer reaction times.

Griffin and Jurinak (1974) studied B desorption kinetics from soil and observed two separate first-order reactions and one very slow reaction. They postulated that the two first-order reactions were due to desorption from two independent B retention sites associated with hydroxy-Al, -Fe,

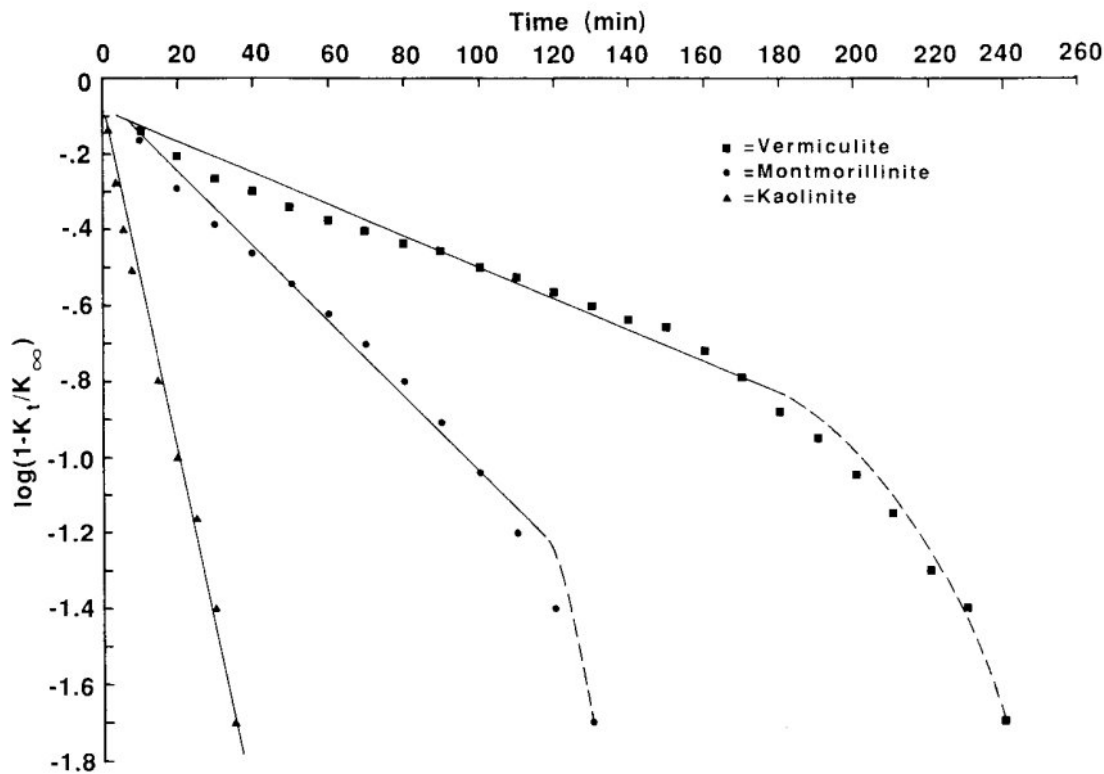


Figure 2.1. First-order plots of potassium adsorption on clay minerals where K_t is quantity of potassium adsorbed at time t and K_∞ is quantity of potassium adsorbed at equilibrium. [From Sparks and Jardine (1984), with permission.]

and $-Mg$ materials in the clay fraction of the soils. The third or lowest reaction rate was attributed to diffusion of B from the interior of clay minerals to the solution phase.

There are dangers, however, in attributing multiple slopes, obtained from plotting time-dependent data according to various kinetic equations, to different sites for reactivity. This is particularly true when the only evidence for such conclusions is multiple slopes. Even if one finds, for example, that data are best described by two first-order reactions, one should not then conclude that two mechanisms are operable. Such conclusions are analogous to deciding that multiple slopes obtained with the Langmuir equation are indicative of different sorption sites and mechanisms (see, e.g., Harter and Smith, 1981) One should refrain from making such judgments unless other lines of evidence also point to multiple reaction sites.

There are several ways to determine kinetically that multiple first-order or other reaction order slopes are present, and that they indicate different sites or mechanisms for sorption. One could determine rate-limiting steps (Chapter 5), E values could be measured, or materials that affect specific

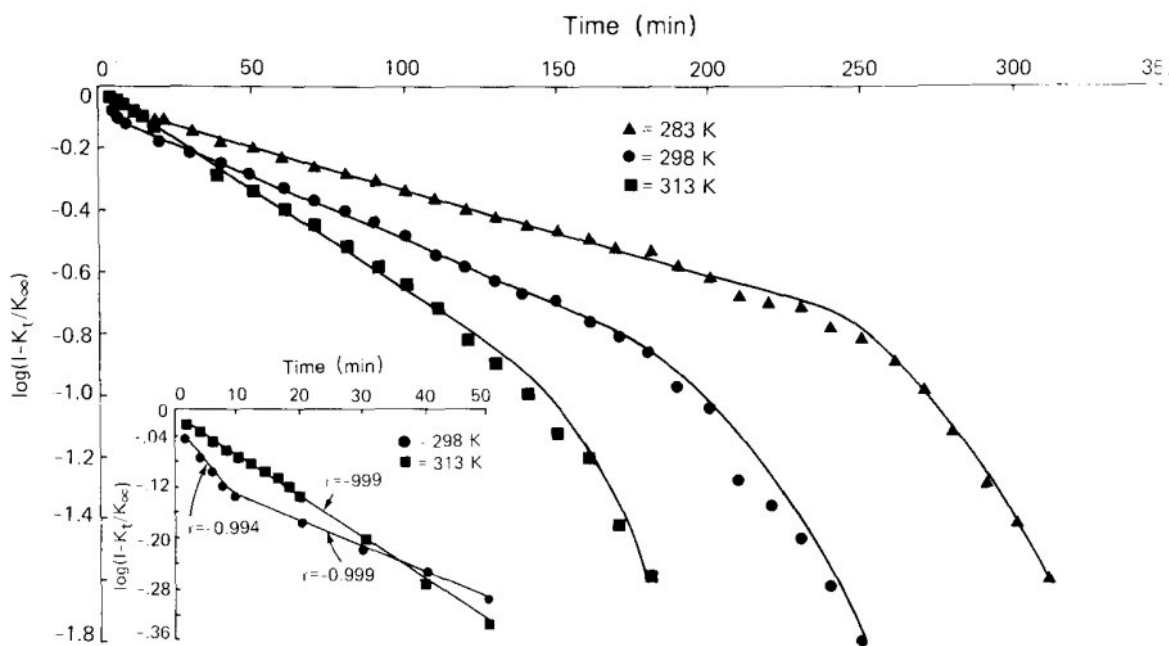


Figure. 2.2. First-order kinetics for potassium adsorption at three temperatures on Evesboro soil, with inset showing the initial 50 min of the first-order plots at 298 and 313 K. Terms are defined in Fig. 1. [From Sparks and Jardine (1984), with permission.]

colloidal sites (blocking agents) could be used to isolate different sorption sites.

An example of the last one can be found in the work of Jardine and Sparks (1984). They found that potassium adsorption and desorption in a soil conformed well to first-order reactions at 283 and 298 K and that two apparent simultaneous first-order reactions existed (Fig. 2.2). The first slope contained both a rapid reaction (rxn 1) and a slow reaction (rxn 2). The second slope described only rxn 2. The difference between the two slopes yielded the slope for rxn 1. The first reaction conformed to first-order kinetics for about 8 min, after which time a second apparent reaction proceeded for many hours. Sparks and Jardine (1984) used different blocking agents, including cetyltrimethylammonium bromide (CTAB), which sorbed only on external surface sites (Fig. 2.3), to show that the two slopes were describing two reactions on different sites for potassium adsorption-desorption. Based on the CTAB results, rxn 1 was ascribed to external surface sites of the organic and inorganic phases of the soil that were readily accessible for cation exchange. Reaction 2 was attributable to less accessible sites of organic matter and interlayer sites of the 2:1 clay minerals such as vermiculitic clays that predominated in the $< 2 \mu\text{m}$ clay fraction.

Another way to more directly prove or disprove mechanisms based on different time-dependent slopes is to use spectroscopic techniques.

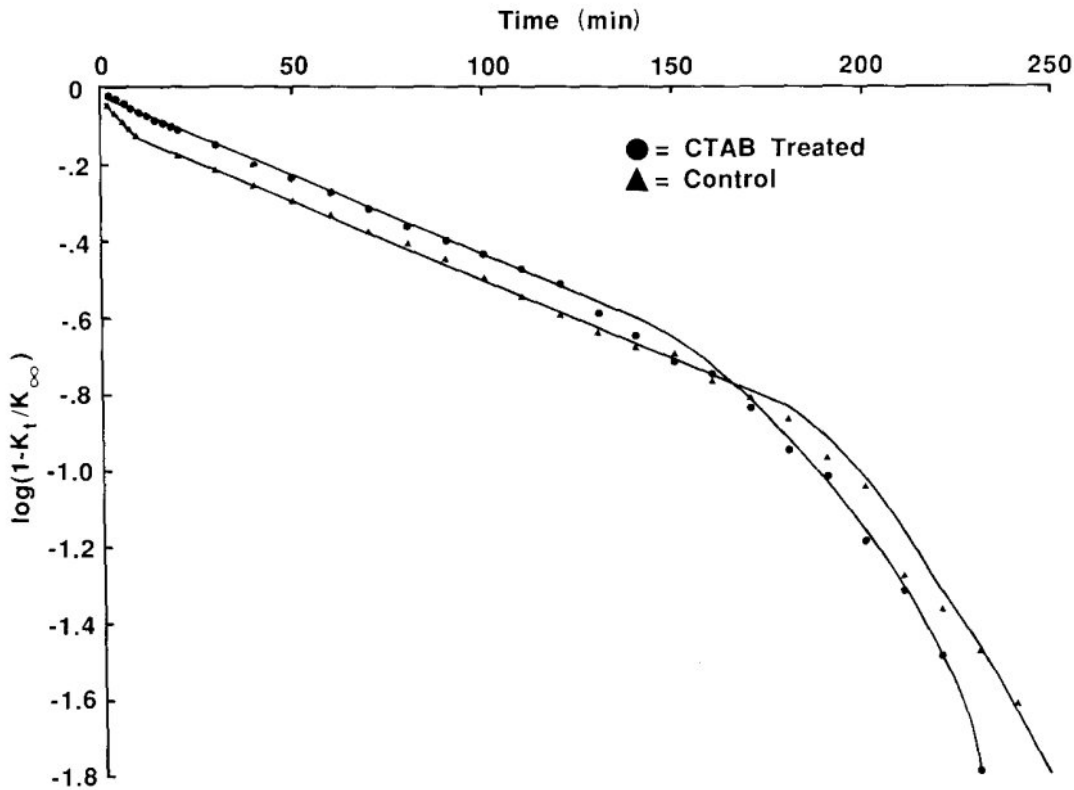


Figure 2.3. First-order kinetics for potassium adsorption at 298 K on Evesboro soil treated with cetyltrimethylammonium bromide (CTAB). Terms are defined in Fig. 1. [From Jardine and Sparks (1984), with permission.]

Methods such as nuclear magnetic resonance (NMR), electron spectroscopy for chemical analysis (ESCA), electron spin resonance (ESR), infrared (IR), and laser raman spectroscopy could be used in conjunction with rate studies to define mechanisms. Another alternative would be to use fast kinetic techniques such as pressure-jump relaxation, electric field pulse, or stopped flow (Chapter 4), where chemical kinetics are measured and mechanisms can be definitively established.

Other Reaction-Order Equations

Zero-Order Reactions. Zero-order reactions have been applied to describe potassium (Mortland, 1958; Burns and Barber, 1961), chromium (Amacher and Baker, 1982), and nitrogen reactions in soils (Patrick, 1961; Broadbent and Clark, 1965; Keeney, 1973).

Second-Order Reactions. If one considers a reaction according to Eq. (2.1), which is overall second-order but first-order in A and first-order

in B, then according to the symbolism used earlier (Bunnett, 1986),

$$\frac{dy}{dt} = k(a - y)(b - y) \quad (2.21)$$

Rearranging,

$$\frac{dy}{(a - y)(b - y)} = k dt$$

Integrating,

$$\frac{1}{a - b} \ln \frac{b(a - y)}{a(b - y)} = kt \quad (2.22)$$

Equation (2.22) is valid only if $a \neq b$. An alternate form of Eq. (2.22) is

$$\ln \frac{a - y}{b - y} + \ln \frac{b}{a} = (a - b)kt \quad (2.23)$$

or,

$$\log \frac{a - y}{b - y} + \log \frac{b}{a} = \frac{(a - b)kt}{2.30} \quad (2.24)$$

Thus, plots of the logarithm of $[(a - y)/(b - y)]$ versus time should be linear with slopes $(a - b)k$ or $(a - b)k/2.30$, depending on which type of logarithm is used.

If the experiment is arranged so that the initial concentrations of A and B are equal or if the reaction is second-order in reactant A, Eq. (2.21) becomes,

$$\frac{dy}{dt} = k(a - y)^2 \quad (2.25)$$

Upon rearrangement and integration,

$$\frac{1}{a - y} - \frac{1}{a} = kt \quad (2.26)$$

a plot of the reciprocal of $(a - y)$ versus time is linear with slope k .

Whereas the half-life for a first-order reaction is independent of reactant concentration, that for a second-order reaction is not. If one inserts $a/2$ for $(a - y)$ in Eq. (2.26), one obtains

$$t_{1/2} = \frac{1}{ak} \quad (2.27)$$

Phosphate reactions on calcite (Kuo and Lotse, 1972; Griffin and Jurinak, 1974) have been described using second-order reactions. Also, recent work on Al reactions in soils has employed second-order reactions (Jardine and Zelazny, 1986).

Kuo and Lotse (1972) derived a second-order equation, which is presented below, and used this equation to describe the rate of PO_4 sorption on CaCO_3 and Ca-kaolinite. This equation considered both the change in PO_4 concentration in solution and the surface saturation of the sorbent during the sorption process. This equation can be written as

$$\frac{dq}{dt} = k_1(C_0 - q)(M - q) - k_{-1}q \quad (2.28)$$

where q is the quantity of ions sorbed, $(C_0 - q)$ is the concentration of ions remaining in solution where C_0 is the initial concentration of ions, and $(M - q)$ is the surface unsaturation.

At equilibrium (eq), dq/dt will equal zero. Then,

$$k_1(C_0 - q)_{\text{eq}}(M - q)_{\text{eq}} = k_{-1}q_{\text{eq}} \quad (2.29)$$

By arranging Eq. (2.29), and expressing q and M in mol kg^{-1} of sorbent rather than in mol ion l^{-1} , the Langmuir equation is obtained,

$$\frac{1}{K_{\text{eq}}M} = \frac{C_{\text{eq}}}{q} - \frac{C_{\text{eq}}}{M} \quad (2.30)$$

where K_{eq} is the equilibrium constant and C_{eq} is the equilibrium concentration of ions. By integrating Eq. (2.28), one obtains

$$\ln\left(\frac{q - A - B}{q + B - A}\right) = 2Ak_1t + \ln\left(\frac{B + A}{B - A}\right) \quad (2.31)$$

where

$$A = \left[\frac{1}{4} \left(C_0 + M + \frac{k_{-1}}{k_1} \right)^2 - C_0M \right]^{1/2} \quad (2.32)$$

and

$$B = \frac{1}{2} \left(C_0 + M + \frac{k_{-1}}{k_1} \right) \quad (2.33)$$

The parameters A and B are constants and contain a concentration unit. By plotting $\ln(q - A - B/q + A - B)$ as a function of t , a straight line is obtained with a slope equal to $2Ak_1$. Kuo and Lotse (1972) found that the second-order rate constant decreased with increasing phosphorus

concentration in the $\text{CaCO}_3\text{-PO}_4$ system, which they explained using the Brønsted-Bjerrum activity-rate theory of ionic reactions in dilute solutions. The Brønsted equation states that “the logarithm of the rate coefficient is inversely proportional to the square root of the ionic strength, when the reaction between the two molecules involves charges of different sign” (Kuo and Lotse, 1972). Kuo and Lotse (1972) determined that k_1 for PO_4 sorption on Ca-kaolinite increased with increasing PO_4 concentration. Novak and Adriano (1975) found that a second-order equation like that given by Kuo and Lotse (1972) described phosphorus kinetics better than other models.

Reactions of Higher or Fractional Order. For reactions of order α in reactant A and of zero-order in other species,

$$\frac{-d[A]}{dt} = k[A]^\alpha \quad (2.34)$$

Letting $[A]_0$ represent the initial concentration of A and $[A]$ its concentration at any time, one may integrate (except when $\alpha = 1$) to obtain, (Bunnett, 1986).

$$\frac{1}{n-1} \left(\frac{1}{[A]^{\alpha-1}} - \frac{1}{[A]_0^{\alpha-1}} \right) = kt \quad (2.35)$$

Eq. (2.26) is the special case of Eq. (2.35) for $n = 2$.

When the order is $\frac{1}{2}$, $\frac{3}{2}$, and 3, Eq. (2.35) assumes the form of Eqs. (2.36), (2.37) and (2.38), respectively.

$$\sqrt{[A]_0} - \sqrt{[A]} = \frac{kt}{2} \quad (\text{half-order}) \quad (2.36)$$

$$\frac{1}{\sqrt{[A]}} - \frac{1}{\sqrt{[A]_0}} = \frac{kt}{2} \quad (\text{three-halves order}) \quad (2.37)$$

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt \quad (\text{third-order}) \quad (2.38)$$

Equations (2.35), (2.37), and (2.38) are also obtained if the reaction is of order $\alpha - 1$ in reactant A and of order one in B, and if the initial concentrations of A and B (and maybe other reactants) are in the ratio of their stoichiometric coefficients.

Often fractional orders best describe soil chemical processes. For example, the reaction order for dissolution of oxides, calcite, feldspars, and ferromagnesian minerals is often <1 (Stumm *et al.*, 1985; Bloom and Erich, 1987).

Two-Constant Rate Equation

Kuo and Lotse (1973) used a two-constant rate equation, derived below, which is adapted from the Freundlich equation to study the kinetics of PO_4 sorption and desorption on hematite and gibbsite.

A kinetic equation was developed by inserting a time-dependent expression into the Freundlich equation. The Freundlich equation can be written as,

$$q = k_F C_f^{c/d} \quad (2.39)$$

where k_F is the Freundlich constant, C_f is the final sorbate concentration, and c and d are both integers with $d > c$.

Kuo and Lotse (1973) presumed that the slope of a Freundlich plot was time independent. The physical meaning of the concentration term exponent in the Freundlich equation is unclear, but has generally been <1 and related to the characteristics of the sorbent. However, the exponent is time-independent, whereas the intercept is time-dependent.

The expression $(1 - e^{-k_2 t})$ can be inserted into Eq. (2.39) such that

$$q^d = k_1 (1 - e^{-k_2 t}) C_f \quad (2.40)$$

where k_1 and k_2 are constants, $k_1 [1 - e^{-k_2 t}] = k^d$

For $t = 0$, $q = 0$, and $t \rightarrow \infty$, Eq. (2.40) is reduced to Eq. (2.39). From Eq. (2.40) one sees that changes in t can only affect the intercept in the Freundlich plot. Rearrangement and successive transformations give,

$$\frac{q}{C_f^{c/d}} = k_1^{1/d} (1 - e^{-k_2 t})^{1/d} \quad (2.41)$$

and

$$\begin{aligned} \ln\left(\frac{q}{C_f^{c/d}}\right) &= \ln k_1^{1/d} + 1/d \ln(1 - e^{-k_2 t}), \\ &= 1/d \ln k_1 + \frac{1}{d} \ln[(1 - (1 - k_2 t) + \eta)] \end{aligned} \quad (2.42)$$

in which η is an error term and equals,

$$\eta = \frac{1}{2!} (k_2 t)^2 - \frac{1}{3!} (k_2 t)^3 + \dots$$

Equation (2.42) contains a total of five unknown constants. To solve the equation, a trial value of the constant k_2 is needed. However, if the constant k_2 (units of h^{-1}) is relatively small, the net effect of η in Eq. (2.42)

can be neglected. Accordingly, Eq. (2.42) can be simplified,

$$\ln\left(\frac{q}{C_f^{c/d}}\right) = 1/d \ln k_1 k_2 + 1/d \ln t \quad (2.43)$$

$$q = A^{1/d} C_f^{c/d} t^{1/d} \quad (2.44)$$

where $A = k_1 k_2$. Since the values of the (c/d) term are $\ll 1$, the change of $C_f^{c/d}$ as a function of time is small. Then $C_f^{c/d}$ can be considered a constant, and Eq. (2.44) is rewritten as

$$q = K C_o t^{1/d} \quad (2.45)$$

where K is a constant

Kuo and Lotse (1973) plotted PO_4 sorbed versus t on a log-log scale and calculated $(1/d)$ and K from the slope and intercept, respectively, of the straight line.

The two-constant rate equation was also used to describe PO_4 desorption from soil (Dalal, 1974), K - Ca exchange on soils (Sparks *et al.*, 1980a), and recently, by Jopony and Young (1987) to study the kinetics of copper desorption from soil and clay minerals.

Elovich Equation

The Elovich equation is one of the most widely used equations to describe the kinetics of heterogeneous chemisorption of gases on solid surfaces (Low, 1960). This equation assumes a heterogeneous distribution of adsorption energies where the E increases linearly with surface coverage (Low, 1960). Parravano and Boudart (1955) criticized using the Elovich equation for describing one unique mechanism since they found that it described a number of different processes, such as bulk or surface diffusion and activation and deactivation of catalytic surfaces. Recent theoretical studies on adsorption-desorption phenomena in oxide-aqueous solution systems illustrated that the applicability and method of fitting kinetic data to the Elovich equation requires accurate data at short reaction times (Aharoni and Ungarish, 1976, 1977). Ungarish and Aharoni (1981) have also pointed out the inappropriateness of the Elovich equation at very low and very high surface coverages (Atkinson *et al.*, 1970; Sharpley, 1983). These types of situations could well exist in soils or on soil constituent systems.

The Elovich equation has been used to describe the kinetics of PO_4 sorption and desorption on soils and soil minerals (Atkinson *et al.*, 1970; Chien and Clayton, 1980; Chien *et al.*, 1980; Sharpley, 1983), potassium reactions in soils (Sparks *et al.*, 1980b; Martin and Sparks, 1983; Sparks and Jardine, 1984; Havlin and Westfall, 1985), borate dissolution from

soils (Peryea *et al.*, 1985), sulfur sorption and desorption kinetics in soils (Hodges and Johnson, 1987), and arsenite sorption on soils (Elkhatib *et al.*, 1984a). In several of these studies, the Elovich equation was claimed to be superior to other kinetic equations based on high r and low SE (standard error) values (Chien and Clayton, 1980; Hodges and Johnson, 1987).

A form of the Elovich equation as applied to the adsorption of gases onto solid surfaces is

$$dq/dt = Xe^{-Yq} \quad (2.46)$$

where q is the amount sorbed at time t and X and Y are constants in a given experiment. The integrated form of Eq. (2.46) is

$$q = (1/Y) \ln(XY) + (1/Y) \ln(\dot{t} + t_0) \quad (2.47)$$

where t_0 is the integration constant. One can make either of two assumptions when studying t_0 (Polyzopoulos *et al.*, 1986) The first assumption is that $t_0 \approx 0$, which indicates that no other processes besides Elovichian ones are occurring; that is, the boundary condition $q = 0$ at $t = 0$ applies. Thus, with the assumption that $t_0 \approx 0$, then

$$q = (1/Y) \ln(XY) + (1/Y) \ln(t) \quad (2.48)$$

Equation (2.48) is a simplified Elovich equation that several investigators have used to study the rates of soil chemical processes. An application of this equation to PO_4 sorption on soils is shown in Fig. 2.4, and one sees a

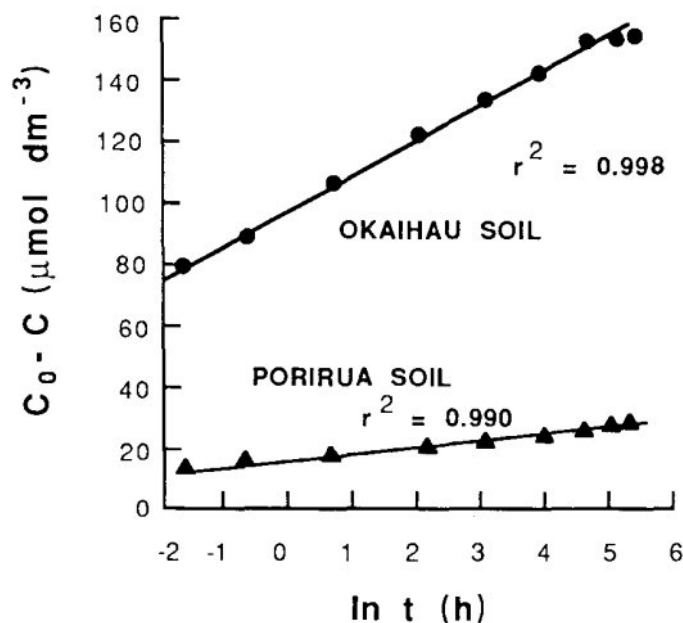
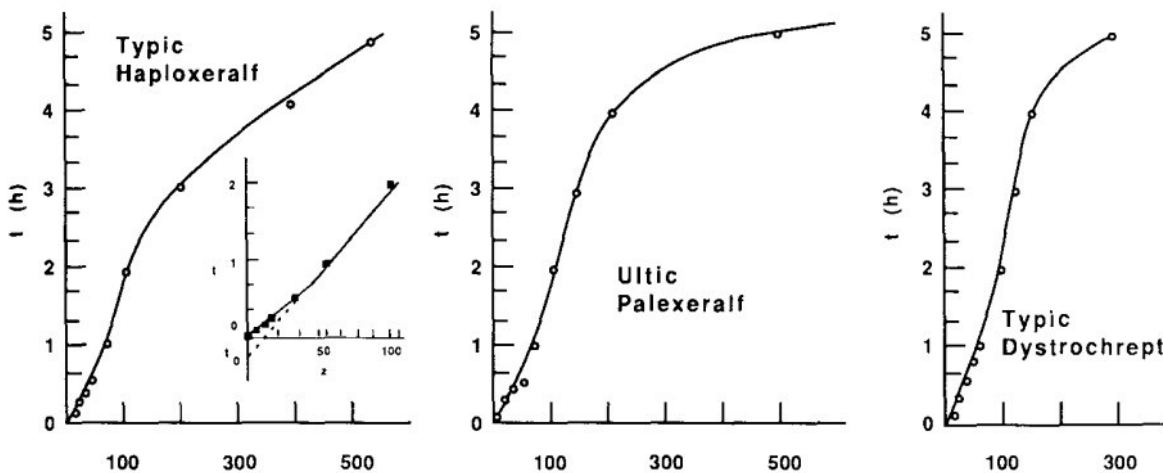


Figure 2.4. Plot of Elovich equation for phosphate (PO_4) sorption on two soils where C_0 is the initial phosphorus concentration added at time zero and C is the phosphorus concentration in the soil solution at time t . [From Chien and Clayton (1980), with permission.]



$$Z = (dq / dt)^{-1}, (\mu\text{g P g}^{-1}\text{h}^{-1})^{-1}$$

Figure 2.6. Plot of t versus Z for phosphate (PO_4) sorption on three Greek soils. [From Polyzopoulous *et al.* (1986), with permission.]

between adsorption and time t that is given in Eq. (2.50),

$$t = Z/Y - t_0 \quad (2.50)$$

where Z is $(dq/dt)^{-1}$ or the reciprocal of the rate. If Eq. (2.50) is valid, t is proportional to Z in any range and extrapolating to $Z = 0$ gives t_0 as an imaginary negative time (Polyzopoulous *et al.*, 1986). At this time the rate is infinity, and as it decreases with increasing q using Eq. (2.46), it coincides with the actual Elovichian rate (Fig. 2.5). Here, t values are given on the ordinate and the y intercept yields t_0 directly.

Equation (2.50) was used by Polyzopoulous *et al.* (1986) to study the rate of PO_4 sorption and release from Greek soils (Fig. 2.6). One sees a linear stage that appears Elovichian, but there is initially a section concave to the t axis. Polyzopoulous *et al.* (1987) ascribe this to a faster rate of PO_4 sorption that is non-Elovichian. One also sees a slow approach to equilibrium with time (Fig. 2.6).

Polyzopoulous *et al.* (1986) calculated t_0 values for the soils by extrapolating to the y -axes regression lines fitted to the linear Elovichian portion of the curves. The t_0 values calculated for the Dystrochrept and Palexeralf soils were greater than zero, which suggests that the assumption that t_0 is close to zero and can be neglected may not be valid.

Some investigators have used Elovich parameters to estimate reaction rates. Chien and Clayton (1980) suggested that a decrease in Y and/or an increase of X would increase reaction rate. However, this may be questionable. The slope of plots using an equation like Eq. (2.48) changes with the

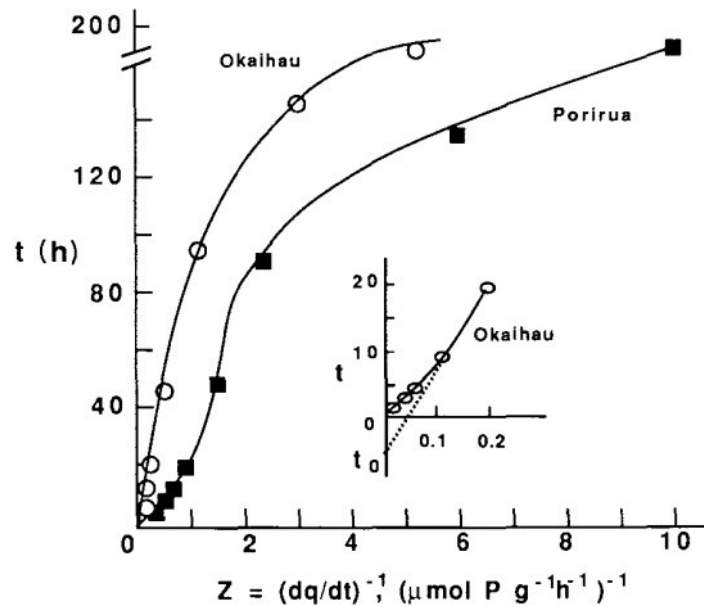


Figure 2.7. Plot of t versus Z for phosphate (PO_4) sorption on Porirua and Okaihau soils. [From Polyzopoulous *et al.* (1986)., with permission.]

level of added ion and with the solution to soil ratio (Sharpley, 1983). Consequently, these slopes are not always characteristic of the soil but depend on various experimental conditions. Sharpley (1983) used the Elovich equation to study soil phosphorus desorption and found that the X and Y values were related to the extractable Al content and CaCO_3 equivalent of acidic and basic soils, respectively.

Another criticism of using Eq. (2.48) is that the pre- and post-Elovichian sections are often not observed and one can erroneously conclude that the entire rate process is explainable using one kinetic law (Polyzopoulous *et al.*, 1986). When kinetic data are plotted according to Eq. (2.50) rather than Eq. (2.31) one sees pre- and post-Elovichian sections (Fig. 2.4 versus Fig. 2.7).

Some investigators have also suggested that “breaks” or multiple linear segments in a q versus $\ln t$ Elovich plot [Eq. (2.48)] could indicate a changeover from one type of binding site to another (Atkinson *et al.*, 1970; Chien and Clayton, 1980). However, one should be cautious about making such mechanistic conclusions from a plot of an empirical equation.

Parabolic Diffusion Equation

The parabolic diffusion law or equation can be used to determine whether diffusion-controlled phenomena are rate-limiting. This equation

was originally derived based on radial diffusion in a cylinder where the ion concentration on the cylindrical surface is constant, and initially the ion concentration throughout the cylinder is uniform. It is also assumed that ion diffusion through the upper and lower faces of the cylinder (corresponding to external cleavage faces) is negligible. Following Crank (1975), if r is the radius of the cylinder, Q_t is the quantity of diffusing substance that has left the cylinder at time t , and Q_∞ is the corresponding quantity after infinite time, then

$$\frac{Q_t}{Q_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{r^2} \right)^{1/2} - \frac{Dt}{r^2} - \frac{1}{3\pi^{1/2}} \left(\frac{Dt}{r^2} \right)^{3/2} \quad (2.51)$$

For the relatively short times in most experiments, the third and subsequent terms may be ignored, and thus

$$\frac{Q_t}{Q_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{r^2} \right)^{1/2} - \frac{Dt}{r^2}$$

or

$$\frac{1}{t} \left(\frac{Q_t}{Q_\infty} \right) = \frac{4}{\pi^{1/2}} \left(\frac{D}{r^2} \right)^{1/2} \frac{1}{t^{1/2}} - \frac{D}{r^2} \quad (2.52)$$

and thus a plot of $\frac{Q_t/Q_\infty}{t}$ versus $1/t^{1/2}$ should give a straight line with a slope

$$\frac{4}{\pi^{1/2}} \left(\frac{D}{r^2} \right)^{1/2}$$

and intercept $(-D/r^2)$. Thus, if r is known, D may be calculated from both the slope and intercept.

A number of researchers have used the parabolic diffusion equation to study the kinetics of reactions on soil constituents (Chute and Quirk, 1967; Sivasubramaniam and Talibudeen, 1972; Evans and Jurinak, 1976; Vig *et al.*, 1979; Feigenbaum *et al.*, 1981; Sparks and Jardine, 1981; Jardine and Sparks, 1984; Havlin and Westfall, 1985; Hodges and Johnson, 1987); feldspar weathering (Wollast, 1967), and pesticide reactions (Weber and Gould, 1966). Sivasubramaniam and Talibudeen (1972) obtained parabolic plots for Al-K exchange on British soils that gave two distinct slopes, which the authors theorized could be indicative of two simultaneous diffusion-controlled reactions. They speculated that the rate-controlling step in Al^{3+} and K^+ adsorption was diffusion of the ions into the sub-surface layers of the solid.

Power-Function Equation

Havlin and Westfall (1985) and Havlin *et al.* (1985) used a power-function equation to describe potassium release from soils. The integrated form of the power-function equation can be expressed (Havlin and Westfall, 1985) as

$$y = at^{\bar{k}} \quad (2.53)$$

The linear transformation is

$$\ln y = \ln a + k(\ln t) \quad (2.54)$$

where y is the quantity of K released at time t , and a and k are constants. The k value is a rate-coefficient value.

Havlin and Westfall (1985) found that the power-function equation described potassium release from soils well. The a and k values were highly correlated with nonexchangeable potassium release. They found that k from Eq. (2.53) was highly correlated with potassium uptake and the relative yield of alfalfa (*Medicago sativa L.*) as shown in Fig. 2.8.

Comparison of Kinetic Equations

Comparisons of different kinetic equations for describing the kinetics of potassium reactions (Martin and Sparks, 1983; Sparks and Jardine, 1984; Havlin and Westfall, 1985), phosphorus sorption and release (Enfield *et al.*, 1976; Chien and Clayton, 1980; Onken and Matheson, 1982), sulfur sorption and desorption (Hodges and Johnson, 1987), and chromium, cadmium, and mercury retention/release (Amacher *et al.*, 1986) have appeared in the soil and environmental sciences literature. Some of these studies are summarized below.

Chien and Clayton (1980) compared several equations for describing PO_4 release from soils and found that the Elovich equation [Eq. (2.49)] was best based on the highest values of the simple correlation coefficient (r^2) and the lowest SE. The two-constant rate equation also described the data satisfactorily. The parabolic diffusion equation was judged unsatisfactory due to low r^2 and high SE values.

Onken and Matheson (1982) studied kinetics of phosphorus dissolution in EDTA (ethylenediamine tetraacetic acid) solution for several soils. They examined eight kinetic models (Table 2.2) and found that phosphorus dissolution in EDTA solution was best described using the two-constant rate, Elovich, and differential rate equations as indicated by high r^2 and low SE values. None of the models best described the dissolution for all soils.

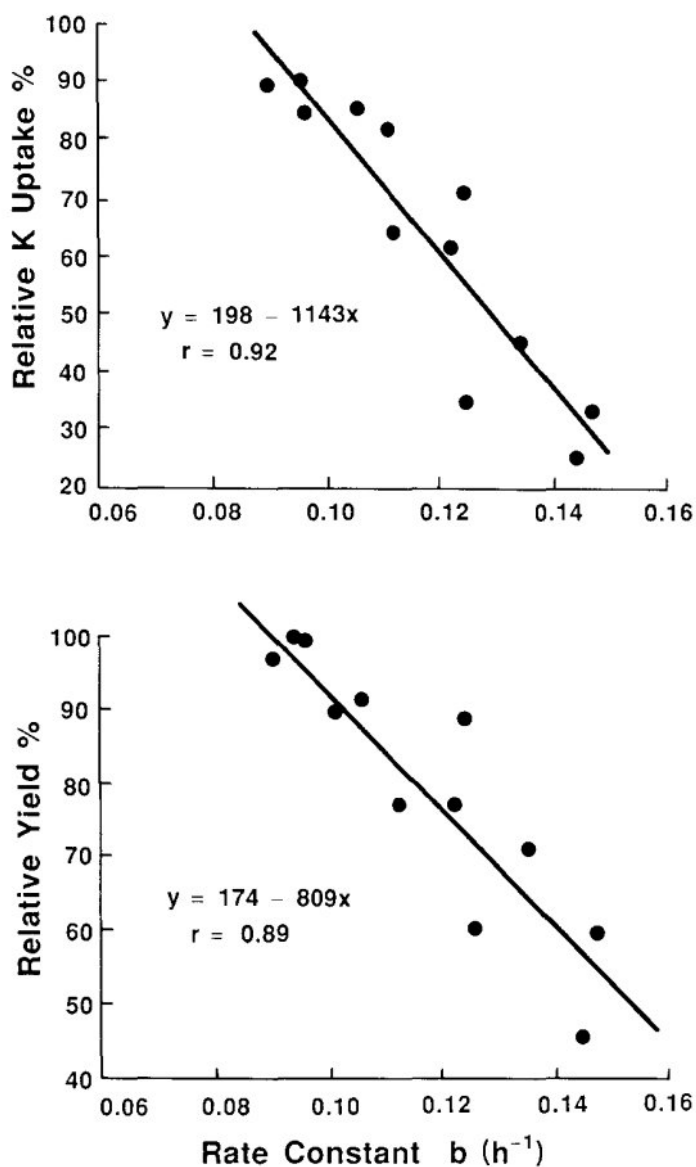


Figure 2.8. Relationship between relative potassium (K) uptake and yield in greenhouse experiment and potassium release constant k , as determined by Ca-resin extraction. [From Havlin and Westfall (1985), with permission.]

Sparks and Jardine (1984) found that the first-order equation best described potassium adsorption kinetics on clay minerals and soils. However, Havlin and Westfall (1985) reported that the power-function equation described nonexchangeable potassium release kinetics better than first-order or a number of other models.

Recently, Hodges and Johnson (1987) used five different kinetic equations to describe sulfur sorption and desorption on soils. Coefficients of determination showed that shell progressive particle diffusion, Elovich,

TABLE 2.2 Summary of r^2 and SE of Eight Kinetic Models for Phosphorus Dissolution in EDTA Solution from Six Test Locations Varying in Plant Response to Applied Phosphorus^a

Kinetic model	Test number											
	1		7		14		15		16		20	
	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE	r^2	SE
Zero-order	0.96	0.04	0.68	0.26	0.87	0.45	0.66	0.30	0.70	0.83	0.86	0.74
First-order	0.92	0.05	0.58	0.34	0.76	0.20	0.55	0.34	0.56	0.39	0.72	0.99
Second-order	0.87	0.07	0.44	0.49	0.63	0.29	0.42	0.44	0.41	0.50	0.56	1.74
Third-order	0.82	0.12	0.41	0.84	0.51	1.23	0.30	2.70	0.30	1.35	0.44	3.06
Parabolic diffusion	0.95	0.05	0.86	0.17	0.97	0.07	0.81	0.22	0.85	0.24	0.96	0.36
Two-constant rate	0.87	0.05	0.93	0.15	0.98	0.05	0.88	0.19	0.91	0.18	0.99	0.26
Elovich-type	0.88	0.07	0.95	0.11	0.95	0.09	0.90	0.16	0.97	0.11	0.97	0.33
Differential rate	0.99	0.0001	0.91	0.0005	0.96	0.0003	0.93	0.001	0.97	0.0002	0.95	0.001

^a From Onken and Matheson (1982), with permission.

and first-order equations described reactions well on the Cecil soil. But the statistical parameters were calculated for only the linear portion of the kinetic plots. When all data points were included, Hodges and Johnson (1987) report that the r^2 and SE values are altered significantly. The desorption data for sulfur reactions on the soils were best described by the shell progressive particle diffusion, Elovich, and parabolic diffusion equations (Hodges and Johnson, 1987).

The above studies clearly show that a number of different equations often describe rate data for soil constituents satisfactorily based on linear regression analyses. However, no single equation best describes every study, and conformity of data to a particular equation does not necessarily indicate that it is the *best* one to use. Moreover, one must be very careful not to attach mechanistic significance to linear plots based on the use of a given model.

TEMPERATURE EFFECTS ON RATES OF REACTION

Arrhenius and van't Hoff Equations

Increasing temperature usually causes a marked increase in reaction rate. Arrhenius observed the following relationship between k and temperature:

$$k = Ae^{-E/RT} \quad (2.55)$$

where k is the rate constant, A is a frequency factor, E is the energy of activation, R is the universal gas constant, and T is absolute temperature. Integrating Eq. (2.55) results in

$$\ln k = (\ln A) - E/RT \quad (2.56)$$

Thus, a plot of $\ln k$ versus $1/T$ would result in a linear relationship with the slope equal to $-E/R$ and the intercept $\ln A$.

Energies of Activation. Low E values ($<42 \text{ kJ mol}^{-1}$) usually indicate diffusion-controlled processes whereas higher E values indicate chemical reaction processes (Sparks, 1985, 1986). For example, E values of $6.7\text{--}26.4 \text{ kJ mol}^{-1}$ were found for pesticide sorption on soils and soil components (Haque *et al.*, 1968; Leenheer and Ahlrichs, 1971; Khan, 1973) while gibbsite dissolution in acid solutions was characterized by E values ranging from 59 ± 4.3 to $67 \pm 0.6 \text{ kJ mol}^{-1}$ (Bloom and Erich, 1987).

Data taken from Huang *et al.* (1968) show the effect of temperature on the rate of potassium release from potassium-bearing minerals (Table 2.3).

TABLE 2.3 Apparent Rate Constants for the Release of Lattice Potassium from Potassium Minerals^a

Mineral	Rate constant (h ⁻¹)	
	Temperature	
	301 K	311 K
Biotite	1.46×10^{-2}	3.09×10^{-4}
Phlogopite	9.01×10^{-4}	2.44×10^{-4}
Muscovite	1.39×10^{-4}	4.15×10^{-4}
Microcline	7.67×10^{-5}	2.63×10^{-4}

^aFrom Huang *et al.* (1968), with permission.

A 10 K rise in temperature during the reaction period resulted in a two- to threefold increase in the rate constant.

One can also derive a relationship between temperature and the equilibrium constant K_{eq} and the standard free enthalpy ΔH° . If the following reversible reaction is operational



and by knowing

$$d(\ln K_{eq})/dT = \Delta H^\circ/RT^2 \quad (2.58)$$

where $K_{eq} = (Y)/(A) = k_a/k_d$ and parentheses denote activity, the van't Hoff relationship can be written:

$$\frac{d(\ln k_a)}{dT} - \frac{d(\ln k_d)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (2.59)$$

where

$$\frac{d(\ln k_a)}{dT} = \frac{E_a}{RT^2} \quad \text{and} \quad \frac{d(\ln k_d)}{dT} = \frac{E_d}{RT^2} \quad (2.60)$$

where k_a and k_d are adsorption and desorption rate coefficients, respectively and E_a and E_d are the energies of activation for adsorption and desorption, respectively.

Specific Studies

A number of researchers have studied the effect of temperature on reaction rates of soil chemical phenomena (Burns and Barber, 1961;

TABLE 2.4 Rate Constants for Indigenous Phosphorus Release from a Thiokol Silt Loam Soil^a

	Surface soil: 0–0.30 m			Subsoil: 0.30–0.40 m		
	284 K	298 K	313 K	284 K	298 K	383 K
(s ⁻¹)	0.19 × 10 ⁻⁴	0.51 × 10 ⁻⁴	0.30 × 10 ⁻⁴	0.24 × 10 ⁻⁴	0.41 × 10 ⁻⁴	0.41 × 10 ⁻⁴
(s ⁻¹)	0.11 × 10 ⁻⁵	0.27 × 10 ⁻⁵	0.16 × 10 ⁻⁵	0.15 × 10 ⁻⁵	0.11 × 10 ⁻⁵	0.26 × 10 ⁻⁵
(s ⁻¹)	0.87 × 10 ⁻⁵	0.13 × 10 ⁻⁶	0.12 × 10 ⁻⁶	0.15 × 10 ⁻⁶	0.93 × 10 ⁻⁷	0.19 × 10 ⁻⁶

^aThe subscripts on k_1 , k_2 , and k_3 represent the first, second, and third phosphorus reactions, respectively. From Evans and Jurinak (1976), with permission.

Huang *et al.*, 1968; Griffin and Jurinak, 1974; Kuo and Lotse, 1974; Barrow and Shaw, 1975; Evans and Jurinak, 1976; Barrow, 1979; Sparks and Jardine, 1981; Ogwada and Sparks, 1986a, Hodges and Johnson, 1987). Evans and Jurinak (1976) studied the rate of phosphorus release from a Thiokol silt loam soil as a function of temperature, using strong anion exchange resins (Table 2.4). Phosphorus released from the surface and subsoil layers of the soil at 284, 298, and 313 K showed that during the initial 4 h of the reaction, the effect of temperature was small, with the rate of release increasing slightly as temperature increased. At times greater than 4 h, the effect of temperature was insignificant.

TRANSITION-STATE THEORY

Theory

Transition-state theory or reaction-rate theory was extensively developed by H. Eyring and collaborators (Glasstone *et al.*, 1941; Frost and Pearson, 1961).

For a given reaction in accordance with the absolute rate theory



where A and B are reactant molecules, $(AB)^{\ddagger}$ is an activated complex, k_1^{\ddagger} is the rate of formation of the activated complex, k_{-1}^{\ddagger} is the rate of decomposition of the activated complex, and K is the rate of product (Y) formation, with

$$K = K_t K^{\ddagger} \quad (2.62)$$

where K_t is the transmittance coefficient and K^{\ddagger} is the pseudothermodynamic equilibrium constant of the activated complex, and

$$K_t = k_B T/h \quad (2.63)$$

where k_B is Boltzmann's constant and h is Planck's constant. Considering the laws of thermodynamics, the following expression may be developed:

$$K^\ddagger = e^{-\Delta G^\ddagger/RT} \quad (2.64)$$

where ΔG^\ddagger is the Gibbs energy of activation. Thus, the parameter, k_1^\ddagger , can be found using,

$$k_1^\ddagger = \left(\frac{k_B T}{h} \right) e^{-\Delta G_1^\ddagger/RT} \quad (2.65)$$

From the reaction rate theory (Frost and Pearson, 1961), it is found that

$$\Delta G_1^\ddagger = \Delta H_1^\ddagger - T \Delta S_1^\ddagger \quad (2.66)$$

where ΔH_1^\ddagger is the enthalpy of activation for the forward reaction and ΔS_1^\ddagger is the entropy of activation for the forward process.

Manipulation of Eq. (2.66) and substitution into Eq. (2.65) give

$$k_1^\ddagger = \frac{k_B T}{h} (e^{\Delta S_1^\ddagger/R - \Delta H_1^\ddagger/RT}) \quad (2.67)$$

Equation (2.67) would enable the calculation of ΔS_1^\ddagger because the following relationship for a unimolecular reaction is true:

$$\Delta H_1^\ddagger = E_1 - RT \quad (2.68)$$

where E_1 refers to an energy of activation for the forward reaction. The ΔG_1^\ddagger may be calculated using Eq. (2.66). Analogous expressions can be obtained for the reverse reaction through the use of E_{-1} and k_{-1}^\ddagger calculated for the reverse process.

The pseudothermodynamic equilibrium constant of the activated complex (K_{eq}^\ddagger) is related to the thermodynamic state functions by

$$\Delta G^{\circ\ddagger} = -RT \ln K_{eq}^\ddagger = \Delta H^{\circ\ddagger} - T \Delta S^{\circ\ddagger} \quad (2.69)$$

where $\Delta G^{\circ\ddagger}$, $\Delta H^{\circ\ddagger}$, and $\Delta S^{\circ\ddagger}$ refer to the standard Gibbs energy of activation, the standard enthalpy of activation, and the standard entropy of activation, respectively.

In each case these parameters represent differences between the state function of the activated complex in a particular standard state and the state function of the reactants referred to in the same standard state. One is giving K_{eq}^\ddagger all the characteristics of a thermodynamic equilibrium constant, although it should be multiplied by a transitional partition function. For ideal systems the magnitude of $\Delta H^{\circ\ddagger}$ does not depend on the choice of standard state, and for most of the nonideal systems that are encountered the dependence is slight. For all systems, the magnitudes of $\Delta G^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$ depend strongly on the choice of standard state, so it is not useful to

say that a particular reaction is characterized by specified numerical values of ΔG^{\ddagger} and ΔS^{\ddagger} unless the standard states associated with these values are clearly identified.

The reaction-rate theory assumes that colliding molecules (e.g., reactions between solution ions and ions held by an exchange complex) must be in a high energy state before a reaction can occur. This energy of activation is the result of van der Waals repulsive forces that occur as two ions approach each other. Without the repulsive forces, all exothermic reactions would have zero or very low activation energies and would be fast (Frost and Pearson, 1961). When these highly energized reactant molecules collide, they form an activated complex. It is a distinct chemical species in equilibrium with the reactants, which has gained one degree of vibrational freedom. This abnormal vibrational freedom causes the complex to lack a "restoring force," a force mandatory for all stable molecules: thus it flies apart in the period of one vibration (Denbigh, 1966). The activated complex is highly unstable and rapidly dissociates to form the eventual product or to reform the original reactants. Once the exchange reaction is complete, pseudothermodynamic parameters for the adsorption and the desorption process may be formulated.

A ΔG^{\ddagger} value may be considered as the free energy change between the activated complex and the reactants from which it was formed, all substances in reference to their standard states (Laidler, 1965). It is the ΔG^{\ddagger} value that determines the rate of the reaction (Glasstone *et al.*, 1941). The ΔG^{\ddagger} values should become larger with temperature, since the tendency of any reaction to proceed is hastened by temperature increases.

The enthalpy of activation ΔH^{\ddagger} is a measure of the energy barrier that must be overcome by reacting molecules (Frost and Pearson, 1961). The energy needed to raise the molecules from their ground state to one of an excited state is the sum of the electronic, vibrational, rotational, and translational energy terms. Thus, the energy needed to change the orientation, structure, and position of an ion from one phase to that of another is the total heat energy required in the process. Variations in ΔH^{\ddagger} with temperature are not the result of energy changes involved in making or breaking bonds, but rather are due to alterations in the heat-capacity behavior of the ions involved in the exchange reaction (Frost and Pearson, 1961).

The entropy of activation ΔS^{\ddagger} may be regarded as the "saddle point of energy" over which reactant molecules must pass as activated complexes (Frost and Pearson, 1961; Laidler, 1965). The ΔS^{\ddagger} conveys whether a particular reaction proceeds more quickly or slowly than another individual reaction. Negative ΔS^{\ddagger} values would depict a system that could ascertain a more ordered molecular arrangement in a shorter period of

time relative to a positive or less negative ΔS^\ddagger parameter. The molecular arrangement would be related to both the aqueous and solid phases where ion hydration and configurational entropy constituents are considered.

Application to Soil Constituent Systems

Griffin and Jurinak (1974) calculated pseudothermodynamic parameters for phosphate interactions with calcite using reaction-rate theory. Gonzalez *et al.* (1982) applied reaction-rate theory to a treatment of adsorption-desorption processes on an Fe-selica gel system. In 1981, Sparks and Jardine applied reaction-rate theory to kinetics of potassium adsorption and desorption in soil systems for the first time (Table 2.5).

In their systems, the ΔG^\ddagger values were higher for desorption than for adsorption, suggesting a greater free-energy requirement for potassium desorption. The ΔG^\ddagger values for both adsorption and desorption were also slightly higher in the B21t than in the Ap soil horizon, suggesting slower

TABLE 2.5 Kinetic Parameters for Potassium Adsorption and Desorption Processes at Three Temperatures in Matapeake Ap and B21t Horizons Using Reaction-Rate Theory^a

Temperature (K)	ΔG^\ddagger (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)
Ap horizon		
Adsorption		
276	67.29	13.74
298	71.44	13.58
313	74.50	13.45
Desorption		
276	72.74	20.83
298	76.85	20.62
313	79.63	20.53
B21t horizon		
Adsorption		
276	68.21	16.30
298	72.28	14.88
313	75.46	14.75
Desorption		
276	73.20	20.66
298	77.10	20.49
313	80.32	20.36

^aFrom Sparks and Jardine (1981), with permission.

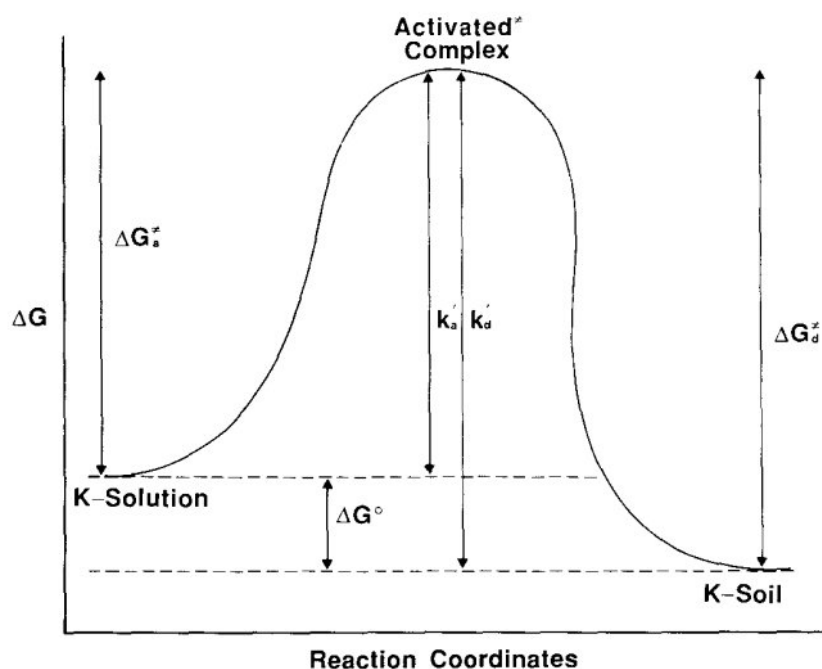


Figure 2.9. Schematic diagram of ΔG versus reaction coordinate for potassium exchange on a Matapeake soil where ΔG is the Gibbs free energy. [From Sparks and Jardine (1981), with permission.]

reactions due to more restrictive binding sites for K in the B21t horizon (Glasstone *et al.*, 1941). Figure 2.9 illustrates a schematic correlation between the pseudothermodynamic parameters and those established using thermodynamics of ion exchange theory. The ΔG_a^\ddagger is the change in free energy required for potassium to cross the barrier of adsorption at an apparent rate of k'_a . The ΔG_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 ΔG° , the Standard Gibbs free energy.

The ΔH^\ddagger values in both horizons were higher for desorption than for adsorption (Table 2.5), suggesting that the heat energy required to overcome the potassium desorption barrier was greater than that for potassium adsorption. This was also seen in the magnitude of the E_a and E_d values calculated (not shown). A schematic correlation between ΔH° and ΔH^\ddagger can be observed like that shown in Fig. 2.9 for ΔG° and ΔG^\ddagger . The ΔH_a^\ddagger represents the change in heat energy needed for K^+ to go from the solution phase to the solid phase (adsorption), whereas ΔH_d^\ddagger is the heat-energy requirement for the desorption reaction. The difference in these two parameters represents ΔH° (Frost and Pearson, 1961).

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