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**Thermodynamics applied to potassium exchange in aluminosilicate minerals
and soils**

K.W.T. GOULDING

*Soils and Plant Nutrition Department, Rothamsted Experimental Station,
Harpenden, Herts, AL5 2JQ, England*

SUMMARY

The enthalpies of Ca-K exchange in 2:1 layer silicate minerals and in soils identify six types of cation exchange site, with up to four in any one soil or clay, which control ion exchange and the extent to which clays swell on adsorption of glycol. It is suggested that these sites are on the planar surfaces of mica, illite, vermiculite and montmorillonite, with a particular type of strongly K selective site at steps, cracks and expansion boundaries (wedge zones) of micaceous clays. Such thermodynamic measurements permit the quantitative determination of very small amounts of 2:1 layer silicate minerals and their K contents in clays and soils with mainly 1:1 or amorphous minerals, and thus a more precise determination of K exchange behaviour, especially selectivity and fixation.

INTRODUCTION

The release of potassium (K) from soil into solution by ion exchange, and the reverse processes of adsorption and fixation, are some of the most important processes in plant nutrition. They are of interest both for determining K availability to crops, and for understanding the adsorption/desorption properties of K in relation to other ions and the nature of the surfaces on which ions are adsorbed. Quémener (1986) recently reviewed these subjects.

For over 30 years classical equilibrium thermodynamics has been applied to ion exchange in soils and clays (for a review, see Goulding, 1983), but the practical advances accruing from this work have been few, and some scientists have been very critical of such an approach (Walsh, 1972). Others, however, see it as having been useful (Cooke & Gething, 1978), particularly in increasing our understanding of the ion exchange process and enabling us to abandon empirical methods of determining ion exchange behaviour.

The approach at Rothamsted was first to apply the thermodynamic method of Gaines and Thomas (1953) to determine exchange isotherms, selectivity coefficients, equilibrium constants, free energies, enthalpies and

entropies of exchange and adsorbed ion activity coefficients. Much information was gleaned on differences between the selectivities of soils or clays for one cation, and on differences in cation selectivities; soil and clay exchange surfaces were generally found to be heterogeneous. However, the thermodynamic quantities determined were not directly measured but calculated from the exchange isotherm. What was required was a direct measurement of the forces controlling ion exchange.

Barrer and his co-workers at Imperial College were obtaining very interesting data on the exchange characteristics of zeolites by directly measuring enthalpies of ion exchange with a calorimeter (e.g. Barrer *et al.*, 1963). We purchased a commercially-made microcalorimeter in 1975, and since that time have been measuring enthalpies of exchange, as well as obtaining free energies and other quantities from exchange isotherm methods. This paper summarizes some of our results, relating them to the recent work of other researchers and suggesting some practical consequences.

MATERIALS AND METHODS

The soils and clays examined and the experimental methods used have been documented elsewhere (Goulding & Talibudeen, 1984). We use a modified LKB 2107 Batch Microcalorimeter to measure enthalpies of exchange and combine these with exchange isotherm data calculated by the method of Gaines and Thomas. The methods are applied to soils, selected for their contrasting mineralogy, pH and organic matter (OM) content (i.e. those properties which control K exchange), and to clay minerals chosen as being typical of the main types of layer silicates that control the ion exchange behaviour of soils of temperate regions and that have been extensively used in other studies of clay chemistry, e.g. Upton montmorillonite (Wyoming bentonite), Camp Berceau montmorillonite, Fithian illite, Montana vermiculite and muscovite mica.

The methods involve first saturating the clays or soils with calcium. The calcium is then gradually exchanged with K, and *vice-versa*, and the enthalpy after each exchange step measured and summed to provide a complete picture of the enthalpy of exchange from 0 to 100% K saturation. The slope of this integral enthalpy (ΔH_X) curve is the differential enthalpy of exchange, $d(\Delta H_X)/dx$ (Fig.1).

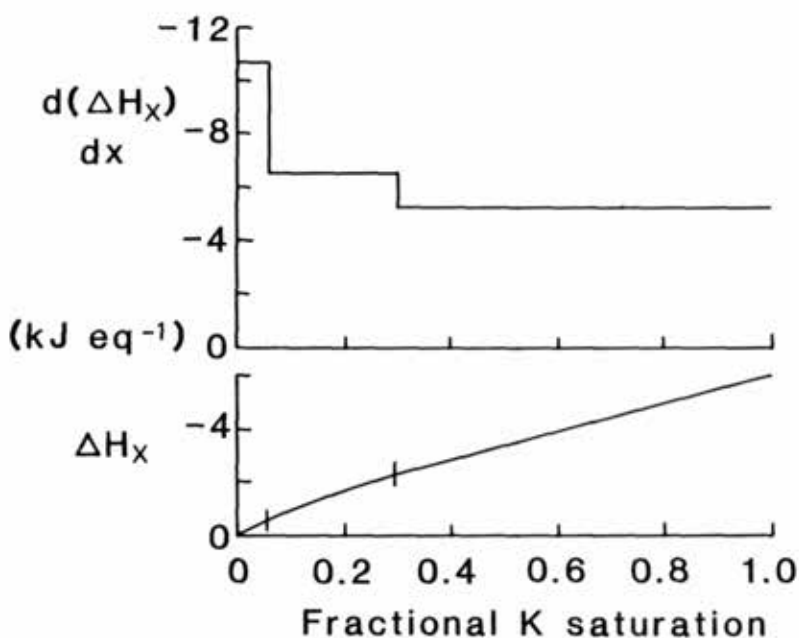


Figure 1. Integral (ΔH_x) and differential ($d(\Delta H_x)/dx$) enthalpy of Ca-K exchange on Upton montmorillonite

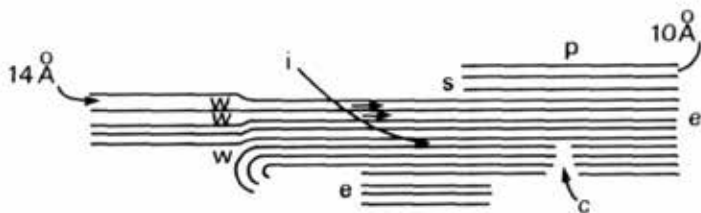


Figure 2. Schematic diagram of a 2:1 layer silicate crystal showing planar (p), edge (e), interlattice (i), wedge (w), crack (c), and step (s) exchange sites

RESULTS AND DISCUSSION

Types of exchange sites

Since the work of Schouwenberg & Schuffelen (1963) and Bolt *et al.* (1963) cation exchange sites have been classified as planar, edge and interlattice, with sites selective for K in wedge-zones at the edge of partially expanded 2:1 layers (Fig.2). While these types of site undoubtedly exist, ion exchange surfaces are somewhat more complex than this.

We found differential enthalpies of Ca-K exchange in 2:1 layer-silicate minerals that appeared to be characteristic of a particular type of exchange site (Table 1). Muscovite mica had only one differential enthalpy of exchange of -10.5 kJ eq^{-1} . Such a value was also found in (i) Fithian illite (an illite being a clay mineral from an argillaceous sediment belonging to the mica group and being somewhat similar to muscovite), (ii) in the coarser fraction of Upton montmorillonite, (iii) in the fine fraction of Camp Berteau montmorillonite, and (iv) in a soil that contained 60-70% mica in its clay fraction (not shown here). We therefore attributed groups of sites with this differential enthalpy to the planar external surface of mica. Others have also deduced that the planar surfaces of muscovite mica have only one type of site (Claesson *et al.*, 1986).

From our studies of some smectites it appeared to us that a true montmorillonite surface had a differential enthalpy value of between -5.2 and -7.6 kJ eq^{-1} , in other words only weak bonding for K. More negative differential enthalpy values were present in some smectite samples (Table 1). Because these more negative differential enthalpies were seen in mica, illite and vermiculite, we suggested that such sites reflected small amounts of those minerals in the smectite.

Up to nine classes of layer charge have been found in montmorillonites using the technique of intercalation of alkylammonium ions (Lagaly, 1981); no one class dominated surface properties. The number and type of exchange site we found did control exchange properties and related closely to the expansion properties of smectites on glycol adsorption (Čičel & Machajdik, 1981). There were three main types of site in the montmorillonites (Table 1): micaceous - strong K bonding, no swelling; illitic - intermediate K bonding, restricted swelling; montmorillonitic - weak K bonding, full swelling. Within the montmorillonitic group there were three sub-groups of sites with slightly different K bonding strengths but with little difference in K selectivity and having no effect on the expansion on glycol adsorption.

Table 1

Groups of exchange sites identified by differential enthalpies ($d(\Delta H_x)/dx$) of Ca+K exchange in some clay minerals.

Clay	$d(\Delta H_x)/dx$ (kJ eq ⁻¹)							
	'Defect sites'	Vermic.	Micaceous	Illitic	Montmorillonitic			
Muscovite mica	-	-	-10.5	-	-	-	-	-
Fithian illite	-20.0	-	-10.9	-	-	-7.6	-6.0	-
Montana vermiculite	-	-15.9	-	-	-	-	-6.3	-
Upton montmorillonite, 0.2-1 μ m	-	-	-10.7	-	-	-	-6.5	-5.2
Upton montmorillonite, <0.2 μ m	-	-	-	-	-	-7.6	-6.7	-
Redhill montmorillonite, <0.2 μ m	-	-	-	-9.4	-	-7.5	-	-5.8
Camp Berteau montmorillonite, <0.2 μ m	-	-	-10.3	-	-6.7	-7.4	-6.0	-
New Mexico montmorillonite <0.2 μ m	-	-11.7	-	-	-8.7	-	-	-

Our data on Fithian illite showed four differential enthalpy values. Two of these groups of sites, with enthalpies of -6.0 and -7.6 kJ eq⁻¹, were the same as those found in montmorillonite and one, with an enthalpy of -10.9 kJ eq⁻¹, was identical to that found in muscovite mica. This agrees with the conclusions of Šrodoň (1984) that Fithian illite is a physical mixture of nonexpanding material with a basal spacing of 10Å and ordered mixed-layer illite/smectite. The fourth group of sites, with an enthalpy of -20.0 kJ eq⁻¹, was unique to this illite. These sites showed great selectivity as well as bonding strength for K over Ca (Table 2). Recently Sposito *et al.* (1985) found an almost identical amount (13% compared to our 15%) of sites, selective for Na over Ca and Mg, in Silver Hill illite. They made no attempt to identify the physical nature of these sites, describing them as 'quasi-crystal exchange sites' or 'high energy exchange sites'. Could these be wedge sites?

Such sites are the best explanation of the strong bonding of, and selectivity for K seen here. But they are not simply wedge zones at the weathered periphery of micaceous clays. They correspond to the defects in micaceous minerals that are found to adsorb uranyl cations strongly (Lee & Jackson, 1977) and to the step edges, cracks, and boundaries of expanded and unexpanded layers in biotite which selectively adsorbed Rb⁺ over Sr²⁺ (Le Roux *et al.*, 1970).

We have interpreted the differential enthalpies of Ca-K exchange measured as reflecting six main groups of exchange sites: micaceous (one type), illitic (three types), vermiculitic (one type) and montmorillonitic (one type). These groupings dominated ion exchange and swelling properties. The occurrence of several types of site in one clay could be explained in terms of interstratification - mixtures of layers in clay crystallites - or in terms of the Nadeau model (Nadeau *et al.*, 1984), physical mixtures of thin fundamental particles.

K selectivity and fixation

Perhaps the most important aspect of the ion exchange behaviour of K is its selective adsorption to the extent that it becomes only slowly-exchangeable in some circumstances, i.e. 'fixed'. Rühlicke (1985) investigating the use of alkylammonium intercalation in the determination of layer charge and its relation to K fixation, found that fixation occurred when the layer charge was -0.75 per formula unit or more. Gaultier (1981), however, found that K was fixed in Wyoming montmorillonite (which has a layer charge $\ll -0.75$) when wetting and drying occurred, and

Eberl & Srodon (1986) came to the same conclusion, although in this case the amount of K fixed increased with layer charge. Thus several factors determine fixation. Below I outline how I think thermodynamic measurements help us to understand this phenomenon.

The ion exchange process is controlled by the Gibbs free energy of exchange. Consider the exchange



If the standard free energy of the reaction is negative then the reaction moves spontaneously to the right; the soil selectively adsorbs K over Ca. Such selectivity is a function of the enthalpy (ΔH_0) and entropy (ΔS_0) of the system as shown by the familiar formula:

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (2)$$

The enthalpy change during a reaction is a measure of the overall bond strength of the two systems. In the case of equation (1) a negative enthalpy change (heat is given out - an exothermic reaction) implies that the bonds formed in the whole K-soil-water/Ca-water system are stronger than those in the Ca-soil-water/K-water system.

The entropy change during a reaction is a measure of the change of order in the system. A negative entropy change in going from Ca-soil to K-soil implies more order (less random arrangement) of the soil, ions and water molecules in the K-soil system. But in the case of entropy, a change to greater disorder favours a process (note the negative sign in equation 2). Thus in equation (1), a positive ΔS_0 value would favour the K-soil system.

We therefore see that selectivity is a function of bond strength and of the order of the system. Thermodynamic measurements cannot prove mechanisms; other data are required before mechanisms can be deduced (Sposito, 1984). Enthalpies and entropies can, however, show how bond strength and order combine to determine selectivity.

In Table 2, the mean free energies (ΔG_1), enthalpies (ΔH_1) and entropies (ΔS_1) of the various groups of exchange sites, distinguished by their differential enthalpies, have been calculated. The single group of exchange sites of muscovite mica was very selective for K over Ca. Although the enthalpy of Ca \rightarrow K exchange was negative, showing K to be bound more strongly, it was by no means large, -10.5 kJ eq^{-1} . The considerable selectivity or preference for K over Ca was caused by a large, positive entropy value ($+29.3 \text{ JK}^{-1} \text{ eq}^{-1}$). What does this reflect?. Potassium ions can form a much more random arrangement on the surface of mica than can

Table 2

Mean free energies (ΔG_i), enthalpies (ΔH_i) and entropies (ΔS_i) of Ca \rightleftharpoons K exchange of groups of exchange sites in some 2:1 layer silicate clays identified by differential enthalpies

Clay	ΔG_i	ΔH_i	ΔS_i
	kJ eq ⁻¹		J k ⁻¹ eq ⁻¹
Muscovite mica	-19.4	-10.5	+29.3
Fithian illite	-15.0	-20.0	-16.5
	-4.0	-10.9	-22.8
	0	-7.6	-25.1
	-8.0	-6.0	+6.6
	-5.0	-15.9	-36.0
Montana vermiculite	-6.0	-6.3	-1.0
	-3.0	-10.7	-25.4
Upton montmorillonite	-1.0	-6.5	-18.2
	-1.0	-5.2	-13.9

Ca²⁺ and this probably dominates ion exchange to make mica surfaces highly selective for K.

By comparison, the highly K selective exchange sites found in Fithian illite were so because of a very large negative enthalpy change (-20.0 kJ eq⁻¹), i.e. much greater bonding strength for K than for Ca. The entropy change accompanying Ca \rightleftharpoons K exchange on these sites was negative (i.e. favouring Ca) and so selectivity here is controlled by binding strength. Brouwer *et al.* (1983) found that the driving force for sites in Morris illite highly selective for Cs⁺ over Rb⁺ was 'exclusively enthalpic', and the entropy of Rb \rightleftharpoons Cs exchange was negative, agreeing with our data. This negative entropy change we would attribute to the rearrangement of expanded 2:1 layers in the illites which precedes their collapse on adsorption of K.

In the Montana vermiculite selectivity was again caused by stronger binding of K than Ca. Entropy changes were negative, implying greater order in the K-clay-water system, and we attribute selectivity and fixation of K to a collapse of the layers with some reorganization and re-alignment following K adsorption and dehydration.

All the clay minerals examined bound K more strongly than Ca, and all were selective for K over Ca. The only cases in which Ca selectivity was observed occurred in a soil which had received large dressings of organic manure for many years, and in two strongly acid soils. The Ca selectivity

of the former was caused solely by a very large negative entropy change in going from a Ca to a K system; K was still bound more strongly. Perhaps the significant effect is that of organic matter (OM) being displaced from mineral surfaces as K replaces Ca and soil-Ca-OM bonds are broken. In the acid soils, H^+ and Al^{3+} ions may well have been present and so studying only K-Ca exchange would give a false picture.

THE FUTURE

Our data do not prove that a particular differential enthalpy is related to one and always to that one mineral surface. To gain a greater insight into what differential enthalpies measure I have begun some collaborative work with Dr Dennis Eberl of the U.S. Geological Survey, and Dr Jan Środoń of the Polish Academy of Sciences. We shall be measuring both the enthalpies and selectivities of ion exchange (probably Na/Ca), of some smectites and the K release and fixation characteristics of some smectites and illites subjected to K fixation by wetting and drying cycles. The structure of the clays will be examined by the most modern XRD techniques both before and after exchange/release and at various points along the exchange isotherm/release curve. We hope that such work will enable us to relate the groups of sites identified by differential enthalpies and the forms of K identified by release curves with the detailed chemistry and layer structure of the clays.

CONCLUSIONS

The application of thermodynamics to the study of potassium exchange in clay minerals and soils has increased our understanding of the adsorption and desorption of K and enabled us to improve our predictions of its exchange behaviour in the field. Future work linking clay structure with K adsorption and release data will enable a better interpretation of thermodynamic data on ion exchange.

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