PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Calculations on a Model Intercalate Containing a Single Layer of Water Molecules: A Study of Potassium Vermiculite, K$_{2x}$Mg$_{6}$(Si$_{4-x}$Al$_{x}$)$_{2}$O$_{20}$(OH)$_{4}$.(H$_{2}$O)$_{4}$, for 1 $\leq$ x $\leq$ 0

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CALCULATIONS ON A MODEL INTERCALATE CONTAINING A SINGLE LAYER OF WATER MOLECULES: A STUDY OF POTASSIUM VERMICULITE, $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$, FOR $1 \leqslant x \leqslant 0$

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CONTENTS

The largest body of information concerning the swelling of clay minerals on exposure to moisture has been accumulated for the vermiculites and the smectites. The experimental findings for a range of phyllosilicates possessing various interlayer charges have shown that for silicates with zero charge on the interlayer (for example talc or pyrophyllite) there is no intercalation of water molecules within the sheets. Maximum water uptake, in this class of minerals, is found to take place in those having a fairly low interlayer charge (for example hectorites, montmorillonite). As the layer charge is increased further uptake falls to zero for fully saturated interlayers (for example beidellite and vermiculites).

This paper represents a comprehensive study from a theoretical standpoint of some of these observations and enables comment to be made on the influence of layer charge on the intercalation process in addition to the examination of other features that have been held to be important (for example tetrahedral or octahedral site substitution) so enabling discussion of the work of the experimenters in this area.

Calculations are reported for the electrostatic energy of a potassium vermiculite, $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$, which contains a single layer of water molecules intercalated into an expanded phlogopite. The crystal structure adopted is such that for $x = 1$, $K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4$, the oxygen atoms of the water molecules form a honeycomb-like network with the potassium ions in the holes.

For $x = 1$, the calculation is straightforward and is based on our 'generic' approach reported previously. This approach also enabled us, in one single calculation, to study the influence of interlayer K^+ ions placed at various levels between the water layer and the silicate layer. It appears that the most favourable position depends on the charge distribution within the water molecule.

The centrally positioned K^+ ion represents the most stable configuration when the charge on the hydrogen atom of the water $q_{H''} \geqslant 0.6$. For $q_{H''}$ below this value the most stable position for the K^+ ions is between the water layer and the plane of the nearest oxygens in the silicate sheet.

For $x < 1$ specific considerations had to be given to the likely arrangement of interlayer K^+ ions and water molecules (taken to be in the plane of the water layer), implying separate calculation of their interaction energies.

The intercalation energy comprises the energy involved in the process of expanding a phlogopite from 10 Å† to 12.5 Å and arranging water molecules in the gap. It emerges that the intercalation is mainly determined by the expansion energy. Both the expansion energy and the arrangement energy depend on the silicate layer charge, which is determined by x.

For large x no intercalation occurs owing to the large amount of energy required for expansion.

For x very close to zero no intercalation occurs owing to the repulsive interaction of the water layer with the silicate layer.

For intermediate values of x intercalation occurs owing to the large K–H_2O interaction energy.

1. INTRODUCTION

Interest in intercalation compounds has increased dramatically in recent years and one of the reasons for this has been the number and variety of reactions found to be capable of taking place within the layers, and the number of types of molecule that can be taken up in such minerals as a guest molecule. Not only are many of the reactions referred to highly specific and often of biological importance (for example formation of polypeptides, (Weiss 1969)) but also conversions of certain organic molecules into others of commercial importance have been achieved, often in very high yields, within intercalates (for example conversion of *trans* 4-4′ diaminostilbene into aniline (Tenakoon *et al.* 1974)). Facile synthesis of esters by direct addition of ammonia from amines (Ballantine *et al.* 1981 *a*) and a novel intermolecular elimination of ammonia from amines

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† $Å = 10^{-10}$ m $= 10^{-1}$ nm.

(Ballantine *et al.* 1981 *b*) within the interlamellar regions of cation-exchanged montmorillonites have very recently been reported.

This paper reports some calculations that seek to examine aspects of the incorporation of water molecules and exchangeable cations within the interlayer of silicates. The calculations represent the first attempt to examine the energetics of such compounds from the standpoint of our 'generic' approach (Jenkins & Hartman 1979).

We begin by describing the structural features and parameters of a model vermiculite, $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$. Then we give the results obtained for the interlayer fully occupied by cations ($x = 1$). We then discuss the modifications that have to be made to the model to treat cases where not all the possible cation interlayer sites are filled ($x < 1$), and present the results for such cases.

Telleria *et al.* (1977) consider the detailed arrangement of the interlamellar cation–H_2O arrangement in barium vermiculite and extend the earlier analyses (Gruner 1934, 1939; Hendricks & Jefferson 1938), which were in substantial agreement regarding the structural features of the silicate layers. Further studies of the general configuration of H_2O molecules and exchangeable cations near silicate surfaces have been made by Mathieson & Walker (1954), Mathieson (1958), Bradley & Serratosa (1960) and Shirozu & Bailey (1966); studies also exist concerning the influence of some exchangeable cations on the relative orientation of the silicate layers (De la Calle 1975 *a*, *b*), and the influence of hydration on the arrangement of cations has been studied by Fernandez *et al.* (1975). Very recently, while the present study was being concluded, a few papers on the structure of the interlayer arrangement appeared. Rausell-Colom *et al.* (1980) and Alcover & Gatineau (1980) determined the interlayer structure of a vermiculite with one layer of water molecules and Mg, Ca, Sr or Ba as interlayer cation, 0.45 of the available sites being occupied ($x = 0.90$ in our formula). The Ba ion is situated between the positions adopted by us for K_B and K_C, but closer to K_C. A further difference between this structure and the model adopted here is that the silicate sheets on opposite sides of the water layer are slightly displaced with respect to each other, with the result that the Ba ion is shifted about 0.5 Å from the centre of the ditrigonal hole.

The present studies represent a first approach to the estimation of the energetics of the process of intercalation and stem from our earlier work which has considered the properties of expanded phlogopite structures (Jenkins & Hartman 1979) and phyllosilicates in general (Jenkins & Hartman 1980). The calculations are made by using the program described by Jenkins & Pratt (1978) to calculate the Jenkins–Hartman coefficients for the basic structure model.

2. NOTATION

$A_{ijklmnpq}$	Jenkins–Hartman coefficients for electrostatic energy of vermiculite
$\boldsymbol{a}, \boldsymbol{b}$	vectors representing axial directions
$\boldsymbol{a}', \boldsymbol{b}'$	vectors representing redefined hexagonal axial directions
a, b, c	unit cell lengths for normal, unexpanded cell
a', b', c'	unit cell lengths for expanded cell
α, β, γ	unit cell angles for unexpanded cell
β'	unit cell angle for expanded phlogopite
d	displacement of interlayer cations from central plane of water molecules
ξ	angle related to β': $\xi = 90° - \beta'$

$E(\mathrm{K{-}H_2O})$	$\mathrm{K^+{-}H_2O}$ interaction energy within interlayer, from first and second nearest neighbour calculations
$E(\mathrm{K{-}K})$	K–K interaction energy within interlayer from nearest neighbour calculations
$E(\mathrm{H_2O{-}H_2O})$	$\mathrm{H_2O{-}H_2O}$ interaction energy within interlayer, from nearest neighbour calculations
$E(\mathrm{H_2O{-}TO})$	interaction energy of water molecules with T and O ions of silicate sheet.
$\Delta H_{\mathrm{vap}}(\mathrm{H_2O})$ (l)	enthalpy of vaporization of water
H''	hydrogen atom of intercalated water molecule
(I), (II), ...	$\mathrm{K^+{-}H_2O}$ specific interaction types
(I)′, (II)′, ...	$\mathrm{H_2O{-}H_2O}$ specific interaction types
i, j, k, l, m, n, p, q	indices of charges in basic electrostatic equation
I_0	$= E(\mathrm{K{-}K})$
I_1	$= E(\mathrm{K{-}H_2O})/q_{\mathrm{H''}}$, coefficient of $q_{\mathrm{H''}}$-dependence of $E(\mathrm{K{-}H_2O})$
I_2	$= E(\mathrm{H_2O{-}H_2O})/q^2_{\mathrm{H''}}$, coefficient of $q^2_{\mathrm{H''}}$-dependence of $E(\mathrm{H_2O{-}H_2O})$
K_{A}	central position of interlayer cation midway between silicate layers
$\mathrm{K_B}$, $\mathrm{K_C}$, $\mathrm{K_D}$, $\mathrm{K_E}$	various positions of interlayer cation within interlayer ($\mathrm{K_C}$ is position of interlayer cation corresponding to distance from $\mathrm{K^+}$ to silicate layer as found in unexpanded phlogopite)
○	water molecule in interlayer that is regarded as freely rotating
$\overset{?}{\ominus\!\!\!\rightarrow}$	water molecule in interlayer for which there is doubt about the actual orientation of the hydrogen atoms
O′	hydroxyl oxygen within vermiculite
O″	oxygen atoms of intercalated water molecule
$\ominus\!\!\!\rightarrow$	water molecules in the interlayer such that line joining the hydrogen atoms, H″, is perpendicular to the (001) plane; arrow points from oxygen atom to mid-point of line joining the hydrogen atoms
$q_{\mathrm{K}}, q_{\mathrm{O''}}, q_{\mathrm{H''}}$	charge on interlayer cation $\mathrm{K^+}$, and the oxygen atom (O″) and hydrogen atoms (H″) of the intercalated water
$q_{\mathrm{Mg}}, q_{\mathrm{O}}, q_{\mathrm{O'}}, q_{\mathrm{H}}$	charge on Mg, oxygen atom (O) of silicate layer, hydroxyl oxygen (O′) atom and its associated hydrogen atom (H)
q_{T}	charge on tetrahedral layer ($q_{\mathrm{T}} = 4 - 0.25x$)
q_{X}	charge on atoms occupying dioctahedral sites X
$q_{\mathrm{X'}}$	charge on atoms occupying trioctahedral site X′
$r(u, v)$	distance of interlayer cation having coordinates (u, v) from reference ion at origin (0, 0)
ΔU_{exp}	expansion energy of phlogopite from 10 Å to 12.5 Å
$\Delta U_{\mathrm{int}}(\mathrm{g})$, $\Delta U_{\mathrm{int}}(\mathrm{l})$	intercalation energies of potassium vermiculite for incorporation of $\mathrm{H_2O(g)}$, $\mathrm{H_2O(l)}$
$\Delta U_{\mathrm{inter}}$	intercalation energy of already expanded phyllosilicate
$U_{\mathrm{elec}}(\mathrm{K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4 \cdot (H_2O)_4})$	electrostatic lattice potential energy of process whereby the crystal $\mathrm{K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4 \cdot (H_2O)_4}$ is converted to gaseous ions at infinite separation
$U'_{\mathrm{elec}}(\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4 \cdot (H_2O)_4})$	electrostatic energy of process whereby the crystal $\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4 \cdot (H_2O)_4}$ is converted to gaseous water molecules and gaseous ions at infinite separation

$U_{\mathrm{H_2\dot{O}-K}}$	electrostatic interaction energy of four H_2O molecules with interlayer
$U_{\mathrm{H_2O-layer}}$	electrostatic interaction energy of four H_2O molecules with silicate layer
$U_{\mathrm{H_2\dot{O}-H_2\dot{O}}}$	interaction energies of intercalated water molecules
$U_{\mathrm{s.e.}}(\mathrm{H_2O})$	self-energy of water molecules
$V_{\mathrm{K}}^{\mathrm{OH}}$	site potential of interlayer cation in hydroxymicas
$V_{\mathrm{K}}^{\mathrm{F}}$	site potential of interlayer cation in fluormicas
ΔV_{K}	difference in site potential of cation of fluorinated and hydroxy micas ($V_{\mathrm{K}}^{\mathrm{F}} - V_{\mathrm{K}}^{\mathrm{OH}}$)
x	interlayer occupancy of K^+ cations in potassium vermiculite
x'	interlayer occupancy of cation Mg^{2+} in magnesium vermiculite
X	site occupied by Mg in trioctahedral micas and by Al in dioctahedral mica
X′	site occupied by Mg in trioctahedral mica and empty in dioctahedral mica

3. Structural parameters for model vermiculite

Telleria *et al.* (1977) have reported an X-ray diffraction study of a barium vermiculite having a triclinic unit cell with parameters

$$a = 5.33\,\text{Å},\quad b = 9.26\,\text{Å},\quad c = 12.47\,\text{Å},\quad \alpha = 100.75°,\quad \beta = 93.5°,\quad \gamma = 90°,$$

and containing one layer of water molecules within the interlayer. The interlayer structure itself has the following features.

(i) In each unit cell four water molecules are arranged in an hexagonal pattern (similar to the arrangement of carbon atoms in a graphite layer).

(ii) In the interstices, or more accurately, above and below these, the Ba^{2+} cations are located (figure 1*a*).

(iii) The layer of Ba^{2+} ions itself lies upon the silicate layer in such a way that the Ba^{2+} ions fit, approximately, into the ditrigonal holes caused by the arrangement of the oxygen atoms. The water molecules lie directly above the three oxygen atoms.

For the present study we adopt the above features of the H_2O geometry, and consider the OH–phlogopite structure (atomic coordinates given in table 1) for which

$$a = 5.308\,\text{Å},\quad b = 9.183\,\text{Å},\quad c = 10.139\,\text{Å},\quad \beta = 100.07°,$$

derived from the structure of fluorphlogopite (McCauley *et al.* 1973) by taking the OH dipole perpendicular to the mica layer with the O′ (hydroxyl) atom at the fluorine position, and assuming an O–H bond length of 1.00 Å. We expand this structure in a direction perpendicular to the (001)-plane such that

$$a = 5.308\,\text{Å},\quad b = 9.183\,\text{Å},\quad c = 12.608\,\text{Å},\quad \beta = 98.08°,$$

as illustrated in the Appendix of Jenkins & Hartman (1980).

In the expanded cell (having space group $P2_1/m$) we place K^+ ions at the position (0, 0, 0) in in the Wyckoff position 2a corresponding to having K^+ ions (labelled K_A in figure 1*b*) midway between the silicate layers. The oxygen atom, O″, of the intercalated water molecule is placed in the position $(0, \frac{1}{3}, 0)$ in 4f. Because we wish to consider the effect of varying the positions of the interlayer cations, similar to the positions established for the Ba^{2+} cations in barium vermiculite (figure 1*a*), we place K^+ atoms also at positions K_B(0.0161, 0.0000, 0.0481), K_C(0.0335, 0.0000, 0.1001), which corresponds to a K–silicate layer distance similar to that found in unexpanded phlogopite, $K_D(0.0509, 0.0000, 0.1522)$, as shown in figure 1*c*, and K_E (not shown in figure 1) at (0.0682, 0.0000, 0.2043), all in Wyckoff positions 2a. This enables us to perform a calculation that includes all these positions (i.e. includes more K^+ ions than the stoichiometry permits) and then, following our 'generic' approach, we can examine the effect on the electrostatic energy of potassium vermiculite by selective systematic exclusion of all K^+ ions except K_i^+, where i = A, B, C, D, E in turn, by placing all charges q_{K_j} $(j \neq i)$ equal to zero.

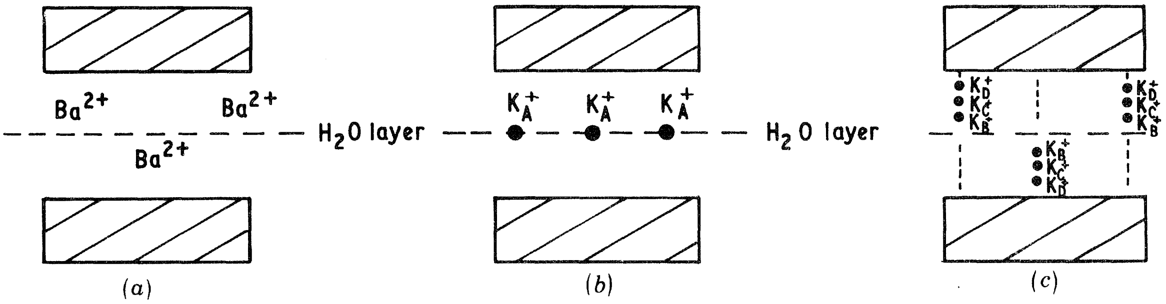


FIGURE 1. (*a*) Schematic arrangement of Ba^{2+} cations between silicate layers as found by Telleria *et al.* (1977) for barium vermiculite. (*b*) Central K^+ positions adopted in the present studies for the ions labelled K_A^+. (*c*) Alternative positions (K_B^+, K_C^+, K_D^+) considered in this paper for K^+ ions (the position K_E^+ is not shown but it lies above and below K_D^+).

TABLE 1. BASIC OH–PHLOGOPITE STRUCTURE BASED ON THAT FOR FLUORPHLOGOPITE GIVEN BY MCCAULEY *et al.* (1973)

(Formula, $KMg_3T_4O_{10}(OH)_2$; space group, C2/m.)

atom type	number in unit cell	Wyckoff position	coordinates *x*	*y*	*z*
K	2	2a	0.0000	0.0000	0.0000
T	8	8j	0.5751	0.1663	0.2245
Mg	4	4h	0.0000	0.8306	0.5000
Mg	2	2d	0.0000	0.5000	0.5000
H	4	4i	0.0992	0.0000	0.3015
O	4	4i	0.5274	0.0000	0.1678
O	8	8j	0.8208	0.2347	0.1682
O	8	8j	0.6291	0.1661	0.3896
O′	4	4i	0.1327	0.0000	0.4017

Cell dimensions:
$a = 5.3080$ Å, $b = 9.1830$ Å, $c = 10.1390$ Å;
$\cos \alpha = 0.0000$, $\cos \beta = -0.1749$, $\cos \gamma = 0.0000$.

When the *z*-coordinate of the interlayer cation is non-zero (K_B, K_C, K_D and K_E), one half of the K^+ ions are at z_K and the other half at $-z_K$; the symmetry of the centred unit cell (C2/m) cannot be maintained and drops to $P2_1/m$.

The distances, *d*, of K^+ ions above the water layer (and hence above the position of the K_A ion) are taken to be 0.6 Å (K_B), 1.25 Å (K_C), 1.90 Å (K_D) and 2.55 Å (K_E), and the relations:

$$x'_K = d \tan \xi / a', \tag{1}$$

$$z'_K = d/c' \cos \xi, \tag{2}$$

are valid, where x'_K and z'_K are the coordinates of the K^+ ions in the $P2_1/m$ cell, and a' and c' are the expanded cell lengths.

To calculate the coordinates of the hydrogen atoms, H″, attached to the oxygen atoms, O″, we have assumed the angle H″O″H″ for water to be 109.47° with an O″–H″ distance of 1.0 Å, where the H″ atoms are above and below the O″ atoms such that the line joining the two hydrogen atoms is perpendicular to the (001)-plane.

Table 2. Structure of a single layer water intercalate, potassium vermiculite

(Formula, $K_2Mg_6T_8O_{20}(OH)_4.(H_2O)_4$; space group, $P2_1/m$.)

atom type	number in unit cell	Wyckoff position	coordinates x	y	z
K_A	2	2a	0.0000	0.0000	0.0000
K_B	2	2a	0.0161	0.0000	0.0481
K_C	2	2a	0.0335	0.0000	0.1001
K_D	2	2a	0.0509	0.0000	0.1522
K_E	2	2a	0.0682	0.0000	0.2043
T	4	4f	0.5935	0.1663	0.2797
T	4	4f	0.0935	0.6663	0.2797
Mg	4	4f	0.0000	0.8306	0.5000
Mg	2	2a	0.0000	0.5000	0.5000
H	2	2a	0.1125	0.0000	0.3413
H	2	2a	0.6125	0.5000	0.3413
H″	4	4f	0.0219	0.3962	0.0654
H″	4	4f	0.9781	0.3962	0.9346
O	2	2a	0.5496	0.0000	0.2343
O	2	2a	0.4504	0.0000	0.7657
O	4	4f	0.8430	0.2347	0.2347
O	4	4f	0.3430	0.7347	0.2347
O	4	4f	0.6365	0.1661	0.4117
O	4	4f	0.1365	0.6661	0.4117
O′	2	2a	0.1393	0.0000	0.4214
O′	2	2a	0.6393	0.5000	0.4214
O″	4	4f	0.0000	0.3333	0.0000

Cell dimensions:

$a = 5.308$ Å, $b = 9.183$ Å, $c = 12.608$ Å;

$\cos\alpha = 0.0000$, $\cos\beta = -0.1406$, $\cos\gamma = 0.0000$.

These considerations, along with the transformation of the coordinates and adjustment of the space group, give rise to the coordinates for potassium vermiculite, $K_2Mg_6T_8O_{20}(OH)_4.(H_2O)_4$, given in table 2. For $x = 1$ in the general vermiculite $K_{2x}Mg_6(Si_{4-x}Al_x)_2$ such an arrangement places the water oxygen atoms, O″, in a hexagonal grid around the K^+ ions as shown in figure 2. $O_{20}(OH)_4.(H_2O)_4$. For x small, different arrangements arise: isolated K^+ ions are surrounded by large numbers of water molecules and for each value of x the orientation of the water molecules is different. Figure 3 illustrates the arrangements diagrammatically for (*a*) $x = 1$ and (*b*) $x \approx 0$. We have, therefore, to give careful consideration to geometrical arrangements of water dipoles.

For $x = 1$, for example, the nearest neighbour K^+–H_2O interaction can be treated as follows. Suppose the H_2O dipole to be such that the hydrogen atoms, H″, are directed away from the K^+ ion as shown schematically in figure 4. Taking our geometrical model for H_2O($\angle$ H″O″H″ = 109.47°, O″–H″ = 1.0 Å) we can calculate the electrostatic energy of this arrangement for a charge on water corresponding to $q_{H''} = 0.5$, $q_{O''} = -1.0$ to be:

$$E(\mathrm{K}\leftarrow\text{-----}\ominus\!\rightarrow) = 81.2\,\mathrm{kJ\,mol^{-1}}. \qquad (3)$$

Considering the other two nearest neighbours and assuming K^+ to be in the position K_A at the same height as the H_2O molecules (figure 3) we have a single water molecule surrounded by three K^+ ions at a distance $\frac{1}{3}b$, and the question immediately arises as to the direction of the dipole. Figure 5 offers two extreme orientations. For (*a*) the interaction energy is calculated to be 41.6 kJ mol^{-1} (or 13.9 kJ mol^{-1} per K^+ ion). For (*b*), which is a less stable arrangement, the interaction energy is calculated to be 32.6 kJ mol^{-1} (or 10.9 kJ mol^{-1} per K^+ atom) for $q_{O''} = -1.0$ and $q_{H''} = 0.5$. The difference between these two extremes is small, some 9.0 kJ mol^{-1}, and suggests that the H_2O molecules in figure 5 might rotate about an axis perpendicular to the interlayer, so

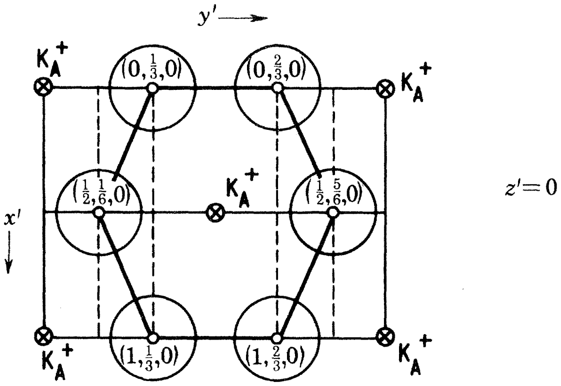


FIGURE 2. Schematic diagram showing positions of oxygen atoms, O″ (large circles) arranged hexagonally around central K_A^+ cation. The dimensions a' and b' are not to scale (deliberately, to facilitate the drawing of more complex situations).

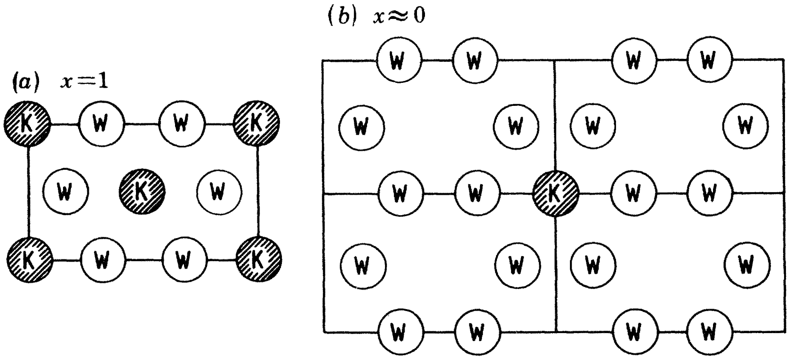


FIGURE 3. Schematic diagram of two extremes of the interlayer arrangement of cations and water molecules Ⓦ. (*a*) When $x = 1$, there is a full complement of K^+ ions surrounded hexagonally by water molecules. (*b*) When $x \approx 0$ and there are few interlayer cations, isolated K^+ ions are surrounded by large numbers of water molecules with most of the sites occupied by K^+ for $x = 1$ now vacant. This changes the orientation of the water dipoles and explicit consideration must be given to each value of x considered.

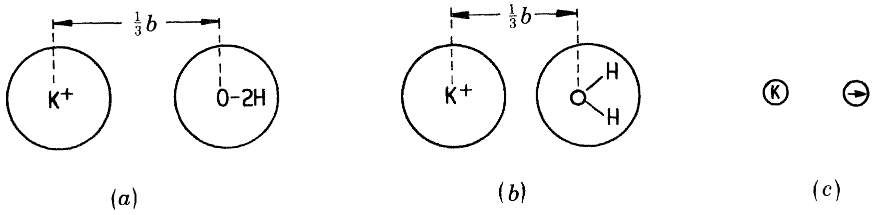
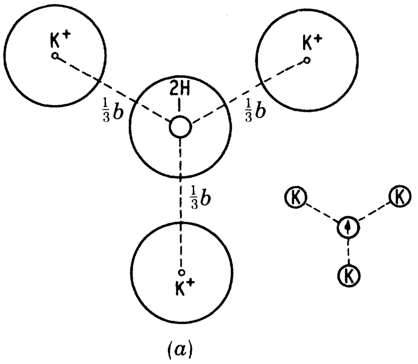


FIGURE 4. Nearest neighbour K–H_2O interaction for $x = 1$ showing: (*a*) interaction viewed in the *a*, *b* plane; (*b*) interaction viewed in the direction of the *a*-axis; (*c*) notation used in this paper to represent the interaction.

that all interactions are possible. We consider the possibility further in the discussion section of this paper, but for the calculations we assume that case (*a*) predominates. This assumption gives rise to figure 6 which shows the suggested arrangement of the water dipoles within the interlayer for $x = 1$.



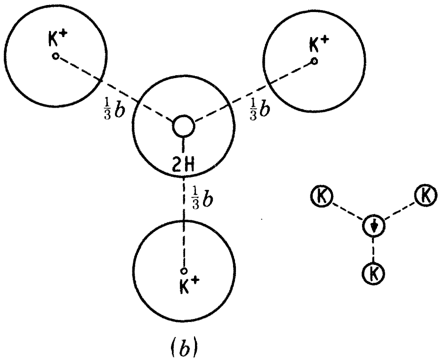


Figure 5. Nearest neighbour K–H_2O interaction for $x = 1$ showing water molecule surrounded by three K^+ ions, and the notation used in this paper to represent these type of interactions. Two extreme positions of the water dipole ↑ (arrow directed towards hydrogen atoms) are illustrated.

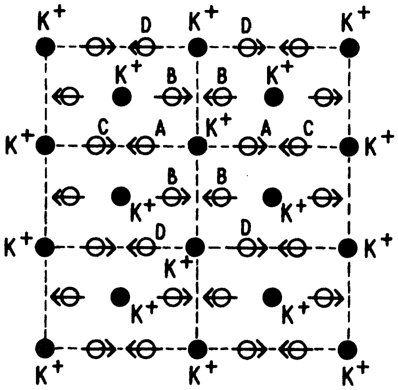


Figure 6. Interlayer arrangement of interlayer cations K^+ and water dipoles (arrow towards hydrogen atoms) for the vermiculite $K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4$ corresponding to $x = 1$ in general formula.

We must now consider the ordering of the K^+ ions for $x < 1$. The pseudo-hexagonal grid formed by the centres of the ditrigonal cells can lead to a (pseudo) hexagonal ordering of the cations. For magnesium vermiculite, $Mg_{x'}Mg_6(Si_{4-x'}Al_{x'})_2O_{20}(OH)_4.(H_2O)_4$, it was found that the magnesium occupies two positions in three unit cells. Here $x' = \frac{2}{3}$, and figure 7 shows the first of a series of hexagonal patterns encountered with diminishing x'. This arrangement found for magnesium vermiculite ($x' = \frac{2}{3}$) enables us to infer the first hexagonal pattern that can be achieved with diminishing x in *potassium* vermiculite, $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$, for the specific value $x = \frac{1}{3}$. This arrangement is shown in figure 8, where the orientation of dipoles is consistent with the considerations for $x = 1$.

As far as calculations involving x in the range $1 > x > \frac{2}{3}$ are concerned, we propose to consider the interlayer as having an ordered arrangement of *vacancies* complementary to the ordering of the K^+ ions in the range $\frac{1}{3} > x > 0$. Thus figure 9 is derived, which shows the ordering of the K^+ ions for $x = \frac{2}{3}$, the water dipoles (arrows towards H″ atoms) being assumed to point towards the

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vacant cation sites. In the range $\frac{2}{3} > x > \frac{1}{3}$, no hexagonal arrangement of K^+ ions or vacancies can be devised.

Figures 10 and 11 show the detailed hexagonal pattern of the K^+ ions in the cells for $x = 1$ and $x = \frac{1}{3}$ respectively. In these diagrams it is convenient to redefine the axial vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ such that

$$\boldsymbol{a}' = \boldsymbol{a}, \tag{4}$$

$$\boldsymbol{b}' = -\tfrac{1}{2}\boldsymbol{a} + \tfrac{1}{2}\boldsymbol{b}, \tag{5}$$

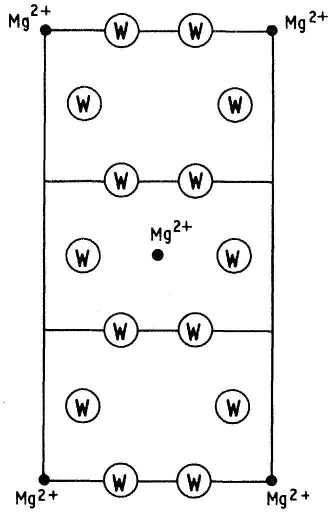

FIGURE 7. Arrangement of Mg^{2+} cations and water molecules (W) in magnesium vermiculite. $Mg_{x'}Mg_6(Si_{4-x'}Al_{x'})_2O_{20}(OH)_4.(H_2O)_4$, corresponding to $x' = \frac{2}{3}$.

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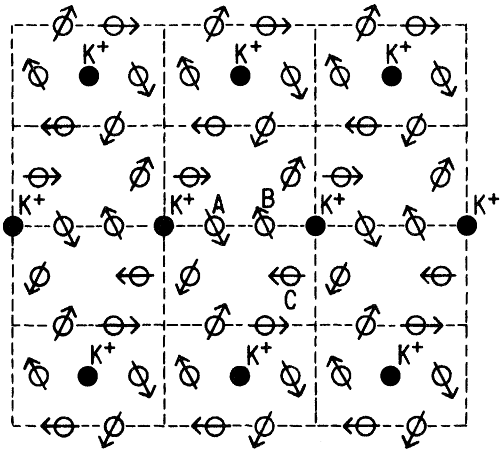

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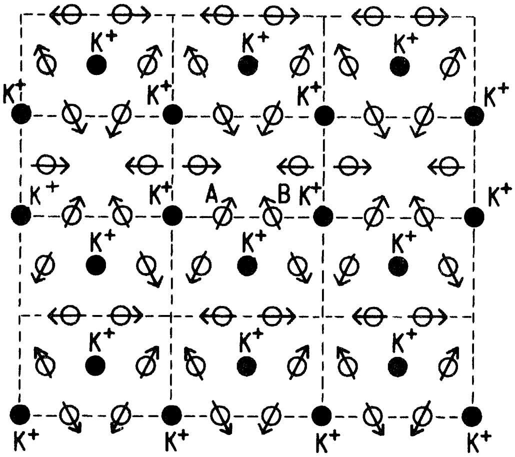


FIGURE 8. Interlayer arrangement of K^+ ions and water molecules for potassium vermiculite when $x = \frac{1}{3}$, $K_{0.66}Mg_6(Si_{3.67}Al_{0.33})_2O_{20}(OH)_4.(H_2O)_4$, inferred by comparison with magnesium vermiculite arrangement (figure 7). Dipole directions are assigned by considerations similar to those used to consider the case $x = 1$.

-+- Represents a vacancy.

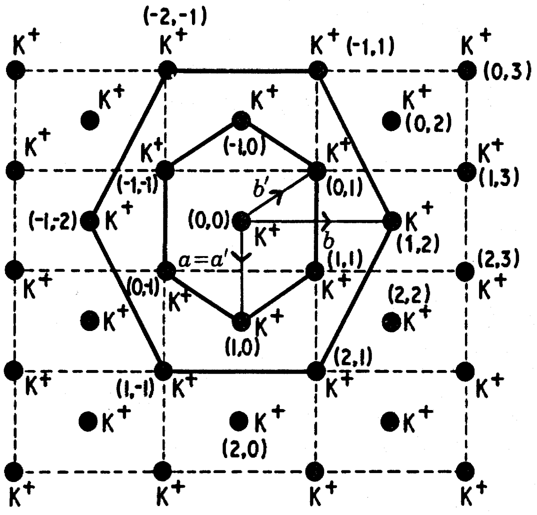
FIGURE 9. Complementary diagram to figure 8 where cations K^+ are interchanged with vacancies and vice versa. The water dipoles are assumed to point towards the vacancies. The arrangement constitutes that for potassium vermiculite, $x = \frac{2}{3}$, $K_{1.34}Mg_6(Si_{3.33}Al_{0.67})_2O_{20}(OH)_4.(H_2O)_4$.

and since $|a'| = |b'|$ the distance $r(u,v)$ of a K^+ ion having coordinates (u,v) from a reference ion at the origin $(0,0)$ is given by

$$r(u,v) = a'(u^2+v^2-uv)^{\frac{1}{2}}. \tag{6}$$

For $x = 1$ (figure 10), the distances of the ions K^+ at (0, 1), (1, 1), (1, 0), (0, −1), (−1, −1) and (−1, 0) from the central reference ion at (0, 0) are given by equation (6) to be a'. The distances of the next hexagonal shell of K^+ ions at (−1, 1), (1, 2), (2, 1), (1, −1), (−1, −2) and (−2, −1) are $\sqrt{3}a'$, etc.

10



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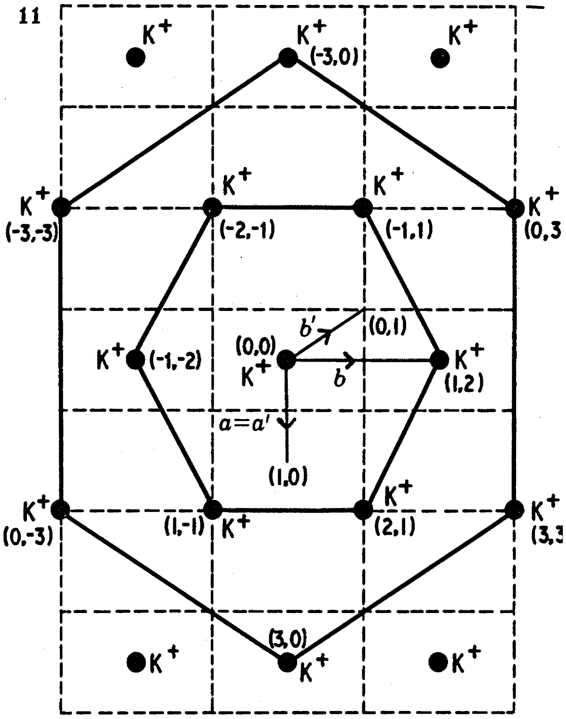

FIGURE 10. Detailed hexagonal arrangement of interlayer K^+ cations for $x = 1$ in potassium vermiculite. The drawing shows the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ defined, respectively, from the origin K^+ ion at (0, 0) to the K^+ ions at (1, 0) and (1, 2). The new hexagonal vectors $\boldsymbol{a}'$ and $\boldsymbol{b}'$ are defined from the origin K^+ ion at (0, 0) to the K^+ ion at (0, 1). Accordingly the K^+ ions on the first hexagonal grid are situated a distance $a' = b'$ from the origin ion, and those lying on the second hexagonal grid out from the origin are at a distance $b = \sqrt{3}a'$. The coordinates are defined with respect to the new axes $\boldsymbol{a}'$ and $\boldsymbol{b}'$.

FIGURE 11. Detailed hexagonal arrangement of interlayer K^+ cations for $x = \frac{1}{3} = 0.333$ in potassium vermiculite. The drawing illustrates the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{b}'$ defined as in figure 10. Accordingly the K^+ ions on the first hexagonal grid are at a distance $b = \sqrt{3}a'$ from the origin K^+ ion at (0, 0), and the ions on the second hexagonal grid out from the origin are at a distance $3b' = 3a'$. The ion coordinates are defined in terms of the new axes $\boldsymbol{a}'$ and $\boldsymbol{b}'$.

For $x = \frac{1}{3}$ (figure 11), the nearest K^+ ions (at (1, 2), (2, 1), (1, −1), (−1, −2), (−2, −1) and (−1, 1)) are at a distance $\sqrt{3}a'$ from the central ion, and the next hexagonal shell is at a distance $3a'$, etc.

For $x = \frac{1}{4}$, $K_{0.50}Mg_6(Si_{3.75}Al_{0.25})_2O_{20}(OH)_4\cdot(H_2O)_4$, (figure 12) the corresponding distances from the origin to the first and second hexagonal shells of K^+ ions are $2a'$ and $\sqrt{12}a'$ respectively.

In general, then, the second hexagonal shell is $\sqrt{3}$ times further away than the first shell from

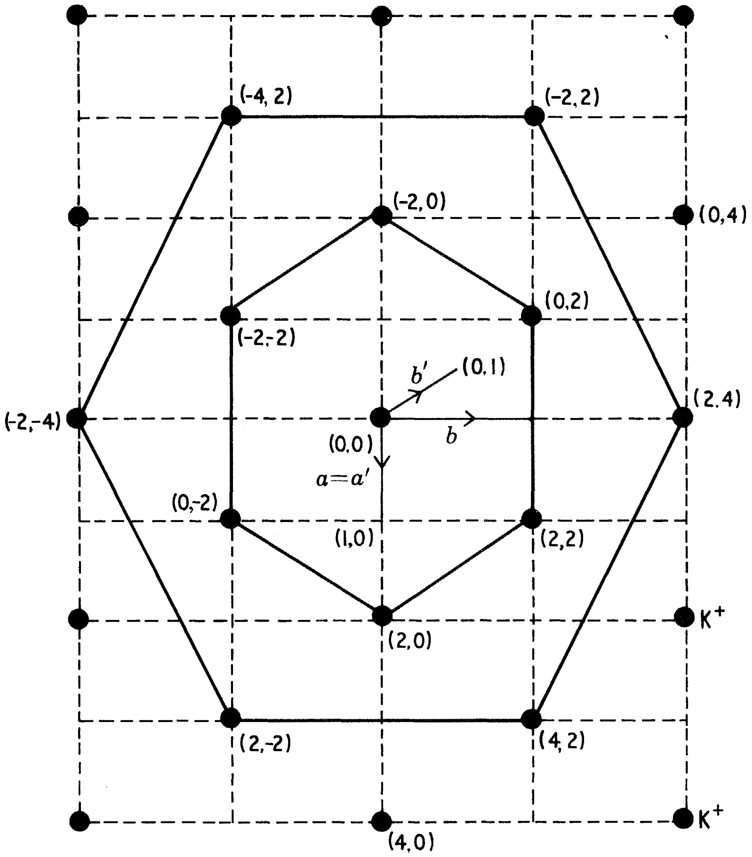

Figure 12. Detailed hexagonal arrangement of interlayer K^+ cations for $x = \frac{1}{4} = 0.25$ in potassium vermiculit The drawing indicates the vectors $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{b}'$ defined as in figure 10. Accordingly the ions in the fir hexagonal grid are at a distance $2b' = 2a'$ from the origin K^+ ion at (0, 0), and the ions in the secon hexagonal grid are at a distance $\sqrt{12}b' = \sqrt{12}a'$. The ion coordinates are defined in terms of the hexagon axes $\boldsymbol{a}'$ and $\boldsymbol{b}'$.

the origin, and the general formula for the distance of the first shell of hexagonal K^+ ions fro the origin is given by $\sqrt{n}\,a'$ where $n = 1/x$.

From an electrostatic viewpoint, therefore, if the K^+–K^+ interaction corresponding to un charges on the K^+ ions ($q_K = 1$) and $x = 1$ is given by A_{KK}, the corresponding interaction ter for $x < 1$ will be given by $A_{KK}/\sqrt{n}$ or $\sqrt{x}\,A_{KK}$. The hexagonal patterns for $x = \frac{1}{7}$ and $x = \frac{1}{9}$ a given in figures 13 and 14 respectively, corresponding to the interlayer cation arrangements i $K_{0.28}Mg_6(Si_{3.86}Al_{0.14})_2O_{20}(OH)_4 \cdot (H_2O)_4$ and $K_{0.22}Mg_6(Si_{3.89}Al_{0.11})_2O_{20}(OH)_4 \cdot (H_2O)_4$.

The arrangement of the water dipoles when placed within the interlayer cation grids can no be deduced. By careful consideration of the interactions involved we generated the arrangemen specified for $x = \frac{1}{4}$ (figure 15) $x = \frac{1}{7}$ (figure 16) and $c = \frac{1}{9}$ (figure 17). Where doubt arose co cerning the most stable orientation of the dipole this is represented in the figures by the symb $\overset{?}{\ominus\!\!\rightarrow}$, the arrow indicating the direction assumed for the calculations. Where we consider th water molecule to be freely rotating, we use the symbol ○.

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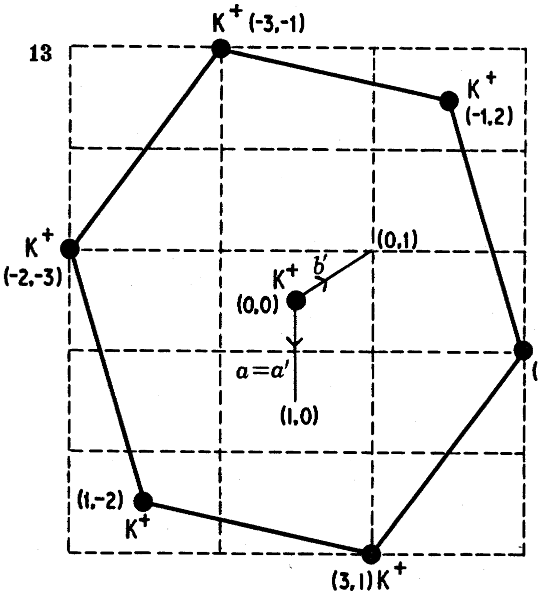

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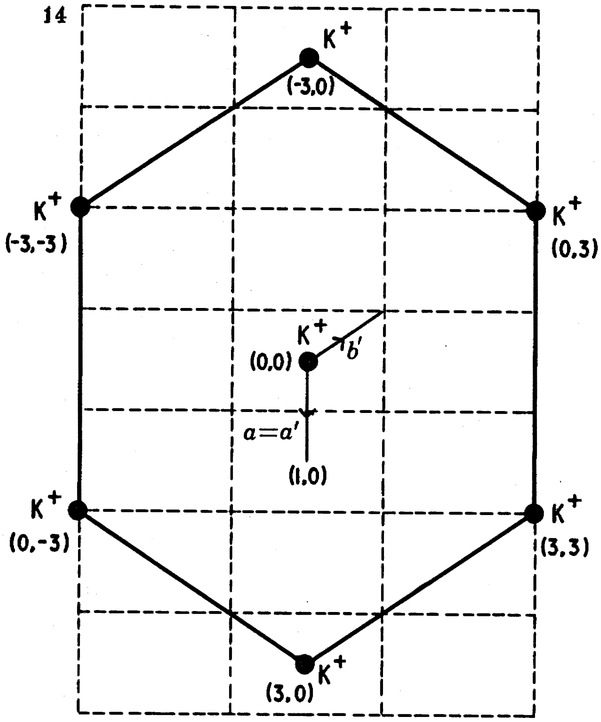


FIGURE 13. Detailed hexagonal grid for arrangement of first neighbour interlayer K^+ cations from central reference K^+ ion at (0,0) for $x = \frac{1}{7} = 0.143$ in potassium vermiculite. The drawing indicates the vectors $\boldsymbol{a}'$ and $\boldsymbol{b}'$, defined as in figure 10. Accordingly the first nearest neighbour K^+ ions are at a distance $\sqrt{7}a'$ from the central ion in this case. The ion coordinates are defined in terms of the hexagonal axes $\boldsymbol{a}'$ and $\boldsymbol{b}'$.

FIGURE 14. Detailed hexagonal arrangement of nearest neighbour interlayer cations from central reference K^+ ion at (0, 0) for $x = \frac{1}{9} = 0.111$ in potassium vermiculite. The drawing indicates the vectors $\boldsymbol{a}'$ and $\boldsymbol{b}'$, defined as in figure 10. Accordingly the first nearest neighbour K^+ ions are at a distance $\sqrt{9a'} = 3a'$ from the central ion in this case. The ion coordinates are defined in terms of the hexagonal axes $\boldsymbol{a}'$ and $\boldsymbol{b}'$.

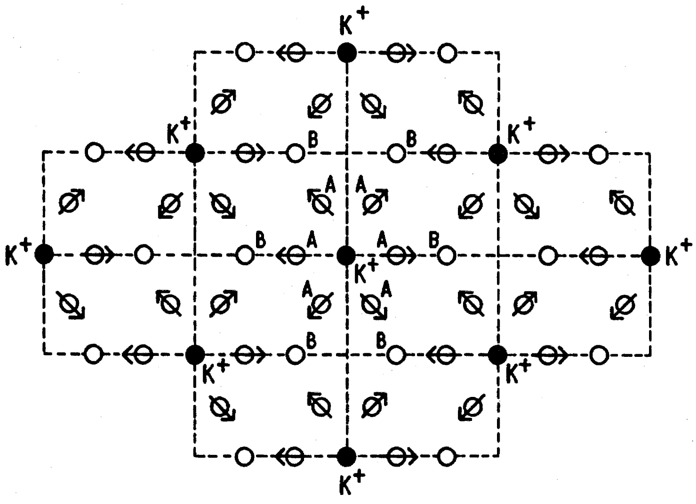
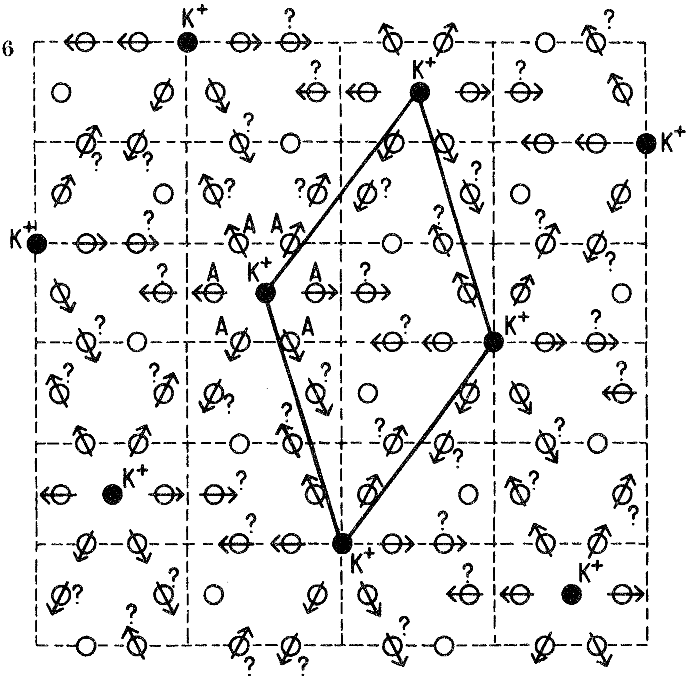


FIGURE 15. Interlayer arrangement of water dipoles (arrow pointing towards H″ atoms) and interlayer cations, deduced from interaction calculations in potassium vermiculite, $K_{0.50}Mg_6(Si_{3.75}Al_{0.25})_2O_{20}(OH)_4 \cdot (H_2O)_4$ for $x = \frac{1}{4}$. In this and subsequent figures ○ represents a freely rotating water molecule and –┼– represents a vacancy.

16



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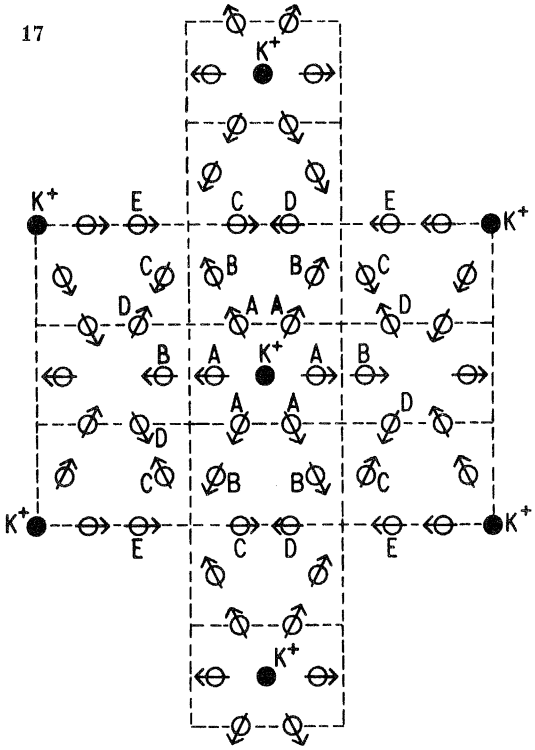

FIGURE 16. Interlayer arrangement of water dipoles (arrow pointing towards H″ atoms) and interlayer cations, deduced from interaction calculations in potassium vermiculite, $K_{0.28}Mg_6(Si_{3.86}Al_{0.14})_2O_{20}(OH)_4 \cdot (H_2O)_4$ for $x = \frac{1}{7}$. In this and subsequent figures $\overset{?}{\ominus\rightarrow}$ indicates that there is some doubt concerning the actual dipole orientation, but the calculation is performed on the assumption that dipole is in the direction indicated by the arrow.

FIGURE 17. Interlayer arrangement of water dipoles (arrow pointing towards H″ atoms) and interlayer cations, deduced from interaction calculations in potassium vermiculite, $K_{0.22}Mg_6(Si_{3.89}Al_{0.11})_2O_{20}(OH)_4 \cdot (H_2O)_4$ for $x = \frac{1}{9}$.

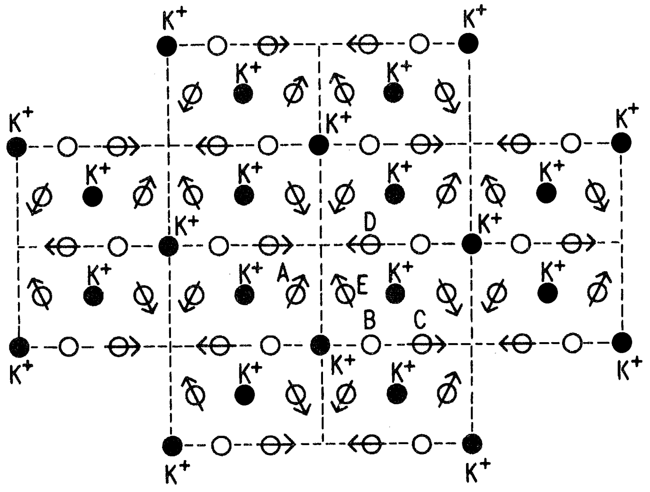

FIGURE 18. Interlayer arrangement of water dipoles (arrow pointing towards the hydrogen atoms) and interlayer cations, deduced from interaction calculations in potassium vermiculite, $K_{1.50}Mg_6(Si_{3.25}Al_{0.75})_2O_{20}(OH)_4 \cdot (H_2O)_4$ for $x = \frac{3}{4}$.

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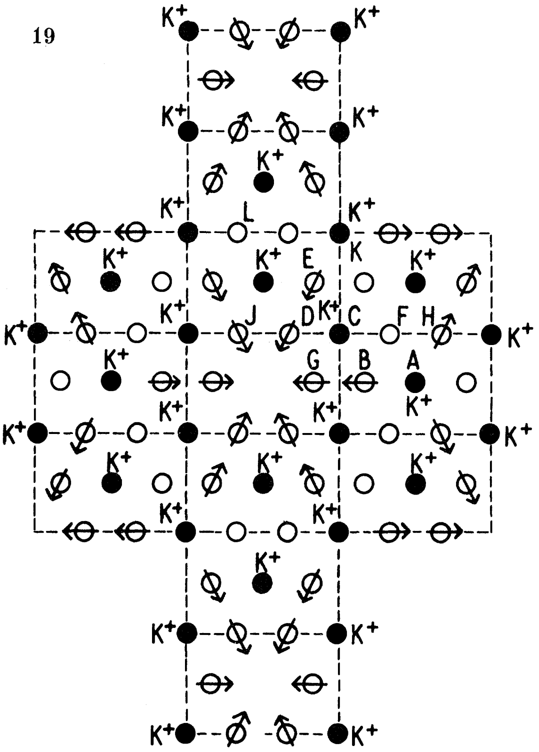

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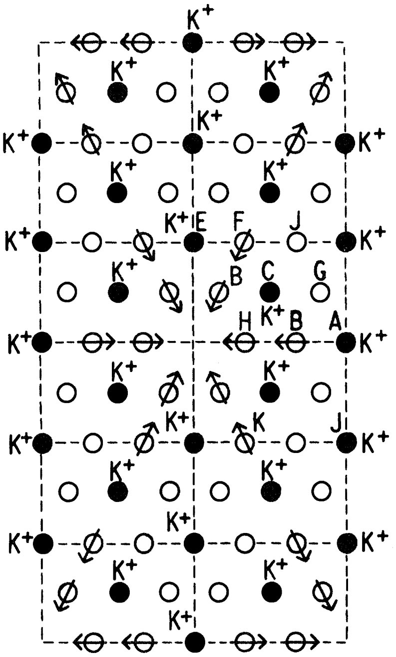

FIGURE 19. Interlayer arrangement of water dipoles (arrow pointing towards the hydrogen atoms) and interlayer cations, deduced from interaction calculations, in potassium vermiculite, $K_{1.78}Mg_6(Si_{3.11}Al_{0.89})_2O_{20}(OH)_4.(H_2O)_4$ for $x = \frac{8}{9}$.

FIGURE 20. Interlayer arrangement of water dipoles (arrow pointing towards hydrogen atoms) and interlayer cations, deduced from interaction calculations, in potassium vermiculite, $K_{1.84}Mg_6(Si_{3.08}Al_{0.92})_2O_{20}(OH)_4.(H_2O)_4$ for $x = \frac{11}{12}$.

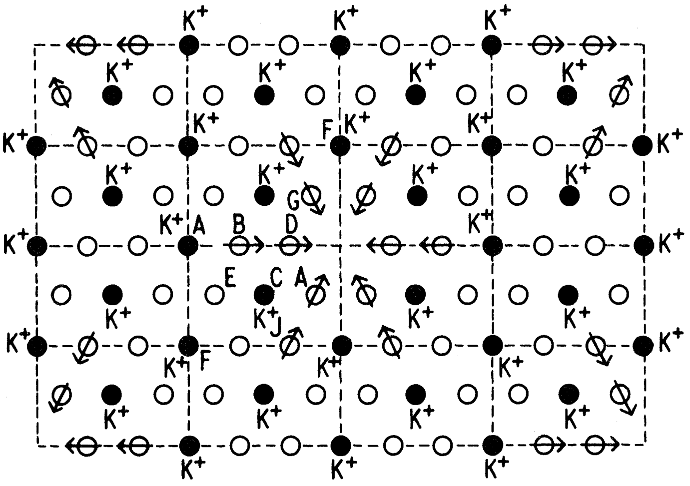

FIGURE 21. Interlayer arrangement of water dipoles (arrows pointing towards hydrogen atoms) and interlayer cations, deduced from interaction calculations, in potassium vermiculite, $K_{1.88}Mg_6(Si_{3.06}Al_{0.94})_2O_{20}(OH)_4.(H_2O)_4$ for $x = \frac{15}{16}$.

The arrangement of water dipoles among the vacant sites can similarly be deduced. In figures 18–21 we give our arrangements for:

$x = \frac{3}{4}$, $K_{1.50}Mg_6(Si_{3.25}Al_{0.75})_2O_{20}(OH)_4.(H_2O)_4$ (figure 18);

$x = \frac{8}{9}$, $K_{1.78}Mg_6(Si_{3.11}Al_{0.89})_2O_{20}(OH)_4.(H_2O)_4$ (figure 19);

$x = \frac{11}{12}$, $K_{1.84}Mg_6(Si_{3.08}Al_{0.92})_2O_{20}(OH)_4.(H_2O)_4$ (figure 20);

$x = \frac{15}{16}$, $K_{1.88}Mg_6(Si_{3.06}Al_{0.94})_2O_{20}(OH)_4.(H_2O)_4$ (figure 21).

4. CALCULATIONS

In accordance with our 'generic' method (Jenkins & Hartman 1979) we used the computer program of Jenkins & Pratt (1978) to obtain the Jenkins–Hartman coefficients for the electrostatic interactions in potassium vermiculite (whose coordinates are listed in table 2) in a similar manner to the treatment described for the phyllosilicates.

From what has gone before, it will be appreciated that while the calculations for $x = 1$ (full interlayer occupancy) follow our normal procedure, the specific K^+–K^+, K^+–H_2O and H_2O–H_2O interactions require specific and detailed consideration for $x < 1$. In the next section of this paper we give, therefore, the general results obtained and then proceed separately to analyse the cases where $x < 1$. The results and discussion of certain features of the model are discussed in the concluding sections of this paper.

The electrostatic energy of potassium vermiculite containing a single layer of intercalated water molecules, $K_{2x}Mg_6T_2O_{20}(OH)_4.(H_2O)_4$, where $T = Si_{4-x}Al_x$, is given by the equation

$$U_{\text{elec}}(K_{2x}Mg_6T_2O_{20}(OH)_4.(H_2O)_4) = \sum_{i=0}^{2}\sum_{j=0}^{2-i}\sum_{k=0}^{2-j}\sum_{l=0}^{2-k}\sum_{m=0}^{2-l}\sum_{n=0}^{2-m}\sum_{p=0}^{2-n}\sum_{q=0}^{2-p} A_{ijklmnpq}\, q_K^i\, q_{Mg}^j\, q_T^k\, q_O^l\, q_{O'}^m\, q_H^n\, q_{O''}^p\, q_{H''}^q, \tag{7}$$

$i+j+k+l+m+n+p+q = 2$, where $A_{ijklmnpq}$ are the Jenkins–Hartman coefficients; and $q_K, q_{Mg}, q_T (= 4-0.25x)$, q_O, $q_{O'}$, q_H, $q_{O''}$, $q_{H''}$ are respectively the charges on the potassium, magnesium, tetrahedral layer, oxygen, hydroxyl oxygen, hydroxyl hydrogen, water oxygen and hydrogen atom of the water molecules. The $A_{ijklmnpq}$ we obtained using a program similar to MADDERIV described by Jenkins & Pratt (1978). The charge-independent coefficients take the values (in kJ mol^{-1} e^{-2}) given in table 3, where q_X and $q_{X'}$ permit distinction between the dioctahedral (X) and trioctahedral (X′) sites.

As mentioned earlier, several positions were simultaneously taken for the interlayer cation positions designated K_A, K_B, K_C, K_D and K_E, and the calculation was made by assigning charges to the atoms of the structure so as to achieve overall electroneutrality. The charge-independent coefficients, $A_{ijklmnpq}$, so calculated could then be used to calculate the electrostatic energy for potassium vermiculite having the various K^+ ion positions by taking realistic atomic charges. The lattice sums required were tested to ensure that convergence had been secured. The coefficients A_{KK}, A_{KT}, A_{KX}, $A_{KX'}$, A_{KO}, A_{KH}, $A_{KO'}$, $A_{KO''}$ and $A_{KH''}$ depend on the position chosen for the interlayer cations K^+ in the interlayer; the various values are listed in table 3.

From this single calculation, using equation (7) above with the calculated coefficients, $A_{ijklmnpq}$, we can generate a wealth of information concerning the properties of vermiculites for varying interlayer charge, $q_K = x$ where x ranges from unity to zero.

TABLE 3. JENKINS AND HARTMAN COEFFICIENTS, $A_{ijklmnpq}$ (IN kJ mol^{-1} e^{-2}) APPROPRIATE TO EQUATION (7) FOR POTASSIUM VERMICULITE

(K_A, K_B, K_C, K_D and K_E relate to the various interlayer K^+ ion positions adopted as described in the text.)

	$A_{ijklmnpq}$				
interaction	K_A	K_B	K_C	K_D	K_E
KK	356.9	378.4	436.8	502.2	548.6
KX	1484.9	1443.5	1305.8	1070.9	739.3
KX′	742.4	721.7	652.8	535.3	369.4
KT	1285.2	1219.6	1012.6	704.5	372.7
KO	3482.3	3316.5	2795.2	2024.3	1194.5
KO′	1369.6	1326.6	1181.5	927.4	546.6
KH	1015.7	67.5	800.5	485.2	−68.2
KO″	−1370.5	−1259.7	−929.7	−474.7	10.2
KH″	−2420.9	−2252.5	−1724.4	−941.3	−53.8

interaction	$A_{ijklmnpq}$	interaction	$A_{ijklmnpq}$	interaction	$A_{ijklmnpq}$
XX	28.4	X′H	−580.1	OO″	6624.7
XX′	−1370.7	X′O″	1484.8	OH″	11616.2
XT	350.1	X′H″	2813.8	O′O′	412.5
XO	−2742.8	TT	2900.4	O′H	−3791.4
XO′	−3051.0	TO	−5605.8	O′O″	2753.4
XH	−1155.1	TO′	380.7	O′H″	5204.8
XO″	2969.7	TH	62.6	HH	1158.1
XH″	5636.3	TO″	2410.7	HO″	2087.1
X′X′	356.9	TH″	4147.5	HH″	3885.9
X′T	176.3	OO	7638.9	O″O″	28.6
X′O	−1368.9	OO′	−1112.8	O″H″	−10696.7
X′O′	−1534.2	OH	−353.5	H″H″	−3059.8

5. RESULTS

(a) *Silicates having a full interlayer charge:* $q_K = x = 1$

(i) *Total electrostatic energy of potassium vermiculite*

Using equation (7) and the $A_{ijklmnpq}$ coefficients listed in table 3 with the charges $q_K = 1$, $q_X = q_{X'} = 2$, $q_T = 3.75$, $q_O = q_{O'} = -2$, $q_H = 1$, and using the fact that, for the intercalated water molecules, the charges on the oxygen, $q_{O''}$, and hydrogen, $q_{H''}$, atoms are related by the equation

$$q_{H''} = -2q_{O''}, \tag{8}$$

since the water molecule is neutrally charged overall, we can generate U_{elec} (in kJ mol^{-1}) for the vermiculite as a function of $q_{H''}$:

$$\begin{aligned} &U_{\text{elec}}(K_2Mg_6(Si_3Al)_2O_{20}(OH)_4\,.\,(H_2O)_4) \\ &\quad = A_{KK} + 3.75A_{KT} + 2A_{KX} + 2A_{KX'} + A_{KH} - 2A_{KO} - 2A_{KO'} + 158\,735.8 \\ &\qquad + [(A_{KH''} - 2A_{KO''}) + 137.2]\, q_{H''} + 18\,448.0\, q_{H''}^2. \end{aligned} \tag{9}$$

The magnitude of the final term in equation (9) is mainly due to the self-energy of the four water molecules. The electrostatic energy $U_{\text{elec}}(K_2Mg_6(Si_3Al)_2O_{20}(OH)_4\,.\,(H_2O)_4)$ corresponds to the energy change for the process

$$K_2Mg_6(Si_3Al)_2O_{20}(OH)_4\,.\,(H_2O)_4(c) \xrightarrow{U_{\text{elec}}} 2K^+(g) + 6Mg^{2+}(g) + 6Si^{4+}(g) + 2Al^{3+}(g) + 24O^{2-}(g) + 4H^+(g) + 8H^{q_{H''}}(g) + 4O^{q_{O''}}(g),$$

while the self-energy of the water molecules, $4U_{\text{s.e.}}(\mathrm{H_2O})$, corresponds to the process

$$4\mathrm{H_2O(g)} \xrightarrow{4U_{\text{s.e.}}(\mathrm{H_2O})} 8\mathrm{H}^{q_{\mathrm{H}''}}\mathrm{(g)} + 4\mathrm{O}^{q_{\mathrm{O}''}}\mathrm{(g)},$$

and amounts to $18825.6\,q^2_{\mathrm{H}''}$ kJ mol^{-1} (see equation (27)).

We can define also a modified electrostatic energy $U'_{\text{elec}}(\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4})$ that corresponds to the process where the water molecules remain intact:

$$\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4}$$
$$\xrightarrow{U'_{\text{elec}}} 2\mathrm{K^+(g)} + 6\mathrm{Mg^{2+}(g)} + 6\mathrm{Si^{4+}(g)} + 2\mathrm{Al^{3+}(g)} + 24\mathrm{O^{2-}(g)} + 4\mathrm{H^+(g)} + 4\mathrm{H_2O(g)}.$$

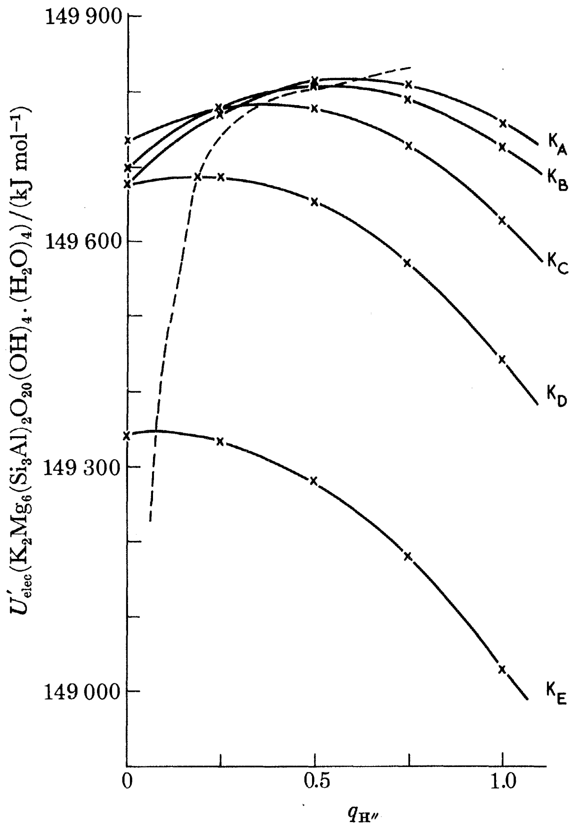

FIGURE 22. Variation of $U'_{\text{elec}}(\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4})$ with $q_{\mathrm{H}''}$, the charge on the hydrogen atoms of the intercalated water molecules, shown for various positions of the interlayer $\mathrm{K^+}$ ions ($\mathrm{K_A}$, $\mathrm{K_B}$, $\mathrm{K_C}$, $\mathrm{K_D}$ and $\mathrm{K_E}$) as described in the text. The dotted line shows the variation in the maximum in U'_{elec} for the various positions and charges.

Using table 3 and evaluating the specific coefficients of equation (9) we find, for the various positions of the interlayer cations, $\mathrm{K^+}$, the following energies, U'_{elec} (in kJ mol^{-1}):

for $\mathrm{K^+}$ in position $\mathrm{K_A}$,

$$U'_{\text{elec}} = 149\,678.6 + 457.3\,q_{\mathrm{H}''} - 377.6\,q^2_{\mathrm{H}''}; \tag{10}$$

for $\mathrm{K^+}$ in position $\mathrm{K_B}$,

$$U'_{\text{elec}} = 149\,699.4 + 404.1\,q_{\mathrm{H}''} - 377.6\,q^2_{\mathrm{H}''}; \tag{11}$$

for K^+ in position K_C,

$$U'_{\text{elec}} = 149\,734.2 + 272.2\,q_{H'} - 377.6\,q^2_{H'}; \tag{12}$$

for K^+ in position K_D,

$$U'_{\text{elec}} = 149\,674.1 + 145.3\,q_{H'} - 377.6\,q^2_{H'}; \tag{13}$$

for K^+ in position K_E,

$$U'_{\text{elec}} = 149\,343.8 + 63.0\,q_{H'} - 377.6\,q^2_{H'}. \tag{14}$$

Figure 22 shows the variation of U'_{elec} as a function of $q_{H'}$ for the various positions of the interlayer cation K^+. The position K_C represents the case where the interlayer cation remains in the same position relative to the silicate layer that it has in the unexpanded phlogopite (see figure 1*c*). For values of $q_{H'} \leqslant 0.25$ it represents the most stable configuration. At larger values of $q_{H'}$, the K^+–H_2O interaction stabilizes configurations where the interlayer cation migrates from its original site position. At values of $q_{H'} \geqslant 0.6$, the centrally positioned interlayer cation represents the most stable configuration.

TABLE 4. INTERACTION OF INTERLAYER CATIONS K^+ WITH THE SILICATE LAYER AS MEASURED BY THE SITE POTENTIALS: V_K^{OH} FOR THE HYDROXYMICA $K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4$ AND V_K^F FOR THE FLUORMICA $K_2Mg_6(Si_3Al)_2O_{20}F_4.(H_2O)_4$

(Various positions of the interlayer cation K^+ are considered (see text). Differences in site potentials: $\Delta V_K = V_K^F - V_K^{OH}$ are also listed.)

position of interlayer cation	V_K^{OH} / kJ mol^{-1} e^{-1}	V_K^F / kJ mol^{-1} e^{-1}	ΔV_K / kJ mol^{-1} e^{-1}
K_A	1299.8	1653.7	353.9
K_B	1342.0	1701.1	359.1
K_C	1435.2	1816.2	381.0
K_D	1440.5	1882.7	442.2
K_E	1161.6	1776.4	614.8

(ii) *Interaction of interlayer* K^+ *cations with the silicate layer*

The potential of the K^+ ion within the vermiculite, V_K, is a measure of the K^+–silicate interaction. It is defined by

$$V_K = \left(\frac{\partial U_{\text{elec}}}{\partial q_K}\right)_{\substack{q_i,\, i \neq K^+,\\ q_{H'} = q_{O'} = 0}}$$

where q_i represents all the other atomic charges (with the exception of K^+) held at their constant-valence values. Equation (7) gives directly, for an hydroxymica $K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4$,

$$V_K^{OH} = 2A_{KK} + 3.75A_{KT} + 2(A_{KX} + A_{KX'}) - 2(A_{KO} + A_{KO'}) + A_{KH}, \tag{15}$$

and for the corresponding fluorinated mica $K_2Mg_6(Si_3Al)_2O_{20}F_4.(H_2O)_4$,

$$V_K^F = 2A_{KK} + 3.75A_{KT} + 2(A_{KX} + A_{KX'}) - 2A_{KO} - 2A_{KO'}. \tag{16}$$

For the latter calculation we assume with reference to the hydroxymica that $q_{O'} = q_F = -1$ and that $q_H = 0$.

The values of the site potentials V_K^{OH} and V_K^F are calculated for varying positions of the interlayer cation K^+; the results are given in table 4, together with the differences, $\Delta V = V_K^F - V_K^{OH}$, in site potentials. It is seen that V_K^{OH} and V_K^F show a maximum when the interlayer cation is in the position near K_D. This is presumably due to the fact that in the expansion of the mica from 10 Å to 12.5 Å there is an additional mutual repulsion created between the interlayer cations K^+, resulting in a force perpendicular to the silicate layer which tends to drive the K^+ ions backward into the ditrigonal holes. Since the K–K repulsive interaction will be diminished in the expande mica with respect to the unexpanded mica we may expect, and indeed find, that V_K-value increase markedly in passing from the unexpanded mica ($V_K^F = 1163\,\mathrm{kJ\,mol^{-1}\,e^{-1}}$) (Jenkins Hartman 1979, equation (39)) to the expanded mica ($V_K^F = 1816.2\,\mathrm{kJ\,mol^{-1}\,e^{-1}}$, table 4). W also observe that $V_K^F > V_K^{OH}$, and explain this fact, as did Giese (1975, 1979), on the basis of th repulsion between the interlayer cation and the hydrogen of the hydroxyl group. This is dramati cally shown by the enormous increase in ΔV_K in going from a situation where the cation is i position K_D to one where it occupies K_E.

(iii) *Interaction of intercalated water molecules with the silicate layer*

The interaction energy of four water molecules with the silicate (excluding the interlayer K ions), $U_{H_2O\text{-layer}}$, is given (taking valence charges) by

$$U_{H_2O\text{-layer}} = (2A_{XH''} + 2A_{X'H''} + 3.75A_{TH''} - 2A_{OH''} - 2A_{O'H''} + A_{HH''} - 4A_{XO''} - 4A_{X'O''} - 7.5A_{TO''} + 4A_{OO''} + 4A_{O'O''} - 2A_{HO''})\,q_{H''}, \qquad \text{(17}$$

which, with the coefficients $A_{ijklmnpq}$ of table 3, gives (in $\mathrm{kJ\,mol^{-1}}$):

$$U_{H_2O\text{-layer}} = 137.2\,q_{H''}. \qquad \text{(1}$$

(iv) *Interaction of intercalated water molecules with interlayer cations*

The interaction of four water molecules with the interlayer cations, $U_{H_2O\text{-}K}$, is given by

$$U_{H_2O\text{-}K} = (A_{KH''} - 2A_{KO''})\,q_{H''}, \qquad \text{(1}$$

and the results for varying K^+ interlayer positions, with the coefficients of table 3, are (i $\mathrm{kJ\,mol^{-1}}$):

for K^+ in position K_A, $$U_{H_2O\text{-}K} = 320.1\,q_{H''}; \qquad \text{(2}$$

for K^+ in position K_B, $$U_{H_2O\text{-}K} = 266.9\,q_{H''}; \qquad \text{(2}$$

for K^+ in position K_C, $$U_{H_2O\text{-}K} = 135.0\,q_{H''}; \qquad \text{(2}$$

for K^+ in position K_D, $$U_{H_2O\text{-}K} = 8.1\,q_{H''}; \qquad \text{(2}$$

for K^+ in position K_E, $$U_{H_2O\text{-}K} = -74.2\,q_{H''}. \qquad \text{(2}$$

The decreasing trend in $U_{H_2O\text{-}K}$ as the interlayer cation migrates from the centralized positio in the interlayer, K_A, to the displaced position K_E is a result of the movement of the interlay cations from the relatively attractive environment (K_A) of the nearest neighbour oxygen aton lying in the same plane to the repulsive environment (K_E) where nearest neighbour hydroge form the major influence. The variation of $U_{H_2O\text{-}K}$ with the movement of the interlayer cation shown in figure 23 from which it is seen to be more marked if the charge $q_{H''}$ on the hydroge atoms of the water is large. This arises because the attraction and repulsion interactions allud to are greater if $q_{H''}$ and hence, (equation (8)) $q_{O''}$, are large in absolute magnitude. The poi where the interaction is zero is, of course, determined by the interlayer cation position corr sponding to the condition $A_{KH''} = 2A_{KO''}$. This occurs closest to the interlayer K^+ positic corresponding to K_D.

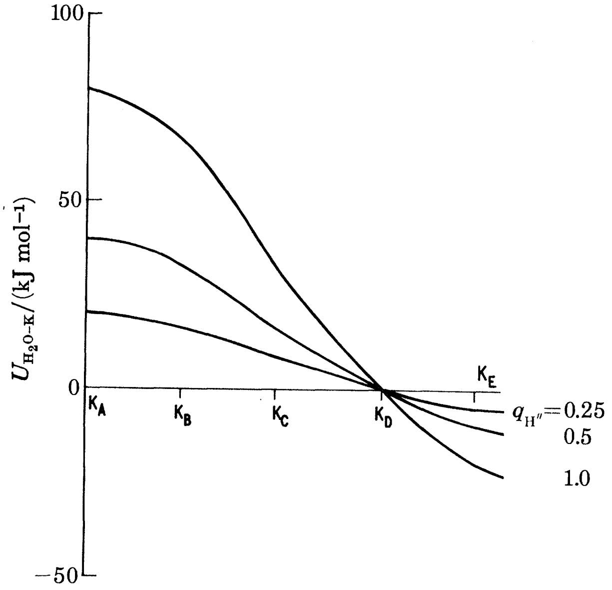

FIGURE 23. Variation of water molecule–interlayer cation interaction, $U_{H_2O\text{-}K}$ with the position of the interlayer cation, which varies from being centrally placed in the interlayer (K_A) to positions (K_B, K_C, K_D, K_E) of increasing displacement from the centre of the interlayer.

(v) H_2O–H_2O *interlayer interaction*

The interaction energy of the water molecules, $U_{H_2O\text{-}H_2O}$, in the interlayer is given by

$$U_{H_2O\text{-}H_2O} = A_{H''H''}q_{H''}^2 + A_{H''O''}q_{H''}q_{O''} + A_{O''O''}q_{O''}^2 - 4U_{s.e.}(H_2O) \tag{25}$$

The term $U_{H_2O\text{-}H_2O}$ represents the intra-water molecule interactions and not the interactions between O″ and H″ atoms within the same molecule, and hence we subtract the self-energy of four water molecules. The self energy $U_{s.e.}(H_2O)$ per molecule is given (in kJ mol^{-1}) by

$$U_{s.e.}(H_2O) = -1389.3(2q_{H''}q_{O''}/R_{OH} + q_{H''}^2/2R_{OH}\sin\theta), \tag{26}$$

where $R_{OH} = 1.00$ Å and $\theta = \frac{1}{2}(\angle H''O''H'') = 54.73°$. With the aid of equation (8) this reduces to

$$U_{s.e.}(H_2O) = 4706.4\,q_{H''}^2, \tag{27}$$

and from equation (25) we find, using the coefficients of table 3,

$$U_{H_2O\text{-}H_2O} = -377.6\,q_{H''}^2. \tag{28}$$

(*b*) *Intercalation energy of potassium vermiculite*, $K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4$, *at negligible pressure*

The energy of the process

$$\underset{\text{(expanded mica)}}{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4(c)} + 4H_2O(g) \xrightarrow{\Delta U'_{\text{inter}}} \underset{\text{(intercalated vermiculite)}}{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4(c)},$$

designated $\Delta U'_{\text{inter}}$, is given by $-(U_{H_2O\text{-}K} + U_{H_2O\text{-layer}} + U_{H_2O\text{-}H_2O})$ which leads, by virtue of equations (18), (20)–(24) and (28), to the following equations (ΔU in kJ mol^{-1}):

for K^+ in position K_A,

$$\Delta U'_{\text{inter}} = -457.3\,q_{H''} + 377.6\,q_{H''}^2; \tag{29}$$

for K^+ in position K_B,
$$\Delta U'_{\mathrm{inter}} = -404.1\,q_{\mathrm{H}''} + 377.6\,q^2_{\mathrm{H}''}; \tag{30}$$

for K^+ in position K_C,
$$\Delta U'_{\mathrm{inter}} = -272.2\,q_{\mathrm{H}''} + 377.6\,q^2_{\mathrm{H}''}; \tag{31}$$

for K^+ in position K_D,
$$\Delta U'_{\mathrm{inter}} = -145.3\,q_{\mathrm{H}''} + 377.6\,q^2_{\mathrm{H}''}; \tag{32}$$

for K^+ in position K_E,
$$\Delta U'_{\mathrm{inter}} = -63.0\,q_{\mathrm{H}''} + 377.6\,q^2_{\mathrm{H}''}. \tag{33}$$

Figure 24 shows the variation of $\Delta U'_{\mathrm{inter}}$ with $q_{\mathrm{H}''}$ for various interlayer cation positions, K_A, K_B, K_C, K_D, and K_E.

For the expansion of phlogopite from 10 Å to 12.5 Å we can calculate the expansion energy, ΔU_{exp}, for the process

$$\underset{\text{(phlogopite)}}{2\mathrm{KMg_3(Si_3Al)\,O_{10}(OH)_2(c)}} \xrightarrow{\Delta U_{\mathrm{exp}}} \underset{\text{(expanded phlogopite)}}{\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4(c)}},$$

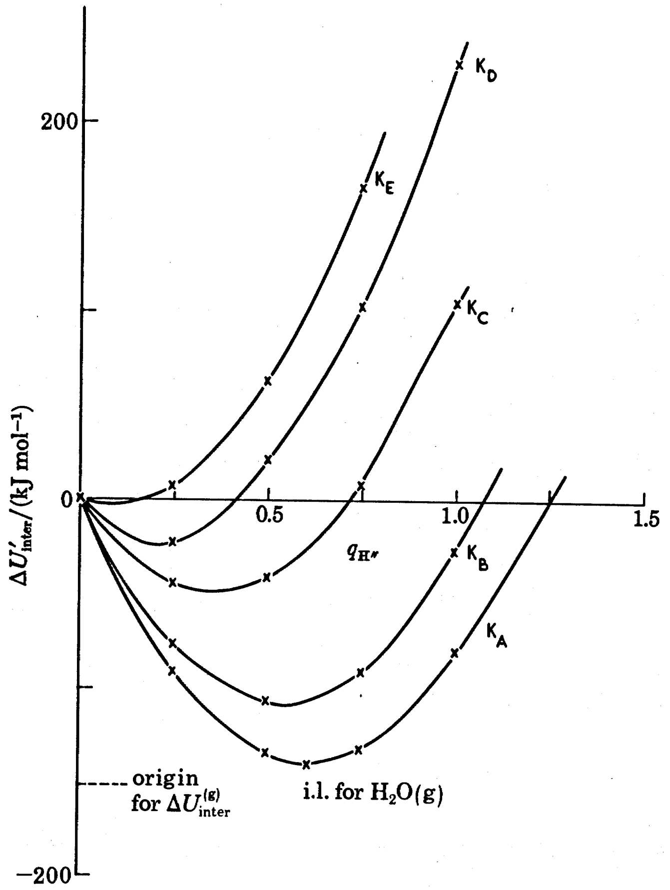

FIGURE 24. Variation of $\Delta U'_{\mathrm{inter}}$ for the process

$$\underset{\text{(expanded)}}{\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4(c)}} + 4\mathrm{H_2O(g)} \longrightarrow \mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4.(H_2O)_4.(c)}$$

with $q_{\mathrm{H}''}$, the charge on the hydrogen atoms of the intercalated water molecules, for various positions of the interlayer cations, K_A, K_B, K_C, K_D, K_E. This energy, $\Delta U'_{\mathrm{inter}}$, represents the change in energy on insertion of gaseous water molecules into the already expanded phlogopite mica. For the process where first normal phlogopite is expanded and then intercalation is attempted, the overall intercalation energy, $\Delta U'^{(g)}_{\mathrm{inter}}$, is 151 kJ mol⁻¹ lower than $\Delta U'_{\mathrm{inter}}$. This origin shift is illustrated in the figure and we see that even for the centralized interlayer cation (K_A), $\Delta U^{(g)}_{\mathrm{inter}}$ is slightly positive, indicating that for the vermiculite with a full charged interlayer no actual intercalation is possible at low pressure.

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using the differences in the electrostatic energies, by virtue of the thermochemical cycle

$$\begin{tikzcd}
2\mathrm{KMg_3(Si_3Al)O_{10}(OH)_2(c)} \arrow[r, "\Delta U_{\mathrm{exp}}"] \arrow[d, "2U_{\mathrm{elec}}\text{ (phlogopite)}"'] & \mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4(c)} \arrow[dl, "U_{\mathrm{elec}}\text{ (expanded phlogopite)}"] \\
2\mathrm{K^+(g)} + 6\mathrm{Mg^{2+}(g)} + 6\mathrm{Si^{4+}(g)} + 2\mathrm{Al^{3+}(g)} + 24\mathrm{O^{2-}(g)} + 4\mathrm{H^+(g)}. &
\end{tikzcd}$$

We have

$$\Delta U_{\mathrm{exp}} = 2U_{\mathrm{elec}}(\text{phlogopite}) - U_{\mathrm{elec}}(\text{expanded phlogopite}), \tag{34}$$

and using the data U_{elec}(phlogopite) $= 74\,915\ \mathrm{kJ\,mol^{-1}}$ (Jenkins & Hartman 1979, table 7) and U_{elec}(expanded phlogopite) $= U_{\mathrm{elec}}$(potassium vermiculite) $= 149\,679\ \mathrm{kJ\,mol^{-1}}$ (table 4 of this paper with $q_{\mathrm{H''}} = q_{\mathrm{O''}} = 0$) gives $\Delta U_{\mathrm{exp}} = 151\ \mathrm{kJ\,mol^{-1}}$.

The intercalation energy, $\Delta U^{(\mathrm{g})}_{\mathrm{inter}}$, for the process of interest:

$$\underset{\text{(normal phlogopite)}}{2\mathrm{KMg_3(Si_3Al)O_{10}(OH)_4(c)}} + 4\mathrm{H_2O(g)} \xrightarrow{\Delta U^{(\mathrm{g})}_{\mathrm{inter}}} \underset{\text{(potassium vermiculite)}}{\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4\,.\,(H_2O)_4(c)}}$$

is given by the equation

$$\Delta U^{(\mathrm{g})}_{\mathrm{inter}} = \Delta U_{\mathrm{exp}} + \Delta U'_{\mathrm{inter}}. \tag{35}$$

The intercalation energy $\Delta U^{(\mathrm{g})}_{\mathrm{inter}}$ differs from $\Delta U'_{\mathrm{inter}}$ by a constant energy of expansion, ΔU_{exp}, and hence for $\mathrm{K_2Mg_6(Si_3Al)_2O_{20}(OH)_4}$ the intercalation energy, $\Delta U^{(\mathrm{g})}_{\mathrm{inter}}$ is given by adding $151\ \mathrm{kJ\,mol^{-1}}$ to each of the $\Delta U'_{\mathrm{inter}}$-values in figure 24. This effects a shift of origin (indicated in figure 24) causing $\Delta U^{(\mathrm{g})}_{\mathrm{inter}}$, even in the most favourable case where $\mathrm{K^+}$ interlayer cations are centrally placed ($\mathrm{K_A}$), to be slightly positive. No intercalation is therefore possible within the fully charged interlayer ($x = 1$) of potassium vermiculite at negligible pressure whatever the actual arrangement of interlayer cations. This conclusion is consistent with the well established fact that normal phlogopite does not take up water.

(c) *Vermiculites having a reduced interlayer charge: $q_{\mathrm{K}} = x < 1$*

(i) *Introduction*

The calculations described above relate to the general formula $\mathrm{K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4\,.\,(H_2O)_4}$ with $x = 1$, where the vermiculite possesses a fully charged interlayer. We must now consider vermiculites having a reduced interlayer charge where $x < 1$ and $q_{\mathrm{K}} = x$, $q_{\mathrm{T}} = (4 - 0.25x)$, parametrizing (by use of equation (8)) in terms of $q_{\mathrm{H''}}$ as before. Equation (7) takes the explicit form (U_{elec} in $\mathrm{kJ\,mol^{-1}}$)

$$\begin{aligned} &U_{\mathrm{elec}}(\mathrm{K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4\,.\,(H_2O)_4}) \\ &\quad = x^2(A_{\mathrm{KK}} - \tfrac{1}{4}A_{\mathrm{KT}} + 181.3) + x[4A_{\mathrm{KT}} + 2A_{\mathrm{KX}} + 2A_{\mathrm{KX'}} + A_{\mathrm{KH}} - 2A_{\mathrm{KO}} - 2A_{\mathrm{KO'}} \\ &\qquad - 8692.2 + (A_{\mathrm{KH''}} - 2A_{\mathrm{KO''}} + 168.5)\,q_{\mathrm{H''}} + 157\,246.7 - 31.3\,q_{\mathrm{H''}} + 18\,448.0q^2_{\mathrm{H''}}, \end{aligned} \tag{36}$$

if we use the coefficients of table 3.

As for equation (9), the magnitude of the final term of equation (36) is mainly due to the self-energy of the four water molecules (see equation (27)) and thus the electrostatic energy for the vermiculite to produce gaseous ions and four discrete water molecules is (in $\mathrm{kJ\,mol^{-1}}$)

$$\begin{aligned} &U'_{\mathrm{elec}}(\mathrm{K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4\,.\,(H_2O)_4}) \\ &\quad = x^2(A_{\mathrm{KK}} - \tfrac{1}{4}A_{\mathrm{KT}} + 181.3) + x[4A_{\mathrm{KT}} + 2A_{\mathrm{KX}} + 2A_{\mathrm{KX'}} + A_{\mathrm{KH}} - 2A_{\mathrm{KO}} - 2A_{\mathrm{KO'}} \\ &\qquad - 8692.2 + (A_{\mathrm{KH''}} - 2A_{\mathrm{KO''}} + 168.5)\,q_{\mathrm{H''}}] + 157\,246.7 - 31.3\,q_{\mathrm{H''}} - 377.6\,q^2_{\mathrm{H''}}. \end{aligned} \tag{37}$$

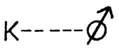
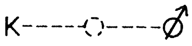
(ii) *Interlayer interaction terms when the interlayer charges are smaller than unity* ($x < 1$)

As the interlayer charges, $q_K = x$, are decreased from unity the vermiculite is correspondingly modified (i) in the interlayer by geometrical changes caused by creation of vacant cation sites and the corresponding adjustments to the orientations of the water molecule dipoles and (ii) in the silicate framework by corresponding occupational changes in the tetrahedral layer sites, $q_T (= 4 - 0.25x)$, required to maintain electroneutrality within the vermiculite. The latter modifications can readily be incorporated within our existing 'generic' approach (Jenkins & Hartman 1979), namely by writing q_T as a function of x, as in equation (37). The former geometrical changes are more complex, varying as they do with the interlayer K^+–H_2O, H_2O–H_2O and K^+–K^+ interactions and the K^+–layer, H_2O–layer interactions with the silicate structure, and we require to consider each situation for a given interlayer charge, x, specifically. For the present calculations for $x < 1$ the interlayer cations K^+ are considered to be located in the central position within the interlayer (position K_A) throughout.

We discussed in § 3 the fact that, for low values of x in the range $\frac{1}{3} \geqslant x > 0$, the K^+–K^+ interactions can be approximated by $\sqrt{x}\,A_{KK}$. This approximation is used in what follows. For x in the range $1 > x \geqslant \frac{2}{3}$, however, a separate calculation for each value of x considered has to be made to treat the ordering of the vacancies explicitly.

(iii) *Explicit* K^+–H_2O *and* H_2O–H_2O *interlayer interactions for various specific values of* x

If we consider the geometrical arrangements of K^+ ions and vacancies that can be deduced for the interlayer as x varies, we can obtain arrangements for $x = 1$ (figure 6), $x = \frac{15}{16}$ (figure 21), $x = \frac{11}{12}$ (figure 20), $x = \frac{8}{9}$ (figure 19), $x = \frac{3}{4}$ (figure 18), $x = \frac{2}{3}$ (figure 9), $x = \frac{1}{3}$ (figure 8), $x = \frac{1}{4}$ (figure 15), $x = \frac{1}{7}$ (figure 16), and $x = \frac{1}{9}$ (figure 17). Consideration of these figures enables us to identify specific types of first and second nearest neighbour K^+–H_2O interactions and of nearest neighbour H_2O–H_2O interactions that occur for the situations we are to consider explicitly, these being labelled (I)–(IX) (for K^+–H_2O interactions) and (I)′–(XII)′ (for H_2O–H_2O interactions) respectively in table 5. In the table each interaction type is designated by a roman numeral, and the following notation is used:

	first nearest neighbour interaction of an interlayer cation K^+ with a water molecule having a dipole orientation with respect to the K–O axis as indicated
	second nearest neighbour interaction of an interlayer cation K^+ with a water molecule having a dipole orientation with respect to the K–O axis as indicated
	first nearest neighbour interaction between two water molecules whose dipoles are orientated with respect to the O–O axis as indicated
○	freely rotating water molecule

The parametric form of the electrostatic energy per interaction is given as a function of $q_{H''}$ for K^+–H_2O interactions and as a function of $q_{H''}^2$ for H_2O–H_2O interactions.

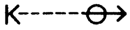
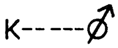
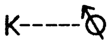
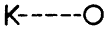
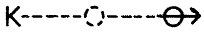
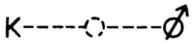
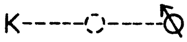
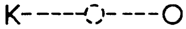
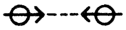
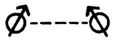
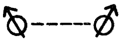
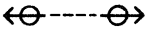
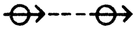
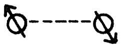
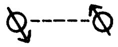
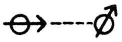
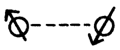
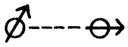
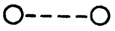
Since we have already calculated the total interaction energy of K^+–H_2O and H_2O–H_2O interactions for $x = 1$ we can compare the total interaction energy calculated using the above approach which takes account of first and second nearest neighbour ion–molecule interactions and nearest neighbour molecule–molecule interactions with the values already cited and obtained from exhaustive lattice summation.

TABLE 5. SUMMARY OF K^+–H_2O AND H_2O–H_2O INTERLAYER INTERACTION TYPES FOUND FOR THE SPECIFIC INTERLAYER ARRANGEMENTS DEDUCED FOR

$x = \frac{15}{16}, \frac{11}{12}, \frac{8}{9}, \frac{3}{4}, \frac{2}{3}, \frac{1}{3}, \frac{1}{4}, \frac{1}{7}, \frac{1}{9}$

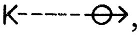
(The energy per interaction is given in parametric form and each interaction type is designated by a roman numeral.)

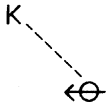
First nearest neighbour K^+–H_2O *interactions*

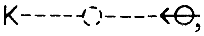
notation	interaction	K–O distance	energy per interaction kJ mol⁻¹
(I)		$\frac{1}{3}b$	$162.4\,q_{\mathrm{H}''}$
(II)		$\frac{1}{3}b$	$110.0\,q_{\mathrm{H}''}$
(III)		$\frac{1}{3}b$	$-39.6\,q_{\mathrm{H}''}$
(IV)		$\frac{1}{3}b$	$12.1\,q_{\mathrm{H}''}$
Second nearest neighbour K^+–H_2O *interactions*			
(V)		$\frac{2}{3}b$	$42.1\,q_{\mathrm{H}''}$
(VI)		$\frac{2}{3}b$	$25.2\,q_{\mathrm{H}''}$
(VII)		$\frac{2}{3}b$	$-16.2\,q_{\mathrm{H}''}$
(VIII)		$\frac{2}{3}b$	$-41.9\,q_{\mathrm{H}''}$
(IX)		$\frac{2}{3}b$	negligible
Nearest neighbour H_2O–H_2O *interactions*			
(I)′		$\frac{1}{3}b$	$-128.6\,q^2_{\mathrm{H}''}$
(II′)		$\frac{1}{3}b$	$-79.5\,q^2_{\mathrm{H}''}$
(III)′		$\frac{1}{3}b$	$-85.5\,q^2_{\mathrm{H}''}$
(IV)′		$\frac{1}{3}b$	$-108.4\,q^2_{\mathrm{H}''}$
(V)′		$\frac{1}{3}b$	$91.7\,q^2_{\mathrm{H}''}$
(VI)′		$\frac{1}{3}b$	$-37.3\,q^2_{\mathrm{H}''}$
(VII)′		$\frac{1}{3}b$	$50.1\,q_{\mathrm{H}''}$
(VIII)′		$\frac{1}{3}b$	$65.5\,q^2_{\mathrm{H}''}$
(IX)′		$\frac{1}{3}b$	$41.9\,q^2_{\mathrm{H}''}$
(X)′		$\frac{1}{3}b$	negligible
(XI)′		$\frac{1}{3}b$	$38.2\,q^2_{\mathrm{H}''}$
(XII)′		$\frac{1}{3}b$	$-9.7\,q^2_{\mathrm{H}''}$ (estimated as an average)

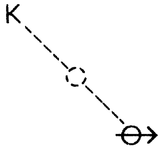
Case A. $x = 1$, $K_2Mg_6(Si_3Al)_2O_{20}(OH)_4 . (H_2O)_4$

If we consider figure 6 in conjunction with table 5 for K^+–H_2O interactions we can identify 2 of type (I),

e.g. ,

48 of type (III), e.g. ,

24 of type (VIII), e.g. ;

and 48 of type (VI), e.g. 

in the six unit cells illustrated. Per unit cell, the interaction energy is therefore given by

$$E(K\text{–}H_2O) = 4(I) + 8(III) + 4(VIII) + 8(VI), \qquad (38$$

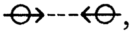
which from table 5 gives (in kJ mol^{-1})

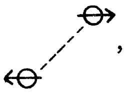
$$E(K\text{–}H_2O) = 366.8\, q_{H''}. \qquad (39$$

This value should be compared with the K^+–H_2O interaction obtained from equation (19) b using the exhaustive lattice sums referred to earlier and equal to (in kJ mol^{-1})

$$E(K\text{–}H_2O) \approx U_{H_2O\text{–}K} = (A_{KH''} - 2A_{KO''})\, q_{H''} = 320.1\, q_{H''}. \qquad (40$$

For the H_2O–H_2O interactions we have 12 of type (I)′,

e.g. ,

and 24 of type (VI)′, e.g. ,

in the six unit cells shown. Hence, per unit cell,

$$E(H_2O\text{–}H_2O) = 2(I)' + 4(VI)', \qquad (41$$

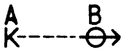
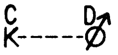
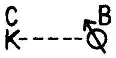
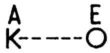
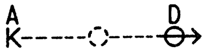
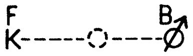
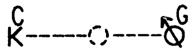
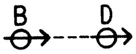
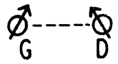
which from table 5 gives (in kJ mol^{-1})

$$E(H_2O\text{–}H_2O) = -406.4\, q^2_{H''}. \qquad (42$$

Second nearest neighbour interactions are disregarded. The energy $E(H_2O\text{–}H_2O)$ should b compared with the total lattice sum calculations for these interactions, $U_{H_2O\text{–}H_2O}$ of equation (28 equal to $-377.6\, q^2_{H''}$.

The above comparisons indicate that our proposed procedure for estimating interlayer inte actions is satisfactory and we now proceed to estimate K^+–H_2O and H_2O–H_2O interactio where the interlayer charge is reduced.

TABLE 6. K^+–H_2O AND H_2O–H_2O INTERACTIONS FOR THE VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{15}{16}$, $K_{1.88}Mg_6(Si_{3.06}Al_{0.94})_2O_{20}(OH)_4.(H_2O)_4$

representative interaction in figure 21	notation for interaction type (table 5)	number of interactions per 16 unit cells	energy per interaction (kJ mol^{-1})
First nearest neighbour K^+–H_2O *interactions*			
	(I)	12	$162.4\,q_{H''}$
	(II)	24	$110.0\,q_{H''}$
	(III)	24	$-39.6\,q_{H''}$
	(IV)	120	$12.1\,q_{H''}$
Second nearest neighbour K^+–H_2O *interactions*			
	(V)	12	$42.1\,q_{H''}$
	(VI)	24	$25.2\,q_{H''}$
	(VII)	24	$-16.2\,q_{H''}$
Nearest neighbour H_2O–H_2O *interactions*			
	(V)′	12	$91.7\,q^2_{H''}$
	(II)′	12	$-79.5\,q^2_{H''}$

Case B. $x = \frac{15}{16}$, $K_{1.88}Mg_6(Si_{3.06}Al_{0.94})_2O_{20}(OH)_4.(H_2O)_4$

Considering figure 21 which shows our interlayer arrangement where the interlayer charge $x = \frac{15}{16}$ we identify four first nearest neighbour K^+–H_2O interactions types (I), (II), (III) and (IV), three K^+–H_2O second nearest neighbour interaction types (V), (VI) and (VII), and two H_2O–H_2O interaction types (V)′ and (II)′. The multiplicity of the various interaction types encountered in the 16 unit cells drawn in figure 21 is summarized in table 6. In the table each interaction type is illustrated by reference to figure 21. The total interactions per unit cell are now seen to be given by

$$E(\text{K–H}_2\text{O}) = \tfrac{3}{4}(\text{I}) + \tfrac{3}{2}(\text{II}) + \tfrac{3}{2}(\text{III}) + \tfrac{15}{2}(\text{IV}) + \tfrac{3}{4}(\text{V}) + \tfrac{3}{2}(\text{VI}) + \tfrac{3}{2}(\text{VII}), \tag{43}$$

where interaction (IV) represents the nearest neighbour interaction of the interlayer cations with rotating water molecules. The procedure used for calculating this interaction is illustrated in Appendix I of this paper.

Evaluation of equation (43) by using the relations given in table 6 generates the value (in kJ mol^{-1}):

$$E(\text{K–H}_2\text{O}) = 363.2\,q_{H''}. \tag{44}$$

The H_2O–H_2O interaction is calculated to be

$$E(\text{H}_2\text{O–H}_2\text{O}) = \tfrac{3}{4}(\text{V})' + \tfrac{3}{4}(\text{II})', \tag{45}$$

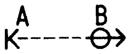
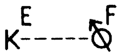
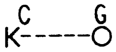
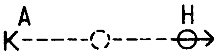
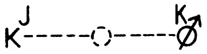
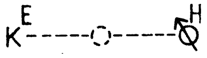
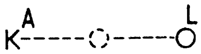
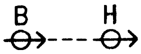
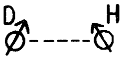
giving (in kJ mol^{-1})

$$E(\text{H}_2\text{O–H}_2\text{O}) = 9.1\,q^2_{H''}. \tag{46}$$

Case C. $x = \frac{11}{12}$, $K_{1.84}Mg_6(Si_{3.08}Al_{0.92})_2O_{20}(OH)_4.(H_2O)_4$

Considering figure 20 which illustrates the arrangement of interlayer cations and wate molecules for the vermiculite having an interlayer charge $x = \frac{11}{12}$, we can identify four firs neighbour K^+–H_2O interactions types (I), (II), (III) and (IV), four second neighbour K^+–H_2 interaction types (V), (VI), (VII) and (IX), and two H_2O–H_2O interaction types (V)′ and (II)′

TABLE 7. K^+–H_2O AND H_2O–H_2O INTERACTIONS FOR THE VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{11}{12}$, $K_{1.84}Mg_6(Si_{3.08}Al_{0.92})_2O_{20}(OH)_4.(H_2O)_4$

representative interaction in figure 20	notation for interaction type (table 5)	number of interactions per 12 unit cells	energy per interaction (kJ mol^{-1})
First nearest neighbour K^+–H_2O *interactions*			
	(I)	12	$162.4\,q_{H''}$
	(II)	24	$110.0\,q_{H''}$
	(III)	24	$-39.6\,q_{H''}$
	(IV)	72	$12.1\,q_{H''}$
Second nearest neighbour K^+–H_2O *interactions*			
	(V)	12	$42.1\,q_{H''}$
	(VI)	24	$25.2\,q_{H''}$
	(VII)	24	$-16.2\,q_{H''}$
	(IX)	72	negligible
Nearest neighbour H_2O–H_2O *interactions*			
	(V)′	12	$91.7\,q^2_{H''}$
	(II)′	12	$-79.5\,q^2_{H''}$

The multiplicity of the various interaction types encountered for the twelve unit cells illustrate in figure 20 is summarized in table 7. Each interaction type is illustrated in the table with referenc to representative interactions labelled in figure 20. The energies of interaction per unit ce (in kJ mol^{-1}) are given by

$$E(K\text{–}H_2O) = (I)+2(II)+2(III)+6(IV)+(V)+2(VI)+2(VII), \quad (47$$

which, if we use the values of the interactions listed in table 7, gives (in kJ mol^{-1})

$$E(K\text{–}H_2O) = 435.9\,q^2_{H''}. \quad (4$$

Further, from table 7,

$$E(H_2O\text{–}H_2O) = (V)'+(II)', \quad (4$$

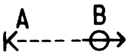
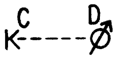
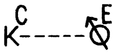
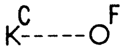
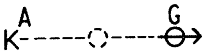
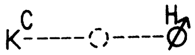
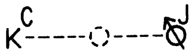
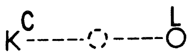
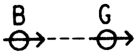
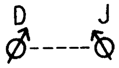
leading to (in kJ mol^{-1})

$$E(H_2O\text{–}H_2O) = 12.2\,q^2_{H''}. \quad (5$$

Case D. $x = \frac{8}{9}$, $K_{1.78}Mg_6(Si_{3.11}Al_{0.89})_2O_{20}(OH)_4.(H_2O)_4$

Figure 19 illustrates the arrangement of the interlayer for the vermiculite bearing interlayer charge $x = \frac{8}{9}$ and we can identify four first nearest neighbour K^+–H_2O interaction types (I), (II), (III) and (IV), four second nearest neighbour K^+–H_2O interaction types (V), (VI), (VII) and (IX), and two H_2O–H_2O interaction types (V)′ and (II)′. Table 8 summarizes the number of interactions of these various types found in the nine unit cells illustrated in figure 19. The total interaction K^+–H_2O per unit cell is then given by

TABLE 8. K^+–H_2O AND H_2O–H_2O INTERACTIONS FOR VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{8}{9}$, $K_{1.78}(Si_{3.11}Al_{0.89})_2O_{20}(OH)_4.(H_2O)_4$

representative interaction in figure 19	notation for interaction type (table 5)	number of interactions per 9 unit cells	energy per interaction (kJ mol^{-1})
First nearest neighbour K^+–H_2O *interactions*			
	(I)	12	$162.4\,q_{H''}$
	(II)	24	$110.0\,q_{H''}$
	(III)	24	$-39.6\,q_{H''}$
	(IV)	36	$12.1\,q_{H''}$
Second nearest neighbour K^+–H_2O *interactions*			
	(V)	12	$42.1\,q_{H''}$
	(VI)	24	$25.2\,q_{H''}$
	(VII)	24	$-16.2\,q_{H''}$
	(IX)	12	negligible
Nearest neighbour H_2O–H_2O *interactions*			
	(V)′	12	$91.7\,q^2_{H''}$
	(II)′	12	$-79.5\,q^2_{H''}$

$$E(K\text{–}H_2O) = \tfrac{4}{3}(I) + \tfrac{8}{3}(II) + \tfrac{8}{3}(III) + 4(IV) + \tfrac{4}{3}(V) + \tfrac{8}{3}(VI) + \tfrac{8}{3}(VII) + \tfrac{4}{3}(IX),$$

whereupon (in kJ mol^{-1})

$$E(K\text{–}H_2O) = 532.8\,q_{H''}. \qquad (52)$$

For the H_2O–H_2O interaction we have

$$E(H_2O\text{–}H_2O) = \tfrac{4}{3}(II)' + \tfrac{4}{3}(V)', \qquad (53)$$

and therefore (in kJ mol^{-1})

$$E(H_2O\text{–}H_2O) = 16.2\,q^2_{H''}. \qquad (54)$$

Case E. $x = \frac{3}{4}$, $K_{1.50}Mg_6(Si_{3.25}Al_{0.75})_2O_{20}(OH)_4.(H_2O)_4$

Figure 18 illustrates the interlayer arrangement of water molecules and cations deduced fo the vermiculite having an interlayer charge $x = \frac{3}{4}$. We can identify two first nearest neighbour (II) and (IV), and two second nearest neighbour, (V) and (VII), K^+–H_2O interaction types anc two, (II)′ and (X)′, H_2O–H_2O interaction types. Table 9 summarizes the number of each o these interactions found per four unit cells in figure 18, from which information we have

$$E(\mathrm{K{-}H_2O}) = 6(\mathrm{II}) + 3(\mathrm{IV}) + 3(\mathrm{V}) + 6(\mathrm{VII}), \quad (55$$

whereupon (in kJ mol⁻¹)

$$E(\mathrm{K{-}H_2O}) = 725.4\,q_{\mathrm{H''}}, \quad (56$$

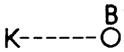
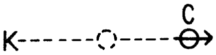
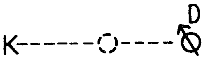
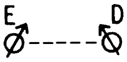
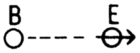
and also

$$E(\mathrm{H_2O{-}H_2O}) = 3(\mathrm{II})' + 3(\mathrm{X})', \quad (57$$

giving (in kJ mol⁻¹)

$$E(\mathrm{H_2O{-}H_2O}) = -238.5\,q^2_{\mathrm{H''}}. \quad (58$$

TABLE 9. K^+–H_2O AND H_2O–H_2O INTERACTIONS FOR VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{3}{4}$, $K_{1.50}Mg_6(Si_{3.25}Al_{0.75})_2O_{20}(OH)_4.(H_2O)_4$

representative interaction in figure 18	notation for interaction type (table 5)	number of interactions per 4 unit cells	energy per interaction (kJ mol⁻¹)
First nearest neighbour K^+–H_2O *interactions*			
	(II)	24	$110.0\,q_{\mathrm{H''}}$
	(IV)	12	$12.1\,q_{\mathrm{H''}}$
Second nearest neighbour K^+–H_2O *interactions*			
	(V)	12	$42.1\,q_{\mathrm{H''}}$
	(VII)	24	$-16.2\,q_{\mathrm{H''}}$
Nearest neighbour H_2O–H_2O *interactions*			
	(II)′	12	$-79.5\,q^2_{\mathrm{H''}}$
	(X)′	12	negligible

Case F. $x = \frac{2}{3}$, $K_{1.34}Mg_6(Si_{3.33}Al_{0.67})_2O_{20}(OH)_4.(H_2O)_4$

Figure 9 illustrates the interlayer arrangement for the vermiculite with interlayer charg $x = \frac{2}{3}$. All first and second nearest neighbour K^+–H_2O interactions are of similar types, (II) anc (VII), and the H_2O–H_2O interactions are of two types (II)′ and (IV)′. The total number o interactions of each type for three unit cells of figure 9 are summarized in table 10 and we finc

$$E(\mathrm{K{-}H_2O}) = 8(\mathrm{II}) + 8(\mathrm{VII}), \quad (59$$

$$E(\mathrm{H_2O{-}H_2O}) = 4(\mathrm{II})' + 2(\mathrm{IV})', \quad (60$$

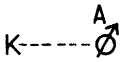
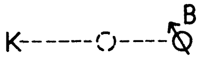
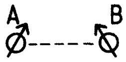
which (in kJ mol⁻¹) become

$$E(\mathrm{K{-}H_2O}) = 750.4\,q_{\mathrm{H''}}, \quad (61$$

and

$$E(\mathrm{H_2O{-}H_2O}) = -534.8\,q^2_{\mathrm{H''}}, \quad (62$$

TABLE 10. K^+–H_2O AND H_2O–H_2O INTERACTIONS FOR VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{2}{3}$, $K_{1.34}Mg_6(Si_{3.33}Al_{0.67})_2O_{20}(OH)_4.(H_2O)_4$

representative interaction in figure 9	notation for interaction type (table 5)	number of interactions per 3 unit cells	energy per interaction (kJ mol^{-1})
First nearest and second nearest neighbour K^+–H_2O *interactions*			
	(II)	24	$110.0\,q_{\mathrm{H}''}$
	(VII)	24	$-16.2\,q_{\mathrm{H}''}$
Nearest neighbour H_2O–H_2O *interactions*			
	(II)′	12	$-79.5\,q^2_{\mathrm{H}''}$
	(IV)′	6	$-108.4\,q^2_{\mathrm{H}''}$

Case G. $x = \frac{1}{3}$, $K_{0.66}Mg_6(Si_{3.67}Al_{0.33})_2O_{20}(OH)_4.(H_2O)_4$

Figure 8 illustrates the interlayer arrangement for the vermiculite having interlayer charge $x = \frac{1}{3}$. First nearest neighbour K^+–H_2O interactions are all of type (II) and second nearest neighbour K^+–H_2O interactions are all of type (VII) while two different types of H_2O–H_2O interaction are identifiable as type (VII)′ and (XI)′. Table 11 gives the specific details of the number of each type of interaction occurring within nine unit cells in figure 8, from which

$$E(\mathrm{K{-}H_2O}) = 4(\mathrm{II}) + 4(\mathrm{VII}), \tag{63}$$

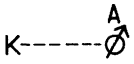
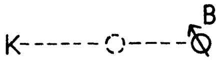
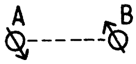
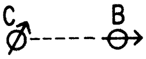
$$E(\mathrm{H_2O{-}H_2O}) = 2(\mathrm{VII})' + 4(\mathrm{XI})', \tag{64}$$

whereupon

$$E(\mathrm{K{-}H_2O}) = 375.2\,q_{\mathrm{H}''}, \tag{65}$$

$$E(\mathrm{H_2O{-}H_2O}) = 253.0\,q^2_{\mathrm{H}''}. \tag{66}$$

TABLE 11. K^+–H_2O AND H_2O–H_2O INTERACTIONS FOR VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{1}{3}$, $K_{0.66}Mg_6(Si_{3.67}Al_{0.33})_2O_{20}(OH)_4.(H_2O)_4$

representative interaction in figure 8	notation for interaction type (table 5)	number of interactions per 9 unit cells	energy per interaction (kJ mol^{-1})
First and second nearest neighbour K^+–H_2O *interactions*			
	(II)	36	$110.0\,q_{\mathrm{H}''}$
	(VII)	36	$-16.2\,q_{\mathrm{H}''}$
Nearest neighbour H_2O–H_2O *interactions*			
	(VII)′	18	$50.1\,q^2_{\mathrm{H}''}$
	(XI)′	36	$38.2\,q^2_{\mathrm{H}''}$

Case H. $x = \frac{1}{4}$, $K_{0.50}Mg_6(Si_{3.75}Al_{0.25})_2O_{20}(OH)_4.(H_2O)_4$

Figure 15 illustrates the interlayer arrangement of water molecules, cations and vacancies for vermiculite having an interlayer charge corresponding to $x = \frac{1}{4}$. First and second nearest neighbour interactions K^+–H_2O are of types (I) and (IX) respectively while all H_2O–H_2O nearest neighbour interactions are of type (III)′. The total number of interactions per four unit cells in figure 15 is summarized in table 12 and leads to the results

$$E(K\text{–}H_2O) = 3(I) + 3(IX), \tag{67}$$

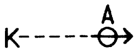
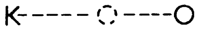
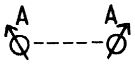
$$E(H_2O\text{–}H_2O) = 3(III)', \tag{68}$$

where (in kJ mol⁻¹)

$$E(K\text{–}H_2O) = 487.2\, q_{H''}, \tag{69}$$

$$E(H_2O\text{–}H_2O) = -256.5\, q^2_{H''}. \tag{70}$$

TABLE 12. K^+–H_2O AND H_2O–H_2O INTERACTIONS FOR VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{1}{4}$, $K_{0.50}Mg_6(Si_{3.75}Al_{0.25})_2O_{20}(OH)_4.(H_2O)_4$

representative interactions in figure 15	notation for interaction type (table 5)	number of interactions per 4 units cells	energy per interaction (kJ mol⁻¹)
First and second nearest neighbour K^+–H_2O *interactions*			
	(I)	12	$162.4\, q_{H''}$
	(IX)	12	negligible
Nearest neighbour H_2O–H_2O *interaction*			
	(III)′	12	$-85.5\, q^2_{H''}$

Case I. $x = \frac{1}{7}$, $K_{0.28}Mg_6(Si_{3.86}Al_{0.14})_2O_{20}(OH)_4.(H_2O)_4$

Figure 16 illustrates the interlayer arrangement for $x = \frac{1}{7}$ for a vermiculite. First nearest neighbour K^+–H_2O interactions are of type (I) but for second nearest neighbour K^+–H_2O interactions there is some doubt concerning the orientation of the water dipoles. For calculation, all were supposed to be of type (V) (table 5). For H_2O–H_2O interactions, three basic interaction types are identified, (V)′, (III)′ and (VII)′, but again there is some uncertainty concerning the dipole *directions* of the water molecules. Table 13 summarizes the number of interactions found of each type in seven unit cells of figure 16. These data lead to the equations

$$E(K\text{–}H_2O) = \tfrac{12}{7}(I) + \tfrac{12}{7}(V), \tag{71}$$

$$E(H_2O\text{–}H_2O) = \tfrac{12}{7}(V)' + \tfrac{12}{7}(III)' + \tfrac{6}{7}(VII)', \tag{72}$$

leading to (in kJ mol⁻¹)

$$E(K\text{–}H_2O) = 350.6\, q_{H''}, \tag{73}$$

$$E(H_2O\text{–}H_2O) = 53.6\, q^2_{H''}. \tag{74}$$

Table 13. K^+–H_2O and H_2O–H_2O interactions for vermiculite having interlayer charge $x = \frac{1}{7}$, $K_{0.28}Mg_6(Si_{3.86}Al_{0.14})_2O_{20}(OH)_4.(H_2O)_4$

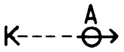
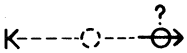
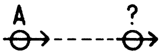
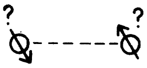
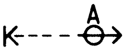
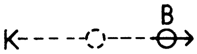
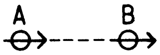
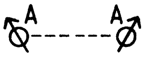
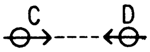
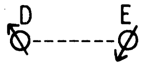
representative interaction in figure 16	notation for interaction type (table 5)	number of interactions per 7 unit cells	energy per interaction (kJ mol^{-1})
First and second nearest neighbour K^+–H_2O *interactions*			
	(I)	12	$162.4\,q_{\mathrm{H}''}$
	(IV)	12	$42.1\,q_{\mathrm{H}''}$
Nearest neighbour H_2O–H_2O *interactions*			
	(V)′	12	$91.7\,q^2_{\mathrm{H}''}$
	(III)′	12	$-85.5\,q^2_{\mathrm{H}''}$
	(VII)′	6	$50.1\,q^2_{\mathrm{H}''}$

Table 14. K^+–H_2O and H_2O–H_2O interactions for vermiculite having interlayer charge $x = \frac{1}{9}$, $K_{0.22}Mg_6(Si_{3.89}Al_{0.11})_2O_{20}(OH)_4.(H_2O)_4$

representative interaction in figure 17	notation for interaction type (table 5)	number of interactions per 9 unit cells	energy per interaction (kJ mol^{-1})
First and second K^+–H_2O *nearest neighbours interactions*			
	(I)	12	$162.4\,q_{\mathrm{H}''}$
	(V)	12	$42.1\,q_{\mathrm{H}''}$
Nearest neighbour H_2O–H_2O *interactions*			
	(V)′	12	$91.7\,q^2_{\mathrm{H}''}$
	(III)′	12	$-85.5\,q^2_{\mathrm{H}''}$
	(I)′	6	$-128.6\,q^2_{\mathrm{H}''}$
	(IX)′	24	$41.9\,q^2_{\mathrm{H}''}$

Case J. $x = \frac{1}{9}$, $K_{0.22}Mg_6(Si_{3.89}Al_{0.11})_2O_{20}(OH)_4.(H_2O)_4$

Figure 17 gives the detailed interlayer arrangement for vermiculite having an interlayer charge corresponding to $x = \frac{1}{9}$. From this arrangement we identify first nearest neighbour interactions K^+–H_2O of type (I) and second nearest neighbour K^+–H_2O interactions of type (V). As regards H_2O–H_2O interactions, four specific types can be identified, (V)′, (III)′, (I)′ and (IX)′, and the detailed summary of the number of each interaction per nine unit cells of figure 17 is given in table 14, from which we can write:

$$E(\mathrm{K{-}H_2O}) = \tfrac{4}{3}(\mathrm{I}) + \tfrac{4}{3}(\mathrm{V}), \tag{75}$$

$$E(\mathrm{H_2O{-}H_2O}) = \tfrac{4}{3}(\mathrm{V})' + \tfrac{4}{3}(\mathrm{III})' + \tfrac{2}{3}(\mathrm{I})' + \tfrac{8}{3}(\mathrm{IX})', \tag{76}$$

which give (in kJ mol^{-1})

$$E(\mathrm{K-H_2O}) = 272.7\,q_{\mathrm{H''}}, \tag{77}$$

$$E(\mathrm{H_2O\text{-}H_2O}) = 34.2\,q^2_{\mathrm{H''}}. \tag{78}$$

Summary of interactions calculated

Table 15 summarizes the results obtained for $E(\mathrm{K\text{-}H_2O})$ and $E(\mathrm{H_2O\text{-}H_2O})$ parametrized as a function of $q_{\mathrm{H''}}$ and $q^2_{\mathrm{H''}}$, for selected values of the interlayer charge, x. The above calculations are based on assumed interlayer arrangements, which have assigned directional dipoles to the water molecules. We believe that these assignments are reasonable although, in some cases, not optimal. For $x = \frac{15}{16}, \frac{11}{12}, \frac{8}{9}, \frac{3}{4}, \frac{2}{3}, \frac{1}{4}, \frac{1}{9}$ and 0 we are reasonably certain of the arrangements while, for $x = 1$, for example, it may be that all the water molecules are freely rotating as opposed to the situation shown in figure 6. For $x = \frac{1}{3}$, the angle between the dipole direction of the water molecule A in figure 8 and the line joining the adjacent $\mathrm{K^+}$ and the oxygen atom of the water molecule was taken to be 120° for our calculations. Presumably this is *not* the optimal angle that gives the largest interaction energy, and preliminary calculations would suggest this angle to be closer to 135°. For the present calculations, however, we have adopted the situations already described. Similar comments can be made for $x = \frac{1}{7}$ (figure 16). For $E(\mathrm{K\text{-}H_2O})$ and $E(\mathrm{H_2O\text{-}H_2O})$ we write, generalizing,

TABLE 15. PARAMETRIC DEPENDENCE OF $E(\mathrm{K\text{-}H_2O})$ AND $E(\mathrm{H_2O\text{-}H_2O})$, FOR VARIOUS VALUES OF INTERLAYER CHARGE x, IN POTASSIUM VERMICULITE

($E(\mathrm{K\text{-}H_2O}) = I_1 q_{\mathrm{H''}}$, $E(\mathrm{H_2O\text{-}H_2O}) = I_2\, q^2_{\mathrm{H''}}$.)

interlayer charge, x	I_1 / (kJ $\mathrm{mol}^{-1}\,\mathrm{e}^{-1}$)	I_2 / (kJ $\mathrm{mol}^{-1}\,\mathrm{e}^{-2}$)	interlayer charge, x	I_1 / (kJ $\mathrm{mol}^{-1}\,\mathrm{e}^{-1}$)	I_2 / (kJ $\mathrm{mol}^{-1}\,\mathrm{e}^{-2}$)
1	320.1†	−377.6†	$\frac{1}{4}$	487.2	−256.5
$\frac{15}{16}$	363.2	9.1	$\frac{1}{7}$	350.6	53.6
$\frac{11}{12}$	435.9	12.2	$\frac{1}{9}$	272.7	34.2
$\frac{8}{9}$	532.8	16.2	$\frac{1}{12}$	204.5	144.9
$\frac{3}{4}$	725.4	−238.5	$\frac{1}{16}$	153.4	65.3
$\frac{2}{3}$	750.4	−534.8	0	0	0
$\frac{1}{3}$	375.2	253.0			

† Exhaustive summation value.

$$E(\mathrm{K\text{-}H_2O}) = I_1 q_{\mathrm{H''}}, \tag{79}$$

$$E(\mathrm{H_2O\text{-}H_2O}) = I_2 q_{\mathrm{H''}}. \tag{80}$$

(iv) K–K *interlayer interactions for various specific values of x*

For the consideration of the mutual interactions of the interlayer cations within the interlayer itself for explicit values of x, two approaches can be adopted, depending on the size of the interlayer charge x. We can attempt rigorous evaluation of the $\mathrm{K^+\text{-}K^+}$ interaction term, or for lower values of x ($x \leqslant \frac{1}{3}$) we can adopt an approximation discussed in § 3, namely

$$E(\mathrm{K\text{-}K}) \approx \surd x A_{\mathrm{KK}}. \tag{81}$$

For the rigorous calculation, substitution of the value $q_{\mathrm{K}} = x$ (where $x \leqslant 1$) into equation (7), all other atom charges being taken as zero, generates the energy of the $\mathrm{K^+\text{-}K^+}$ interactions of a potassium vermiculite having a completely *uniform arrangement* of interlayer cations *each bearing a reduced charge* $+x$ and having the arrangement in figure 6 (water molecules being ignored). In reality, in vermiculites where the interlayer charge is reduced, the charge x is *not* spread uniformly over the lattice but sites (K″) are created where fully charged interlayer cations having $q_{K''} = 1$ are resident and corresponding sites (K′) are created where vacancies, $q_{K'} = 0$, exist. To utilize our generic method fully (and accordingly save, literally, vast amounts of computer time) we can adopt a subterfuge to calculate K^+–K^+ interactions rigorously as x is decreased from unity.

Generalizing, for potassium vermiculite of formula $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$ having interlayer charge x we can calculate E(K–K), the K^+–K^+ interaction energy, by calculating the lattice energy of a cell containing interlayer cations in positions K″ and vacancies in positions K′ corresponding to the arrangements previously discussed for the specific values of x. For the calculation when $x = \frac{15}{16}$, for example, (and hence also for the complementary case where vacancies and cations are interchanged, $x = \frac{1}{16}$) we take the cell described in table 16 having $a = 21.232$ Å, $b = 36.732$ Å and $c = 12.608$ Å. When $x = \frac{11}{12}$ (and hence for the complementary case, $x = \frac{1}{12}$) we take the cell described in table 18 having $a = 31.848$ Å, $b = 18.366$ Å and $c = 12.608$ Å. For $x = \frac{8}{9}$ (and hence for the complementary case, $x = \frac{1}{9}$) we calculate the lattice energy of the cell described in table 20 having $a = 15.924$ Å, $b = 27.549$ Å and $c = 12.608$ Å. When $x = \frac{3}{4}$ (and hence also for the complementary case, $x = \frac{1}{4}$) we use the cell defined in table 22 having $a = 10.616$ Å, $b = 18.366$ Å and $c = 12.608$ Å. Finally, when $x = \frac{2}{3}$ (and hence also for the complementary case $x = \frac{1}{3}$) we can use the cell defined in table 24 having $a = 15.924$ Å, $b = 9.183$ Å and $c = 12.608$ Å. Generalizing, to generate the interlayer cation pattern specific to a given value of x we need to devise a cell which is $1/(1-x)$ times as large as the original expanded phlogopite cell in the a, b-plane to generate a complete unit cell for the specific interlayer arrangement corresponding to x. Each of these larger cells contains two vacancies (K′) and $2x/(1-x)$ interlayer cations (K″) each bearing a charge $+1$. The lattice energy, E(K–K), for the $K'_2K''_{2x/(1-x)}$ arrangement is given by

$$E(\mathrm{K{-}K}) = A_{K'K'}q_{K'}^2 + A_{K'K''}q_{K'}q_{K''} + A_{K''K''}q_{K''}^2. \tag{82}$$

For $q_{K'} = q_{K''} = 1$ (corresponding to potassium vermiculite in which every interlayer site is fully occupied) we have

$$E(\mathrm{K{-}K})_{x=1} = A_{K'K'} + A_{K'K''} + A_{K''K''}. \tag{83}$$

From equation (7) if we put $q_K = 1$ and the charges on all other atoms (Mg, T, O, O′, H, O″, H″) equal to zero, we have:

$$E(\mathrm{K{-}K})_{x=1} = A_{KK}. \tag{84}$$

Combining equations (83) and (84) which give the K'–K^+ interaction for the same arrangement we therefore have the relation

$$A_{K'K'} + A_{K'K''} + A_{K''K''} = A_{KK} \tag{85}$$

connecting the coefficients $A_{K'K'}$, $A_{K'K''}$ and $A_{K''K''}$, which can be calculated for the specific interlayer arrangements described above, with the A_{KK} coefficient for the full calculation ($356.9\ \mathrm{kJ\ mol^{-1}\ e^{-2}}$) listed in table 3 and for K^+ ions in positions K_A.

For the general case where the interlayer charge is x in $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$, we devise a cell having $q_{K''} = 0$, $q_{K''} = 1$ and for which

$$E(\mathrm{K{-}K})_x = A_{K''K''}. \tag{86}$$

If we now interchange vacancies and interlayer cations, the new arrangement corresponds to an interlayer charge of $1-x$ and a formula $K_{2(1-x)}Mg_6(Si_{3+x}Al_{1-x})_2O_{20}(OH)_4(H_2O)_4$, and has $q_{K'} = 1$ and $q_{K''} = 0$. Therefore

$$E(\mathrm{K{-}K})_{1-x} = A_{K'K'}. \tag{87}$$

Thus $A_{\mathrm{K''K''}}$ represents the $\mathrm{K^+}$–$\mathrm{K^+}$ interaction energy for the cell having formula $\mathrm{K'_2K''_{2x/(1-}}$ with two vacancies and all other cations bearing charges of +1 while $A_{\mathrm{K'K'}}$ represents the $\mathrm{K^+}$-K interaction energy for the cell $\mathrm{K'_{2x/(1-x)}K''_2}$ with two cations each bearing a charge +1, th remaining sites being vacant. The energy $A_{\mathrm{K'K'}}-A_{\mathrm{K''K''}}$ therefore corresponds to the creation ($(2x/1-x)-2$ or $(4x-2)/(1-x)$ vacancies in $1/(1-x)$ original cells, or $4x-2$ vacancies per cel The energy of each vacancy creation per cell is therefore given by

$$E_{\mathrm{vac}} = (A_{\mathrm{K'K'}}-A_{\mathrm{K''K''}})/(4x-2), \qquad (8$$

and, since A_{KK} represents the energy of two $\mathrm{K^+}$ ions per cell, $-2E_{\mathrm{vac}} = A_{\mathrm{KK}}$ or

$$A_{\mathrm{KK}} = (A_{\mathrm{K''K''}}-A_{\mathrm{K'K'}})/(2x-1). \qquad (8$$

Relations of the type (85) and (89) are therefore expected to exist between our explicitly calcu lated coefficients $A_{\mathrm{K'K'}}$, $A_{\mathrm{K'K''}}$ and $A_{\mathrm{K''K''}}$ for various geometrical arrangements correspondin to interlayer charge x and the original coefficient A_{KK} obtained for the fully charged vermiculit

An alternative, but less satisfactory, approach can be considered to calculate $E(\mathrm{K–K})$ fo specific interlayer charge arrangements. This approach is mentioned here because it uses ou generic approach in a slightly different way to the above approach and yet achieves the sam results but less directly. It may, however, be useful in other contexts and for similar types (problem. The argument is formulated as follows. The magnitude of the $\mathrm{K^+}$–$\mathrm{K^+}$ interaction fo the uniform distribution of cations described above and having the reduced ion charge q_{K} = is given by equation (7)

$$E(\mathrm{K–K})_{\mathrm{uni}} = x^2A_{\mathrm{KK}}. \qquad (9$$

Each reduced interlayer charge in a vermiculite produces, as we have seen, specific arrang ments of interlayer cations and vacant sites for a given value of x. Equation (90) gives the $\mathrm{K^+}$–K interaction for a uniform array of charges situated in the interlayer and bearing a charge $+x$. we were to superimpose on this uniform array a lattice containing atoms in identical site positio but with some atoms (K′) bearing a charge $q_{\mathrm{K'}} = -x$ and the remaining atoms (K″) bearing charge $q_{\mathrm{K''}} = 1-x$, the effect of the combined lattice arrangement would be to create vacanci at sites K′ and fully charged interlayer $\mathrm{K^+}$ ions at K″ sites. Since the energy of the superimpose lattice can be made the subject of a separate calculation, we can obtain the $\mathrm{K^+}$–$\mathrm{K^+}$ interaction i this case in terms of our coefficients in the conventional way:

$$E(\mathrm{K–K})_{\mathrm{super}} = q^2_{\mathrm{K'}}A_{\mathrm{K'K'}}+q_{\mathrm{K'}}q_{\mathrm{K''}}A_{\mathrm{K'K''}}+q^2_{\mathrm{K''}}A_{\mathrm{K''K''}}, \qquad (9$$

and since $q_{\mathrm{K'}} = -x$ and $q_{\mathrm{K''}} = 1-x$ we have

$$E(\mathrm{K–K})_{\mathrm{super}} = x^2(A_{\mathrm{K'K'}}+A_{\mathrm{K'K''}}+A_{\mathrm{K''K''}})-x(A_{\mathrm{K'K''}}+2A_{\mathrm{K''K''}})+A_{\mathrm{K''K''}}. \qquad (9$$

We can clearly adjust our specification of the superimposable cell so that, for each value of superimposition of the new cell on a grid of uniform charges ($q_{\mathrm{K}} = x$) generates the precise inte layer geometry already specified for the given x. The corresponding $\mathrm{K^+}$- $\mathrm{K^+}$ interaction energ for the present interlayer arrangement required, $E(\mathrm{K–K})$, is then simply:

$$E(\mathrm{K–K}) = E(\mathrm{K–K})_{\mathrm{uni}}+E(\mathrm{K–K})_{\mathrm{super}}, \qquad (9$$

or, in terms of our coefficients,

$$E(\mathrm{K–K}) = x^2(A_{\mathrm{KK}}+A_{\mathrm{K'K'}}+A_{\mathrm{K'K''}}+A_{\mathrm{K''K''}}) -x(A_{\mathrm{K'K''}}+2A_{\mathrm{K''K''}})+A_{\mathrm{K''K''}}. \qquad (9$$

This procedure for the evaluation of the K^+–K^+ interactions could be used for interlayer charges within the range $1 > x \geqslant \tfrac{2}{3}$, the approximate relation of equation (90) being retained when the value of the interlayer charge $x \leqslant \tfrac{1}{3}$. An example of the operation of this calculation is given as case (A) below.

The examples that follow give explicit consideration to the superimposable cells, which we need to evaluate explicitly the K^+–K^+ interaction energy for specific values of x.

Table 16. Atomic coordinates of superimposable cell used to obtain K^+–K^+ interaction term, for potassium vermiculite having interlayer charge $x = \tfrac{15}{16}$, by simulating the interlayer K^+ arrangement shown in figure 21

(Formula, $K'_2K''_{30}$; space group, C2/m.)

atom type	number in unit cell	Wyckoff position	coordinates x	y	z
K′	2	2a	0.0000	0.0000	0.0000
K″	4	4e	0.2500	0.0000	0.0000
K″	2	2b	0.5000	0.0000	0.0000
K″	8	8j	0.1250	0.1250	0.0000
K″	8	8j	0.3750	0.1250	0.0000
K″	4	4g	0.0000	0.2500	0.0000
K″	4	4e	0.2500	0.2500	0.0000

Cell dimensions:
$a = 21.232$ Å, $b = 36.732$ Å, $c = 12.608$ Å;
$\cos\alpha = 0.0000$, $\cos\beta = -0.1406$, $\cos\gamma = 0.0000$.

Table 17. Jenkins–Hartman coefficients for K′K′, K′K″ and K″K″ interactions in the superimposable cell of table 16, for $x = \tfrac{15}{16}$

ij	$A_{ij}/(\mathrm{kJ\ mol^{-1}\ e^{-2}})$
K′K′	13.7
K′K″	17.3
K″K″	326.5
KK†	356.9

† From table 3, for K_A position.

Case A. $x = \tfrac{15}{16}$, $K_{1.88}Mg_6(Si_{3.06}Al_{0.94})_2O_{20}(OH)_4.(H_2O)_4$ *and*
$x = \tfrac{1}{16}$, $K_{0.12}Mg_6(Si_{3.94}Al_{0.06})_2O_{20}(OH)_4.(H_2O)_4$

If we regard K′ positions to be vacancies and K″ positions to be fully charged interlayer K^+ cations, the atomic coordinates of table 16 can be regarded as corresponding to the arrangement shown in figure 21 for $x = \tfrac{15}{16}$. From equation (86) the K^+–K^+ interaction energy is then given by

$$E(\mathrm{K{-}K})_{x=\frac{15}{16}} = A_{\mathrm{K''K''}} = 326.5\ \mathrm{kJ\ mol^{-1}}, \tag{95}$$

where the value $A_{\mathrm{K''K''}}$ is extracted from table 17, which gives the Jenkins–Hartman (1979) coefficients calculated for the cell specified in table 16. Interchange of vacancies and cations in figure 21 generates the complementary situation for $x = \tfrac{1}{16}$ and accordingly, from equation (87),

$$E(\mathrm{K{-}K})_{x=\frac{1}{16}} = A_{\mathrm{K'K'}} = 13.7\ \mathrm{kJ\ mol^{-1}} \tag{96}$$

where the $A_{\mathrm{K'K'}}$ value is given in table 17.

If we choose to adopt the alternative way of calculating the energy $E(\mathrm{K{-}K})_{x=\frac{15}{16}}$ using th principle, described above, of superimposable cells, we have to regard the cell specified in table 1 and the results listed in table 17 differently. Equation (90) gives the $\mathrm{K^+{-}K^+}$ interaction for th cell having the arrangement of interlayer cations shown in figure 6, each bearing a charge which for $x = \frac{15}{16}$ leads to

$$E(\mathrm{K{-}K})_{\substack{\mathrm{uni} \\ x=\frac{15}{16}}} = A_{\mathrm{KK}}x^2 = 356.9x^2 = 313.7\,\mathrm{kJ\,mol^{-1}}. \qquad (9$$

If we now place a charge on K′ equal to $-\frac{15}{16}$ and a charge of $+\frac{1}{16}$ on K″ in the unit cell describe in table 16, the energy is given by

$$E(\mathrm{K{-}K})_{\mathrm{super}} = (-\tfrac{15}{16})^2 A_{\mathrm{K'K'}} + \tfrac{1}{16}(-\tfrac{15}{16})\,A_{\mathrm{K'K''}} + (\tfrac{1}{16})^2 A_{\mathrm{K''K''}}, \qquad (9$$

which with the values of the coefficients given in table 17 leads to

$$E(\mathrm{K{-}K})_{\mathrm{super}} = 12.3\,\mathrm{kJ\,mol^{-1}}. \qquad (9$$

Superimposition of the above cell charge arrangement on a lattice possessing the uniform ce charge configuration leads to a cell arrangement corresponding to that shown in figure 21 whe fully charged ions and vacancies are located at the same place. The total interaction energy given by equation (93) and leads to

$$E(\mathrm{K{-}K})_{x=\frac{15}{16}} = 313.7 + 12.3 = 326.0\,\mathrm{kJ\,mol^{-1}}, \qquad (10$$

which should be compared with equation (95). The above superimposition calculation can b repeated now to obtain the $\mathrm{K^+{-}K^+}$ interaction term for $x = \frac{1}{16}$ by taking the superimposed ce to have $q_{\mathrm{K'}} = +\frac{15}{16}$ and $q_{\mathrm{K''}} = -\frac{1}{16}$, this cell arrangement being superimposed on one consistin of a uniformly charged cell where each cation bears a charge $+\frac{1}{16}$. In the latter cell

$$E(\mathrm{K{-}K})_{\substack{\mathrm{uni} \\ x=\frac{1}{16}}} = A_{\mathrm{KK}}x^2 = 356.9x^2 = 1.3\,\mathrm{kJ\,mol^{-1}}, \qquad (10$$

whereas the superimposed cell corresponds to that considered previously except that the signs the charges on K′ and K″ have been reversed. The energy of the superimposed cell will remai unchanged by this operation and is therefore given by equation (99). Addition of the two cel (corresponding to figure 21 with vacancies and occupancies reversed for the cations) leads to value

$$E(\mathrm{K{-}K})_{x=\frac{1}{16}} = 1.3 + 12.3 = 13.6\,\mathrm{kJ\,mol^{-1}}, \qquad (10$$

in close agreement with the calculation of equation (96).

In what follows, further description of the superimposition calculation will not be given, sin the coefficients $A_{\mathrm{K'K'}}$ and $A_{\mathrm{K''K''}}$ give the required interaction energies directly. A test of t relations (85) and (89) in respect of the coefficients of table 17 is used to ensure that convergen has been achieved in their calculation. Similar tests have been made for other values of x but w not be further described.

Case B. $x = \frac{11}{12}$, $\mathrm{K_{1.84}Mg_6(Si_{3.08}Al_{0.92})_2O_{20}(OH)_4.(H_2O)_4}$ *and*

$x = \frac{1}{12}$, $\mathrm{K_{0.16}Mg_6(Si_{3.92}Al_{0.08})_2O_{20}(OH)_4.(H_2O)_4}$

The cell used for this calculation is described in table 18, and the results obtained for t coefficients of equation (82) are listed in table 19. Using equations (86) and (87) we find

$$E(\mathrm{K{-}K})_{x=\frac{11}{12}} = A_{\mathrm{K''K''}} = 318.9\,\mathrm{kJ\,mol^{-1}} \qquad (10$$

and

$$E(\mathrm{K{-}K})_{x=\frac{1}{12}} = A_{\mathrm{K'K'}} = 20.9\,\mathrm{kJ\,mol^{-1}}. \qquad (10$$

Equation (103) thus corresponds to the energy of the cation and vacancy arrangements illustrated in figure 20 while equation (104) gives the K^+–K^+ interaction when mutual exchange of cations for vacancies and vice versa is effected on the arrangement in figure 20.

TABLE 18. ATOMIC COORDINATES OF SUPERIMPOSABLE CELL USED TO OBTAIN K^+–K^+ INTERACTION TERMS, FOR POTASSIUM VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{11}{12}$, BY SIMULATING THE INTERLAYER K^+ ARRANGEMENT SHOWN IN FIGURE 20

(Formula, $K'_2K''_{22}$; space group, C2/m.)

atom type	number in unit cell	Wyckoff position	coordinates		
			x	y	z
K′	2	2a	0.0000	0.0000	0.0000
K″	4	4i	0.1667	0.0000	0.0000
K″	4	4i	0.3333	0.0000	0.0000
K″	2	2b	0.5000	0.0000	0.0000
K″	8	8j	0.0833	0.2500	0.0000
K″	4	4e	0.2500	0.2500	0.0000

Cell dimensions:

$a = 31.848$ Å, $b = 18.366$ Å, $c = 12.608$ Å;

$\cos\alpha = 0.0000$, $\cos\beta = -0.1406$, $\cos\gamma = 0.0000$.

TABLE 19. JENKINS–HARTMAN COEFFICIENTS FOR K′K′, K′K″ AND K″K″ INTERACTIONS IN SUPERIMPOSABLE CELL OF TABLE 18, FOR $x = \frac{11}{12}$

ij	$A_{ij}/(\text{kJ mol}^{-1}\,\text{e}^{-2})$
K′K′	20.9
K′K″	17.8
K″K″	318.9
KK†	356.9

† From table 3, for K_A position.

Case C. $x = \frac{8}{9}$, $K_{1.78}Mg_6(Si_{3.11}Al_{0.89})_2O_{20}(OH)_4.(H_2O)_4$ *and*

$x = \frac{1}{9}$, $K_{0.22}Mg_6(Si_{3.89}Al_{0.11})_2O_{20}(OH)_4.(H_2O)_4$

Table 20 gives the atomic coordinates and cell constants used to compute the interlayer cation interaction terms for $x = \frac{8}{9}$ and $x = \frac{1}{9}$. Table 21 gives the Jenkins–Hartman (1979) coefficients obtained. Using equations (86) and (87) we have

$$E(\text{K–K})_{x=\frac{8}{9}} = A_{K''K''} = 309.4\,\text{kJ mol}^{-1}, \tag{105}$$

which is the K^+–K^+ interaction exhibited by the cation and vacancy arrangements illustrated in figure 19. Further,

$$E(\text{K–K})_{x=\frac{1}{9}} = A_{K'K'} = 31.3\,\text{kJ mol}^{-1}, \tag{106}$$

which corresponds to the geometrical arrangement in figure 19 when cations and vacancies are interchanged on each site.

Case D. $x = \frac{3}{4}$, $K_{1.50}Mg_6(Si_{3.25}Al_{0.75})_2O_{20}(OH)_4.(H_2O)_4$ *and*

$x = \frac{1}{4}$, $K_{0.50}Mg_6(Si_{3.75}Al_{0.25})_2O_{20}(OH)_4.(H_2O)_4$

Table 22 defines the cell used to calculate E for $x = \frac{3}{4}$ and $x = \frac{1}{4}$. Table 23 gives the coefficients generated. Using equations (86) and (87) we have

$$E(\text{K–K})_{x=\frac{3}{4}} = A_{K''K''} = 270.0\,\text{kJ mol}^{-1}, \tag{107}$$

Table 20. Atomic coordinates of superimposable cell used to obtain K^+–K^+ interactio terms, for potassium vermiculite having interlayer charge $x = \frac{8}{9}$, by simulatin the interlayer K^+ arrangement shown in figure 19

(Formula, $K'_2K''_{16}$; space group, C2/m.)

				coordinates	
atom type	number in unit cell	Wyckoff position	x	y	z
K′	2	2a	0.0000	0.0000	0.0000
K″	4	4i	0.3333	0.0000	0.0000
K″	8	8j	0.1667	0.1667	0.0000
K″	4	4g	0.5000	0.1667	0.0000

Cell dimensions:

$a = 15.924$ Å, $b = 27.549$ Å, $c = 12.608$ Å;
$\cos \alpha = 0.0000$, $\cos \beta = -0.1406$, $\cos \gamma = 0.0000$.

Table 21. Jenkins–Hartman coefficients for K′K′, K′K″ and K″K″ interactions in the superimposable cell of table 20, for $x = \frac{8}{9}$

ij	$A_{ij}/(\text{kJ mol}^{-1}\ \text{e}^{-2})$
K′K′	31.3
K′K″	16.8
K″K″	309.4
KK†	356.9

† From table 3, for K_A position.

Table 22. Atomic coordinates of superimposable cell used to obtain K^+–K^+ interactio terms, for potassium vermiculite having a charge $x = \frac{3}{4}$, by simulating the inte layer K^+ arrangement shown in figure 18

(Formula, $K'_2K''_6$; space group, C2/m.)

				coordinates	
atom type	number in unit cell	Wyckoff position	x	y	z
K′	2	2a	0.0000	0.0000	0.0000
K″	2	2b	0.5000	0.0000	0.0000
K″	4	4e	0.2500	0.2500	0.0000

Cell dimensions:

$a = 10.616$ Å, $b = 18.366$ Å, $c = 12.608$ Å;
$\cos \alpha = 0.0000$, $\cos \beta = -0.1406$, $\cos \gamma = 0.0000$.

Table 23. Jenkins–Hartman coefficients for K′K′, K′K″ and K″K″ interactions in superimposable cell of table 22, for $x = \frac{3}{4}$

ij	$A_{ij}/(\text{kJ mol}^{-1}\ \text{e}^{-2})$
K′K′	91.3
K′K″	−3.8
K″K″	270.0
KK†	356.9

† From table 3, for K_A position.

which is the K^+–K^+ interaction exhibited by the cation arrangement illustrated in figure 18. Further,

$$E(\mathrm{K{-}K})_{x=\frac{1}{4}} = \mathrm{A}_{\mathrm{K'K'}} = 91.3\,\mathrm{kJ\,mol^{-1}}, \tag{108}$$

which corresponds to interchange of cations and vacancies illustrated in figure 19.

TABLE 24. ATOMIC COORDINATES OF SUPERIMPOSABLE CELL USED TO OBTAIN K^+–K^+ INTERACTION TERMS, FOR POTASSIUM VERMICULITE HAVING INTERLAYER CHARGE $x = \frac{2}{3}$, BY SIMULATING THE INTERLAYER K^+ ARRANGEMENT SHOWN IN FIGURE 9

(Formula, $K'_2K''_4$; space group, C2/m.)

			coordinates		
atom type	number in unit cell	Wyckoff position	x	y	z
K′	2	2a	0.0000	0.0000	0.0000
K″	4	4i	0.3333	0.0000	0.0000

Cell dimensions:

$a = 15.924$ Å, $b = 9.183$ Å, $c = 12.608$ Å;

$\cos\alpha = 0.0000$, $\cos\beta = -0.1406$, $\cos\gamma = 0.0000$.

TABLE 25. JENKINS–HARTMAN COEFFICIENTS FOR K′K′, K′K″ AND K″K″ INTERACTIONS IN SUPERIMPOSABLE CELL OF TABLE 24 FOR $x = \frac{2}{3}$

ij	$A_{ij}/(\mathrm{kJ\ mol^{-1}\ e^{-2}})$
K′K′	129.7
K′K″	−20.6
K″K″	248.6
KK†	356.9

† From table 3, for K_A position.

Case E. $x = \frac{2}{3}$, $K_{1.34}Mg_6(Si_{3.33}Al_{0.67})_2O_{20}(OH)_4.(H_2O)_4$ *and*
$x = \frac{1}{3}$, $K_{0.66}Mg_6(Si_{3.67}Al_{0.33})_2O_{20}(OH)_4.(H_2O)_4$

Table 24 gives the atomic coordinates and cell constants used to calculate the K^+–K^+ interactions for $x = \frac{2}{3}$ and $x = \frac{1}{3}$. The generated coefficients are listed in table 25. Using equations (86) and (87) we have

$$E(\mathrm{K{-}K})_{x=\frac{2}{3}} = A_{\mathrm{K''K''}} = 248.6\,\mathrm{kJ\,mol^{-1}}, \tag{109}$$

which is the interaction illustrated in figure 9. Further,

$$E(\mathrm{K{-}K})_{x=\frac{1}{3}} = A_{\mathrm{K'K'}} = 129.7\,\mathrm{kJ\,mol^{-1}}, \tag{110}$$

which corresponds to the interlayer geometry shown in figure 9 with cation and vacant sites interchanged.

Case F. $x = \frac{1}{7}$, $K_{0.28}Mg_6(Si_{3.86}Al_{0.14})_2O_{20}(OH)_4.(H_2O)_4$ *and*
$x = \frac{1}{9}$, $K_{0.22}Mg_6(Si_{3.89}Al_{0.11})_2O_{20}(OH)_4.(H_2O_4)$.

Equation (81) is used to evaluate $E(\mathrm{K{-}K})$ for $x = \frac{1}{7}$ and $x = \frac{1}{9}$. Taking the centrally placed (K_A) position of K^+ in the interlayer to generate A_{KK} we have

$$E(\mathrm{K{-}K}) = 356.9\,\mathrm{kJ\,mol^{-1}}, \tag{111}$$

leading to

$$E(\mathrm{K{-}K})_{x=\frac{1}{7}} = 134.9\,\mathrm{kJ\,mol^{-1}}, \tag{112}$$

$$E(\mathrm{K{-}K})_{x=\frac{1}{9}} = 119.0\,\mathrm{kJ\,mol^{-1}}. \tag{113}$$

Summary of interactions calculated

Table 26 summarizes the values obtained for E(K–K) for the various interlayer charges, x, an compares the results obtained with the approximate value generated by equation (81). The tab shows that for x in the range $\frac{1}{9} \leqslant x < \frac{3}{4}$, E(K–K) deviates markedly from $\sqrt{x}A_{KK}$, so justifyin the explicit evaluation of E(K–K) for these cases as performed in the foregoing cases A–E.

TABLE 26. E(K–K) AS OBTAINED FROM EXPLICIT CALCULATION COMPARED WITH THE VALUE GENERATED BY USING EQUATION (81) FOR x IN THE RANGE $1 \geqslant x \geqslant 0$

x	$I_0 = E$(K–K)/(kJ mol^{-1})	$\sqrt{x}A_{KK}$/(kJ mol^{-1})
1	356.9	356.9
$\frac{16}{16}$	326.5	345.6
$\frac{11}{12}$	318.9	341.7
$\frac{8}{9}$	309.4	336.4
$\frac{3}{4}$	270.0	309.1
$\frac{2}{3}$	248.6	291.4
$\frac{1}{3}$	129.7	206.1
$\frac{1}{4}$	91.3	178.4
$\frac{1}{7}$	46.0	134.9
$\frac{1}{9}$	31.3	119.0
0	0	0

(v) *Total interlayer interactions*

If we add the K^+–K^+, K^+–H_2O and H_2O–H_2O interlayer interactions these take the parametr form

$$E(\mathrm{K{-}H_2O}) + E(\mathrm{H_2O{-}H_2O}) + E(\mathrm{K{-}K}) = \sum_{i=0}^{2} I_i q^i_{\mathrm{H''}} \qquad (11$$

where the coefficient I_0 is given in table 26, and the coefficients I_1 and I_2 are given in table 15.

(vi) *Calculation of total electrostatic energy of vermiculites*, $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$, *f* $x < 1$

Equation (37) gives the electrostatic energy, $U'_{\mathrm{elec}}(K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4)$, fc the process whereby potassium vermiculite, having a fully occupied interlayer of cation charg on every site equal to x and the arrangement of water molecules as indicated in figure 6, is co verted to gaseous ions and four discrete water molecules. The previous §§ 5 (*c*iii) and 5 (*c*iv) hav been concerned with the specific evaluation of K–K, K–H_2O and H_2O–H_2O interactions fc explicit interlayer geometries. To calculate $U'_{\mathrm{elec}}(K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4)$ fc decreasing x, while taking full account of the interlayer geometry, we can modify equation (37

Two modifications are required. First, to take account of the ordering of the cations, we om the term x^2A_{KK} (which is appropriate only when all cation sites in the interlayer are fully occupie (no vacancies) with cations of charge x) and replace it by the E(K–K) term specifically calculate for individual x-values. Secondly, to account for the varying arrangements of water dipol encountered as x is decreased, we must remove from equation (37) K–H_2O and H_2O–H_2O inte actions applicable only to the arrangement shown in figure 6, and replace these terms by th specific values of E(K–H_2O) and E(H_2O–H_2O) calculated for the specific x-values. We perfor this latter modification of equation (37) by eliminating terms involving $A_{KO''}$ and A_{K} (specifying the original H_2O–K interactions), by deleting the final term in $q^2_{H''}$ (specifying th original H_2O–H_2O interactions), the self-energies of the water molecules having already bee removed when $U_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4)$ in equation (36) was replaced by $U'_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4)$ in equation (37). Finally, we complete the modification by adding the specific terms $E(\mathrm{K{-}H_2O})$ and $E(\mathrm{H_2O{-}H_2O})$ calculated above (table 15) for specific values of x.

Accordingly, for the process

$$\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4(\mathrm{c})$$

$$\xrightarrow{U'_{\text{elec}}} 2\mathrm{K}^{x+}(\mathrm{g}) + 6\mathrm{Mg}^{2+}(\mathrm{g}) + (8-2x)\,\mathrm{Si}^{4+}(\mathrm{g}) + 24\mathrm{O}^{2-}(\mathrm{g}) + 4\mathrm{H}^+(\mathrm{g}) + 4\mathrm{H_2O}(\mathrm{g}),$$

we have

$$U'_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4)\ (\mathrm{c})$$
$$= x^2(181.3 - \tfrac{1}{4}A_{\mathrm{KT}}) + x(4A_{\mathrm{KT}} + 2A_{\mathrm{KX}} + 2A_{\mathrm{KX'}} + A_{\mathrm{KH}} - 2A_{\mathrm{KO}} - 2A_{\mathrm{KO'}} - 8692.2 + 168.5\,q_{\mathrm{H''}})$$
$$+ 157\,246.7 - 31.3\,q_{\mathrm{H''}} + E(\mathrm{K{-}K}) + E(\mathrm{K{-}H_2O}) + E(\mathrm{H_2O{-}H_2O}), \qquad (115)$$

whereupon, using table 3 and equation (114), and assuming the interlayer K^+ cations to be in the centralized position, $\mathrm{K_A}$,

$$U'_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4)$$
$$= -140.0x^2 + [168.5\,q_{\mathrm{H''}} - 7784.9]x + I_2 q^2_{\mathrm{H''}} + (I_1 - 31.3)\,q_{\mathrm{H''}} + (157\,246.7 + I_0). \qquad (116)$$

TABLE 27. $U'_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4)$ IN kJ mol^{-1} AS A FUNCTION OF x AND $q_{\mathrm{H''}}$

x \ $q_{\mathrm{H''}}$	1	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	0
1	149758.4	149809.3	149813.0	149789.2	149769.4	149678.7
$\frac{15}{16}$	150650.9	150524.4	150399.1	150316.2	150274.9	150151.9
$\frac{11}{12}$	150883.0	150738.5	150594.5	150499.6	150452.4	150311.8
$\frac{8}{9}$	151193.1	151023.2	150855.3	150744.6	150689.4	150525.6
$\frac{3}{4}$	152181.2	152080.4	151949.9	151846.3	151789.5	151599.2
$\frac{2}{3}$	152538.8	152565.9	152525.2	152461.0	152417.7	152243.2
$\frac{1}{3}$	155418.9	155208.1	155029.2	154927.3	154881.6	154765.8
$\frac{1}{4}$	155624.5	155612.2	155568.0	155520.6	155491.5	155383.0
$\frac{1}{7}$	156663.6	156554.4	156451.7	156387.1	156355.9	156266.6
$\frac{1}{9}$	156705.6	156625.5	156550.8	156501.8	156478.5	156411.3
0	157215.4	157223.2	157231.1	157236.3	157238.9	157246.7

Table 27 gives the values of $U'_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4)$ for various values of $q_{\mathrm{H''}}$ and x. For $1 \geqslant x \geqslant \frac{1}{9}$, $U'_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_4)$ *decreases* with *decreasing* $q_{\mathrm{H''}}$, the charge on the hydrogen atoms of the water. However, for $x = 0$ (i.e. in the absence of interlayer cations) $U'_{\text{elec}}(\mathrm{K}_{2x}\mathrm{Mg}_6(\mathrm{Si}_{4-x}\mathrm{Al}_x)_2\mathrm{O}_{20}(\mathrm{OH})_4\,.\,(\mathrm{H_2O})_2)$ *increases* with *decreasing* $q_{\mathrm{H''}}$.

It is not necessary that the calculations for $x < 1$ should be restricted to examining the case where the interlayer cations are centrally placed and remain in positions $\mathrm{K_A}$ (figure 1). Any of the other configurations ($\mathrm{K_B}$, $\mathrm{K_C}$, $\mathrm{K_D}$, $\mathrm{K_E}$, etc.) could be chosen. By using the appropriate coefficients A_{KT}, A_{KX}, $A_{\mathrm{KX'}}$, A_{KH}, A_{KO}, $A_{\mathrm{KO'}}$ as given in table 3 for each interlayer K^+ position, $\mathrm{K_B}$, $\mathrm{K_C}$, $\mathrm{K_D}$ or $\mathrm{K_E}$, we then need to calculate the specific $\mathrm{K^+{-}K^+}$, $\mathrm{K^+{-}H_2O}$ and $\mathrm{H_2O{-}H_2O}$ interactions for the non-centralized K^+ ions, which influence the orientation of the water dipoles and hence $E(\mathrm{H_2O{-}H_2O})$ differently for each position taken for K^+. The attendant tilting of the water dipoles out of the plane of the oxygen atoms would be a major consideration.

(*d*) *Intercalation energy of* $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4$, *for various values of* x, *at negligible pressure*

The energy of the process

$$K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4(c) + 4H_2O(g) \xrightarrow{\Delta U'_{\text{inter}}} K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4(c),$$
$$\text{(expanded phlogopite)} \qquad\qquad \text{(vermiculite)}$$

is given by

$$\Delta U'_{\text{inter}} = U_{\text{elec}}(K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4) - U'_{\text{elec}}(K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4), \qquad (117)$$

where the second term corresponds to that given in equation (116) and the first term corresponds to that given in equation (116) under the substitution $q_{H''} = 0$. Hence (in kJ mol^{-1})

$$\Delta U'_{\text{inter}} = -I_2 q^2_{H''} - (I_1 - 31.3 + 168.5x)\, q_{H''}, \qquad (118)$$

which for $x = 1$ reduces to equation (29) as is expected. The values of $\Delta U'_{\text{inter}}$ are given in table 28.

Table 28. Energy of intercalation, $\Delta U'_{\text{inter}}$, of four molecules of H_2O into an expanded mica, in kJ mol^{-1}, as a function of x and $q_{H''}$

x \ $q_{H''}$	1	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$
1	−79.7	−130.6	−134.3	−110.5	−90.7
$\frac{15}{16}$	−499.0	−372.5	−247.2	−164.3	−123.0
$\frac{11}{12}$	−571.2	−426.2	−282.7	−187.8	−140.6
$\frac{8}{9}$	−667.5	−497.6	−329.7	−219.0	−163.8
$\frac{3}{4}$	−582.0	−481.2	−350.7	−247.1	−190.3
$\frac{2}{3}$	−296.6	−322.7	−282.0	−217.8	−174.5
$\frac{1}{3}$	−653.1	−442.3	−263.4	−161.5	−115.8
$\frac{1}{4}$	−241.5	−229.2	−185.0	−137.6	−108.5
$\frac{1}{7}$	−397.0	−287.8	−185.1	−120.5	−89.3
$\frac{1}{9}$	−294.3	−214.2	−138.8	−90.5	−67.2
$\frac{1}{12}$	−332.1	−221.9	−129.8	−78.5	−55.9
$\frac{1}{16}$	−197.9	−136.2	−82.6	−51.5	−6.2
0	31.3	23.5	15.6	10.4	7.8

The intercalation energy of the process

$$2K_xMg_3(Si_{4-x}Al_x)O_{10}(OH)_4(c) + 4H_2O(g) \xrightarrow{\Delta U^{(g)}_{\text{inter}}} K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4.(H_2O)_4(c),$$

is given by equation (35)

$$\Delta U^{(g)}_{\text{inter}} = \Delta U'_{\text{inter}} + \Delta U_{\text{exp}}, \qquad (119)$$

where ΔU_{exp} is the expansion energy as defined in equation (34) for the process

$$2K_xMg_3(Si_{4-x}Al_x)O_{10}(OH)_2(c) \xrightarrow{\Delta U_{\text{exp}}} \underset{\text{(expanded)}}{K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4(c)}.$$

The expansion energy of one mole of $K_xMg_3(Si_{4-x}Al_x)O_{10}(OH)_2(c)$ is given by equation (5) o our previous paper (Jenkins & Hartman 1980) for $a = 2.5$ Å. In the present context therefore:

$$\Delta U_{\text{exp}} = 2U^{\Delta}_{\text{exp}} = 2D_1x^2 + 2D_2x + 2D_3, \qquad (120)$$

where the coefficients D_1–D_3 are given in table 6 of Jenkins & Hartman (1980). Referring to this paper we have (in kJ mol^{-1})

$$\Delta U_{\text{exp}} = 421.0x^2 - 150.0x - 7.6, \qquad (121)$$

the values for which are listed in table 29.

TABLE 29. ΔU_{exp}, FOR VARIOUS VALUES OF x, FOR THE PROCESS

$$2\text{K}_x\text{Mg}_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2(\text{c}) \longrightarrow \text{K}_{2x}\text{Mg}_6(\text{Si}_{4-x}\text{Al}_x)_2\text{O}_{20}(\text{OH})_4(\text{c})$$

x	$\Delta U_{\text{exp}}/(\text{kJ mol}^{-1})$	x	$\Delta U_{\text{exp}}/(\text{kJ mol}^{-1})$
1	263.4	$\frac{1}{4}$	−18.9
$\frac{15}{16}$	221.8	$\frac{1}{7}$	−20.4
$\frac{11}{12}$	208.7	$\frac{1}{9}$	−19.1
$\frac{8}{9}$	191.7	$\frac{1}{12}$	−17.2
$\frac{3}{4}$	116.7	$\frac{1}{16}$	−15.3
$\frac{2}{3}$	79.5	0	−7.6
$\frac{1}{3}$	−10.8		

TABLE 30. ENERGY OF INTERCALATION, $\Delta U_{\text{inter}}^{(\text{g})}$, OF FOUR MOLECULES OF H_2O AT NEGLIGIBLE PRESSURE INTO VERMICULITE, WITH THE EXPANSION ENERGY TAKEN INTO ACCOUNT, IN kJ mol^{-1}, AS A FUNCTION OF x AND $q_{\text{H}''}$

x \\ $q_{\text{H}''}$	1	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$
1	+183.7	+132.8	+129.1	+152.9	+172.7
$\frac{15}{16}$	−277.2	−150.7	−25.5	+57.4	+98.7
$\frac{11}{12}$	−362.5	−217.5	−74.0	+20.9	+68.1
$\frac{8}{9}$	−475.8	−305.9	−138.0	−27.3	+27.9
$\frac{3}{4}$	−465.3	−364.5	−234.0	−130.4	−73.6
$\frac{2}{3}$	−271.1	−243.2	−202.5	−138.3	−95.0
$\frac{1}{3}$	−663.9	−453.1	−274.2	−172.3	−126.6
$\frac{1}{4}$	−260.4	−248.1	−203.9	−156.5	−127.4
$\frac{1}{7}$	−417.4	−308.2	−205.5	−140.9	−109.7
$\frac{1}{9}$	−313.4	−233.3	−157.9	−109.6	−86.3
$\frac{1}{12}$	−349.3	−239.1	−147.0	−95.7	−73.0
$\frac{1}{16}$	−213.3	−151.5	−98.0	−66.8	−52.6
0	23.7	15.9	8.0	2.8	0.2

Combination of equations (118) and (121) leads to (in kJ mol^{-1})

$$\Delta U_{\text{inter}}^{(\text{g})} = 421.0\,x^2 - x(168.5\,q_{\text{H}''} + 150.0) - I_2 q_{\text{H}''}^2 - (I_1 - 31.3)\,q_{\text{H}''} - 7.6 \qquad (122)$$

and the values of $\Delta U_{\text{inter}}^{(\text{g})}$ generated for explicit values of x in $\text{K}_{2x}\text{Mg}_6(\text{Si}_{4-x}\text{Al}_x)_2\text{O}_{20}(\text{OH})_4 . (\text{H}_2\text{O})_4$ are listed in table 30.

In figure 25 we show the variation of $\Delta U_{\text{inter}}^{(\text{g})}$ as a function of x for $q_{\text{H}''} = \frac{1}{2}, \frac{1}{3}$ and $\frac{1}{4}$. The curves are based on the results given in table 15 and incorporated into equation (122). The term $\Delta U_{\text{inter}}^{(\text{g})}$ represents the intercalation process whereby H_2O molecules in the gas phase are incorporated into the expanded structure. When $\Delta U_{\text{inter}}^{(\text{g})}$ is negative our prediction is that intercalation will proceed spontaneously, at least from a thermodynamic standpoint, and hence the abscissa of the graph is labelled "intercalation limit H_2O(g)".

If we consider the process:

$$\underset{(\text{unexpanded})}{2\text{K}_x\text{Mg}_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2(\text{c})} + 4\text{H}_2\text{O}(\text{l}) \xrightarrow{\Delta U_{\text{inter}}^{(1)}} \text{K}_{2x}\text{Mg}_6(\text{Si}_{4-x}\text{Al}_x)_2\text{O}_{20}(\text{OH})_4 . (\text{H}_2\text{O})_4(\text{c})$$

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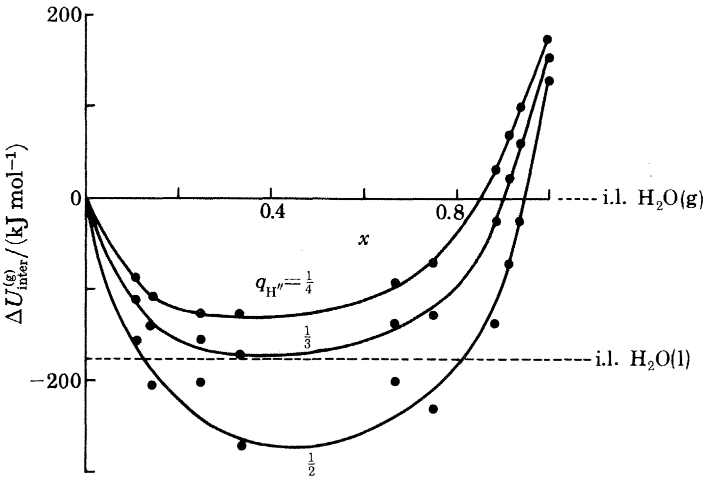

FIGURE 25. Variation of $\Delta U^{(g)}_{\text{inter}}$ with x for values of water molecule hydrogen charge, $q_{H''}$, of $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{4}$. Intercalation limits (i.l.) for liquid and gaseous H_2O molecules are shown. For $\Delta U^{(g)}_{\text{inter}}$-values below these limits intercalation is possible.

we have

$$\Delta U^{(g)}_{\text{inter}} = \Delta U^{(l)}_{\text{inter}} + 4\Delta H_{\text{vap}}(H_2O)(l) \tag{123}$$

where $\Delta H_{\text{vap}}(H_2O)(l)$ is the enthalpy of vaporization of water which, from standard sources (Wagman *et al.* 1968) has a value 44 kJ mol^{-1}. Hence the intercalation energy for $H_2O(l)$ requires 176 kJ mol^{-1} more than that for intercalation of gaseous water. In figure 25 we show the intercalation limit for $H_2O(l)$ for the above process. For hydrogen charges less than or equal to $\frac{1}{3}$, no intercalation of liquid water is predicted as possible, while values of $q_{H''}$ in excess of $\frac{1}{3}$ permit intercalation of water.

6. DISCUSSION

This study of a potassium vermiculite, $K_{2x}Mg_6(Si_{4-x}Al_x)_2O_{20}(OH)_4 . (H_2O)_4$ has provided intercalation energies. These energies are given by equation (122) and are presented numerically in table 30, for various values of x and $q_{H''}$. To appreciate the significance of the various contributions we write equation (122) in the form

$$\Delta U^{(g)}_{\text{inter}} = -E(\text{K–H}_2\text{O}) - E(\text{H}_2\text{O–H}_2\text{O}) - E(\text{H}_2\text{O–silicate layer}) + \Delta U_{\text{exp}} \tag{124}$$

where

$$E(\text{K–H}_2\text{O}) = I_1 q_{H''}, \tag{125}$$

$$E(\text{H}_2\text{O–H}_2\text{O}) = I_2 q^2_{H''}, \tag{126}$$

$$E(\text{H}_2\text{O–silicate layer}) = (168.5x - 31.3)\, q_{H''}, \tag{127}$$

while ΔU_{exp} is given by equation (121). The first three terms represent the energy gained by the process of intercalation of water into an expanded mica, while the final term represents the energy of expansion.

Tables 31 and 29 show the values of U_W and ΔU_{exp}:

$$U_W = -E(\text{K–H}_2\text{O}) - E(\text{H}_2\text{O–H}_2\text{O}) - E(\text{H}_2\text{O–silicate layer}), \tag{128}$$

$$\Delta U^{(g)}_{\text{inter}} = U_W + \Delta U_{\text{exp}}, \tag{129}$$

for $q_{\mathrm{H}''} = \frac{1}{3}$. Figure 26 shows the energy gain, U_{W}, of equation (128) and ΔU_{exp}, the expansion energy (table 29, $q_{\mathrm{H}''} = \frac{1}{3}$), which make up $\Delta U^{(\mathrm{g})}_{\mathrm{inter}}$ for $q_{\mathrm{H}''} = \frac{1}{3}$. It is clear that ΔU_{exp}, plays an important role only when $x > 0.4$. For $x \leqslant 0.4$, the intercalation energy $\Delta U^{(\mathrm{g})}_{\mathrm{inter}} \approx U_{\mathrm{W}}$, the interaction energy of the water molecules with the expanded structure. The predominant term is $E(\mathrm{K{-}H_2O})$, while the interaction of the water molecules with the silicate layer is vanishingly small. It is interesting to note the irregular way in which $E(\mathrm{H_2O{-}H_2O})$ varies with x, owing of course to the various assignments we adopted for the water dipoles. In spite of this the energy gain emerges as a rather smooth function as x is varied; this in turn comes about because $E(\mathrm{K{-}H_2O})$ changes irregularly.

Table 31. Energy gain by intercalation of water into expanded mica, U_{W}, for $q_{\mathrm{H}''} = \frac{1}{3}$

x	$U_{\mathrm{W}}/(\mathrm{kJ\ mol^{-1}})$	x	$U_{\mathrm{W}}/(\mathrm{kJ\ mol^{-1}})$
1	−110.5	$\frac{1}{4}$	−137.6
$\frac{15}{16}$	−164.4	$\frac{1}{7}$	−120.5
$\frac{11}{12}$	−187.8	$\frac{1}{9}$	−90.5
$\frac{8}{9}$	−219.0	$\frac{1}{12}$	−78.5
$\frac{3}{4}$	−247.1	$\frac{1}{16}$	−51.5
$\frac{2}{3}$	−217.8	0	10.4
$\frac{1}{3}$	−161.5		

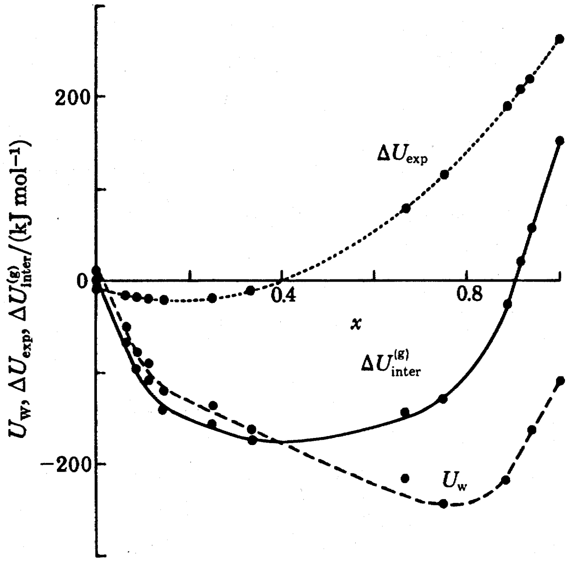

Figure 26. Component terms U_{W} and ΔU_{exp} of $\Delta U^{(\mathrm{g})}_{\mathrm{inter}}$. The figure shows the variation of component terms and the composite term as a function of x for $q_{\mathrm{H}''} = \frac{1}{3}$.

When we take $q_{\mathrm{H}''} = \frac{1}{2}$ it is seen from table 30 that the interaction energy is no longer a smooth function of x. The specific values of x ($\frac{1}{3}$ and $\frac{3}{4}$) associated with a special arrangement of water dipoles favour the intercalation. The interaction of water molecules with the silicate layer becomes a relatively important factor only when $x > 0.5$ in this case.

With regard to the absolute values of the energies calculated, the following remarks must be made. First, we have considered only the electrostatic part of the lattice energies, neglecting the Born–Mayer repulsion and dispersion interactions. Since repulsion energies are larger than the corresponding dispersion energies the absolute energies will decrease if these additional terms are included. Secondly, the calculated energies have been parametrized (purposely) as functions of the charge distribution of the water molecules. We neglected the quadrupole moment and induced dipole moment in H_2O. In procedures for determining the hydrogen positions in crystal structures (see Jenkins & Waddington 1982) from lattice energy studies it has been common practice to take $q_{H''} = \frac{1}{2}$. In view of the results presented in figure 26 a closer estimation of $q_{H''}$ is necessary to interpret the results more fully. Thirdly, the actual charge distribution within the silicate sheet plays a role. This affects the charges q_T and q_0, and from the electroneutrality condition we have

$$q_T = \tfrac{1}{4}(10q_0 + x + 4). \tag{130}$$

The interaction energy of H_2O molecules with only the T and O ions becomes, if we adopt the coefficients in table 3 (in $kJ\,mol^{-1}$),

$$E(H_2O\text{–}TO) = [51.5q_O + 168.5(x+4)]q_{H''}. \tag{131}$$

If we take $q_O = -1.5$ instead of -2.0 and $q_{H''} = 0.5$, this interaction energy changes by approximately $13\,kJ\,mol^{-1}$, and the low magnitude of this energy difference justifies the neglect of this factor in the present calculations.

Finally, we wish to compare these theoretical results with the experimental data. It is well known that Mg–vermiculites with a basal spacing of 14.4 Å collapse to 10.0 Å when the interlayer Mg^{2+} ions are exchanged against K^+ ions. Not all vermiculites contract in this way and Walker (1961) states that 'failure of the lattice to contract does not exclude the possibility of a vermiculite of low layer charge'. Schultz (1969) stresses the importance of layer charge and concludes that the actual location of the charge is of minor importance. Harward *et al.* (1969) concluded that a differentiation can be made between vermiculite, montmorillonite and beidellite by considering the collapse on K^+ saturation to about 10 Å. In dry air all three minerals collapse, while at 54 % relative humidity only vermiculite collapses. On the basis of the present work the latter distinction becomes questionable since it seems that the major factor is the layer charge and that for a given layer charge the type of substitution, whether tetrahedral or octahedral, is very much a factor of secondary importance. This is in agreement with Schultz's (1969) conclusions.

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APPENDIX. APPROACH USED FOR CALCULATING THE INTERACTION OF K^+ IONS WITH FREELY ROTATING WATER MOLECULES AT A DISTANCE K–O CORRESPONDING TO $\frac{1}{3}b$ Å

For a specific position of an H_2O molecule situated at $\frac{1}{3}b$ Å from a K^+ cation we have

$$-E(\text{K-----O}) = q_{\text{K}}q_{\text{O}''}/\tfrac{1}{3}b + 2q_{\text{K}}q_{\text{H}''}/r, \tag{132}$$

where (in Å^{-1})

$$1/r = 1/[(\tfrac{1}{3}b)^2 + (r_{\text{OH}}{}^2) + (2br_{\text{OH}}\cos\theta)/3\sqrt{3}], \tag{133}$$

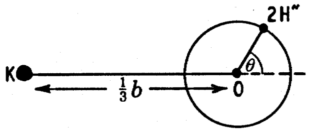

FIGURE 27. Definition of the angle θ in equation (133). The hydrogen atoms H″ of the water are projected onto a plane containing the K and O atoms and the midpoint of the line joining the two hydrogen atoms of the water. The angle θ is then as shown.

and θ is the angle defined as shown in figure 27, r is the K–H″ distance and r_{OH} represents the O–H bond length. When the H_2O molecule rotates, the average value of $1/r$ becomes (in Å^{-1})

$$\overline{1/r} = \frac{2}{2\pi}\int_0^{\pi}\frac{\mathrm{d}\theta}{r} = \frac{4}{2\pi}\int_0^{\frac{1}{2}\pi}\frac{\mathrm{d}\alpha}{r} \tag{134}$$

where $\alpha = \frac{1}{2}\theta$. Taking $b = 9.183$ Å, $r_{\text{OH}} = 1.0$ Å we calculate

$$\overline{1/r} = \frac{0.53\,636}{\pi}\int_0^{\frac{1}{2}\pi}\frac{\mathrm{d}\alpha}{(1-0.50\,841\sin^2\alpha)^{\frac{1}{2}}} = 0.3177\ \text{Å}^{-1}. \tag{135}$$

The first term of equation (132) can be written in terms of $q_{\text{H}''}$ ($q_{\text{O}''} = -2q_{\text{H}''}$) and, when combined with the second, gives (in kJ mol^{-1})

$$E(\text{K-----O}) = 12.1\,q_{\text{H}''}. \tag{136}$$

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