A STUDY OF Na/K FELDSPAR SOLID SOLUTION USING STATISTICAL MECHANICS

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ABSTRACT

Thermal behaviour of various solid feldspars are different, namely those of bivalent cations show no change in the distribution of Al and Si atoms, whereas feldspars of univalent cations become more disordered with raising temperature. In the latter case Al atoms migrate from the sites they occupy at low temperatures and interchange positions with the Si atoms. At high temperatures (but still below the melting point) the mixture of the two feldspars forms a solid solution, while at low temperatures two almost pure phases separate out from each other. The behaviour of pure feldspar (like albite) have been theoretically studied by various methods, while solid solutions of feldspars of univalent cations have not been studied (due to their complexity). In this paper statistical mechanical methods are used to study sodium and potassium feldspar solutions.

INTRODUCTION

Feldspar is an anhydrous aluminum silicate with the general formula $MT_4O_8$, where $M$ represents the cation contained in the feldspar. For univalent cations (metals) like Na, K, ..., one of the Ts is an Al atom and the other three are Si atoms, while for bivalent cations like Ca, Ba, ..., two of the T's are Al atoms and the other two are Si atoms. The three dimensional network of this compound is formed by linking of $TO_4$ tetrahedral units, wherein oxygen atoms are located at the

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vertices and T(Al or Si) atoms at the center of the tetrahedra. Each oxygen atom in the feldspar lattice lies between two T atoms (such that the T and O atoms alternate in the structure). Since the sites of the oxygens can only be occupied by these atoms, there is only one way to distribute the oxygen atoms, while the T sites can be occupied by either of the two types of atoms (Al or Si). The distribution of oxygen atoms will thus not be further discussed. In the case of pure feldspars only the distribution of Al and Si atoms among the T sites need be considered, while in their solutions, the distribution of the cations must also be considered. The T sites which are occupied by Al or Si atoms are called the primary sites and those occupied by cations (Na, K, ...) are called the secondary sites. For more information the reader is referred to references [1] and [2].

It has been experimentally observed that two Al atoms cannot be located on two adjacent T sites; this phenomena is called the principle of aluminum avoidance [3]. It states that distributions in which two Al atoms are on two adjacent T sites are disallowed, and consequently the distribution of Al and Si atoms among the T sites is not random. This, in turn, causes a decrease in the number of configurations, hence the entropy of the system.

There are four distinct types of primary crystallographic sites, which are shown as, $T_1(o), T_2(o), T_1(m)$, and $T_2(m)$ [3]. On the basis of experimental evidence, it is observed that Al atoms prefer to occupy the $T_1(o)$ sites (due to site preference energy which is dominant in the low temperature region). Such a preference arises from the interaction energy between $T_1(o)$ sites and Al atoms. The positional randomness of Al atoms on the primary sites increases with an increase in temperature and at a high temperature limit Al atoms may occupy all types of primary sites with equal probabilities [1]. Contrary to many cases, order disorder in feldspars is mainly due to atom-site interaction energies rather than interatomic interactions. Usually the $T_1(o)$ site is shown simply by "a" and the three other sites by "b". In feldspar lattice each "a" site is surrounded by four "b" sites and each "b" site (on the average) by 4/3 "a" and 8/3 "b" sites.

The first statistical mechanical investigation on sodium feldspar (albite) was done by Mazo [3]. In these calculations while using the QC (quasi chemical) method, a diamond-like lattice was assumed for albite in which the Si and Al atoms replaced the carbon atoms, i.e. instead of the main structure a simple model was used. Later
Andersen and Mazo[4] introduced the idea of local charge neutrality, on the basis of which in addition to electroneutrality in the entire lattice, different regions or locations (which will later be designated as units) also have to be electrically neutral. On the basis of this suggestion and to simplify calculations as far as possible, they chose locations which are electrically neutral to be as small as possible (actually one molecular unit). Their model is shown in Fig.1. In this figure the corners of the squares are T sites, X marks show the site of cations the open circles represent "a" sites and the filled ones "b" sites. In this model each square that has an X is considered to be a unit, and in order to be neutral it must have one Al and three Si atoms. In spite of the two dimensional character of the model, the coordination number of four for each T site is the same as the actual coordination number in the three dimensional lattice. Because the real feldspar lattice is complex, the choice of a simple model as the given two dimensional model seems unavoidable.

A new method for the statistical mechanical study of albite was introduced in 1986[6]. In this method the T sites were artificially divided into two groups. Sodium and calcium (or any bivalent cation) feldspars have been studied recently with the QC method using the two dimensional model of Andersen and Mazo[7]. The study of sodium and potassium feldspar mixtures seems to be more complicated, due to the fact that the interchange of Al and Si atoms with changing temperature occurs in both feldspars, and perhaps because of this complexity such an investigation has not yet been performed. Such a study is the goal of this paper.

![Figure 1](image-url)

**Fig.1-** Andersen and Mazo's model of the feldspar minerals. Open circles represent "a" sites, filled circles "b" sites, and X the cationic sites.

**STATISTICAL MECHANICAL STUDY OF SODIUM AND POTASSIUM FELDSPAR MIXTURES**

To accomplish this goal, the two dimensional model of Andersen and Mazo will be used in order to calculate the number of distributions and all available information will be imposed by using appropriate constraints. To do so, the following points...
will be considered:

1. In order to follow the aluminum avoidance principle, only distributions will be accepted in which no two Al atoms are adjacent.

2. To take the site preference energy into consideration, a negative site energy is given for each Al atom on the T_1 (o) site. Other site energies are taken to be zero.

3. Since different units prefer not to be adjacent, a positive interaction energy will be given to them such that the interaction energies between two adjacent cations of the same kind are zero.

4. To follow the principle of local charge neutrality, one alkali metal atom, one Al atom, and three Si atoms will be devoted to each unit.

In the feldspar mixture two types of distribution must be considered; first the distribution of the units (or cations), for which the QC method [3-5] will be used to calculate the number of such distributions, and second, the distribution of Al atoms on the T sites, for which the SCM (sequential construction method) [6] will be used. These distributions will be performed in two separate steps in the following order:

A—Distribution of alkali metal cations (Na and K)

According to the model chosen, each unit must contain one alkali metal cation, one Al atom, and three Si atoms. The distribution of cations is actually the distribution of the units, and thus, instead of considering the cations, the distribution of units A (NaAlSi_3O_8) and B (KAISi_3O_8) will be considered. Assume that the interaction energies between the units are shown as E_{AA}, E_{AB}, and E_{BB}, which represent the interaction energies between units of A with A, A with B, and B with B, respectively (the interaction energy between two units is actually related to that of two cations). With a decrease in temperature A and B units separate, which shows that AB pairs possess a repulsion energy greater than the energy between two units of the same kind:

\[ 2E_{AB} > E_{AA} + E_{BB} \]

If the number of AA, AB, BA, and BB pairs are shown with N_{AA}, N_{AB}, N_{BA}, and N_{BB}, respectively, the following general relationship will exist between them:

\[ CN = 2N_{AA} + N_{AB} \]  \hspace{1cm} (1)

\[ C(M-N) = 2N_{BB} + N_{BA} \]  \hspace{1cm} (2)

Where M is the total number of units, N the number of A units, and C the coordination number of the units.

To distribute the units, the QC approximation will be used. In this approximation it is initially assumed that the pairs are independent of each other, meaning that they do not share any site. In such case the
number of distributions, $\omega$, will be:

$$\omega = \frac{(CM/2)!}{CN_{\text{AB}}\left(C(M-N)-N_{\text{AB}}\right)!\left(N_{\text{AB}}\right)^2}$$

(3).

Using eq. (3) the number of distributions can now be calculated for each $N_{\text{AB}}$. To calculate the total number of distributions we must sum the right hand side of eq. (3) over all possible values of $N_{\text{AB}}$. It can be shown that in such a sum, only one term which is called the maximum term is of importance and others in respect, are negligible. In other words, the only value of $N_{\text{AB}}$ which has to be used in eq. (3) is the value which maximizes $\omega$. This value will be shown by $N_{\text{AB}}^*$. Thus we will have:

$$\Sigma_{N_{\text{AB}}} \omega(M,N,N_{\text{AB}}^*) \sim \omega(M,N,N_{\text{AB}}^*)$$

The interaction energies between the units will be given by:

$$E = N_{\text{AA}}E_{\text{AA}} + N_{\text{AB}}E_{\text{AB}} + N_{\text{BA}}E_{\text{BA}} + N_{\text{BB}}E_{\text{BB}}$$

(4).

Knowing the energy and the number of distributions (using the QC approximation) the Helmholtz function of the system can be calculated:

$$A = E - TS = E - T\text{ln}\omega + C'$$

where $C'$ is a constant related to the difference between the real number of distributions ($q$) and $\omega$.

To obtain the most stable state (equilibrium), $A$ must be minimized with respect to $N_{\text{AB}}$. The final result is:

$$N_{\text{AB}}^* = \text{CMR}$$

$$R = -\left[Z(1\pm\sqrt{1+4(1-Z)F(1-F)/Z})\right]/[2(1-Z)]$$

$$Z = \exp\left(F_{\text{AA}} - 2F_{\text{AB}} + F_{\text{BB}}\right)$$

For the sake of brevity $N_{\text{AB}}^*$ will be shown as $N_{\text{AB}}$ from now on. From the relation between the pairs, eq. (1), and eq. (2), we have:

$$N_{\text{AA}} = CM(F-R)/2$$

$$N_{\text{BB}} = CM(1-F-R)/2$$

in which: $F=N/M$

Thus the probability that a pair in the lattice has AA, AB, or BB configuration is:

$$P_{\text{AA}} = N_{\text{AA}}/(N_{\text{AA}} + N_{\text{AB}} + N_{\text{BA}} + N_{\text{BB}}) = F-R$$

$$P_{\text{AB}} = R$$

$$P_{\text{BB}} = 1-F-R$$

The values of $P_{\text{AA}}, P_{\text{AB}},$ and $P_{\text{BB}}$ will be used in the later calculations.

B - Calculation of the number of distributions of Al atoms on T sites

The alkali metal cations have been previously distributed and the distribution of Al atoms on T sites is wanted. In distributing Al atoms we must be careful not to place two Al atoms adjacent to each other (the aluminum avoidance principle). The two dimensional model of Andersen and Mazo will be used in this calculation and to follow the local charge neutrality one Al atom will be devoted to each unit. The distribution of Al atoms will be performed by using the
SCM approximation. In this method the units are hypothetically divided into black and white classes (Fig. 2) such that each black unit can only be surrounded by four white units and each white unit only by four black units, so that A and B units are divided into black and white A and B units. The probability for occupying "a" sites of the A units is shown by P, and the probability for occupying "a" sites of the B units is shown by P'.

PN atoms of aluminum are initially distributed on the "a" sites of the A units. The number of ways for such a distribution, \( \omega(a) \) is:

\[
\omega(a) = \frac{N!}{(PN)! [(1-P)N]}
\]

Now \( P'(M-N) \) Al atoms are distributed among "a" sites of B units. The number of ways for this kind of distribution, \( \omega(a') \) is:

\[
\omega(a') = \frac{(M-N)!}{[P'(M-N)] [(1-P')(M-N)]}
\]

**Step two: Distribution of Al atoms on "b" sites of black units**

In the first step of the distribution, \((1-P)N/2 \) black type units were not given any Al atoms. We now want to distribute \((1-P)N/2 \) Al atoms on the "b" sites of these units in such a manner that aluminum avoidance and the local charge neutrality are followed. Each of the two "b" sites of a black A unit are adjacent to one "a" site of a white unit, and this white unit has a probability of \( P_{AA} \) of being of the A type and \( P_{AB} \) of being of the B type. Thus the probability that the "a" site of this white unit has been occupied in the first step is \( (PP_{AA}+P'P_{AB}) \). The probability that the two "b" sites attainable is thus 2-2(PP_{AA}+P'P_{AB}).

The third "b" site of this black unit is adjacent to two "b" sites of the two white units (Fig.2) which are still unoccupied. It is obvious that this site is completely attainable.

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**Fig. 2** The classification of the Andersen and Mazo's model into white and black units.

The interaction energies between Al atoms and "a" sites of the A and B units are shown by \( E_a \) and \( E'a \) respectively, these being the site preference energies discussed previously.

The distribution of Al atoms is performed in several steps:

**Step one: Distribution of Al atoms on "a" sites**

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for occupation by Al atoms and so the probability of its being occupied is unity. Thus the total probability of attaining three b sites is equal to 
\[ \Delta = 3 - 2 \left( P_{AA}^P + P_{AB}^P \right) \]. The number of ways for this type of distribution \( \omega(s) \) will thus be:

\[ \omega(s) = [\Delta] (1-P)(M-N)/2 \]

Similarly we distribute \( (1-P')x(M-N)/2 \) Al atoms on the "b" sites of the black B units which have not been occupied previously with Al atoms. It can be shown that for this distribution we have:

\[ \Delta' = 3 - 2 \left( P_{BB}^P + P_{BA}^P \right) \]

\[ \omega(s') = [\Delta'] (1-P')(M-N)/2 \]

In which \( \Delta' \) is the average number of attainable "b" sites and \( \omega(s') \) is the number of ways for such a distribution.

**Step three: Distribution of Al atoms among the "b" sites of white units**

We next distribute \( (1-P)N/2 \) Al atoms on the "b" sites of the white units whose "a" sites have not been given any Al atom in their first step. By using arguments similar to those given previously it can be shown that:

\[ 3 - 2 \left( P_{AA}^P + P_{AB}^P \right) - (4/3) \left[ P_{AA}^P (1-P) + P_{BB}^P (1-P') \right] = \Delta - \lambda \]

\[ \omega(N) = [\Delta - \lambda] (1-P)N/2 \]

in which \( \Delta - \lambda \) is the average number of attainable "b" sites of each of the white A unit and \( \omega(N) \) is the number of ways for such a distribution. Similarly, we distribute \( (1-P')(M-N)/2 \) Al atoms on the "b" sites of the \( (1-P')x(M-N)/2 \) white B units (those on which no Al atom was located on their "a" site previously). It can be shown that:

\[ 3 - 2 \left( P_{BB}^P + P_{BA}^P \right) - (4/3) \left[ P_{BB}^P (1-P') + P_{BA}^P (1-P) \right] = \Delta' - \lambda' \]

\[ \omega(N') = [\Delta' - \lambda'] (1-P')(M-N)/2 \]

again \( \Delta' - \lambda' \) is the average number of "b" sites in each of the white B units and \( \omega(N') \) is the number of ways for such a distribution.

All Al atoms have been distributed on the T sites in several steps and in each step the number of distributions has been calculated. Thus the total number of distribution, \( g_{Al} \), is:

\[ g_{Al} = \omega(a)\omega(a')\omega(s)\omega(s')\omega(N)\omega(N') \]

Using the Boltzmann equation \( S_{Al} = k \ln(g_{Al}) \), the entropy related to the distribution of the Al atoms can be calculated. The energy due to the interaction of the Al atoms with the sites is:

\[ E = P_{AA}^P + P_{BA}^P (M-N)E^a \]

Knowing \( S \) and \( E \) the Helmholtz free energy \( A = E - TS \) can be calculated. Finally, to find the most stable state (equilibrium) we minimize this with respect to \( P \) and \( P' \). The final
results are:

\[ u' = \frac{\ln[(1-P)/P] - 1/2 \ln(A-1-P)P_{AA}/\Delta' - (1-P')P_{BB}/\Delta}{(1-P)P_{AA}/3(\Delta'-\lambda') - 1/3(1-P')P_{BB} / \Delta} \times (\Delta'-\lambda') = 0, u = E_a / kT \]  

Finally by adding these two entropies, the total entropy of the binary feldspar mixture was calculated.

In Fig.3 the entropy of the system is drawn versus the energy of the units of A(\ud). In these calculations F=0.3, u\ud=1.37, and the repulsion energy between two different types of units were kept constant (w=1). As shown in this figure the entropy reduces by increasing the absolute value of the energy.

RESULTS

In the previous section eq. (8) was obtained for finding AA, AB, and BB unit pairs and equations (9) and (10) were found for the calculation of the thermodynamic quantities P and P'. For any value of the repulsion energy between A and B units and the fraction of sodium units in the mixture, eq. (8) can be solved by computer to obtain the probabilities P_{AA}, P_{AB}, and P_{BB}. Next these values and the site preference energies u and u' were used in another computer program to solve equations (9) and (10) numerically for P and P' at the same time. Having the probability parameters P_{AA}, P_{AB}, and P_{BB}, the number of distributions of the units and the entropy of these distributions were calculated (stage A distribution). Knowing the parameters P and P', the number of distributions of the Al and Si atoms and thus their entropy was calculated (stage B distribution).

In order to investigate the effect of repulsion energy between units (w), the entropy is plotted against this quantity in Fig.4, while the other quantities are held constant. Such behaviour as seen in this graph is plausible, because strong repulsion causes the separation of unlike units which leads to the reduction of the
entropy.

In Fig. 5 the effect of the mole fraction of sodium feldspar on the entropy of the system is shown. As expected, for F = 0.5 the entropy has the maximum amount, because the number of distributions is the greatest in this case.

The effect of temperature on the entropy of the system is shown in Fig. 6, and Fig. 7 shows the effect of temperature on the entropy of the immiscible binary mixture, on the one hand, and of the solid solution of the two feldspars, on the other hand, in the same condition. The results of the last two figures will be discussed in the next section.

Fig. 4- Variation of entropy with the interaction energy

Fig. 5- Variation of entropy with the mole fraction of A type unit

Fig. 6- Variation of entropy with the temperature
Fig. 7- Variation of entropy with temperature.

Curve 1. Immiscible feldspar mixtures
Curve 2. Feldspar solutions

DISCUSSION

Fig. 6 shows the effect of temperature on the entropy of the system and it predicts that the system's entropy show different behaviours at low, medium, and high temperatures. At low temperatures the entropy changes quickly with temperature because displacement of units and that of Al and Si atoms in the lattice both occur quickly leading to rapid increase in disorder. At intermediate temperatures (where the variation of entropy is smaller) the displacements in one of these processes has probably reached its maximum (the process which has reached the maximum in its displacement rate is determined by the ratios of $u_a/w$ and $u_a'/w$). Finally at high temperatures where the displacements in both processes have reached their maximum an increase in temperature does not cause any change in the entropy.

In Fig. 7 the entropy of the solid solution of sodium and potassium feldspars (curve 2) is given on the one hand and the entropy of the two immiscible feldspars (curve 1) on the other hand. Since these two curves were drawn for the same site energies, the entropy of the immiscible feldspars and that of the solution will show the relative thermodynamic stability of these two systems to some extent. Since at the higher temperatures the entropy of the solution is appreciably greater than the entropy of the immiscible mixture, it is thermodynamically predicted that the feldspars will form a solution in these conditions (as they actually do). While at the low temperatures where the difference in entropy is low, the effect of the repulsion is more important than the entropy difference, and it can be expected that the two feldspars will separate (as they actually do)[1].

In the distribution of alkali metal cations (A and B units) the QC approximation was used. This method is largely used to avoid the mathematical complexity of the problem. In the absence of mathematical difficulties it would be preferred to use the Kikuchi method which is more general than the QC method[8 and 9].
In distribution of the Al and Si atoms on the T sites the SCM was used. The main approximation in this method is the fact that the equivalent units are hypothetically divided into black and white classes. Since in this method the distribution of Al atoms on these units is not performed simultaneously (first among the black units then among the white units), they actually are not considered to be equivalent. To clarify this point consider a hypothetical lattice with four sites all in one direction. Assume that we want to distribute two Al atoms among them following the principle of aluminum avoidance. Three ways exist for performing this (the actual number of distributions). According to the SCM the sites are divided into two groups, "a" and "b", such that similar sites are not adjacent ("a" and "b" alternate). We first distribute half of the Al atoms (one Al atom in this case) on the "a" sites. It is obvious that such a distribution can be performed in two ways. We now distribute the other Al atom on the "b" sites. For the aluminum avoidance to be followed on the average only 1/2 of a way will exist for this distribution. Thus in this case the number of distributions is 2 x 1/2 = 1 (distributions based on the SCM). If we reduce the hypothetical difference between the black and white sites by any method possible, it can be expected that a better approximation will be obtained. For this purpose the MS CM (modified sequential construction method) has recently been suggested [10]. In this method, instead of giving different values to the availability of the black and white "b" sites, an equal-average value is given to each.

Andersen and Mazo have introduced NaAlSi₃O₈ as the local charge unit in the model (meaning each square with a single Na atom in the middle). This is the smallest possible local charge unit. A small size for the local charge unit simplifies the mathematical operations. Before the introduction of the theory, the entire lattice was considered as the electroneutral unit [3]. In spite of the complexity of the mathematical operations, it seems sounder to use larger units. It has been suggested that use of units three times larger than the units of Andersen and Mazo is more appropriate [10, 11]. Finally to find the equilibrium state, the Helmholtz free energy of the system was divided into two independent parts, one for the distribution of the units and the other for the distribution of the Al atoms. Each distribution was given a Helmholtz free energy and each part was minimized independently. If it was not for avoiding the mathematical operations, it would be sounder to minimize the
function relative to all independent variables in one step.

REFERENCES