

## Statistical mechanical calculation of aluminum–silicon disorder in albite

ROBERT M. MAZO

*Institute of Theoretical Science and Department of Chemistry  
University of Oregon, Eugene, Oregon 97403*

### Abstract

Equilibrium silicon–aluminum disorder in albite is computed on the basis of statistical-mechanical order–disorder theory. The quasi-chemical approximation is used, and the aluminum avoidance principle is taken into account. A limiting high temperature configurational entropy of  $1.57 R$  per mole of Al is obtained. It is argued that a  $T_{10}$  site preference energy, as well as Al–Si interaction energy, is required for the model to be realistic. The configurational entropy and order parameter are calculated as functions of temperature.

### Introduction

The properties, and in particular, the thermodynamic properties, of feldspar minerals are affected by aluminum–silicon disorder (Ribbe, 1975). In an attempt to understand better the behavior of this cation disorder, it seemed worthwhile to undertake a calculation on the basis of statistical mechanics. A particular aim of the calculation is to gain some insight into the effect of the so-called aluminum-avoidance principle on the disordering process.

Except for one case, the 2-dimensional Ising model, no exact solutions of the statistical-mechanical order–disorder problem are known. We can hardly expect to improve this situation on an example as complex as a feldspar crystal. Nevertheless, we believe that a calculation based on the simplest non-trivial approximation which takes shortrange order into account gives useful qualitative insight, and such a calculation is presented here.

The system treated is the low albite–high albite transformation. The approximation used is the quasi-chemical approximation, which is equivalent to the Bethe method. This method originated in the theory of order–disorder in metallic alloys, and has been applied to the theory of solutions and to magnetic problems (Guggenheim, 1952). It is not quantitatively accurate, especially in the neighborhood of critical points (Stanley, 1971) but does portray the main essential features of the phenomena it purports to describe. The conclusions to be drawn from our calculations are therefore qualitative ones, even though we shall present quantitative results of the formalism.

Statistical mechanical methods have previously been applied to petrological problems but, as far as we are aware, only to systems which are, in one sense or another, ideal (*e.g.* Kerrick and Darken, 1975). We hope to demonstrate that certain more complex cases can, in fact, be approached by these methods.

### The model

Albite,  $\text{NaAlSi}_3\text{O}_8$ , has the typical feldspar structure. The Al and Si atoms lie at the centers of tetrahedra of oxygen which share corners. The Al and Si cations can be thought of as lying on the corners of a “double-crankshaft.” These “crankshafts” are linked to form a 3-dimensional network. The Na atoms lie in mushroom-shaped cavities formed by the joined crankshafts. We shall not be concerned explicitly with the Na atoms in what follows. For a more complete description of the crystal structures of the feldspars, see Smith (1974).

The tetrahedrally coordinated cation sites are not equivalent. There are four nonequivalent types for which the usual nomenclature is  $T_{01}$ ,  $T_{0m}$ ,  $T_{10}$ ,  $T_{1m}$ . At low temperatures in equilibrated samples, the Al atoms are found on the  $T_{10}$  sites. Thus low albite has an ordered structure. As the temperature is raised, Al atoms migrate to the other three types of sites, and the structure becomes disordered with respect to tetrahedral cation placement. The kinetics of this process are very slow, and poorly understood. In this paper we shall be exclusively concerned with the equilibrium situation.

In feldspar crystallography, there is a guiding principle based on empirical observation known as the aluminum avoidance principle. This says that two

oxygen tetrahedra sharing a corner cannot both contain aluminum. Clearly, there must be an energetic reason for this. We formulate our model in terms of an arbitrary amount of aluminum avoidance, but only make numerical calculations for the case of total aluminum avoidance.

The quantities which we shall calculate are the entropy,  $S$ , and the order parameter,  $p$ , as functions of temperature. The order parameter is the fraction of  $T_{10}$  sites occupied by Al atoms at equilibrium; it varies from 1 at low temperatures to  $1/4$  at high temperatures. The model assumes that the  $T_{1m}$ ,  $T_{20}$ , and  $T_{2m}$  sites are energetically equivalent with respect to Al or Si occupancy. Thus there is only one distinguished type of site,  $T_{10}$ , and one order parameter,  $p$ , as far as the order-disorder problem is concerned. The entropy calculated is the configurational entropy due to Al-Si disorder. We do not consider the vibrational entropy, nor interactions between vibrations and disorder.

Our model is the following. We consider a lattice of  $N$  tetrahedrally coordinated sites.  $N/4$  sites are type  $a$  sites ( $T_{10}$ ), while  $3N/4$  sites are type  $b$  sites ( $T_{1m}$ ,  $T_{20}$ ,  $T_{2m}$ ). Each  $a$  site has 4  $b$  sites as neighbors. Each  $b$  site has  $4/3$  type  $a$  neighbors and  $8/3$  type  $b$  neighbors. The  $T_{1m}$  and  $T_{20}$  sites each have one  $T_{10}$  neighbor, while a  $T_{2m}$  site has two. Since our model lumps  $T_{1m}$ ,  $T_{2m}$ , and  $T_{20}$  sites together, we give each  $b$  site its average coordination. This accounts for the peculiar looking fractions.

Order-disorder phenomena are usually governed by the interaction between atoms on the various sites; we consider only nearest-neighbor interactions. Let  $n$  denote the number of Al atoms on  $a$  sites. Let  $r_{ij}$  denote the number of nearest-neighbor pairs of atoms consisting of an atom of type  $i$  on an  $a$  site, and one of type  $j$  on a  $b$  site. Let  $s_{ij}$  denote the number of nearest-neighbor  $i, j$  pairs, both members of which are on  $b$  sites. If the interaction energy between an  $i, j$  nearest-neighbor pair is  $\epsilon_{ij}$ , then the total interaction energy of the system is

$$E_I(r, s) = \epsilon_{AA}(r_{AA} + s_{AA}) + \epsilon_{BB}(r_{BB} + s_{BB}) + \epsilon_{AB}(r_{AB} + r_{BA} + s_{AB}) \quad (1)$$

To avoid having multiliteral subscripts we have here denoted Al atoms by  $A$  and Si atoms by  $B$ . Note that  $r_{AB} \neq r_{BA}$ , but  $s_{AB} = s_{BA}$ . The  $r_{ij}$ 's and  $s_{ij}$ 's are not all independent. In fact, they can all be expressed in terms of  $r_{AA}$ ,  $s_{AA}$ , and  $n$  as follows.

$$\begin{aligned} r_{AB} &= 4n - r_{AA} \\ r_{BA} &= N/3 - 4n/3 - r_{AA} \\ r_{BB} &= 2N/3 - 8n/3 + r_{AA} \end{aligned} \quad (2a)$$

$$\begin{aligned} s_{AB} &= 2N/3 - 8n/3 - 2s_{AA} \\ s_{BB} &= N/3 + 8n/3 + s_{AA} \end{aligned} \quad (2b)$$

Using Eq.'s (2) we can express  $E_I$  as

$$\begin{aligned} E_I &= w(r_{AA} + s_{AA}) + \text{constant} \\ w &= \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} \end{aligned} \quad (3)$$

The constant in (3) depends on the  $\epsilon$ 's, but not on the configuration, *i.e.* not on the  $r$ 's,  $s$ 's, or  $n$ . It plays no role in what follows, and so we ignore it from here on.

In addition to the interaction energy between sites, we will permit our model to possess a site-preference energy. That is an  $A$  (Al) atom on an  $a$  site will have an energy  $u_A$ , a  $B$  (Si) atom on an  $a$  site will have an energy  $u_B$ . An  $A$  atom on a  $b$  site will have an energy  $v_A$ , while a  $B$  on a  $b$  site will have an energy  $v_B$ . These energies do not depend on the neighbors of the site in question. All neighbor-dependent energies in the model have already been included in  $E_I$ , by hypothesis. Then the site-preference energy is

$$\begin{aligned} E_S &= un + \text{constant} \\ u &= u_A + v_B - u_B - v_A \end{aligned} \quad (4)$$

The remarks concerning the constant in (3) also refer to the constant in (4). Thus the total energy for a given configuration is

$$E = w(r_{AA} + s_{AA}) + un \quad (5)$$

The thermodynamic properties of the system are determined by the partition function

$$Q = \sum_{r,s,n} g(r, s, n) \exp[-\beta E(r, s, n)] \quad \beta = (kT)^{-1} \quad (6)$$

where  $g$  is the number of possible configurations with specified  $r$ ,  $s$ , and  $n$ . It is purely combinatorial quantity. Within the confines of our model, the expression for  $E$  in (5) is exact. The problem is to find an expression for  $g$ ; this has not been done exactly.

We shall make the quasi-chemical approximation for pairs. That is, we shall take  $g$  to be proportional to the number of ways that *independent pairs* can be arranged on the lattice consistent with the given  $r$ ,  $s$ ,  $n$ . It is obvious that this is not exact, since two pairs sharing a common site cannot be independent.

Having now explained the model, we sketch the evaluation of  $Q$ , relegating many of the technical details to the Appendix.  $Q$  is determined by the maximum term method for each  $n$ .

$$Q = g(r_{AA}, s_{AA}, n) \exp[-\beta E(r_{AA}, s_{AA}, n)] \quad (7)$$

where the values of  $r_{AA}$  and  $s_{AA}$  to be used are deter-

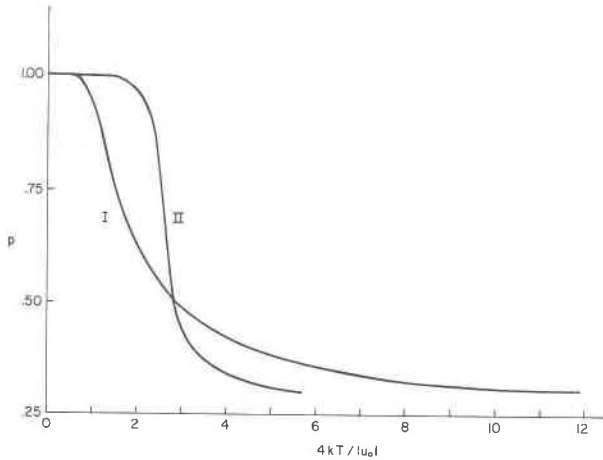


Fig. 1. Order parameter versus  $kT$  temperature in reduced units. Curve I: constant site-preference energy. Curve II: site-preference energy a linear function of order parameter.

mined by quasi-chemical equations given in the appendix. Once  $r_{AA}$  and  $s_{AA}$  are found as functions of  $n$  (and  $w$ ), one minimizes the Helmholtz free energy,  $-kT \ln Q$ , with respect to  $n$ , to find the equilibrium value of  $n$ . Before carrying out this program, we wish to make a simplification.

We said earlier that the extent of aluminum avoidance must be determined on energetic grounds. It is clear that, in the present model, the aluminum avoidance is determined by the parameter  $w$ . In fact, aluminum avoidance means  $w \gg kT$  for any temperatures of interest. Aluminum avoidance means  $r_{AA} = s_{AA} = 0$ . Now,  $r_{AA}$  and  $s_{AA}$  depend on  $w/kT$  exponentially, from the quasi-chemical equations. Hence  $E_I = 0$  in the complete aluminum avoidance limit. This has the pleasant effect of reducing a two-parameter theory ( $w$  and  $u$ ) to a one-parameter theory (only  $u$ ), and is the simplification referred to above.

Let us introduce the order parameter,  $p$ , mentioned earlier, by

$$p = 4n/N \quad (8)$$

$p$  varies from 1, for complete order, to  $1/4$ , for complete disorder. In terms of  $p$ , the free energy,  $F$ , becomes

$$\begin{aligned} -F/kT(N/4) = & (1/4)\{(1 + 4p) \ln 1/3 + (4/3) \\ & (1 - p) \ln 1/4 - p \ln p - (2/3)(1 - p) \ln (1 - p) \\ & + 3(2 + p) \ln (2 + p) \\ & - (4/3)(1 + 2p) \ln (1 + 2p)\} - up/4kT \quad (9) \end{aligned}$$

The division by  $N/4$  is so as to give the free energy per Al atom. Differentiating (9) with respect to  $p$  and setting the derivative equal to zero determines  $p$  in an

equilibrated crystal. The equation is

$$\begin{aligned} -\ln 3 + (1/3) \ln 4 - (1/4) \ln p + (1/6) \ln (1 - p) \\ + (3/4) \ln (2 + p) - (2/3) \ln (1 + 2p) = u/4kT \quad (10) \end{aligned}$$

This equation can be solved numerically for  $p$  as a function of the dimensionless temperature  $4kT/|u|$ . Recall that  $u$  must be negative if the  $a$  sites are to be preferred energetically. The results of this calculation are shown in Figure 1.

Once  $p$  has been determined, through (10), the entropy,  $S$ , can be determined by noting that  $S/(N/4)k$  is the first term on the right-hand side of Eq. (9). The entropy is plotted in Figure 2 as a function of  $T$ .

Of some interest is the high-temperature limit of  $S/R$ , under the assumption of aluminum-avoidance. This requires some explanation. We have identified aluminum-avoidance with  $w/kT \gg 1$ . Clearly, if  $T$  is high enough, for any finite  $w$  this inequality cannot hold. Presumably, before  $T$  got that high, the crystal would melt, and the whole model becomes meaningless. So, by high-temperature limit with aluminum avoidance, we mean  $u/kT \ll 1$ ,  $w/kT \gg 1$ .

To compute  $S$  in this limit, we merely put  $p = 1/4$  in the formula for  $S$ . The result is  $S = 1.570 R$ , or  $3.12 \text{ cal}/^\circ\text{K}$  per mole of Al. This is to be compared to the value  $2.249 R$  or  $4.47 \text{ cal}/^\circ\text{K}$  for complete random mixing. Kerrick and Darken (1975) have given an estimate of  $1.469 R$  or  $2.92 \text{ cal}/^\circ\text{K}$  for complete aluminum-avoidance. Their calculation was based on an approximate geometrical counting argument, whereas ours is based on the quasi-chemical approximation. It is quite gratifying that their estimate and

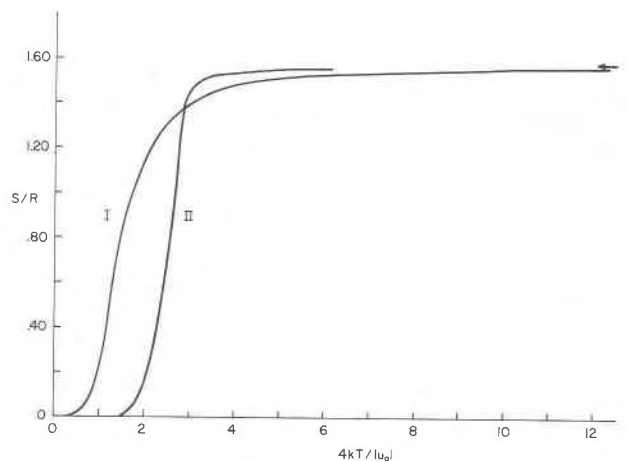


Fig. 2. Configurational entropy versus reduced temperature. Curve I: constant site-preference energy. Curve II: site-preference energy a linear function of order parameter. The arrow denotes the high-temperature limit.

ours are so close to each other. When one considers the different characters of the approximations used, the concordance of the results leads one to believe that they are both more or less right. We have obtained  $S$  for all temperatures, whereas they have considered only the high-temperature limit.

### Discussion

The first question one should ask is why we had to introduce the site-preference energy parameter,  $u$ . After all, most order-disorder problems can be adequately modeled without it. Firstly, the  $T_{10}$  sites in albite do appear to be different from the other sites. The framework is distorted, presumably because of the small size of the Na atom relative to the cavity size (Ribbe, 1975, Fig. R-9). This could conceivably be a minor perturbation and not an essential point. But let us consider a completely ordered configuration,  $p = 1$ , at  $T = 0$ . Each  $T_{10}$  site has an adjacent  $T_{1m}$  site. If we randomly switch Al atoms from their sites in the ordered configuration to the neighboring  $T_{1m}$  sites (not to an arbitrary  $T_{1m}$  site), we do not change the coordination of an Al atom, and hence do not change its interaction energy. But the number of such configuration is  $2^N$ , which would give an entropy contribution of  $R \ln 2$ . And of course, there may be other isoenergetic configurations which would raise this value. For our purposes, it is sufficient to note that the above argument shows that there are at least enough configurations to give an entropy of order  $R$  (per mole of Al) at  $T = 0$ . Thus  $p = 1$  is not the stable state at  $T = 0$  when only interaction energy is present. On the other hand, even a small amount of site-preference energy stabilizes the ordered ground state.

In the case of the alloy  $\text{Cu}_3\text{Au}$ , which has the same atom ratio as the Si/Al ratio in albite, the quasi-chemical method based on pairs of sites with no site-preference energy yields no order-disorder transition. But a higher approximation, based on tetramers of sites, does yield a transition similar to that observed. The argument we have just given shows that our model is not ordered at  $T = 0$ , if  $u = 0$ , independent of the approximation used. A better approximation (with the same model) would not yield a transition. The difference between albite and  $\text{Cu}_3\text{Au}$ , for present purposes, lies in the open tetrahedral structure of albite, as contrasted to the close-packed, 12-coordinated structure of the alloy.

Secondly, one should ask "What is the experimental situation?" Our theory predicts no phase transition. Rather, as  $T$  increases from zero, the order

parameter,  $p$ , drops rapidly and then, rather gradually, approaches its asymptotic value of  $1/4$ . McKenzie (1957) has performed annealing experiments on low albite, and these data were analyzed by Stewart and Ribbe (1969), to determine  $p$  as a function of  $T$ . Figure 6 of Stewart and Ribbe (1969) shows a remarkable qualitative accord with Figure 1 of this paper. Unfortunately, the quantitative accord is not so good. If one looks carefully at the temperature axes in our graph and that of Stewart and Ribbe, one sees that the change of  $p$  with  $T$  is much more abrupt in actuality than is predicted by our theory.

It is easy to understand why this should be so. The site-preference energy is caused by distortion of the framework around the Na atoms. As the temperature increases, the occupancy of the various sites becomes more and more alike, and the amplitude of atomic vibrations becomes larger. One would expect the site-preference energy to become smaller. That is,  $u$  should not be a constant, but rather  $u = u(p)$ , decreasing (in absolute value) as  $p$  decreases. The smaller  $u$ , the lower  $p$ , at a given temperature. Hence this mechanism would give a more rapid decrease of  $p$  with  $T$  than does our constant  $u$  model, and would give better agreement with experiment. This can be looked upon as a manifestation of the coupling of cation configuration and atomic motions, which has been explicitly left out of our model.

It is possible to carry out a calculation similar to the one presented here if one knows how  $u(p)$  depends on  $p$ . The simplest guess,  $u = (4/3)u_0(p - 1/4)$ , says that  $u$  decreases linearly from  $u_0$  to 0 as  $p$  goes from 1 to  $1/4$ ; this guess is free of additional parameters, but probably overestimates the  $p$  dependence of  $u$ . A calculation shows that, indeed, the  $p$ - $T$  curve computed on this hypothesis looks much more like the experimental one. This is also shown in Figure 1. But since the form of  $u(p)$  used was rather *ad hoc*, we do not wish to dwell on this point, even though the improvement is appreciable. We have also plotted the entropy for this case in Figure 2. For the present we shall be content with asserting that the lowering of  $u$  as  $p$  decreases most probably occurs and, if it occurs, will certainly make the  $p$  versus  $T$  curve more abrupt, more like the experimental curve.

If, instead of letting  $w$  tend toward infinity, we had kept  $w$  finite (incomplete aluminum avoidance), we could have computed  $p$  and  $S$  with some additional labor, but not an inordinate amount. The problem is not with the calculation, but with the presentation of results. The work presented here had one parameter,

$u$ , which entered the theory only as a dimensional reduction parameter for the temperature. Thus the fact that we do not know  $u$  *a priori* is relatively unimportant for qualitative results. If we had to account for both  $u$  and  $w$ , neither of which is known, only one of these parameters could be incorporated into a dimensionless temperature, and a large range of parameter space would have to be investigated for each  $T$ .

We could, of course, compute the energy, heat capacity, *etc.* of this order-disorder system also; we already have all of the ingredients. We have not done so because it seems to us that the main interest of this work at its present stage is in the qualitative insight it gives into the order, and entropies are usually more sensitive indicators of order than energies, especially when an approximate theory is being used.

The conclusions to be drawn are, first, that the ordering process in albite is gradual, and not a true phase transition. Secondly, the primary ordering factor is not the interaction energy between tetrahedrally coordinated cations, but is a site-preference energy for  $T_{10}$  sites. Thirdly, the aluminum-avoidance principle implies a considerable reduction of the configurational entropy of high albite. Both the order parameter and the entropy make a relatively rapid, though smooth change from their low-temperature values, as the temperature rises above 1 (in units of 4  $|u|/k$ ), followed by a much more gradual change toward their ultimate asymptotic limits.

Could this model also apply to potassium feldspar (low-microcline, sanidine)? The high-temperature entropy estimate would apply, just as for albite; the combinatorics are the same. But the constant  $u$  model cannot apply for the  $p$  versus  $T$  or  $S$  versus  $T$  curves, over the entire temperature range, for the crystal symmetry changes from triclinic to monoclinic as the temperature is raised. This does not change the local coordination appreciably, but will probably affect the site-preference energy. Thus we expect our constant  $u$  model to be of dubious validity for the K-feldspar case, except at high temperatures.

For feldspars with different Al/Si ratios, the model would have to be modified, but it should not be too difficult to do so. The calculations could then be extended to solid solution of, say, albite and anorthite.

### Appendix

We outline here some of the mathematical development of the calculation. Much of this will be elementary for those already familiar with the quasi-chem-

ical approximation. An excellent source for details is the book by Guggenheim (1954).

In Eq. (7), we approximate  $g(r_{AA}, s_{AA}, n)$  by the number of ways *independent pairs* of  $A$  and  $B$  particles can be put on the lattice. Thus

$$g(r_{AA}, s_{AA}, n) = [h(n)(N/4)!]/[r_{AA}! r_{BB}! r_{AB}! r_{BA}!] \times [2^{s_{AB}}(3N/4)!]/[s_{AA}! s_{AB}! s_{BB}!] \quad (\text{A.1})$$

where the relations (2a, b) hold.  $h(n)$  is a correction factor to take account of the normalization required by the meaning of  $g$ :

$$\sum_{r,s} g(r, s, n) = [(N/4)! (3N/4)!]/[n!(N/2 + n)! \{(N/4 - n)!\}^2] \quad (\text{A.2})$$

which would automatically be satisfied if the hypothesis of independent pairs were really true.

$h(n)$  is determined by approximating the logarithm of the sum in (A.2) by the logarithm of the largest term (maximum term method), and one obtains

$$h(n) = [n!(N/2 + n)! \{(N/4 - n)!\}^2]^{-1} \times r_{AA}^0! r_{AB}^0! r_{BA}^0! r_{BB}^0! s_{AA}^0! s_{BB}^0! s_{AB}^0! 2^{-s_{AB}^0} \quad (\text{A.3})$$

Here the zero superscript on the  $r$ 's and  $s$ 's refers to the values of the  $r$ 's and  $s$ 's for a completely random distribution. In particular  $r_{AA}^0 = Np(1-p)/3$ ,  $s_{AA}^0 = N(1-p)^2/9$ .

The sum in Eq. (7) is then also evaluated by the maximum term method. This leads to the quasi-chemical equations

$$[(4n - r_{AA})(N/3 - 4n/3 - r_{AA})]/[r_{AA}(2N/3 - 8n/3 + r_{AA})] = \exp(\beta w) \quad (\text{A4a})$$

$$(N/3 - n/3 - s_{AA})^2/[s_{AA}(N/3 + 8n/3 + s_{AA})] = \exp(\beta w) \quad (\text{A4b})$$

$r_{AA}^0$  and  $s_{AA}^0$  are the solutions of these equations when  $w = 0$ .

In the text, we have computed only the case  $w \rightarrow \infty$ , *i.e.*  $r_{AA} = 0$ ,  $s_{AA} = 0$ , the case of strict aluminum avoidance. However, it is clear that these equations can be solved for any value of  $w$  we please, by numerical methods.

Having determined  $r_{AA}$  and  $s_{AA}$  in terms of  $p$  (and  $T$  too, of course) one minimizes  $F(p)/NkT = \beta E(p) - \ln g(p)$  as a function of  $p$ , which we did by solving  $\partial F/\partial p = 0$  numerically. The value of  $p$  which gives the minimum is the equilibrium value, and it is this which is plotted in Figure 1. In  $g$  can then be calculated easily, and this is what is shown in Figure 2.

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