

## Statistical mechanical models for aluminum–silicon disorder in plagioclases

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### Abstract

The equilibrium aluminum–silicon disorder which occurs in plagioclase solid solutions is computed using an extension of the statistical mechanical model of Mazo. The model includes aluminum avoidance and a composition-dependent  $T_{10}$  site preference energy. The configurational entropy and order parameter are calculated as functions of the temperature and composition, and reasonable qualitative agreement is obtained with the known composition dependence of the order parameter. A two-dimensional analogue model of albite is introduced which includes local charge balance. A limiting high-temperature configurational entropy of  $1.12R$  per mole of Al is obtained in the two-dimensional model when local charge balance is rigorously obeyed.

### Introduction

A variety of silicate minerals exhibit order–disorder phenomena similar to those seen in binary alloys. However, the complex nature of the silicate minerals has greatly limited the understanding of the ordering phenomena in these systems. While there have been some theoretical studies of silicate solid solutions using simple thermodynamic solution models (Saxena, 1973), little work has been attempted using statistical mechanical methods. Thus little is known about the connection between the microscopic ordering process and the bulk thermodynamic properties of these systems. Recently, a statistical mechanical model has been proposed by one of us (Mazo, 1977) (hereafter referred to as I) for the low albite–high albite transformation. The work of I gave a reasonable qualitative description of the ordering phenomena in albite and demonstrated that tractable statistical mechanical models can be developed which deal with order–disorder phenomena in complex mineral systems. Another example, for a different system, is the work of Navrotsky and Loucks (1977).

The aluminum–silicon ordering which occurs in albite is also present, in varying degrees, in plagioclases of various compositions. These systems are particularly interesting since the ordering is found to be composition- as well as temperature-dependent. Statistical mechanical models have been previously proposed for plagioclase mixtures (Kerrick and

Darken, 1975); however, they have not dealt with the temperature dependence of the ordering nor have they considered what effects the ordering has on the thermodynamic properties of the mixture. In addition, these models assume that plagioclases are, in some sense, ideal mixtures of albite and anorthite, while the experimental evidence strongly suggests otherwise (Seck, 1971).

This paper extends the model of I to plagioclase mixtures. The advantage of the approach of I over the models of Kerrick and Darken (1975) is that interatomic interactions thought to be important in feldspars can be incorporated into the theory. Consequently we will be particularly interested in determining the effect of short-range order due to aluminum avoidance on the long-range ordering of the aluminum atoms in the mixture.

The paper is organized as follows. In the remainder of the Introduction we briefly describe the ordering phenomena which occur in calcic and sodic feldspars. In Section II we define the model and describe some of its order-dependent thermodynamic properties. In the third and final section we discuss some of the shortcomings of the model.

Albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) both have typical feldspar structures in which the aluminum and silicon atoms are tetrahedrally bonded to oxygen atoms. The key structural unit in the crystal is that of four-member rings of  $\text{TO}_4$  ( $T = \text{Al, Si}$ ) tetrahedra which are bound together in a

three-dimensional network of crankshaft-like chains (Smith, 1974, Chapter 2). The sodium and calcium atoms lie in mushroom-like cavities formed by the joined crankshafts. Here we are only interested in the aluminosilicate network and will therefore essentially ignore the sodium and calcium cations. We discuss the ramifications of this approximation in Section III. The tetrahedrally-coordinated cation sites are not all equivalent and can be divided into four classes, usually labeled  $T_{10}$ ,  $T_{1M}$ ,  $T_{2O}$ , and  $T_{2M}$ . Experimentally one finds in both albite and certain plagioclases that the  $T_{10}$  sites are preferentially occupied by Al atoms at low temperatures. As the temperature is increased, the occupation of the various sites by Al becomes more random. At sufficiently high temperatures ( $\sim 800^\circ\text{C}$ ) the distribution of Al among the T sites in albite is essentially uniform. The situation in anorthite and some Al-rich plagioclases is different, since aluminum avoidance precludes a completely random distribution of the Al and Si atoms even at high temperatures.

Below the melting point of feldspars one observes strict adherence to the principle of aluminum avoidance. This principle states that two oxygen tetrahedra sharing a corner cannot both contain aluminum. Experimental evidence (Megaw *et al.*, 1962) suggests that the tetrahedral cation distribution of anorthite is completely determined by aluminum avoidance. Aluminum avoidance in anorthite produces a completely ordered structure characterized by alternation of Al and Si atoms throughout the aluminosilicate framework. This geometry results in exactly half of the  $T_{10}$  sites being occupied by Al. While aluminum avoidance does not completely dictate the ordering in albite as it does in anorthite, it causes a substantial reduction in albite's configurational entropy. In plagioclases one sees a competition between these two ordering processes. For compositions near pure albite, Al atoms tend to occupy  $T_{10}$  sites. However, for compositions near pure anorthite, aluminum avoidance dominates the ordering process and drives the Al atoms from the  $T_{10}$  sites, which results in a more anorthite-like crystal structure.

We should briefly mention that the ordering of the Al atoms in the  $T_{10}$  sites, especially for albite, appears to result from a site preference energy rather than from nearest-neighbor interactions. Smith (1974, p. 79-80) has suggested that such a site preference by Al results from the fact that the four oxygen atoms surrounding the  $T_{10}$  site are more closely bonded to the respective sodium or calcium cation than those coordinating  $T_{1M}$ ,  $T_{2O}$ , or  $T_{2M}$ . Thus, since

there are fewer electrons involved in the T-O bond to  $T_{10}$  than to the other three sites, trivalent aluminum prefers  $T_{10}$ . It can be expected that such a site preference energy will depend strongly on which atom, sodium or calcium, is in close proximity to the oxygen atoms surrounding the  $T_{10}$  sites. Such a site preference energy was included in the model of I. In the model to be presented we will again want to include a site preference energy which favors the occupation of  $T_{10}$  sites by Al atoms, but will now allow it to depend on the composition.

### The model

Our model starts with a set of  $N$  tetrahedrally coordinated sites of which  $N/4$  are type  $a$  sites ( $T_{10}$ ) and  $3N/4$  are type  $b$  sites ( $T_{1M}$ ,  $T_{2O}$ ,  $T_{2M}$ ). Notice that the model assumes that the non- $T_{10}$  sites are energetically equivalent with respect to Al and Si occupancy. Each  $a$  site has  $4b$  sites as nearest neighbors. Each  $b$  site has, on the average,  $4/3$  type  $a$  sites and  $8/3$  type  $b$  sites as nearest neighbors. The number of aluminum and silicon atoms in the lattice can be expressed in terms of  $x$ , the mole fraction of albite, by the following:

$$\begin{aligned} N_{\text{Al}} &= \frac{N}{4} (2 - x) \\ N_{\text{Si}} &= \frac{N}{4} (2 + x) \end{aligned} \quad (1)$$

Like I, the present model includes interactions between nearest-neighbor Al and Si atoms in the aluminosilicate framework. Let  $n$  be the number of Al atoms on  $a$  sites. Let  $r_{ij}$  denote the number of nearest-neighbor pairs of atoms where an atom of type  $i$  is on an  $a$  site and an atom of type  $j$  on a  $b$  site. Let  $s_{ij}$  denote the number of nearest-neighbor pairs of atoms of type  $i$  and  $j$  where both atoms are on  $b$  sites. If the interaction energy between an  $ij$  nearest-neighbor pair is  $E_{ij}$ , then the energy due to nearest neighbor interactions is

$$\begin{aligned} E_I &= E_{AA}(r_{AA} + s_{AA}) + E_{BB}(r_{BB} + s_{BB}) \\ &+ E_{AB}(r_{AB} + s_{AB}) \end{aligned} \quad (2)$$

where we have denoted aluminum and silicon by A and B respectively. The various  $r_{ij}$  and  $s_{ij}$  are not independent and can be expressed in terms of  $r_{AA}$ ,  $s_{AA}$ ,  $n$ , and  $x$  as follows:

$$\begin{aligned}
 r_{AB} &= 4n - r_{AA} \\
 r_{BA} &= \frac{N}{3} \left( 2 - x - \frac{4n}{N} \right) - r_{AA} \\
 r_{BB} &= \frac{N}{3} \left( 1 + x - \frac{8n}{N} \right) + r_{AA} \\
 s_{AB} &= \frac{2N}{3} \left( 2 - x - \frac{4n}{N} \right) - 2s_{AA} \\
 s_{BB} &= \frac{N}{3} \left( 2x - 1 + \frac{8n}{N} \right) + s_{AA}
 \end{aligned} \tag{3a}$$

$$\begin{aligned}
 s_{BB} &= \frac{N}{3} \left( 2x - 1 + \frac{8n}{N} \right) + s_{AA}
 \end{aligned} \tag{3b}$$

Using equations 3a and 3b we can re-express the interaction energy  $E_i$  as follows:

$$E_i = w(r_{AA} + s_{AA}) + \text{Constant} \tag{4}$$

where

$$w = E_{AA} + E_{BB} - 2E_{AB} \tag{5}$$

The constant in equation 4 depends on the  $E$ 's and on the composition but is independent of the configuration, *i.e.* independent of  $r_{AA}$ ,  $s_{AA}$ , and  $n$ . All of the thermodynamic quantities we are concerned with are independent of such constant terms and therefore we will disregard the constant from this point on.

We also include a site preference energy which favors  $a$  sites being occupied by Al. If we accept the argument given in the Introduction for the origin of the site preference energy, then it is reasonable to expect that this energy will depend on which cation, sodium or calcium, is in close proximity to the  $T_{10}$  site. Thus, to write down an exact expression for the total site preference energy would require the specification of how many of the occupied  $T_{10}$  sites are in the coordination spheres of each of the two types of cation. This greatly complicates the model, since it would require knowing the configurational state of the surroundings of sodium and calcium atoms in the lattice, a feature we have elected to ignore. Therefore we will define a *mean* site preference energy that varies linearly with the composition. That is, an A atom on an  $a$  site will have energy  $c_1 + d_1x$ , a B atom on an  $a$  site will have energy  $c_2 + d_2x$ . An A atom on a  $b$  site will have energy  $c_3 + d_3x$ , and a B atom on a  $b$  site will have energy  $c_4 + d_4x$ . The site preference energy in the lattice is therefore

$$E_s = (u + vx)n + \text{Constant} \tag{6}$$

where

$$\begin{aligned}
 u &= c_1 + c_4 - c_2 - c_3 \\
 v &= d_1 + d_4 - d_2 - d_3
 \end{aligned} \tag{7}$$

As in equation 4 the constant term in the energy expression is independent of the configuration and so will be disregarded. The total energy for a given configuration is therefore

$$E = w(r_{AA} + s_{AA}) + (u + vx)n \tag{8}$$

The assumption of *linear* dependence of  $E_s$  on composition is made solely for simplicity.

The canonical partition function for the system is

$$Q(N, T, x) = \sum_{r,s,n} g(r, s, n, x) e^{-\beta E(r,s,n,x)} \tag{9}$$

where

$$\beta = (kT)^{-1} \tag{10}$$

and  $g(r, s, n, x)$  is the number of possible configurations of the atoms consistent with a given value of  $r$ ,  $s$ ,  $x$ , and  $n$ . We make the quasi-chemical approximation for  $g$  which assumes that this quantity is proportional to the number of ways that independent pairs can be arranged on the lattice consistent with the given  $r$ ,  $s$ ,  $n$ , and  $x$ . The specific form of  $g$  is given in Appendix A.<sup>1</sup> The summation in equation 9 is difficult, and therefore we use the maximum term method. The partition function is then

$$Q(N, T, x) = g(r, s, n, x) e^{-\beta E(r, s, n, x)} \tag{11}$$

Normally the values of  $r_{AA}$  and  $s_{AA}$  at any given temperature would be found by solving a set of equations arising from the determination of the maximum term of (9), the quasi-chemical equations. However, in all of our calculation we assume complete aluminum avoidance and therefore  $r_{AA} = s_{AA} = 0$  at all temperatures. This simplification also means that the total energy of the system is dependent on only two adjustable parameters,  $u$  and  $v$ .

Let us introduce the order parameter,  $p$ , defined as

$$p = \frac{4n}{N} \tag{12}$$

The order parameter is exactly one-half in anorthite and varies between  $\frac{1}{4}$  and 1 in albite as the system goes from a completely disordered to a completely ordered state.

The Helmholtz free energy for the system is given by

$$A = -kT \ln Q \tag{13}$$

<sup>1</sup>To receive a copy of Appendices A and B, order Document AM-80-123 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

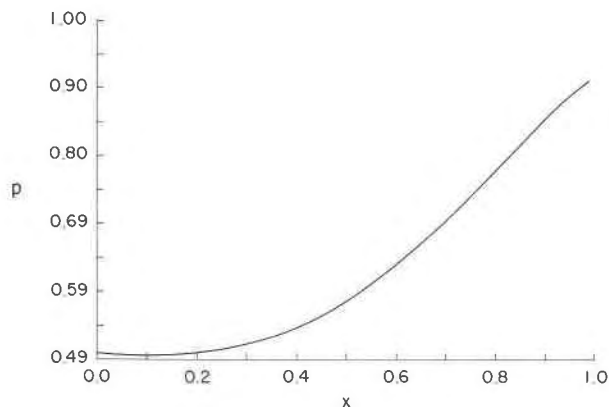


Fig. 1. Order parameter vs. the mole fraction of albite when the reduced temperature,  $4kT/|u+v|$ , is equal to 0.8 and the ratio  $v/u$  is equal to 10.

and we refer the reader to Appendix A for its detailed form. The equilibrium value of  $p$  is found by minimizing the free energy with respect to  $p$ . The equation determining the equilibrium value of  $p$  for any temperature is also given in Appendix A.

If we use the quantity  $|u+v|/4k$  to scale the temperature, then the only remaining independent adjustable parameter in the model can be chosen to be the ratio  $v/u$ . We assume that both  $u$  and  $v$  are negative in order that  $a$  sites be preferred energetically for all compositions. In Figure 1 we show a  $p$  vs. composition curve when the reduced temperature,  $4kT/|u+v|$ , is equal to 0.8 and the ratio  $v/u$  is equal to 10. This value of the reduced temperature produces a virtually completely ordered structure in albite. The composition dependence of the order parameter shown in Figure 1 is qualitatively very similar to that

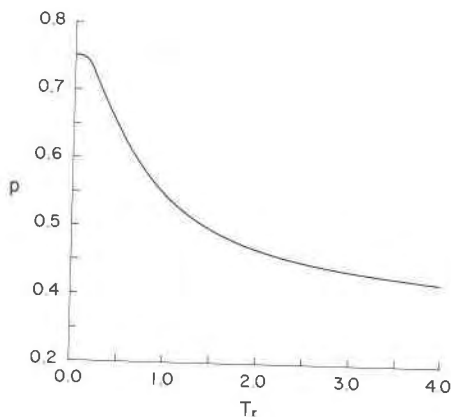


Fig. 2. Order parameter vs. reduced temperature when the mole fraction of albite is equal to 0.5. The ratio  $v/u$  is the same as that of Fig. 1.

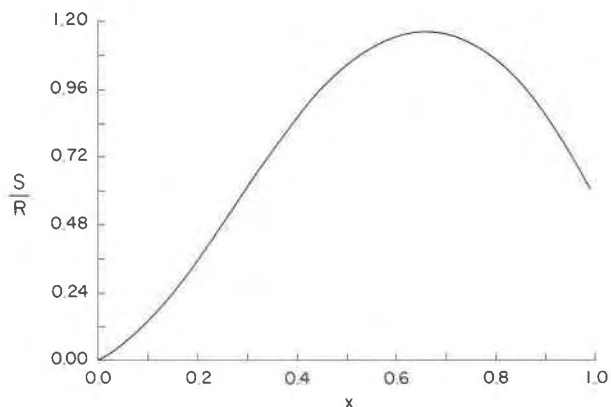


Fig. 3. Reduced entropy (per mole of Na, Ca cation) vs. the mole fraction of albite. The values of the reduced temperature and ratio  $v/u$  are the same as those for Fig. 1.

which is found in plagioclases which have been equilibrated at relatively low temperatures (Ribbe, 1975). In Figure 2 we show a  $p$  vs. reduced temperature curve for  $v/u$  equal to that of Figure 1 when  $x$  is equal to 0.5.

The configurational entropy of the mixture is essentially given by the logarithm of the combinatorial factor  $g$ . In Figures 3 and 4 we show reduced entropy,  $S/R$ , per mole of cation (Na,Ca) curves as a function of the composition and reduced temperature respectively. In both figures the ratio  $v/u$  is equal to 10. It should be mentioned that the general shape of the entropy vs. composition curve (Fig. 3), *i.e.* its asymmetry, is relatively insensitive to the value of  $v/u$ .

## Discussion

It seems reasonable to believe that aluminum-silicon order-disorder must be properly accounted for if

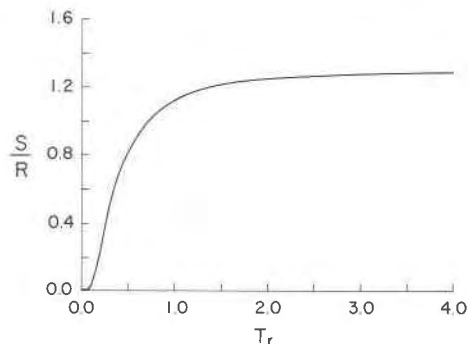


Fig. 4. Reduced entropy vs. reduced temperature when the mole fraction of albite and the ratio  $v/u$  are equal to 0.5 and 10 respectively.

a good thermodynamic model for plagioclase solid solutions is to be developed. The model presented here appears to give a reasonable qualitative description of some of the order-dependent thermodynamic properties of plagioclases and thus might be particularly useful as a model for plagioclase solid solutions near the melting point of the solid. At these temperatures the contribution of the sodium and calcium cations to the configurational entropy might be adequately approximated by an ideal entropy of mixing term. The entropy reported here may be useful as an ingredient for computing solid-liquid equilibrium in plagioclases, though, by itself, it is not sufficient.

In all our calculations we assume that the structure of the lattice does not change as a function of the composition or the temperature. Some evidence suggests that such structural changes do indeed occur. It can then be expected that the various site preference energies will not remain constant but vary, possibly discontinuously, as a function of the composition. It was previously demonstrated in I that a more realistic temperature dependence for the order parameter could be obtained if the site preference energy was allowed to be a function of the order. In a similar manner a more realistic composition dependence for the order parameter in our model might be obtained by allowing the mean site preference energy to be a nonlinear function of the composition. This would require only trivial changes in the model; this possibility has not been pursued since it would be just a kind of curve fitting in the present state of our knowledge.

The most serious shortcoming of the model is its failure to incorporate the ordering of sodium and calcium atoms into the lattice structure. In both the pure components and in the mixture one can expect that these atoms have a significant effect on the configurational entropy of the mixture through local charge-balance requirements. Local charge balance would imply that the stoichiometry of the coordination sphere of a sodium or calcium atom, in terms of Al and Si, would be that of pure albite and anorthite respectively. This criterion is satisfied identically for anorthite and ordered albite in the model but is violated for albite at elevated temperatures. This arises from the feature that the incomplete ordering of the Al atoms in the *a* sites implies that many configurations will be counted in our combinatorial factor, *g*, which do not strictly adhere to local charge balance. Thus the estimate of the high-temperature limit for the configurational entropy of albite given in I most

likely represents an upper bound to the true value. A similar overcounting of configurations is expected to occur in the present model for the plagioclase mixture.

It might also be expected that equivalent results could be obtained from the model with a smaller site preference energy if local charge balance were properly accounted for. This can be inferred from the fact that the site preference energy in the model, in conjunction with aluminum avoidance and overall charge balance, preferentially weights those configurations in which local charge balance is satisfied. Thus if local charge balance were rigorously obeyed it seems plausible that a smaller site preference energy would be needed to obtain an equivalent temperature dependence for the order parameter.

The complex nature of the feldspar lattice and specifically the structural relationship between the sodium and calcium atoms and Al and Si atoms have prevented us from incorporating, unambiguously, local charge balance into the model. However, a two-dimensional analog model of plagioclase can be constructed for which it is straightforward to include charge balance constraints. While we have not investigated the model in detail, we have calculated the high-temperature limiting value for the configurational entropy of the two-dimensional analog of albite. The calculation is outlined in Appendix B.<sup>1</sup> We find a substantial reduction in the entropy of "two-dimensional albite" due to charge balance and expect a similar reduction, although not of the same magnitude, in the three-dimensional case.

Lastly, we have ignored the possibility of a phase separation of the mixture into albite-like and anorthite-like solid solutions. It is conceivable that such a phase separation could result from the ordering process in the aluminosilicate framework. We are currently investigating this possibility.

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