

## On the formulation of simple mixing models for complex phases

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### ABSTRACT

In activity-composition relationships for multisite phases, it often occurs that end-members possess individual sites that contain more than one element. For example, in hornblende,  $\square\text{Ca}_2\text{Mg}_3[\text{MgAl}][\text{AlSi}_3]\text{Si}_4\text{O}_{22}(\text{OH})_2$ , the M2 site contains one Mg and one Al, and the T1 site contains one Al and three Si. In such cases, normalization is required to ensure that the ideal mixing activity and the activity coefficient of each end-member are each unity for the pure end-member. Such normalization is well known for the former, but not for the latter. A new formulation of normalization for activity coefficients is presented. In the context of symmetric (regular and reciprocal) interactions, the formulation is used to show that the thermodynamics can always be written in terms of  $\frac{1}{2}n(n-1)$  interaction parameters, where  $n$  is the minimum number of components needed to represent the composition of the phase. These macroscopic interaction parameters are particular linear combinations of the constituent regular and reciprocal model microscopic interaction parameters. With this, a further generalization leads to a dramatic simplification in the writing of activity coefficients: for any end-member,  $a$ , of a complex phase, including all symmetric microscopic interactions:

$$RT \ln \gamma_a = - \sum_i \sum_{j>i} (p_i^0 - p_i)(p_j^0 - p_j)W_{ij}$$

in which  $p_k$  is the proportion of end-member,  $k$ , in the phase,  $p_k^0$  is the value of  $p_k$  in pure  $a$ , and  $W_{ij}$  is the macroscopic interaction parameter for the  $ij$  binary. The summations are over an independent set of end-members chosen to represent the composition of the phase.

### INTRODUCTION

The lack of knowledge of activity-composition ( $a$ - $x$ ) relationships for minerals is still a major shortcoming in the reliable calculation of the conditions of formation of rocks and the calculation of geologically appropriate phase diagrams (Powell and Holland, 1988, p. 187–190). This lack of knowledge stems not only from the shortage of experimental data that can be used to constrain  $a$ - $x$  relations, but also from the formulation of the  $a$ - $x$  relations themselves. The task is not straightforward. The complexity of minerals, in terms of crystal structure and the differences in size and charge among the atoms mixing on the sites, means that a simple mixing model that can be routinely applied to minerals is unlikely. In particular, the presence of significant long-range and short-range order in minerals makes the task of formulating  $a$ - $x$  relations in a physically and chemically realistic way daunting. The formulation of entropy of mixing, and thus of thermodynamic mole fractions (or ideal mixing activities), for phases with even a small amount of nonideality is quite approximate (Guggenheim, 1966; Powell, 1983) and is impossible for the degree of nonideality characteristic of minerals. This is because the entropy of mixing

is directly related to the number of ways of organizing the atoms or molecules in the structure of the phase, for example, in terms of the numbers of nearest neighbors of different types. In turn, these numbers must depend on the interaction parameters (e.g., Guggenheim, 1966). Thus nonunit activity coefficients require thermodynamic mole fractions that depend on the interaction parameters. However, counting the number of ways of organizing the atoms or molecules turns out to be impossible unless very restrictive approximations are made. Thus, for all the models normally used (regular, subregular, reciprocal), thermodynamic mole fractions are written in terms of ideal mixing, with the activity coefficient terms written separately, for simplicity, and in the absence of a general way of doing otherwise.

In this paper, thermodynamic mole fractions (ideal mixing activities) are formulated with ideal mixing on all sites, representing a disordered solution, and nonideality is formulated involving enthalpic interactions involving all sites, which may be taken to account at least partially for any ordering in the structure. In this framework, it is shown how  $a$ - $x$  relationships may be simplified. Moreover, the logic developed can apply to other formulations, including those in which order parameters are involved

explicitly (e.g., Thompson, 1969). In this latter case, the logic applies prior to determining the equilibrium values of the order parameters, with or without the inclusion of additional ways of representing the order-disorder (e.g., Ghiorso, 1990; Holland, 1990).

Before this logic can be developed, a subsidiary but central problem must be solved. It concerns normalization, which ensures that both the thermodynamic mole fraction and the activity coefficient of each end-member goes to unity as the proportion of that end-member goes to unity. Normalization is necessary for end-members in multicomponent phases that do not involve sites filled with just one element, as for example in diopside Ca-Tschermak's, in which the two tetrahedral sites in Ca-Tschermak's involve Al and Si. Although normalization in ideal mixing activities is well known (e.g., Kerrick and Darken, 1975; Powell, 1977), that is not true for activity coefficients.

Simple symmetric formulations of nonideality will be considered here. For contributions to activity coefficients from interactions within any one site, the regular model will be used, whereas for contributions from interactions between sites, expressions of the Bragg-Williams (or reciprocal) type will be used. These will be referred to as the same-site and cross-site models, respectively. First, normalization of activity coefficients is discussed, then it is shown how the resulting activity coefficient expressions may be combined in a useful way.

#### NORMALIZATION OF ACTIVITY COEFFICIENTS

In a multicomponent multisite phase, for a general end-member,  $a$ , using a pure end-member standard state (so  $\mu_a^0$  refers to pure  $a$ ), the activity coefficient of  $a$ ,  $\gamma_a$ , is given by

$$\mu'_a = \mu_a^0 + RT \ln \gamma_a = \left( \frac{\partial G'}{\partial N_a} \right) \quad (1)$$

in which  $G'$  is the Gibbs energy of the phase without the ideal mixing term, so that  $\mu'_a$  is the chemical potential of  $a$  without the ideal mixing activity, and  $N_a$  is the number of moles of the end-member,  $a$ . Symbol usage is summarized in Table 1. The activity coefficient can be derived directly from Equation 1 by the methods of the next two sections if the end-member,  $a$ , does not have more than one element on any site. However, this is not possible otherwise, and this excluded case is the one for which normalization is required. But Equation 1 can be transformed so that the activity coefficient can be derived by the methods below. By using the chain rule in Equation 1,

$$\mu'_a = \sum_k \left( \frac{\partial G'}{\partial N_k} \right) \left( \frac{\partial N_k}{\partial N_a} \right) = \sum_k x_k^0 (\mu_k^0 + RT \ln \gamma_k). \quad (2)$$

The summation is over an independent set of components for which it is straightforward to derive activity coefficients by means of Equation 1. To write  $RT \ln \gamma_a$  in terms of the  $RT \ln \gamma_k$ , it is not sufficient just to equate terms between Equations 1 and 2; in order for  $RT \ln \gamma_a$

TABLE 1. Definitions of symbols used in text

Sym- bol	Definition
$\mu'_k$	chemical potential of end-member $k$ without the ideal mixing term (Eq. 1)
$G'$	Gibbs energy without the ideal mixing term (Eq. 1)
$N_k$	no. of moles of end-member $K$ (Eq. 1)
$RT$	gas constant times the temperature (Eq. 1)
$\gamma_i$	activity coefficient of $i$ (Eq. 1)
$\gamma_i^0$	activity coefficient of $i$ in a pure end-member (Eq. 3)
$x_i$	site fraction of $i$ (Eq. 7)
$x_i^0$	site fraction of $i$ in a pure end-member (Eq. 2)
$n_{ij}$	no. of moles of nearest neighbor $i$ - $j$ pair (Eq. 5)
$\epsilon_{ij}$	energy of nearest neighbor $i$ - $j$ pair (Eq. 5)
$w_{ij}$	same-site interaction energy involving $ij$ (Eq. 7)
$w_{kl}$	cross-site interaction energy involving $ij$ on one site and $kl$ on another (Eq. 14)
$y_k$	normalized $-x_k$ (Eq. 14)
$p_k$	proportion of end-member $k$ in an independent set (Eq. 20)
$q_k$	normalized $-p_k$ (Eq. 20)
$W_{kl}$	macroscopic interaction energy for the $k$ - $l$ binary (Eq. 20)

Note: the equation numbers given are those in which the respective symbols were first used. Additional superscripts may be involved to clarify which sites are referred to, for example, in  $x_i$  and  $w_{ij}$ ; they are omitted, as in this table, if there is no ambiguity.

to be appropriately normalized,

$$RT \ln \gamma_a = \sum_k x_k^0 RT \ln \frac{\gamma_k}{\gamma_k^0} \quad (3)$$

and

$$\mu_a^0 = \sum_k x_k^0 (\mu_k^0 + RT \ln \gamma_k^0) \quad (4)$$

in which  $\gamma_k^0$  is  $\gamma_k$  in pure end-member  $a$ . The two  $\gamma_k^0$  terms cancel as required when Equations 3 and 4 are combined. Equation 3 is a general expression for the normalized activity coefficient, regardless of the model used for the activity coefficient.

#### GENERALIZED $a$ - $x$ RELATIONSHIPS FOR SAME-SITE MIXING

The contribution to the Gibbs energy of a phase,  $G'$ , from same-site mixing on each of its sites can be modeled by the pair-wise nearest-neighbor approximation of, for example,

$$G' = \sum_i \sum_{j \geq i} n_{ij} \epsilon_{ij} \quad (5)$$

(Guggenheim, 1966) in which  $n_{ij}$  is the number of nearest neighbor  $i$ - $j$  pairs,  $\epsilon_{ij}$  is the energy of a nearest neighbor  $i$ - $j$  pair, and both sums are over the number of elements on the site (e.g., Powell, 1977). Subsumed in the  $\epsilon_{ij}$  are the factors coming from the duplicate counting of nearest neighbors, in proportion to their coordination. Strictly, Equation 5 is a virtual Gibbs energy (Powell, 1983) because the  $n_{ij}$  are not independent.

For an element,  $k$ , on the site, substituting Equation 5 into Equation 1 and applying the chain rule give

$$\mu'_k = \left( \frac{\partial G'}{\partial N_k} \right) = \sum_i \sum_j \left( \frac{\partial G'}{\partial n_{ij}} \right) \left( \frac{\partial n_{ij}}{\partial N_k} \right) = \sum_i \sum_j \left( \frac{\partial n_{ij}}{\partial N_k} \right) \epsilon_{ij}. \quad (6)$$

With the assumption of ideal mixing on sites, the  $n_{ij}$  are specified in terms of the  $N_k$  because the number of pairs is equal to the probability of an  $i$  being a nearest neighbor to a  $j$  as a proportion of the total number of pairs. Each probability is just the mole fraction, so  $n_{ij} = nx_i x_j$ , with  $x_k$  the mole fraction of  $k$ ,  $N_k/\sum_i N_i$ , on the site, and  $n$  the total number of pairs on this site,  $\sum \sum n_{kl}$ . Substituting this expression for  $n_{ij}$  into Equation 6, differentiating, and rearranging give

$$RT \ln \gamma_k = \sum_{i \neq k} x_i (1 - x_k) w_{ik} - \sum_{i \neq k} \sum_{j \neq k} x_i x_j w_{ij} \quad (7)$$

with  $\mu_k^0 = \epsilon_{kk}$  and  $w_{ij} = 2\epsilon_{ij} - \epsilon_{ii} - \epsilon_{jj}$ , reflecting whether  $i$ - $i$  and  $j$ - $j$  are preferred over  $i$ - $j$  nearest neighbors in the structure. This, or an equivalent formulation, is well known (e.g., Powell, 1977).

Substituting Equation 7 into Equation 3 and rearranging give the normalized contribution of same-site mixing to the activity coefficient of an arbitrary end-member,  $a$ :

$$\begin{aligned} RT \ln \gamma_a &= - \sum_i \sum_{j>i} (x_i^0 - x_i)(x_j^0 - x_j) w_{ij} \\ &\equiv - \sum_i \sum_{j>i} y_i y_j w_{ij} \end{aligned} \quad (8)$$

in which  $x_k$  is the mole fraction of atom  $k$  on the site being considered and  $x_k^0$  is the  $x_k$  in pure  $a$ . In Equation 8,  $y_k = x_k^0 - x_k$  can be considered to be the normalized value of  $-x_k$ . This formulation is new; its generality may be appreciated by considering two simple examples of its use.

The mixing of Ca, Na, and K on the A site of feldspar is a simple ternary example of same-site mixing. From Equation 8, for  $a$  being the Na end-member, with  $y_{Ca} = -x_{Ca}$ ,  $y_{Na} = 1 - x_{Na}$ , and  $y_K = -x_K$ , then

$$\begin{aligned} RT \ln \gamma_{Na} &= -(1 - x_{Na})(-x_{Ca}) w_{NaCa} \\ &\quad - (1 - x_{Na})(-x_K) w_{NaK} - (-x_K)(-x_{Ca}) w_{KCa} \\ &= x_{Ca}(1 - x_{Na}) w_{NaCa} + x_K(1 - x_{Na}) w_{NaK} \\ &\quad - x_K x_{Ca} w_{KCa} \end{aligned} \quad (9)$$

which is recognizable as the well-known ternary regular solution model expression (e.g., Wohl, 1946).

As an example of a binary mineral with an intermediate end-member, mixing in disordered epidote is considered, in the solid solution between clinozoisite {cz,  $\text{CaAl}[\text{Al}_2]\text{Si}_3\text{O}_{10}(\text{OH})$ } and pistacite {ps,  $\text{CaAl}[\text{Fe}_2]\text{Si}_3\text{O}_{10}(\text{OH})$ }. The internal bracket notation indicates the grouping of atoms on the sites, following Holland and Powell (1990). These formulae have been written assuming Al and  $\text{Fe}^{3+}$  mix (randomly) on two octahedral sites, referred to here as M13; in nature Fe orders in the M3 site and Al in the M1 site at lower temperatures. Using Equation 8, the same-site contribution from mixing in M13 to the activity coefficient of the epidote end-member, with  $y_{Al} = \frac{1}{2} - x_{Al}$  and  $y_{Fe} = \frac{1}{2} - x_{Fe}$ , is

$$\begin{aligned} RT \ln \gamma_{ep} &= -(\frac{1}{2} - x_{Al})(\frac{1}{2} - x_{Fe}) w_{FeAl} \\ &= (\frac{1}{2} - x_{Al})^2 w_{FeAl} \end{aligned} \quad (10)$$

as  $x_{Fe} = 1 - x_{Al}$ . This is just a special case of an intermediate end-member,  $A_m B_n$ , in a binary phase between A and B; Equation 8 gives

$$\begin{aligned} RT \ln \gamma_{A_m B_n} &= - \left( \frac{m}{n+m} - x_A \right) \left( \frac{n}{n+m} - x_B \right) w_{AB}. \end{aligned} \quad (11)$$

In addition, the system may be examined graphically (Fig. 1). In this, a tangent to the  $G^{\text{ex}}$  loop, say at  $x_B$ , gives  $RT \ln \gamma$  of the end-members, A and B, of a phase of this composition, from the intercepts of the tangent at pure A and pure B, respectively. Similarly, the activity coefficient of the intermediate end-member,  $A_m B_n$ , is given by the distance between this tangent and the  $G^{\text{ex}}$  loop at the composition of  $A_m B_n$ . For same-site mixing,  $G^{\text{ex}} = x_A x_B w_{AB}$ , and, from the geometry of the graph,  $RT \ln \gamma_{A_m B_n}$  is just

$$\begin{aligned} RT \ln \gamma_{A_m B_n} &= x_A x_B w_{AB} + \left( \frac{\partial G^{\text{ex}}}{\partial x_B} \right) \left( \frac{n}{n+m} - x_B \right) \\ &\quad - w_{AB} \frac{n}{n+m} \frac{m}{n+m}. \end{aligned} \quad (12)$$

Performing the differentiation in Equation 12 and rearranging give the same result as in Equation 11, as expected.

#### GENERALIZED $a$ - $x$ RELATIONSHIPS FOR CROSS-SITE MIXING

The contribution to the Gibbs energy of a phase,  $G'$ , from cross-site mixing involving two of its sites can be modeled by the pair-wise nearest-neighbor approximation, analogous to Equation 5:

$$G' = \sum_i \sum_j n_{ij} \epsilon_{ij} \quad (13)$$

with the  $i$  and  $j$  elements on the different sites. In this case, with the logic above and with M1 denoting one site and M2 the other,

$$\mu_{kl}^0 = \mu_{kl}^0 + \sum_{i \neq k} \sum_{j \neq l} x_i^{M1} x_j^{M2} w_{ijkl} \quad (14)$$

in which  $\mu_k^0 = \epsilon_{kl}$  and  $w_{ijkl} = \epsilon_{il} + \epsilon_{kj} - \epsilon_{ij} - \epsilon_{kl}$ , reflecting whether  $il$  and  $kj$  are preferred to  $ij$  and  $kl$  nearest neighbors between the two sites. There is a complication concerning the interaction parameters in the cross-site model in that not all the  $w_{ijkl}$  that can be written are independent (Powell, 1977). For two sites, with  $m_1$  elements in the first and  $m_2$  elements in the second, there are  $\frac{1}{2} m_1(m_1 - 1) m_2(m_2 - 1) w$  parameters, but only  $(m_1 - 1)(m_2 - 1)$  independent ones. However, an independent set of interaction parameters can be formed if a pair of elements is chosen to be involved in every one. If this pair is  $rs$ , then,

from Equation 14,

$$RT \ln \gamma_{kl} = \sum_{i \neq r} \sum_{j \neq s} (\delta_{ki} - x_{i1})(\delta_{lj} - x_{j2})w_{rsij} \quad (15)$$

in which  $\delta_{ab} = 1$  when  $a = b$  and equals 0 otherwise, and the independent interaction parameters are  $w_{rsij}$ , with  $i \neq r$  and  $j \neq s$ . This equation replaces the equivalent expression in Powell (1977), which, unfortunately, is in error.

Substituting Equation 15 into Equation 3 and rearranging give the formulation of the normalized contribution of cross-site mixing to the activity coefficient of an arbitrary end-member,  $a$ :

$$\begin{aligned} RT \ln \gamma_a &= \sum_{i \neq r} \sum_{j \neq s} [(x_i^A)^0 - x_i^A][x_j^B - x_j^B]w_{rsij}^{AB} \\ &= \sum_{i \neq r} \sum_{j \neq s} y_i^A y_j^B w_{rsij}^{AB} \end{aligned} \quad (16)$$

in which  $x_k^s$  is the site fraction of  $k$  on site  $S$ , and  $(x_k^s)^0$  is the value of the site fraction in pure  $a$ . In Equation 16,  $y_k^s = (x_k^s)^0 - x_k^s$  can be considered to be the normalized value of  $-x_k^s$ . This is a new formulation.

In garnet in  $\text{CaO-MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$ , an example requiring no normalization, Ca and Mg mix on the cubic site (M1), and Al and Cr on the octahedral site (M2), with end-members grossularite (gr,  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), pyrope (py,  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), uvarovite (uv,  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ), and knorringite (kn,  $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ). Using Equation 16 and choosing the interaction parameter to be  $w_{\text{CaAlMgCr}}$ , we have

$$\begin{aligned} RT \ln \gamma_{\text{gr}} &= (-x_{\text{Mg}}^{\text{M1}})(-x_{\text{Cr}}^{\text{M2}})w_{\text{CaAlMgCr}} \\ &= x_{\text{Mg}}^{\text{M1}}x_{\text{Cr}}^{\text{M2}}w_{\text{CaAlMgCr}} \\ RT \ln \gamma_{\text{py}} &= (1 - x_{\text{Mg}}^{\text{M1}})(-x_{\text{Cr}}^{\text{M2}})w_{\text{CaAlMgCr}} \\ &= -x_{\text{Ca}}^{\text{M1}}x_{\text{Cr}}^{\text{M2}}w_{\text{CaAlMgCr}} \\ RT \ln \gamma_{\text{uv}} &= (-x_{\text{Mg}}^{\text{M1}})(1 - x_{\text{Cr}}^{\text{M2}})w_{\text{CaAlMgCr}} \\ &= -x_{\text{Mg}}^{\text{M1}}x_{\text{Al}}^{\text{M2}}w_{\text{CaAlMgCr}} \\ RT \ln \gamma_{\text{kn}} &= (1 - x_{\text{Mg}}^{\text{M1}})(1 - x_{\text{Cr}}^{\text{M2}})w_{\text{CaAlMgCr}} \\ &= x_{\text{Ca}}^{\text{M1}}x_{\text{Al}}^{\text{M2}}w_{\text{CaAlMgCr}} \end{aligned} \quad (17)$$

The results in Equation 17 are seen to be identical to the familiar reciprocal expressions of Powell (1977) and Wood and Nicholls (1978).

In feldspar in  $\text{CaO-Na}_2\text{O-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ , an example in which normalization is required, Na, K, and Ca mix on the A site, and Al and Si mix on the four tetrahedral sites, with end-members anorthite (an,  $\text{Ca}[\text{Al}_2\text{Si}_2]\text{O}_8$ ), albite (ab,  $\text{Na}[\text{AlSi}_3]\text{O}_8$ ), and orthoclase (or,  $\text{K}[\text{AlSi}_3]\text{O}_8$ ). The cross-site contribution to the activity coefficient of albite can be written down directly using Equation 16. There are two independent cross-site interaction parameters, which, if the fixed pair  $rs$  is CaAl, are  $w_{\text{CaAlKSi}}^{\text{AT}}$  and  $w_{\text{CaAlNaSi}}^{\text{AT}}$ . For albite,  $y_{\text{K}}^{\text{A}} = -x_{\text{K}}^{\text{A}}$ ,  $y_{\text{Ca}}^{\text{A}} = -x_{\text{Ca}}^{\text{A}}$ ,  $y_{\text{Na}}^{\text{A}} = 1 - x_{\text{Na}}^{\text{A}}$ ,  $y_{\text{Al}}^{\text{T}} = 1/4 - x_{\text{Al}}^{\text{T}}$ ,  $y_{\text{Si}}^{\text{T}} = 3/4 - x_{\text{Si}}^{\text{T}}$ , and similarly for the

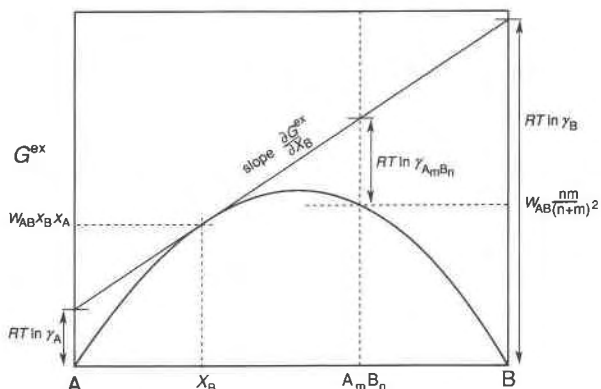


Fig. 1. Graphical demonstration of the form of normalization in a binary system with regular mixing between the end-members A and B (see text).

other end-members, then, from Equation 16:

$$\begin{aligned} RT \ln \gamma_{\text{ab}} &= w_{\text{CaAlKSi}}^{\text{AT}}(-x_{\text{K}}^{\text{A}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ &\quad + w_{\text{CaAlNaSi}}^{\text{AT}}(1 - x_{\text{Na}}^{\text{A}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ RT \ln \gamma_{\text{or}} &= w_{\text{CaAlKSi}}^{\text{AT}}(1 - x_{\text{K}}^{\text{A}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ &\quad + w_{\text{CaAlNaSi}}^{\text{AT}}(-x_{\text{Na}}^{\text{A}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ RT \ln \gamma_{\text{an}} &= w_{\text{CaAlKSi}}^{\text{AT}}(-x_{\text{K}}^{\text{A}})(1/2 - x_{\text{Si}}^{\text{T}}) \\ &\quad + w_{\text{CaAlNaSi}}^{\text{AT}}(-x_{\text{Na}}^{\text{A}})(1/2 - x_{\text{Si}}^{\text{T}}). \end{aligned} \quad (18)$$

In amphibole in  $\text{CaO-Na}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ , Table 2 (but, for this example, excluding Na from the M4 site), there are cross-site contributions to the activity coefficients from interactions between Na and  $\square$  on the A site, Mg and Al on the two M2 sites, and Si and Al on four of the T sites. Using the independent set of interaction parameters,  $w_{\text{AlAlMgSi}}^{\text{M2T}}$ ,  $w_{\text{NaAlMg}}^{\text{AM2}}$ , and  $w_{\text{NaAlSi}}^{\text{AT}}$  then, from Equation 16, for example:

$$\begin{aligned} RT \ln \gamma_{\text{tr}} &= w_{\text{AlAlMgSi}}^{\text{M2T}}(1 - x_{\text{Mg}}^{\text{M2}})(1 - x_{\text{Si}}^{\text{T}}) \\ &\quad + w_{\text{NaAlMg}}^{\text{AM2}}(1 - x_{\text{Al}}^{\text{A}})(1 - x_{\text{Mg}}^{\text{M2}}) \\ &\quad + w_{\text{NaAlSi}}^{\text{AT}}(1 - x_{\text{Al}}^{\text{A}})(1 - x_{\text{Si}}^{\text{T}}) \\ RT \ln \gamma_{\text{ed}} &= w_{\text{AlAlMgSi}}^{\text{M2T}}(1 - x_{\text{Mg}}^{\text{M2}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ &\quad + w_{\text{NaAlMg}}^{\text{AM2}}(-x_{\text{Al}}^{\text{A}})(1 - x_{\text{Mg}}^{\text{M2}}) \\ &\quad + w_{\text{NaAlSi}}^{\text{AT}}(-x_{\text{Al}}^{\text{A}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ RT \ln \gamma_{\text{hb}} &= w_{\text{AlAlMgSi}}^{\text{M2T}}(1/2 - x_{\text{Mg}}^{\text{M2}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ &\quad + w_{\text{NaAlMg}}^{\text{AM2}}(1 - x_{\text{Al}}^{\text{A}})(1/2 - x_{\text{Mg}}^{\text{M2}}) \\ &\quad + w_{\text{NaAlSi}}^{\text{AT}}(1 - x_{\text{Al}}^{\text{A}})(3/4 - x_{\text{Si}}^{\text{T}}) \\ RT \ln \gamma_{\text{ts}} &= w_{\text{AlAlMgSi}}^{\text{M2T}}(-x_{\text{Mg}}^{\text{M2}})(1/2 - x_{\text{Si}}^{\text{T}}) \\ &\quad + w_{\text{NaAlMg}}^{\text{AM2}}(1 - x_{\text{Al}}^{\text{A}})(-x_{\text{Mg}}^{\text{M2}}) \\ &\quad + w_{\text{NaAlSi}}^{\text{AT}}(1 - x_{\text{Al}}^{\text{A}})(1/2 - x_{\text{Si}}^{\text{T}}). \end{aligned} \quad (19)$$

TABLE 2. Amphibole formulae and site allocations

	A	M4	M13	M2	T1	T2
Tremolite	□	Ca <sub>2</sub>	Mg <sub>3</sub>	Mg <sub>2</sub>	Si <sub>4</sub>	Si <sub>4</sub>
Edenite	Na	Ca <sub>2</sub>	Mg <sub>3</sub>	Mg <sub>2</sub>	AlSi <sub>3</sub>	Si <sub>4</sub>
Hornblende	□	Ca <sub>2</sub>	Mg <sub>3</sub>	MgAl	AlSi <sub>3</sub>	Si <sub>4</sub>
Tschemakite	□	Ca <sub>2</sub>	Mg <sub>3</sub>	Al <sub>2</sub>	Al <sub>2</sub> Si <sub>2</sub>	Si <sub>4</sub>
Pargasite	Na	Ca <sub>2</sub>	Mg <sub>3</sub>	MgAl	Al <sub>2</sub> Si <sub>2</sub>	Si <sub>4</sub>
Glaucofane	□	Na <sub>2</sub>	Mg <sub>3</sub>	Al <sub>2</sub>	Si <sub>4</sub>	Si <sub>4</sub>
Richterite	Na	NaCa	Mg <sub>3</sub>	Mg <sub>2</sub>	Si <sub>4</sub>	Si <sub>4</sub>

### MACROSCOPIC THERMODYNAMICS

As can be seen above, when activity coefficient expressions involving same-site and cross-site terms are written out, there is a proliferation of interaction energy parameters. Even for a ternary phase there are already many interaction parameters, if mixing occurs on several sites. For example, in ternary anorthite albite orthoclase feldspar, with mixing on two sites, there are two cross-site terms and four same-site terms (three for the A site and one for the tetrahedral site). In ternary tremolite hornblende edenite amphibole, with mixing on three sites, there are three cross-site terms and three same-site terms. For larger systems there is a rapid increase in the number of terms. However two lines of argument suggest that a simplification is possible. The first is the similar forms of the activity coefficient contributions from Equations 8 and 16. The second is that there are many more  $y$  terms than independent compositional terms. Thus for the ternary feldspars above there are five  $y$  terms ( $y_{\text{Na}}^{\text{A}}$ ,  $y_{\text{Ca}}^{\text{A}}$ ,  $y_{\text{Al}}^{\text{A}}$ ,  $y_{\text{Si}}^{\text{T}}$ ) but only three compositional terms, of which two are independent (as the phase is ternary). These compositional terms can be taken to be the proportions of a set of independent end-members. An independent set of end-members is just a minimum set of end-members from which all other end-members of the phase can be constructed, and which can be used to represent any composition of the phase (e.g., Thompson, 1982). The proportions of the end-members in an independent set will be denoted  $p_k$ . In the ternary feldspar case, the choice of an independent set is straightforward—albite, anorthite, and orthoclase—with  $p_{\text{ab}} = x_{\text{Na}}^{\text{A}}$ ,  $p_{\text{an}} = x_{\text{Ca}}^{\text{A}}$ , and  $p_{\text{or}} = x_{\text{K}}^{\text{A}}$ . In the ternary amphibole case, several choices of an independent set can be made. For the independent set tremolite-hornblende-edenite, the proportions of the end-members in terms of site fractions are  $p_{\text{ed}} = x_{\text{Na}}^{\text{A}}$ ,  $p_{\text{hb}} = 2x_{\text{Ca}}^{\text{A}}$ , and, by difference,  $p_{\text{tr}} = 1 - p_{\text{hb}} - p_{\text{ed}}$ .

For the activity coefficient of a general end-member  $a$ , the  $y$  terms in Equations 8 and 16 can be written as a linear combination of  $q_k = p_k^0 - p_k$ , in which  $p_k^0$  is the proportion of  $k$  in pure  $a$ . Multiplying out each  $y_i y_j$  term with the appropriate linear combination substituted for each  $y$  and then summing produce a result involving terms in every  $q_k q_l$  combination, each involving a linear combination of the same-site and cross-site interaction parameters. For an  $n$ -component system, there are  ${}^nC_2 = n!/(n-2)! = \frac{1}{2}n(n-1)$  different  $q_k q_l$  combinations, and so there are also this number of linear combinations

of interaction parameters, regardless of the number of sites on which the mixing takes place. The linear combinations of (microscopic) interaction parameters may be termed macroscopic interaction parameters and will be denoted  $W_{kl}$ . Thus, in a general multisite phase, the activity coefficient of any end-member,  $a$ , of the phase from all symmetric interactions can be written as

$$RT \ln \gamma_a = - \sum_k \sum_{l>k} (p_k^0 - p_k)(p_l^0 - p_l) W_{kl} \\ \equiv - \sum_k \sum_{l>k} q_k q_l W_{kl} \quad (20)$$

in which  $q_k = p_k^0 - p_k$  is the normalized value of  $-p_k$ . The summation is over an independent set of end-members. This new equation is general, allowing activity coefficients to be formulated for dependent end-members, as well as members of the chosen independent set, taking into account the same-site and cross-site interactions being considered here. The corresponding equation for  $G^{\text{ex}}$  of the phase is

$$G^{\text{ex}} = \sum_k \sum_{l>k} p_k p_l W_{kl} \quad (21)$$

Thus the formulation of activity coefficients in complex phases arising from symmetric interactions can be written down directly using Equation 20 once an independent set of end-members is chosen, and the proportions of these end-members are cast in terms of site fractions.

The logic leading to Equation 20 is illustrated using a binary enstatite Mg-Tschemak's pyroxene, with enstatite (en,  $\text{MgMg}[\text{Si}_2]\text{O}_6$ ) and Mg-Tschemak's (Mg-ts,  $\text{MgAl}[\text{AlSi}]\text{O}_6$ ) chosen as the independent set. The proportions of these are just  $p_{\text{en}} = x_{\text{Mg}}^{\text{M1}}$  and  $p_{\text{Mg-ts}} = x_{\text{Al}}^{\text{M1}}$ , in terms of the mole fractions of the elements on sites. Writing the activity coefficients using Equations 8 and 16, with same-site terms involving  $w_{\text{MgAl}}^{\text{M1}}$  and  $w_{\text{AlSi}}^{\text{T}}$ , and the cross-site term involving  $w_{\text{AlAlMgSi}}^{\text{M1T}}$ , we then have

$$RT \ln \gamma_{\text{en}} = w_{\text{MgAl}}^{\text{M1}}(1 - x_{\text{Mg}}^{\text{M1}})^2 + w_{\text{AlSi}}^{\text{T}}(1 - x_{\text{Si}}^{\text{T}})^2 \\ + w_{\text{AlAlMgSi}}^{\text{M1T}}(1 - x_{\text{Mg}}^{\text{M1}})(1 - x_{\text{Si}}^{\text{T}}) \\ RT \ln \gamma_{\text{Mg-ts}} = w_{\text{MgAl}}^{\text{M1}}(1 - x_{\text{Al}}^{\text{M1}})^2 + w_{\text{AlSi}}^{\text{T}}(\frac{1}{2} - x_{\text{Al}}^{\text{T}})^2 \\ + w_{\text{AlAlMgSi}}^{\text{M1T}}(-x_{\text{Mg}}^{\text{M1}})(\frac{1}{2} - x_{\text{Si}}^{\text{T}}). \quad (22)$$

Note that in Equation 22 multipliers to represent the number of sites in the formula unit are not included; any multipliers have been subsumed into the  $w$  parameters, which are bulk interaction parameters (also see Discussion). Substituting  $x_{\text{Mg}}^{\text{M1}} = 1 - p_{\text{Mg-ts}}$  and  $x_{\text{Al}}^{\text{M1}} = p_{\text{Mg-ts}}$  gives

$$RT \ln \gamma_{\text{en}} \\ = (1 - p_{\text{en}})p_{\text{Mg-ts}}(w_{\text{MgAl}}^{\text{M1}} + \frac{1}{4}w_{\text{AlSi}}^{\text{T}} + \frac{1}{2}w_{\text{AlAlMgSi}}^{\text{M1T}}) \\ RT \ln \gamma_{\text{Mg-ts}} \\ = p_{\text{en}}(1 - p_{\text{Mg-ts}})(w_{\text{MgAl}}^{\text{M1}} + \frac{1}{4}w_{\text{AlSi}}^{\text{T}} + \frac{1}{2}w_{\text{AlAlMgSi}}^{\text{M1T}}) \quad (23)$$

and

TABLE 3. The linear combinations of the macroscopic interaction parameters for amphibole, with tr-hb-ed-gl as the independent set

Mult	$W_{\text{CaNa}}^{\text{A}}$	$W_{\text{MgAl}}^{\text{M2}}$	$W_{\text{CaNa}}^{\text{M4}}$	$W_{\text{SiAl}}^{\text{T}}$	$W_{\text{NaAlMg}}^{\text{AM2}}$	$W_{\text{NaCaCa}}^{\text{AM4}}$	$W_{\text{AlNaMgCa}}^{\text{M2M4}}$	$W_{\text{NaAlSi}}^{\text{AT}}$	$W_{\text{AlAlMgSi}}^{\text{M2T}}$	$W_{\text{NaAlCaSi}}^{\text{M4T}}$
$W_{\text{tr-hb}}$	$\frac{1}{2}$	4	—	1	—	—	—	—	2	—
$W_{\text{tr-ed}}$	$\frac{1}{2}$	16	—	1	—	—	—	4	—	—
$W_{\text{hb-ed}}$	$\frac{1}{4}$	4	1	—	-2	—	—	—	—	—
$W_{\text{tr-gl}}$	1	—	1	—	—	—	1	—	—	—
$W_{\text{hb-gl}}$	$\frac{1}{2}$	—	4	16	1	—	8	—	-2	-4
$W_{\text{ed-gl}}$	$\frac{1}{2}$	16	16	16	1	-16	16	4	-4	-4

Note: tr = tremolite, hb = hornblende, ed = edenite, gl = glaucophane. Each row of the table defines a linear combination, with the number in the Mult column the multiplier; thus from the first row:  $W_{\text{tr-hb}} = \frac{1}{2}(4W_{\text{MgAl}}^{\text{M2}} + W_{\text{SiAl}}^{\text{T}} + 2W_{\text{AlAlMgSi}}^{\text{M2T}})$ . See Table 1 for formulae.

$$G^{\text{ex}} = p_{\text{en}}RT \ln \gamma_{\text{en}} + p_{\text{Mg-ts}}RT \ln \gamma_{\text{Mg-ts}}$$

$$= p_{\text{Mg-ts}}p_{\text{en}}(w_{\text{MgAl}}^{\text{M1}} + \frac{1}{4}w_{\text{AlSi}}^{\text{T}} + \frac{1}{2}w_{\text{AlAlMgSi}}^{\text{M1T}}). \quad (24)$$

Therefore, although there are three interaction parameters in Equations 23 and 24, they only occur in one linear combination,  $w_{\text{MgAl}}^{\text{M1}} + \frac{1}{4}w_{\text{AlSi}}^{\text{T}} + \frac{1}{2}w_{\text{AlAlMgSi}}^{\text{M1T}}$ , which can be referred to as  $W_{\text{en-Mg-ts}}$ , which is a macroscopic interaction parameter. These equations correspond to those obtained through Equations 20 and 21. In addition, the activity coefficient of the fictive garnet end-member, orthopyroxene (opy), in this binary may be obtained using Equation 20. This end-member is  $\text{Mg}_{\frac{3}{2}}\text{Al}_{\frac{1}{2}}\text{Si}_{\frac{3}{2}}$ ; it can be represented by  $\text{opy} = (\text{en} + \text{Mg-ts})/2$ . Thus, for orthopyroxene,  $q_{\text{en}} = \frac{1}{2} - p_{\text{en}}$  and  $q_{\text{Mg-ts}} = \frac{1}{2} - p_{\text{Mg-ts}}$ , and

$$RT \ln \gamma_{\text{opy}} = (\frac{1}{2} - p_{\text{en}})(\frac{1}{2} - p_{\text{Mg-ts}})W_{\text{en-Mg-ts}}. \quad (25)$$

Considering macroscopic interaction parameters, for example,  $W_{\text{en-Mg-ts}}$  in Equation 25, we find it useful to be able to write down the linear combinations of interaction parameters directly, without having to resort to Equations 8 and 16. In the enstatite Mg-Tschermak's case above, there is just one macroscopic interaction parameter, but in large systems there are many. However, each linear combination of same-site and cross-site interaction parameters involves only those in the corresponding binary. With the enstatite Mg-Tschermak's binary, with  $p \equiv p_{\text{Mg-ts}}$  and therefore  $p_{\text{en}} = 1 - p$ , then  $x_{\text{Al}}^{\text{M1}} = p$ ,  $x_{\text{Mg}}^{\text{M1}} = 1 - p$ ,  $x_{\text{Al}}^{\text{T}} = \frac{1}{2}$ , and  $x_{\text{Si}}^{\text{T}} = (2 - p)/2$ . To find the multipliers on the constituent  $w$  parameters, the denominators in these expressions are examined, noting that two such denominators are involved in each activity coefficient contribution. Thus, for  $w_{\text{MgAl}}^{\text{M1}}$  it is  $1 \cdot 1 = 1$ , for  $w_{\text{AlSi}}^{\text{T}}$  it is  $\frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$ , and for  $w_{\text{AlAlMgSi}}^{\text{M1T}}$  it is  $1 \cdot \frac{1}{2} = \frac{1}{2}$ , giving, as expected,

$W_{\text{en-Mg-ts}} = w_{\text{MgAl}}^{\text{M1}} + \frac{1}{4}w_{\text{AlSi}}^{\text{T}} + \frac{1}{2}w_{\text{AlAlMgSi}}^{\text{M1T}}$ , as given by Equation 22.

A simple example showing the application of Equation 20 and the procedure of the last paragraph involves the ternary feldspar system. As a consequence  $W_{\text{ab-an}} = w_{\text{NaCl}}^{\text{A}} + \frac{1}{16}w_{\text{AlSi}}^{\text{T}} + \frac{1}{4}w_{\text{CaAlNaSi}}^{\text{AT}}$ ,  $W_{\text{or-an}} = w_{\text{KCa}}^{\text{A}} + \frac{1}{16}w_{\text{AlSi}}^{\text{T}} + \frac{1}{4}w_{\text{CaAlKSi}}^{\text{AT}}$ ,  $W_{\text{ab-or}} = w_{\text{KNa}}^{\text{A}}$ , and

$$RT \ln \gamma_{\text{ab}} = -(1 - p_{\text{ab}})(-p_{\text{an}})W_{\text{ab-an}} - (-p_{\text{or}})(-p_{\text{an}})W_{\text{or-an}}$$

$$- (1 - p_{\text{ab}})(-p_{\text{or}})W_{\text{ab-or}}$$

$$RT \ln \gamma_{\text{or}} = -(-p_{\text{ab}})(-p_{\text{an}})W_{\text{ab-an}} - (1 - p_{\text{or}})(-p_{\text{an}})W_{\text{or-an}}$$

$$- (-p_{\text{ab}})(1 - p_{\text{or}})W_{\text{ab-or}}$$

$$RT \ln \gamma_{\text{an}} = -(-p_{\text{ab}})(1 - p_{\text{an}})W_{\text{ab-an}}$$

$$- (-p_{\text{or}})(1 - p_{\text{an}})W_{\text{or-an}}$$

$$- (-p_{\text{ab}})(-p_{\text{or}})W_{\text{ab-or}}. \quad (26)$$

In relation to the description of the thermodynamics of plagioclase of Holland and Powell (1992),  $w_{\text{C1}}$  for example, was considered to relate only to mixing of Ca and Na in the CT structure. In fact, the interaction parameters estimated actually refer to  $w_{\text{NaCa}}^{\text{A}} + \frac{1}{16}w_{\text{AlSi}}^{\text{T}} + \frac{1}{4}w_{\text{CaAlNaSi}}^{\text{AT}}$ , not just to  $w_{\text{NaCa}}^{\text{A}}$ ; otherwise the logic used there is entirely consistent with this study.

A more complex example showing the application of Equation 20 involves amphibole (Table 2), with Na-□ mixing on one A site, Mg-Al mixing on two M2 sites, Na-Ca mixing on two M4 sites, and Al-Si mixing on four T sites, and choosing tremolite (tr), hornblende (hb), edenite (ed), and glaucophane (gl) as the independent set of end-members. With this choice,  $p_{\text{ed}} = x_{\text{Na}}^{\text{A}}$ ,  $p_{\text{gl}} = x_{\text{Na}}^{\text{M4}}$ ,

TABLE 4. The formulation of activity coefficients for amphibole, with tr-hb-ed-gl as the independent set

	$W_{\text{tr-hb}}$	$W_{\text{tr-ed}}$	$W_{\text{hb-ed}}$	$W_{\text{tr-gl}}$	$W_{\text{hb-gl}}$	$W_{\text{ed-gl}}$
$RT \ln \gamma_{\text{tr}}$	$-(1 - p_{\text{tr}})(-p_{\text{hb}})$	$-(1 - p_{\text{tr}})(-p_{\text{ed}})$	$-(-p_{\text{hb}})(-p_{\text{ed}})$	$-(1 - p_{\text{tr}})(-p_{\text{gl}})$	$-(-p_{\text{hb}})(-p_{\text{gl}})$	$-(-p_{\text{ed}})(-p_{\text{gl}})$
$RT \ln \gamma_{\text{hb}}$	$-(-p_{\text{tr}})(1 - p_{\text{hb}})$	$-(-p_{\text{tr}})(-p_{\text{ed}})$	$-(1 - p_{\text{hb}})(-p_{\text{ed}})$	$-(-p_{\text{tr}})(-p_{\text{gl}})$	$-(1 - p_{\text{hb}})(-p_{\text{gl}})$	$-(-p_{\text{ed}})(-p_{\text{gl}})$
$RT \ln \gamma_{\text{ed}}$	$-(-p_{\text{tr}})(-p_{\text{hb}})$	$-(-p_{\text{tr}})(1 - p_{\text{ed}})$	$-(-p_{\text{hb}})(1 - p_{\text{ed}})$	$-(-p_{\text{tr}})(-p_{\text{gl}})$	$-(-p_{\text{hb}})(-p_{\text{gl}})$	$-(1 - p_{\text{ed}})(-p_{\text{gl}})$
$RT \ln \gamma_{\text{gl}}$	$-(-p_{\text{tr}})(-p_{\text{hb}})$	$-(-p_{\text{tr}})(-p_{\text{ed}})$	$-(-p_{\text{hb}})(-p_{\text{ed}})$	$-(-p_{\text{tr}})(1 - p_{\text{gl}})$	$-(-p_{\text{hb}})(1 - p_{\text{gl}})$	$-(-p_{\text{ed}})(1 - p_{\text{gl}})$
$RT \ln \gamma_{\text{ts}}$	$-(-1 - p_{\text{tr}})(2 - p_{\text{hb}})$	$-(-1 - p_{\text{tr}})(-p_{\text{ed}})$	$-(2 - p_{\text{hb}})(-p_{\text{ed}})$	$-(-1 - p_{\text{tr}})(-p_{\text{gl}})$	$-(2 - p_{\text{hb}})(-p_{\text{gl}})$	$-(-p_{\text{ed}})(-p_{\text{gl}})$
$RT \ln \gamma_{\text{ri}}$	$-(\frac{1}{2} - p_{\text{tr}})(-1 - p_{\text{hb}})$	$-(\frac{1}{2} - p_{\text{tr}})(1 - p_{\text{ed}})$	$-(-1 - p_{\text{hb}})(1 - p_{\text{ed}})$	$-(\frac{1}{2} - p_{\text{tr}})(\frac{1}{2} - p_{\text{gl}})$	$-(-1 - p_{\text{hb}})(\frac{1}{2} - p_{\text{gl}})$	$-(1 - p_{\text{ed}})(\frac{1}{2} - p_{\text{gl}})$
$RT \ln \gamma_{\text{pa}}$	$-(-1 - p_{\text{tr}})(1 - p_{\text{hb}})$	$-(-1 - p_{\text{tr}})(1 - p_{\text{ed}})$	$-(1 - p_{\text{hb}})(1 - p_{\text{ed}})$	$-(-1 - p_{\text{tr}})(-p_{\text{gl}})$	$-(-1 - p_{\text{hb}})(-p_{\text{gl}})$	$-(1 - p_{\text{ed}})(-p_{\text{gl}})$

Note: ts = tschermakite, ri = richterite, pa = pargasite. Each row defines the activity coefficient given in the first column. The first four columns are for the end-members in the independent set; the last three columns are for dependent end-members. The proportions of the end-members in the independent set in terms of site fractions are  $p_{\text{ed}} = x_{\text{Na}}^{\text{A}}$ ,  $p_{\text{gl}} = x_{\text{Na}}^{\text{M4}}$ ,  $p_{\text{hb}} = 2(x_{\text{Al}}^{\text{M2}} - x_{\text{Na}}^{\text{M4}})$ , and  $p_{\text{tr}}$  is found by difference. See Table 1 for formulae.

$p_{hb} = 2(x_{Al}^{M2} - x_{Na}^{M4})$ , and  $p_{tr}$  is found by difference. The dependent end-members in Table 1 are related to the end-members in the independent set by tschermakite ( $ts = 2hb - tr$ ), pargasite ( $pa = ed + hb - tr$ ), and richterite [ $ri = \frac{1}{2}(gl + tr) + ed - hb$ ]. Thus, for example, for richterite,  $p_{tr}^0 = \frac{1}{2}$ ,  $p_{hb}^0 = -1$ ,  $p_{ed}^0 = 1$ , and  $p_{gl}^0 = \frac{1}{2}$ . The resulting activity coefficients are given in Tables 3 and 4.

### DISCUSSION

The logic developed above shows how the number of interaction parameters required to represent  $a$ - $x$  relationships in multisite multicomponent phases can be minimized when cross-site and same-site interaction parameters are considered in linear combination. This symmetric formalism dramatically simplifies the writing of  $a$ - $x$  relationships and brings out the underlying form of the thermodynamics. It also has the merit of appearing to be a macroscopic phenomenological description of the phase, even though it is derived from a microscopic description.

In the formulations it is important to note that the same-site and cross-site interaction parameters used are bulk ones for the stated size of the formula unit. Although it would have been straightforward to have included a multiplicity in the same-site activity coefficient expressions, as commonly done in the literature, simply equal to the number of sites on which mixing occurs in the formula unit, it is not easily done for the cross-site activity coefficients. Thus, if one considers same-site mixing in garnet, with an  $A_3B_2Si_3O_{12}$  formula, the interaction parameters to be used in, for example, Equation 3, may be considered to represent, for example,

$$w_{CaMg} = 3(2\epsilon_{CaMg} - \epsilon_{CaCa} - \epsilon_{MgMg}) \quad (27)$$

and in cross-site mixing,

$$w_{CaAlMgCr} = \epsilon_{Ca_2Cr_3} + \epsilon_{Mg_2Al_3} - \epsilon_{Mg_2Cr_3} - \epsilon_{Ca_2Al_3}. \quad (28)$$

No difficulty arises in this, although, if for some reason a larger or smaller formula unit is chosen for a mineral, the interaction parameters must be varied in proportion.

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