

## The use of thermodynamic excess functions in the Nernst distribution law: discussion

JAMES GUY BLENCOE

Department of Geosciences, The Pennsylvania State University  
University Park, Pennsylvania 16802

### Abstract

Holst (1978) has used thermodynamic theory to derive a Nernst distribution equation in which nonideal behavior of coexisting phases is represented by excess functions rather than activity coefficients. This equation was employed in a thermodynamic and geothermometric evaluation of 30 kbar orthoehstatite–diopside solvus data to illustrate a practical application of the theory. However, Holst did not include crystal structure as a factor in his thermodynamic analysis.

This paper presents thermodynamic theory which illustrates some of the complexities and constraints in applications of the Nernst distribution law to crystalline solutions. It is concluded that a strict accounting for the effects of crystal structure is required for a rigorous thermodynamic assessment of equilibria between coexisting, mutually-soluble crystalline solutions with different structures.

### Introduction

Holst (1978) has derived a Nernst distribution equation for application to: (1) analysis of solvus data for binary systems, (2) geothermometry, and (3) trace-element distribution among coexisting phases. The main purpose of this communication is to show that applications of the Nernst distribution law to coexisting crystalline solutions are usually more complicated than implied in Holst's treatment.

### Basic theory

Thermodynamic theory applicable to the equilibrium coexistence of two mutually-soluble binary crystalline solutions has been discussed in detail by Blencoe (1977), so only a brief summary will be given here [thermochemical terms used in this paper are defined in Table 1 of Blencoe (1977)]. The chemical potential of a crystalline component *i*, with the standard-state conditions  $P^\circ = P$ ,  $T^\circ = T$ , and  $X_i^\circ = 1$ , is given by the generalized equation

$$\mu_{i,P,T} = \mu_{i,P,T}^\circ + RT \ln a_{i,P,T} \quad (1)$$

[Blencoe, 1977, equation (5)].<sup>1</sup> For equilibrium be-

<sup>1</sup> Actually, the equation presented by Blencoe (1977) is:  $\mu_{i,P,T} = \mu_{i,P,T}^\circ + \alpha RT \ln a_{i,P,T}$ , where " $\alpha$ " is the number of mixing sites in the standard formulae for the components of a crystalline solution series (Thompson, 1967, p. 342). This equation is always appli-

tween coexisting crystalline solutions A and B in a binary system 1–2 at constant *P* and *T*, we have  $\mu_{1A} = \mu_{1B}$  and  $\mu_{2A} = \mu_{2B}$ , and by substituting equation (1) into each of these relations we obtain

$$\mu_{1A}^\circ + RT \ln a_{1A} = \mu_{1B}^\circ + RT \ln a_{1B} \quad (2a)$$

and

$$\mu_{2A}^\circ + RT \ln a_{2A} = \mu_{2B}^\circ + RT \ln a_{2B} \quad (2b)$$

(Throughout this paper, "A" and "B" will refer to the two phases of a crystalline solvus-pair in a binary or multicomponent system at an arbitrary but fixed *P* and *T*, with  $X_{1A} \geq X_{1B}$ .) A and B can be either isostructural or nonisostructural,<sup>2</sup> and if they are iso-

structural, they are also equivalent. The term "equivalent" is applicable to crystalline solutions with one or more equivalent mixing sites, but in other instances its use may be quite improper [e.g., for binary plagioclase feldspars when the mixing properties of the crystalline solutions are assumed to conform to certain crystallographic constraints (Kerrick and Darken, 1975)]. With the proviso that  $a_i$  can be a model-dependent expression of any appropriate mathematical form, it can be stated simply that equation (1) is a completely correct but generalized equation for the chemical potential of component *i*.

<sup>2</sup> The term "isostructural" refers to coexisting phases of a single crystalline solution series (stable, metastable, or unstable) in which there are: (1) no abrupt changes in crystal structure with changing composition, and (2) no structural differences which are independent of the structural differences attributable to mixing of the components (Blencoe, 1977). [This definition is completely compatible

structural the mixing properties of both phases are properly represented by a single equation of state. On the other hand, for coexisting nonisostructural crystals it is necessary not only to have separate equations of state for each phase [because the structural configuration (state) of each phase is different], but also to specify the structure(s) of the crystalline components in their standard state(s). In this regard it is useful to consider two alternative standard states; viz., the standard state of a component can be taken as: (1) the pure crystalline component with the same structure as *one* of the coexisting crystalline phases at system *P* and *T*, or (2) the pure crystalline component with the same structure as the crystalline phase under consideration at system *P* and *T*. For coexisting isostructural crystalline solutions these two standard states are equivalent. However, for nonisostructural crystalline solutions standard state (2) gives different standard-state chemical potentials for each component in each phase [a total of four different  $\mu_i^\circ$  terms, two for each component, while standard state (1) would involve only two  $\mu_i^\circ$  terms, one for each component]. For reasons discussed in detail by Blencoe (1977), standard state (2) is the more convenient of the two alternatives, and with this standard state we have: (1) for isostructural A–B pairs,  $\mu_{1A}^\circ = \mu_{1B}^\circ$ ,  $\mu_{2A}^\circ = \mu_{2B}^\circ$  and, consequently,  $a_{1A} = a_{1B}$  and  $a_{2A} = a_{2B}$ ; and (2) for nonisostructural A–B pairs,  $\mu_{1A}^\circ \neq \mu_{1B}^\circ$ ,  $\mu_{2A}^\circ \neq \mu_{2B}^\circ$  and, consequently,  $a_{1A} \neq a_{1B}$  and  $a_{2A} \neq a_{2B}$ . Furthermore, for subsequent discussion it is useful to define  $\Delta G_1^\circ = \mu_{1B}^\circ - \mu_{1A}^\circ$  and  $\Delta G_2^\circ = \mu_{2A}^\circ - \mu_{2B}^\circ$ , so we also have: (1) for isostructural A–B pairs,  $\Delta G_1^\circ$

= 0 and  $\Delta G_2^\circ = 0$ ; and (2) for nonisostructural A–B pairs,  $\Delta G_1^\circ \neq 0$  and  $\Delta G_2^\circ \neq 0$ . By selecting standard state (2), the nonzero values of  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$  for nonisostructural A–B pairs are directly attributable to and completely account for the different free energies of the crystal structures of the coexisting phases. Moreover, with this standard state the activity terms in equations (2) are relative activities by definition (Guggenheim, 1967, p. 181), and this is convenient because many of the commonly-used formulations for the excess properties of binary crystalline solutions [e.g., the two-parameter Margules formulation described by Thompson (1967)] yield relative activities for the components in the phases. Consequently, for a binary isostructural solvus, the compositions of A and B (and, therefore, the symmetry of the solvus) are dictated by the “activity–equivalence conditions”  $a_{1A} = a_{1B}$  and  $a_{2A} = a_{2B}$ , and these activities are a function of *P*, *T* and *X*. However, when A and B are nonisostructural, the symmetry of the binary solvus is a function of not only the activities of the components in A and B, but also  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$ , the latter two quantities being a function of *P* and *T* but not *X*.

### Discussion

#### *The Nernst distribution law for isostructural binary A–B solvus-pairs*

Defining  $a_i = \gamma_i X_i$  and  $\mu_{i\phi}^{\text{ex}} = RT \ln \gamma_{i\phi}$ , where the subscript  $\phi$  indicates a phase (either A or B), equation (2a) may be rewritten for isostructural A–B pairs as:

$$\mu_{1A}^\circ + RT \ln X_{1A} + \mu_{1A}^{\text{ex}} = \mu_{1B}^\circ + RT \ln X_{1B} + \mu_{1B}^{\text{ex}} \quad (3)$$

where  $\mu_{1A}^\circ = \mu_{1B}^\circ$  [Holst, 1978, equation (8)]. Following Holst (1978), we may also define  $K_D = X_{1A}/X_{1B}$  and  $\Delta G_1^{\text{ex}} = \mu_{1A}^{\text{ex}} - \mu_{1B}^{\text{ex}}$ , so from equation (3) we have the following thermodynamic definitions of the Nernst distribution law for *isostructural* binary A–B pairs:<sup>3</sup>

$$\ln K_D = \ln (\gamma_{1B}/\gamma_{1A}) = -(\mu_{1A}^{\text{ex}} - \mu_{1B}^{\text{ex}})/RT = -\Delta G_1^{\text{ex}}/RT \quad (4)$$

[Holst, 1978, equation (9)]. Furthermore, equation

<sup>3</sup> Since “ $\Delta G^{\text{xs}}$ ,” “ $\Delta H^{\text{xs}}$ ,” and “ $\Delta S^{\text{xs}}$ ” as defined by Holst (1978) refer only to component 1, it is appropriate to add the subscript “1” to these terms. Therefore, for example,  $\Delta G^{\text{xs}}$  (Holst, 1978) =  $\Delta G_1^{\text{ex}}$  (this paper).  $\Delta G_1^{\text{ex}}$  should not be confused with  $G^{\text{ex}}$  which, for binary crystalline solutions, is defined by the relation  $G^{\text{ex}} = RT(X_1 \ln \gamma_1 + X_2 \ln \gamma_2)$ .

with discussion presented by Navrotsky and Loucks (1977, p. 119), who describe such crystalline solution series as being characterized structurally by “a continuous set of distortions of bond lengths, bond angles, and positional parameters.” Accordingly, the term “nonisostructural” refers to coexisting phases which do not conform to either or both of the conditions (1) and (2) listed above, and in this situation the phases should be treated as belonging to separate crystalline solution series. In the present discussion, the terms “isostructural” and “nonisostructural” will be used as adjectives to describe not only coexisting mutually-soluble crystalline solutions (A–B pairs), but also the miscibility gap (solvus) described in *P–T–X* space by the equilibrium coexistence of these phases. Using this terminology, *any* miscibility gap (at a given pressure) which shows a *continuous* increase in mutual solubility of the coexisting crystalline solutions with increasing temperature is conveniently and definitively described as either an isostructural solvus or a nonisostructural solvus (*cf.* Navrotsky and Loucks, 1977, p. 119). A fundamental difference between these two types of solvi is that, owing to the different structures of the coexisting phases, a nonisostructural solvus cannot have a stable or metastable critical point.

(4) ( $\ln K_D = -\Delta G_1^{\text{ex}}/RT$ ) can be used to derive the relation

$$\Delta G_1^{\text{ex}} = \Delta H_1^{\text{ex}} - T\Delta S_1^{\text{ex}} \quad (5)$$

[see Holst, 1978, equations (9)–(15)].

From equation (4) we have the equalities  $\Delta G_1^{\text{ex}} = -RT \ln (X_{1A}/X_{1B}) = -RT \ln (\gamma_{1B}/\gamma_{1A})$ , and because  $R$  and  $T$  are positive quantities, and  $1 > X_{1A} \geq X_{1B} > 0$ , we also have, at any given *subsolvus*  $P$  and  $T$ ,  $\gamma_{1B} > \gamma_{1A}$  and  $\Delta G_1^{\text{ex}} < 0$ . Furthermore, because  $\Delta G_1^{\text{ex}} = f(T, X_{1A}, X_{1B})$ ,  $X_{1A} = f(T)$ , and  $X_{1B} = f(T)$ , it is evident that values of  $\Delta G_1^{\text{ex}}$  [and  $(\partial \Delta G_1^{\text{ex}}/\partial T)_P$ ] will be strongly dependent upon the symmetry of the solvus. But regardless of the form of the solvus,  $X_{1A}/X_{1B} = 1$  at the upper-consolute point (high-temperature critical point), so from equation (4) we have at this point  $\Delta G_1^{\text{ex}} = 0$ .

*The Nernst distribution law for nonisostructural binary A–B solvus-pairs*

Mathematical expressions of the Nernst distribution law for nonisostructural binary A–B solvus-pairs can be developed using thermodynamic analysis similar to that described for isostructural A–B pairs. Thus, with the definitions of  $a_i$ ,  $\mu_i^{\text{ex}}$ , and  $K_D$  given previously, equation (2a) may be rewritten for nonisostructural A–B pairs as:

$$RT \ln X_{1A} + \mu_{1A}^{\text{ex}} = \Delta G_1^{\circ} + RT \ln X_{1B} + \mu_{1B}^{\text{ex}} \quad (6)$$

where  $\Delta G_1^{\circ} = \mu_{1B}^{\circ} - \mu_{1A}^{\circ} \neq 0$ . By substituting and rearranging terms in equation (6), we derive the following definitions of the Nernst distribution law for *nonisostructural* binary A–B pairs:

$$\begin{aligned} \ln K_D &= \Delta G_1^{\circ}/RT + \ln(\gamma_{1B}/\gamma_{1A}) \\ &= [\Delta G_1^{\circ} - (\mu_{1A}^{\text{ex}} - \mu_{1B}^{\text{ex}})]/RT \\ &= (\Delta G_1^{\circ} - \Delta G_1^{\text{ex}})/RT \end{aligned} \quad (7)$$

Comparison of equations (4) and (7) shows that the effect of A and B having different crystal structures is expressed thermodynamically by  $\Delta G_1^{\circ}/RT$  in equation (7).

From equation (7) we have the equality  $\Delta G_1^{\text{ex}} = \Delta G_1^{\circ} - RT \ln(X_{1A}/X_{1B})$ , and this relation shows that  $\Delta G_1^{\text{ex}}$  is now partly a function of  $\Delta G_1^{\circ}$ . This result is not attributable to the standard state adopted here because, as noted previously,  $\Delta G_1^{\circ}$  represents the difference between the free energies of crystalline component 1 in the structures of A and B. Therefore, defining  $\Delta G_1^{\text{ex}}$  by the relation  $\Delta G_1^{\text{ex}} = -RT \ln (X_{1A}/X_{1B})$  [Holst, 1978, equation (9)] is invalid for noniso-

structural crystalline solutions. However, the other definition of  $\Delta G_1^{\text{ex}}$  given by Holst, *i.e.*,  $\Delta G_1^{\text{ex}} = \mu_{1A}^{\text{ex}} - \mu_{1B}^{\text{ex}}$  [Holst, 1978, equation (9)], is valid for both isostructural and nonisostructural crystalline solutions, and this definition [for the equivalent relation,  $\Delta G_1^{\text{ex}} = RT \ln (\gamma_{1A}/\gamma_{1B})$ ] will be used in the remaining discussion presented here.

*The Nernst distribution law applied to  $Mg_2Si_2O_6(en)$ – $CaMgSi_2O_6(di)$  orthoenstatite–diopside solvus-pairs*

Equation (3) is identical to equation (8) of Holst (1978), so it is evident that his thermodynamic relations for crystal-pairs at equilibrium [Holst, 1978, equations (8)–(16)] are applicable only to coexisting isostructural crystalline solutions.<sup>4</sup> Furthermore, he has applied these equations, and the relation  $\Delta G_1^{\text{ex}} = -RT \ln (X_{1A}/X_{1B})$  in particular, in a thermodynamic analysis of binary orthoenstatite–diopside solvus data, and these crystalline solutions are *nonisostructural* (diopside is monoclinic). These observations, along with thermodynamic theory presented here, have the following implications regarding the validity of the thermodynamic analysis presented by Holst (following Holst, in this paper  $Mg_2Si_2O_6$  is component 1,  $CaMgSi_2O_6$  is component 2 and, consequently,  $X_{en}^{\text{opx}} = X_{1A}$  and  $X_{en}^{\text{cpx}} = X_{1B}$ ):

(1)  $\Delta G_1^{\text{ex}}$  values for nonisostructural solvus-pairs cannot be derived from solvus data alone. Rather, these data give values for  $\Delta G_1^{\text{ex}} - \Delta G_1^{\circ}$  [ $= -RT \ln (X_{1A}/X_{1B})$ ], and it is these values for 30 kbar orthoenstatite–diopside solvus data that Holst (1978) has plotted in his Figure 1. Furthermore, because  $R$  and  $T$  are positive quantities, and  $X_{en}^{\text{opx}} > X_{en}^{\text{cpx}}$ , “excess free energy” (here  $\Delta G_1^{\text{ex}} - \Delta G_1^{\circ}$ ) values on the abscissa of Figure 1 in Holst (1978) should be negative rather than positive, and his orthoenstatite–diopside geothermometric equation (Holst, 1978, p. 85) should be:

$$-RT \ln (X_{en}^{\text{opx}}/X_{en}^{\text{cpx}}) = 4800 - 18.9T + 0.00829T^2$$

(2) The form of an isobaric  $-RT \ln (X_{1A}/X_{1B})$  vs.  $T$  curve [*e.g.*, as in Fig. 1 of Holst (1978)] is a function of values of  $\Delta G_1^{\text{ex}}$ ,  $\Delta G_1^{\circ}$  and their derivatives with respect to temperature. For most nonisostructural solvi,  $\Delta G_1^{\text{ex}}$  values increase continuously toward zero with increasing temperature.<sup>5</sup> On the other hand,  $\Delta G_1^{\circ}$  val-

<sup>4</sup> Equation (16) of Holst (1978, p. 85) is mislabeled as equation (6).

<sup>5</sup> It has been demonstrated that  $\gamma_{1B} \geq \gamma_{1A}$  for isostructural binary A–B solvus-pairs, and without elaboration it will be assumed here that this is also true for nonisostructural binary A–B solvus-

ues may either increase or decrease with increasing temperature. It is likely that  $\Delta G_1^\circ$  values will display an approximately-linear variation with temperature, because this is true for  $\mu$  values of most pure crystalline components, but significant curvature in an isobaric  $\Delta G_1^\circ$  vs.  $T$  function remains a theoretical possibility in the absence of definitive phase-equilibrium and/or calorimetric data. For any nonisostructural solvus, however,  $(\partial\Delta G_1^{\text{ex}}/\partial T)_P$  and  $(\partial\Delta G_1^\circ/\partial T)_P$  must be continuous functions, and the writer agrees with Holst (1978, p. 84) that a *discontinuity* in the slope of a  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  curve indicates a first-order phase transformation or a reaction. The writer also agrees with Holst that inflections in  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  curves *generally* can be attributed to inaccuracies in solvus experimental data, but it should be recognized that such inflections are not intrinsically invalid. Several different unusual circumstances can produce inflections in  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  curves, but the most likely is the situation in which  $\Delta G_1^{\text{ex}}$  increases toward zero with increasing temperature and reaches a value of zero (or near zero) at a subsolvus temperature. In this regard, it may be noted that the 30 kbar orthoenstatite–diopside solvus of Mori and Green (1976) is consistent with an inflection in the  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  curve for that solvus near 1900K. Holst (1978) attributes this inflection to experimental error (which is a distinct possibility), but an alternative *schematic* explanation is illustrated in Figure 1. Obviously, additional accurate 30 kbar orthoenstatite–diopside solvus data in the range 1700–2000K are needed to settle this matter.

(3) The orthoenstatite–diopside geothermometric equation listed by Holst (1978, p. 84), which is attributed to Wood and Banno (1973), is not equivalent (theoretically) to the equation presented by these investigators [Wood and Banno, 1973, equation (22)]. The equation listed by Holst is

$$\begin{aligned} \ln(X_{\text{en}}^{\text{cpx}}/X_{\text{en}}^{\text{opx}}) &= -\Delta H/RT + \Delta S/R \\ &= -10202/T + 5.35 \end{aligned} \quad (8)$$

while the equation presented by Wood and Banno is

$$\begin{aligned} \ln(a_{\text{en}}^{\text{cpx}}/a_{\text{en}}^{\text{opx}}) &= -\Delta H^\circ/RT + \Delta S^\circ/R \\ &= -10202/T + 5.35 \end{aligned} \quad (9)$$

Because the terms on the left-hand side of equation (9) are activities and *not* mole fractions, we have

pairs. Therefore, from the relation  $\Delta G_1^{\text{ex}} = RT \ln(\gamma_{1A}/\gamma_{1B})$ , we have  $\Delta G_1^{\text{ex}} \leq 0$  for both isostructural and nonisostructural binary A–B solvus-pairs.

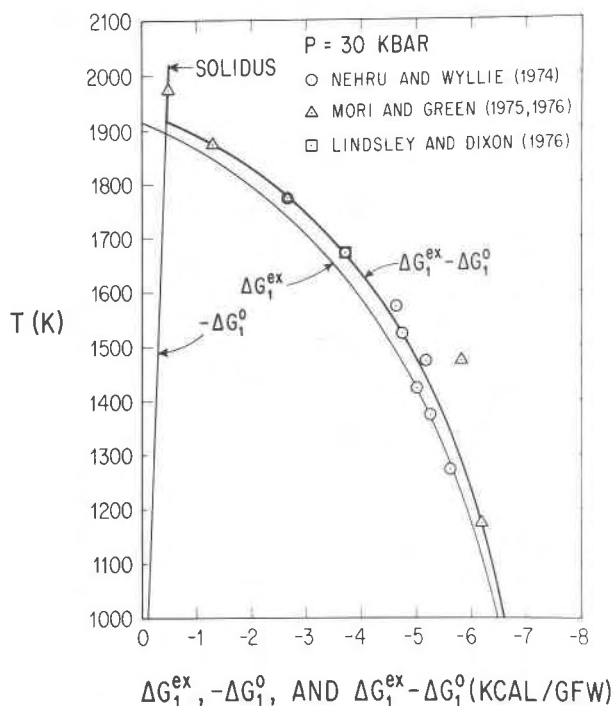


Fig. 1. Semi-schematic diagram illustrating: (1) hypothetical 30 kbar orthoenstatite–diopside  $\Delta G_1^{\text{ex}}-T$  and  $-\Delta G_1^\circ-T$  relations; and (2) a  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  vs.  $T$  curve based upon the 30 kbar orthoenstatite–diopside solvus data of Nehru and Wyllie (1974), Mori and Green (1975, 1976), and Lindsley and Dixon (1976). The sharp *inflection* in the  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  curve occurs at 1910K because orthoenstatite–diopside solvus-pairs are coexisting ideal, nonisostructural crystalline solutions at this and higher temperatures (that is,  $\gamma_{\text{en}}^{\text{opx}} = 1$ ,  $\gamma_{\text{en}}^{\text{cpx}} = 1$  and, therefore,  $\Delta G_1^{\text{ex}} = 0$  at  $T \geq 1910\text{K}$ ). The  $\Delta G_1^{\text{ex}}$  and  $\Delta G_1^\circ$  vs.  $T$  curves in this figure (as well as the inflection in the  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  curve at 1915K) are entirely schematic, and they are illustrated simply to demonstrate that it is theoretically possible to have inflections in  $\Delta G_1^{\text{ex}} - \Delta G_1^\circ$  curves for nonisostructural solvi.

from equation (2a) (using the notation of Wood and Banno)

$$\ln(a_{\text{en}}^{\text{cpx}}/a_{\text{en}}^{\text{opx}}) = -\Delta G^\circ/RT \quad (10)$$

[Wood and Banno, 1973, equation (20)] where  $\Delta G^\circ$  is equivalent to  $\Delta G_1^\circ$  in this paper. Therefore, as indicated by Wood and Banno (1973, p. 117), and by the superscript “ $^\circ$ ” in  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ , equations (9)–(10) refer to the transfer of  $\text{Mg}_2\text{Si}_2\text{O}_6$  from orthopyroxene to clinopyroxene *in the standard state* (pure  $\text{Mg}_2\text{Si}_2\text{O}_6$  at system  $P$  and  $T$ ). Consequently, nonzero values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  in equations (9)–(10) are ostensibly due *entirely* to the different free energies of the orthorhombic and monoclinic structures of pure  $\text{Mg}_2\text{Si}_2\text{O}_6$ . In contrast, the terms on the left-hand side of equation (8) are mole fractions, so

the  $\Delta H$  and  $\Delta S$  terms in this equation are not equivalent (theoretically) to  $\Delta H^\circ$  and  $\Delta S^\circ$ , respectively, in equation (9). According to thermodynamic analysis and notation presented by Holst,  $\Delta H$  in equation (8) should be  $\Delta H^{xs}$ , and  $\Delta S$  should be  $\Delta S^{xs}$ , but even with these modifications equation (8) would still be invalid because orthoenstatite and diopside are nonisostructural.

Although equation (8) is thermodynamically invalid and not equivalent to equation (9) (which is valid), theoretical treatment by Wood and Banno yields "idealized" activities which are equivalent to mole fractions, and in this instance equations (8) and (9) give identical *numerical* results. According to Wood and Banno (1973, p. 118),  $a_{\text{en}}^{\text{cpx}}$  and  $a_{\text{en}}^{\text{opx}}$  in equation (9) can be estimated from the generalized relation

$$a_{\text{en}} = \left( \frac{\text{Mg}^{2+}}{\text{Mg}^{2+} + \text{Ca}^{2+}} \right)_{\text{M2}} \cdot \left( \frac{\text{Mg}^{2+}}{\text{Mg}^{2+} + \text{Ca}^{2+}} \right)_{\text{M1}} \quad (11)$$

thereby yielding (using the notation of Wood and Banno)

$$a_{\text{en}}^{\text{cpx}} = (X_{\text{Mg}}^{\text{M2}} \cdot X_{\text{Mg}}^{\text{M1}})_{\text{cpx}}$$

and

$$a_{\text{en}}^{\text{opx}} = (X_{\text{Mg}}^{\text{M2}} \cdot X_{\text{Mg}}^{\text{M1}})_{\text{opx}}$$

[Wood and Banno, 1973, equations (21)]. However, Wood and Banno assume that  $\text{Ca}^{2+}$  in orthopyroxene and clinopyroxene is restricted to the larger M2 site [*i.e.*,  $(\text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Ca}^{2+}))_{\text{M1}} = 1$  in binary Mg–Ca orthoenstatite and diopside], and with this assumption equation (11) reduces to

$$a_{\text{en}} = \left( \frac{\text{Mg}^{2+}}{\text{Mg}^{2+} + \text{Ca}^{2+}} \right)_{\text{M2}} = X_{\text{en}} \text{ (Raoult's law)}$$

Thus, although the form of equation (9) is valid thermodynamically, the numerical evaluations of  $\ln(a_{\text{en}}^{\text{cpx}}/a_{\text{en}}^{\text{opx}})$  [at  $950 \leq T(^{\circ}\text{C}) \leq 1400$ ] by Wood and Banno are based upon the assumption that orthoenstatite–diopside solvus-pairs can be treated approximately as coexisting *ideal* crystalline solutions. Consequently, since the nonideality of the crystalline solutions has not been accounted for in the activity terms in equation (9), the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  in this equation (20.27 kcal/gfw and 10.63 cal/deg-gfw, respectively) are a function of not only the different free energies of the crystal structures, but also the excess properties of the crystalline solutions. However, because these values are only *partly* a function of the

nonideality of the crystalline solutions,  $\Delta H^\circ$  and  $\Delta S^\circ$  in equation (9) cannot properly be described as thermodynamic excess functions (*cf.* Holst, 1978, p. 84). (4) Phase relations of coexisting, nonisostructural crystalline solutions are dictated in part by the values of  $\Delta G_1^\circ$  and *relative* activities for the components calculated from solvus data will be inaccurate if these values are not taken into account. This is well exemplified by the phase relations and thermodynamics of the  $\text{Mg}_2\text{Si}_2\text{O}_6$ – $\text{CaMgSi}_2\text{O}_6$  system, because orthoenstatite–diopside solvus-pairs are stable and show continuously-increasing mutual crystalline solution to extraordinarily high temperatures.<sup>6</sup> At 20 kbar, orthoenstatite + diopside is stable up to at least 1600°C, and Mori and Green (1976) report that, at this  $P$  and  $T$ ,  $X_{2A} = 0.1048$  and  $X_{2B} = 0.208$ . At 1600°C it is probably valid to assume that the pyroxenes are nearly ideal and, accordingly (provided that Mori and Green's solvus data are accurate), from equations (2) we obtain the following *maximum* values for  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$  at this temperature:

$$\Delta G_1^\circ \cong RT \ln (X_{1A}/X_{1B}) = 456 \text{ cal/gfw}$$

and

$$\Delta G_2^\circ \cong RT \ln (X_{2B}/X_{2A}) = 2552 \text{ cal/gfw}$$

The result  $\Delta G_2^\circ \gg \Delta G_1^\circ$  suggests that the unusual topology of the orthoenstatite–diopside solvus (that is, the marked shift of the diopside limb of the solvus toward  $\text{Mg}_2\text{Si}_2\text{O}_6$  at high temperatures) is attributable to the extreme instability of orthorhombic diopside, and this is in complete accord with the fact that this phase has never been observed in either natural rocks or experimental samples.

From equations (2) it is also apparent that  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$  values should be accounted for in calculations of relative activities for the components in the pyroxenes at low temperatures where the phases must be

<sup>6</sup> It is inappropriate here to discuss the controversy regarding the existence of an "iron-free pigeonite"–diopside solvus in the  $\text{Mg}_2\text{Si}_2\text{O}_6$ – $\text{CaMgSi}_2\text{O}_6$  system (for comprehensive discussions, see Mori and Green, 1975, 1976, and Navrotsky and Loucks, 1977). To simplify the discussion, it will be assumed that the orthoenstatite–diopside miscibility gap is a nonisostructural solvus up to solidus temperatures at 20 kbar (Mori and Green, 1976). If, on the other hand, a "pigeonite"–diopside solvus is stable at this pressure, then analysis presented here will be partly invalid. In particular, if this solvus is present and stable up to the solidus ( $\cong 1650^\circ\text{C}$ ) as suggested by Kushiro (1969), this would indicate (contrary to analysis given here) that Mg-rich  $\text{Mg}_2\text{Si}_2\text{O}_6$ – $\text{CaMgSi}_2\text{O}_6$  pyroxenes are appreciably nonideal at 20 kbar, 1600°C.

appreciably nonideal. For example, for diopside in equilibrium with orthoenstatite we have from equation (2a)

$$RT \ln a_{\text{en}}^{\text{cpX}} = -\Delta G_1^\circ + RT \ln a_{\text{en}}^{\text{opX}}$$

and this relation shows that, because  $\Delta G_1^\circ$  is positive,  $a_{\text{en}}^{\text{cpX}}$  is always less than  $a_{\text{en}}^{\text{opX}}$  by a factor of  $\exp(-\Delta G_1^\circ/RT)$ . However, because  $\Delta G_1^\circ$  decreases with decreasing temperature, the difference between  $a_{\text{en}}^{\text{cpX}}$  and  $a_{\text{en}}^{\text{opX}}$  also will decrease with decreasing temperature. (5) Holst (1978, p. 85) calculated  $a_{\text{en}}^{\text{cpX}}$  and  $\gamma_{\text{en}}^{\text{cpX}}$  for diopside in equilibrium with orthoenstatite at 30 kbar and 1100°C, but his results are erroneous for several reasons. First, the value of “ $\Delta G^{\text{xs}}$ ” that he used in his calculations should have been  $-5275$  cal/gfw rather than  $5275$  cal/gfw. Furthermore, it can be shown that his activity equation reduces to

$$a_{\text{en}}^{\text{cpX}} = X_{\text{en}}^{\text{cpX}} \text{ (Raoult's law)}$$

Therefore, his method of estimating  $a_{\text{en}}^{\text{cpX}}$  fails to account for not only the different free energies of the crystal structures of pure orthoenstatite and clinoenstatite ( $\Delta G_1^\circ$ ), but also any nonideal behavior of the  $\text{Mg}_2\text{Si}_2\text{O}_6$  component in diopside.

#### *The Nernst distribution law for multicomponent A-B solvus-pairs*

The mathematical (thermodynamic) definitions of the Nernst distribution law for isostructural and non-isostructural binary A-B pairs listed previously [equations (4) and (7)] are also valid for multicomponent A-B pairs, but applications of these equations are more complicated for multicomponent crystalline solutions. When A and B are binary,  $X_{1A}$ ,  $X_{1B}$  and  $K_D$  are fixed values. However, when A and B are multicomponent crystalline solutions,  $X_{1A}$  and  $X_{1B}$  are a function of the bulk composition of the system, and  $K_D$  may or may not be constant depending upon the thermodynamic properties of the crystalline solutions. For example, suppose A and B are non-ideal ternary crystalline solutions each containing a trace amount of component 1. If the amount of component 1 in each phase is sufficiently small to be in the compositional range of Henrian behavior, then  $\gamma_{1A}$ ,  $\gamma_{1B}$  and  $K_D$  will be essentially constant with small changes of  $X_1$  in A and B (for nonisostructural crystalline solutions,  $\Delta G_1^\circ$  is always constant at a fixed  $P$  and  $T$ ). However, if component 1 is present in A and B in greater than “Henrian quantities,” then  $\gamma_{1A}$ ,  $\gamma_{1B}$ , and  $K_D$  will be a function of the bulk composition of the system. For additional discussion of Henrian be-

havior of trace elements in crystalline solutions, and precautions required in interpretation of trace-element data, see Dowty (1977), Mysen (1978), and Navrotsky (1978).

Crystal-structure effects also must be considered in a thermodynamic analysis of trace-element distribution between coexisting crystalline solutions. For example, when component 1 is a trace component in multicomponent and isostructural phases A and B coexisting at equilibrium at a fixed  $P$  and  $T$ , we have from equation (4),  $\ln K_D = \ln (\gamma_{1B}/\gamma_{1A})$ , so equipartitioning ( $K_D = 1$ ) can occur only when  $\gamma_{1A} = \gamma_{1B}$ . On the other hand, if A and B are nonisostructural, then we have from equation (7),  $\ln K_D = \Delta G_1^\circ/RT + \ln (\gamma_{1B}/\gamma_{1A})$ , and in this instance equipartitioning can occur only when  $\gamma_{1A} = \gamma_{1B} \exp (\Delta G_1^\circ/RT)$  (cf. Holst, 1978, p. 85).

### Conclusions

It has been demonstrated that applications of the Nernst distribution law to coexisting crystalline solutions can be considerably more complex than indicated by Holst (1978). In particular, Holst did not consider the complexities and constraints introduced when the coexisting phases are nonisostructural. A strict accounting for the effects of crystal structure is particularly important in a thermodynamic analysis of orthoenstatite–diopside equilibria because these phases have significantly different structures.

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### References

- Blencoe, J. G. (1977) Computation of thermodynamic mixing parameters for isostructural, binary crystalline solutions using solvus experimental data. *Computers & Geosciences*, 3, 1–18.
- Dowty, E. (1977) The importance of adsorption in igneous partitioning of trace elements. *Geochim. Cosmochim. Acta*, 41, 1643–1646.
- Guggenheim, E. A. (1967) *Thermodynamics*. North-Holland, Amsterdam.
- Holst, N. B., Jr. (1978) The use of thermodynamic excess functions in the Nernst distribution law. *Am. Mineral.*, 63, 83–86.
- Kerrick, D. M. and L. S. Darken (1975) Statistical thermodynamic models for ideal oxide and silicate solid solutions, with application to plagioclase. *Geochim. Cosmochim. Acta*, 39, 1431–1442.
- Kushiro, I. (1969) The system forsterite–diopside–silica with and without water at high pressures. *Am. J. Sci.*, 267A (Schairer Vol.), 269–294.

- Lindsley, D. H. and S. A. Dixon (1976) Diopside–enstatite equilibria at 850°C to 1400°C, 5 to 35 kb. *Am. J. Sci.*, 276, 1285–1301.
- Mori, T. and D. H. Green (1975) Pyroxenes in the system  $\text{Mg}_2\text{Si}_2\text{O}_6$ – $\text{CaMgSi}_2\text{O}_6$  at high pressure. *Earth Planet. Sci. Lett.*, 26, 277–286.
- and ——— (1976) Subsolidus equilibria between pyroxenes in the  $\text{CaO}$ – $\text{MgO}$ – $\text{SiO}_2$  system at high pressures and temperatures. *Am. Mineral.*, 61, 616–625.
- Mysen, B. O. (1978) Limits of solution of trace elements in minerals according to Henry's law: review of experimental data. *Geochim. Cosmochim. Acta*, 42, 871–885.
- Navrotsky, A. (1978) Thermodynamics of element partitioning: (1) systematics of transition metals in crystalline and molten silicates and (2) defect chemistry and "the Henry's law problem." *Geochim. Cosmochim. Acta*, 42, 887–902.
- and D. Loucks (1977) Calculation of subsolidus phase relations in carbonates and pyroxenes. *Phys. Chem. Minerals*, 1, 109–127.
- Nehru, C. E. and P. J. Wyllie (1974) Electron microprobe measurement of pyroxenes coexisting with  $\text{H}_2\text{O}$ -undersaturated liquid in the join  $\text{CaMgSi}_2\text{O}_6$ – $\text{Mg}_2\text{Si}_2\text{O}_6$ – $\text{H}_2\text{O}$  at 30 kilobars, with applications to geothermometry. *Contrib. Mineral. Petrol.*, 48, 221–228.
- Thompson, J. B., Jr. (1967) Thermodynamic properties of simple solutions. In P. H. Abelson, Ed., *Researches in Geochemistry*, Vol. 2, p. 340–361. Wiley, New York.
- Wood, B. J. and S. Banno (1973) Garnet–orthopyroxene and orthopyroxene–clinopyroxene relationships in simple and complex systems. *Contrib. Mineral. Petrol.*, 42, 109–124.

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