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

NORMAN B. HOLST, JR.

Harza Associates of Virginia, Mountain Grove Route
Warm Springs, Virginia 24484

Abstract

The form of the Nernst distribution law derived by Holst (1978) utilizes the conventions of classical thermodynamics. As such it only accounts for changes in free energy without attributing them to any particular phenomenon on the atomic scale. It does not offer any conceptual framework within which to view these changes. However, it is the most general approach which can be applied to any binary solvus pair, since the excess function is not rigidly defined and crystal structure is not considered. The excess free energy change is defined simply as any free energy change which cannot be attributed to the ideal free energy change with the standard state taken as the pure substance in its stable form at standard conditions.

Discussion

Classical thermodynamics deals only with the interchanges of energy, work, and matter as systems evolve through physical and chemical changes on the macroscopic scale. Swalin (1972, p. 1) writes: "The application of thermodynamics to the study of crystals offers a powerful quantitative tool for the investigation of important properties. With the aid of thermodynamics, for example, one is able to control the structure of a material without the necessity of knowing atomic details of the crystals. One of the principal reasons for this power is that one does not need to postulate any specific model of the crystal." Indeed the works of Maxwell, Clausius, and Nernst in laying the foundations of thermodynamics were all done in the latter half of the last century, while the elucidation of crystal structures did not begin until the work of the Braggs early in this century.

In dealing with solutions, classical thermodynamics defines an ideal solution as one in which the chemical potential of each component is a function of the chemical potential of the pure component and its mole fraction in the solution only,

$$\mu_1^{\mathrm{B}} = \mu_1^{\mathrm{P}} + RT \ln X_1^{\mathrm{B}} \qquad (1)$$

The chemical potential of the pure component (μ_1^{P}) is commonly that in the most stable form at standard conditions, Blencoe's (1979) first alternative. For many reasons most solutions, especially solid solutions, are not ideal. The chemical potentials of the individual components do not conform to equation 1. This is accounted for by adding an excess term:

$$\mu_1^{\mathrm{B}} = \mu_1^{\mathrm{P}} + RT \ln X_1^{\mathrm{B}} + \mu_1^{\mathrm{Bxs}} \qquad (2)$$

This is the simplest and most general approach which can be applied to any phase without regard to atomic structures. These are the conventions I used (Holst, 1978) in deriving a form of the Nernst distribution law applicable to solvus pairs.

Blencoe (1979) derived a form of the Nernst distribution law for nonisostructual binary solvus pairs which includes the modern conceptual refinement that the two phases and, therefore, their components exist in different crystal structures. There is a free energy change associated with transferring component 1 (pure phase A) into phase B that is due to the change of crystal structure from that of A to that of B. This he defines as $\Delta G_1^{\circ} = \mu_{1\mathrm{B}}^{\circ} - \mu_{1\mathrm{A}}^{\circ}$ where $\mu_{1\mathrm{B}}^{\circ}$ and $\mu_{1\mathrm{A}}^{\circ}$ are the chemical potentials of pure component 1 in the B and the A crystal structures respectively. From Blencoe's (1979) equation 6 it is apparent that

$$\mu_{1\mathrm{B}} = \mu_{1\mathrm{B}}^{\circ} + RT \ln X_{1\mathrm{B}} + \mu_{1\mathrm{B}}^{\mathrm{ex}} \qquad (3)$$

From Blencoe's (1979) equation 7 we have

$$RT \ln (X_{1\mathrm{A}}/X_{1\mathrm{B}}) = \Delta G_1^{\circ} - \Delta G_1^{\mathrm{ex}} \qquad (4)$$

Blencoe's (1979) notations $\mu_{1\mathrm{A}}^{\circ}$, $X_{1\mathrm{A}}$, $\mu_{1\mathrm{B}}$, and $X_{1\mathrm{B}}$ are equivalent to Holst's (1978) notations μ_1^{P}, X_1^{A}, μ_1^{B},

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and X_1^B in that order. Comparing equations 2 and 3 one obtains

$$\mu_1^{Bxs} = \Delta G^{\circ}_{1B} + \mu^{ex} \tag{5}$$

Holst's (1978) equation 9 is

$$RT \ln (X_1^A / X_1^B) = -\Delta G^{xs} \tag{6}$$

Comparing it to equation 4 one finds that

$$\Delta G^{xs} = \Delta G_1^{ex} - \Delta G_1^{\circ} \tag{7}$$

In each case the original excess function as defined by Holst (1978) is equated to two terms, a term associated with the change in crystal structure and a new excess function which is not attributed to any specific phenomenon. The minus sign in the second case (equation 7) is present because ΔG_1° and the excess term are defined in the opposite sense: $\Delta G_1^{ex} = \mu_{1A}^{ex} - \mu_{1B}^{ex}$ and $\Delta G_1^{\circ} = \mu^{\circ}_{1B} - \mu^{\circ}_{1A}$.

Blencoe (1979) has demonstrated that, in the case of nonisostructural binary solvus pairs, parts of the original excess functions are due to the difference in crystal structure. We could take the excess functions as defined by Blencoe for nonisostructural solvus pairs and apportion them to free energy changes associated with other phenomena on the atomic scale. It may be useful for some purposes, but it is not necessary. The classical approach is still valid, and it is the most general.

The original conclusions of my paper are not affected. Whether one chooses equation 4 or equation 6, a thermodynamic excess function is present. This accounts for the non-ideal behavior however one defines it. It is not necessary to introduce activities into plots such as that made by Wood and Banno (1973) for the orthoenstatite–diopside solvus.

I certainly did not wish to misrepresent the orthoenstatite–diopside geothermometric equation developed by Wood and Banno (1973). Their original equation as presented in their original paper does contain activity terms, not mole fractions. However, as is capably demonstrated by Blencoe (1979), the mixing assumptions made by Wood and Banno (1973) result in the equality

$$a_{Mg_2Si_2O_6} = X_{Mg_2Si_2O_6} \tag{8}$$

I substituted this into their original equation without presenting it formally in the interest of brevity. I believed that my earlier comments in the paper (Holst, 1978) made it clear that they did use activities.

After reviewing my original paper (Holst, 1978) it becomes very apparent that, as pointed out by Blencoe (1979), in actual calculations done by me on the orthoenstatite–diopside solvus the positive and negative signs are not correct. This error is carried over into my accompanying figure. How that happened is not known to me at this time but it certainly should be mentioned. I can only offer apologies.

Conclusions

The form of the Nernst distribution law derived by Holst (1978) using thermodynamic excess functions is based on the conventions of classical thermodynamics. These simply account for changes in free energy without attributing them to specific changes in atomic or crystal structure. As such it does not provide one with a conceptual or theoretical framework for understanding the changes in free energy that accompany the formation of a non-ideal solution. It also may not be as convenient for the application of various mathematical models of solutions. However, it is a general approach which can be applied to any binary solvus pair, and it quantitatively accounts for all the changes in free energy and chemical potential which occur on the formation of such solutions. This includes the nonisostructural solutions on the orthoenstatite–diopside solvus.

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