The Polynomial Representation of Thermodynamic Properties in Dilute Solutions

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Attempts to extend the interaction parameter formalism to higher-order polynomials and to render it thermodynamically consistent at finite solute concentrations have resulted in much confusion. The literature is reviewed with a view to clarifying the issues. The problem is best and most simply resolved through extension of the quadratic formalism, which has a sound theoretical foundation. A new and general set of equations for estimating higher-order parameters from binary parameters is derived. The applicability of using molar ratios rather than mole fractions in the polynomial expansions is discussed. The formation of associate species (such as the formation of "AlO" associates in molten Fe) is treated. In such cases of strong solute-solute interactions, the usual practice of expressing the interaction parameters as linear functions of $(1/T)$ is invalid. Finally, for more concentrated solutions, the advantage of using the Kohler or Toop interpolation models rather than the commonly used Muggianu model is shown.

I. INTRODUCTION

THE well-known first-order interaction parameter formalism of Wagner[1] for a dilute solution of components 1-2-3 ... -N, where component 1 is the solvent, may be written as

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_{i2} X_2 + \varepsilon_{i3} X_3 + ... + \varepsilon_{iN} X_N \ (i \geq 2) \quad [1]$$

where γ_i is the activity coefficient of solute i defined as

$$\gamma_i = a_i/X_i \quad [2]$$

where a_i is the activity of i and X_i is the mole fraction of i defined as

$$X_i = n_i/(n_1 + n_2 + ... + n_N) \quad [3]$$

where n_i is the number of moles of i in solution. The activity coefficient at infinite dilution (where $X_1 \rightarrow 1$) is denoted by γ_i^0. The parameters ε_{ij} are called "first-order interaction parameters."

From the Gibbs–Duhem equation,

$$\sum X_i \, d \ln \gamma_i = 0 \quad [4]$$

it can be shown that in the limit at infinite dilution,

$$\varepsilon_{ij} = \varepsilon_{ji} \quad [5]$$

and

$$\ln \gamma_1 = -\frac{1}{2} \sum_{i=2}^{N} \sum_{j=2}^{N} \varepsilon_{ij} X_i X_j \quad [6]$$

The Wagner formalism is very simple and useful but has frequently been misunderstood or misapplied. Much of the confusion has arisen because Eqs. [1] and [6] only obey the Gibbs–Duhem equation in the limit of infinite dilution, and because the formalism does not obey the following

necessary thermodynamic relationship except at infinite dilution:

$$(\partial \ln \gamma_i/\partial n_j) = (\partial \ln \gamma_j/\partial n_i) \quad [7]$$

This problem was simply resolved many years ago for the case of the first-order formalism for 2- and 3-component systems by Darken[2,3] in two articles, which have not received sufficient attention.

Darken's Quadratic Formalism

In a binary system 1-2 (where 1 is the solvent), Darken proposed a "quadratic formalism":

$$g^E/RT = a_{12} X_1 X_2 + C_2 X_2 \quad [8]$$

where g^E is the excess molar Gibbs energy:

$$g^E/RT = \sum_{i=1}^{N} X_i \ln \gamma_i \quad [9]$$

and where α_{ij} and C_2 are constants. By differentiation,

$$\ln \gamma_2 = a_{12} X_1^2 + C_2 \quad [10]$$
$$= (a_{12} + C_2) - 2a_{12} X_2 + a_{12} X_2^2$$
$$\ln \gamma_1 = a_{12} X_2^2 \quad [11]$$

When $C_2 = 0$, the quadratic formalism reduces to the regular solution equations.

It has been observed that many simple binary solutions conform quite closely to the quadratic formalism up to relatively large values of X_2. This observation can be rationalized by a simple regular solution model. Assume a random distribution of atoms or molecules of components 1 and 2 on a quasilattice. Let E_{ij} be the bond energy of one mole of i-j nearest-neighbor pairs. The probabilities that a given pair is a 1-1, a 2-2, or a 1-2 pair are X_1^2, X_2^2, and $2 X_1 X_2$, respectively. The excess Gibbs energy is then equal to the sum of the energies of the pair bonds in 1 mole of solution, less the energy of the 1-1 bonds in X_1 moles of pure component 1 and the energy of the 2-2 bonds in 1 mole of pure component 2:

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$$g^E = (Z/2)(2X_1 X_2 E_{12} + X_1^2 E_{11} + X_2^2 E_{22})$$
$$- (Z/2) X_1 E_{11} - (Z^0/2) X_2 E_{22}^0 \quad [12]$$
$$= (Z/2)(2E_{12} - E_{11} - E_{22}) X_1 X_2 + X_2$$
$$(ZE_{22} - Z^0 E_{22}^0)/2$$

where Z is the coordination number and there are $(Z/2)$ pairs per mole of solution. It is assumed that Z, E_{11}, E_{22}, and E_{12} are independent of composition for solutions in which X_1 is sufficiently large, and that Z^0 and E_{22}^0 are the values in pure component 2. Equation [12] is then identical to Eq. [8].

The extension of the quadratic formalism to ternary solutions is obvious:

$$g^E/RT = (a_{12} X_1 X_2 + a_{23} X_2 X_3 + a_{31} X_3 X_1) \quad [13]$$
$$+ (C_2 X_2 + C_3 X_3)$$

and partial properties are given by differentiation:

$$\ln \gamma_1 = a_{12} X_2^2 + a_{13} X_3^2 + (a_{12} + a_{31} - a_{23}) X_2 X_3 \quad [14]$$

$$\ln \gamma_2 = (a_{12} + C_2) - 2a_{12} X_2 - (a_{12} + a_{31} - a_{23}) X_3 \quad [15]$$
$$+ [a_{12} X_2^2 + a_{31} X_3^2 + (a_{12} + a_{31} - a_{23}) X_2 X_3]$$

$$\ln \gamma_3 = (a_{31} + C_3) - 2a_{31} X_3 - (a_{12} + a_{31} - a_{23}) X_2 \quad [16]$$
$$+ [a_{12} X_2^2 + a_{31} X_3^2 + (a_{12} + a_{31} - a_{23}) X_2 X_3]$$

The extension to N-component systems can be made by simply adding similar terms.

II. THE UNIFIED INTERACTION PARAMETER FORMALISM

A unified interaction parameter formalism for the polynomial representation of the thermodynamic properties of dilute solutions was proposed by Bale and Pelton.[4,5] The interaction parameter formalism was modified to be consistent with the quadratic formalism, as well as with the Gibbs–Duhem equation and Eq. [7]. The equations were generalized for N-component systems and higher-order terms.

A. First-Order Formalism—Binary Systems

If the following substitutions are made in the binary quadratic formalism:

$$\ln \gamma_2^0 = (a_{12} + C_2) \quad [17]$$
$$\varepsilon_{22} = -2a_{12} \quad [18]$$

Equations [10] and [11] then become

$$\ln \gamma_2 = \ln \gamma_2^0 + \varepsilon_{22} (X_2 - X_2^2/2) \quad [19]$$

$$\ln \gamma_1 = -\left(\frac{\varepsilon_{22}}{2}\right) X_2^2 \quad [20]$$

Equation [19] reduces to the Wagner formalism in the limit as $X_2 \to 0$, and Eq. [20] is identical to Eq. [6] for a binary system. Equations [19] and [20] are thus a modified interaction parameter formalism that is identical to the quadratic formalism and reduces to the Wagner formalism at infinite dilution, but that is consistent with the Gibbs–Duhem Eq. [4] and with Eq. [7] at finite solute concentrations.

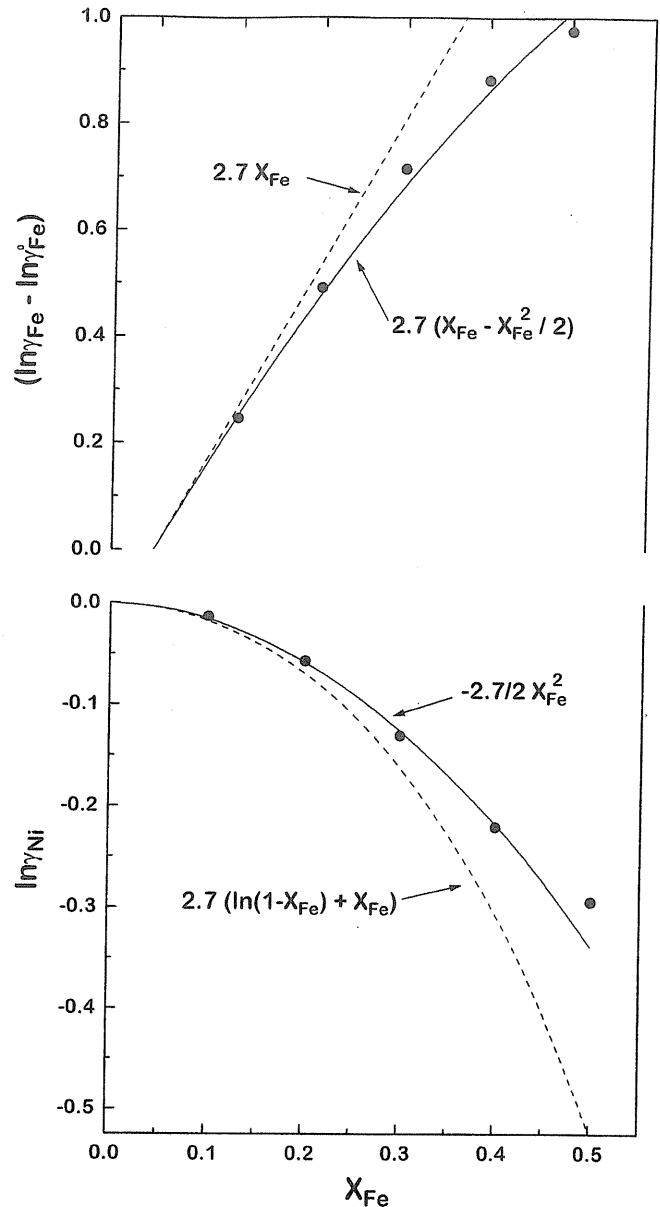As an example, for Ni-Fe liquid solutions at 1600 °C,

Fig. 1—Activity coefficients[6] of Fe and Ni in liquid Ni-Fe solutions at 1600 °C. Solid lines show agreement with unified interaction parameter formalism with $\varepsilon_{\text{FeFe}} = 2.7$. Dashed lines show agreement with linear formalism.

where Ni is the solvent (Ni = 1, Fe = 2), activity coefficients[6] of Fe and Ni are plotted in Figure 1. It can be seen that Equations [19] and [20] with $\varepsilon_{\text{FeFe}} = 2.7$ provide a very good representation of both $\ln \gamma_{\text{Fe}}$ and $\ln \gamma_{\text{Ni}}$ for solute concentrations up to $X_{\text{Fe}} = 0.5$. The linear Wagner formalism, on the other hand, does not give a good representation of the data for $\ln \gamma_{\text{Fe}}$ when $X_{\text{Fe}} > 0.1$.

Suppose, nevertheless, that one wishes to maintain the Wagner formalism even to finite concentrations:

$$\ln \gamma_2 = \ln \gamma_2^0 + \varepsilon_{22} X_2 \quad [21]$$

By substituting Eq. [21] into the Gibbs–Duhem Eq. [4], the following equation is obtained by integration:

$$\ln \gamma_1 = \varepsilon_{22} [\ln (1 - X_2) + X_2] \quad [22]$$

Hajra *et al.*[7] propose the use of Eqs. [21] and [22].

From Figure 1, it can be seen that Eq. [22] gives a poor representation of $\ln \gamma_{Ni}$ at higher solute concentrations, because Eq. [21] gives a poor representation of $(\ln \gamma_{Fe} - \ln \gamma^0_{Fe})$ at higher solute concentrations. Of course, for some binary systems, the linear Wagner formalism, Eq. [21], may give a closer fit to the experimental points than the modified formalism, Eq. [19]. In this case, Eq. [22] for $\ln \gamma_1$ will be better than Eq. [21]. However, in general, there is no sound theoretical foundation for the use of Eqs. [21] and [22] as there is for Eqs. [19] and [20], which are identical to the quadratic formalism. If only data for very dilute solutions are available, then Eqs. [19] and [20] are more likely to provide a good extrapolation to higher solute concentrations, although, of course, there will be exceptions.

B. First-Order Formalism-Ternary Systems

Although it is possible to maintain the linear Wagner formalism, Eq. [21], for a binary system by choosing an expression for $\ln \gamma_1$, Eq. [22], consistent with the Gibbs–Duhem equation, this is no longer possible in the case of a ternary system, where the Wagner formalism,

$$\ln \gamma_2 = \ln \gamma^0_2 + \varepsilon_{22} X_2 + \varepsilon_{23} X_3 \quad [23]$$
$$\ln \gamma_3 = \ln \gamma^0_3 + \varepsilon_{32} X_2 + \varepsilon_{33} X_3 \quad [24]$$

is inconsistent with the relationship of Eq. [7] no matter what expression is chosen for $\ln \gamma_1$. This point appears to have been missed by Srikanth and Jacob,[8] who proposed a complex "integration path dependent" expression for $\ln \gamma_1$, based upon Eqs. [23] and [24] and consistent with the Gibbs–Duhem equation. The problem is that consistency with the Gibbs–Duhem equation is necessary but not sufficient. Equation [7] must also be obeyed.

Hajra *et al.*[7] recognized this requirement and proposed the following ternary expressions:

$$\ln \gamma_2 = \ln \gamma^0_2 + X_2 \varepsilon_{22} + X_3 \varepsilon_{33} + (\varepsilon_{33} - \varepsilon_{23}) \ln (1 - X_3) \quad [25]$$

$$\ln \gamma_3 = \ln \gamma^0_3 + X_2 \varepsilon_{22} + X_3 \varepsilon_{33} + (\varepsilon_{22} - \varepsilon_{23}) \ln (1 - X_2) \quad [26]$$

$$\ln \gamma_1 = \varepsilon_{22} \ln (1 - X_2) + \varepsilon_{33} \ln (1 - X_3) + X_2 \varepsilon_{22} \quad [27]$$

$$+ X_3 \varepsilon_{33} - \varepsilon_{23} \ln \frac{(1 - X_2)(1 - X_3)}{(1 - X_2 - X_3)}$$

Equations [25] through [27], while thermodynamically consistent with Eqs. [4] and [7], do not preserve the simple form of the original Wagner Eq. [1]. Furthermore, they are not based upon a theoretical model as is the quadratic formalism. Of course, for certain composition regions in certain systems, Eqs. [25] through [27] may provide a reasonable representation of the data. This is the case in Ni-Fe-Cr liquid alloys when Ni is the solvent, mainly because binary solutions of Cr in liquid Ni are better represented by Eqs. [21] and [22] than by Eqs. [19] and [20] (although neither set of equations is satisfactory; a second-order parameter is required). Based upon this one example, Hajra *et al.* concluded that Eqs. [25] through [27] are superior to the quadratic formalism. This conclusion is not justified.

For ternary systems, it is simpler, and more theoretically justifiable, to use the quadratic formalism of Eqs. [14] and [16]. With the following substitutions in Eqs. [14] through [16],

$$\ln \gamma^0_i = (\alpha_{1i} + C_i) \quad i = 2,3 \quad [28]$$

$$\varepsilon_{ii} = -2\alpha_{1i} \quad i = 2,3 \quad [29]$$

$$\varepsilon_{23} = -(\alpha_{12} + \alpha_{31} - \alpha_{23}) \quad [30]$$

the following equations of the unified interaction parameter formalism[4,5] result:

$$\ln \gamma_1 = -\left(\frac{\varepsilon_{22}}{2} X_2^2 + \frac{\varepsilon_{33}}{2} X_3^2 + \varepsilon_{33} X_2 X_3 \right) \quad [31]$$

$$\ln \gamma_2 = \ln \gamma^0_2 + \varepsilon_{22} X_2 + \varepsilon_{23} X_3 \quad [32]$$

$$- \left(\frac{\varepsilon_{22}}{2} X_2^2 + \frac{\varepsilon_{33}}{2} X_3^2 + \varepsilon_{23} X_2 X_3 \right)$$

$$= \ln \gamma^0_2 + \varepsilon_{22} X_2 + \varepsilon_{23} X_3 + (\ln \gamma_1)$$

Similarly,

$$\ln \gamma_3 = \ln \gamma^0_3 + \varepsilon_{32} X_3 + \varepsilon_{33} X_3 + (\ln \gamma_1) \quad [33]$$

where $(\ln \gamma_1)$ in Eqs. [32] and [33] is given by Eq. [31] and $\varepsilon_{23} = \varepsilon_{32}$.

Equations [32] and [33] are identical to Wagner's formalism, Eq. [1], in the limit of infinite dilution (where the $\ln \gamma_1$ term becomes vanishingly small relative to the other terms), and the parameters ε_{22}, ε_{33}, and ε_{23} are identical to those of the Wagner formalism. However, Eqs. [31] through [33] are consistent with the Gibbs–Duhem Eq. [4] and with Eq. [7].

Equation [31] for $\ln \gamma_1$ is identical to Eq. [6]. Because Eqs. [1] and [6] are thermodynamically consistent only at infinite dilution, Srikanth and Jacob[8] incorrectly concluded that the same is true of Eqs. [31] through [33]. In fact, Eqs. [31] through [33] are thermodynamically consistent at all compositions.

Approximation for ε_{23}

If ε_{22} and ε_{33} have been determined from measurements in the 1-2 and 1-3 binary systems, and one wishes to estimate the properties of the ternary solutions, then, as a first approximation, one might assume that 2-3 interactions are negligible. Because ε_{23} is an "interaction parameter," one might then propose setting $\varepsilon_{23} = 0$. However, it is clear from Eqs. [8] and [12] that it is α_{23} that should be set to zero. From Eqs. [29] and [30], then, it follows that a better first approximation to ε_{23} is

$$\varepsilon_{23} = (\varepsilon_{22} + \varepsilon_{33})/2 \quad [34]$$

Clearly, Eq. [34] should only be used if, in fact, 2-3 interactions can be reasonably assumed to be small as, for example, in a case of two metallic solutes in a metallic solvent. For a case of a metallic and a nonmetallic solute in a metallic solvent (*e.g.*, Al and O in Fe), the interactions are likely to be strong, and Eq. [34] should not be used.

C. General Unified Formalism—N Components, Higher-Order Terms

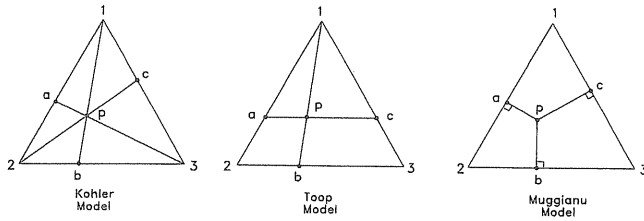The unified formalism has been generalized as follows:[4,5]

Fig. 2—Three geometric models for estimating thermodynamic properties of ternary solutions from binary data.

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{N} \varepsilon_{ij} X_j + \sum_{j,k=2}^{N} \varepsilon_{ijk} X_j X_k$$
$$+ \sum_{j,k,l=2}^{N} \varepsilon_{ijkl} X_j X_k X_l + ... + (\ln \gamma_1) \quad (i \geq 2) \quad [35]$$

where $(\ln \gamma_1)$ for the solvent is given by

$$\ln \gamma_1 = -\frac{1}{2} \sum_{j,k=2}^{N} \varepsilon_{jk} X_j X_k - \frac{2}{3} \sum_{j,k,l=2}^{N} \varepsilon_{jkl} X_j X_k X_l$$
$$-\frac{3}{4} \sum_{j,k,l,m=2}^{N} \varepsilon_{jklm} X_j X_k X_l X_m - ... \quad [36]$$

where the parameters ε_{ij}, ε_{ijk}, ε_{ijkl}, ... may be called first-order, second-order, third-order, etc. interaction parameters.

Equations [35] and [36] may be shown to satisfy the relationship of Eq. [7]. By substituting Eqs. [35] and [36] into Eq. [4] and collecting like terms, it may be shown that the Gibbs–Duhem equation is satisfied and, furthermore, that a very simple relationship exists among the higher-order parameters, namely,

$$\varepsilon_{ijk} = \varepsilon_{ikj} = \varepsilon_{jik} = \varepsilon_{jki} = \varepsilon_{kij} = \varepsilon_{kji} \quad [37]$$
$$\varepsilon_{ijkl} = \varepsilon_{jikl} = \varepsilon_{kjil} = ...$$

That is, the order of the subscripts is immaterial just as in Eq. [5] for the first-order parameters. Equation [37] also holds when two or more subscripts are identical. For example,

$$\varepsilon_{ijj} = \varepsilon_{jji} = \varepsilon_{jij} \quad [38]$$

Note in Eqs. [35] and [36] that the summations are over all values of all indices. For example, the sum $\Sigma \varepsilon_{jkl} X_j X_k X_l$ contains terms $\varepsilon_{123} X_1 X_2 X_3 + \varepsilon_{132} X_1 X_3 X_2 + \varepsilon_{213} X_2 X_1 X_3 + ...$ for all possible permutations. These terms are all equal by virtue of Eq. [37].

Srikanth and Jacob[8] stated that Eqs. [35] and [36] are thermodynamically consistent only at infinite dilution. This is incorrect. Equations [4] and [7] are satisfied at all concentrations.

Although it was not given by Bale and Pelton, the following simple expression for the integral excess Gibbs energy (Eq. [9]) may be written by substituting Eqs. [35] and [36] into Eq. [9]:

$$g^E/RT = \sum_{i=2}^{N} X_i \ln \gamma_i^0 + \frac{1}{2} \sum_{i,j=2}^{N} \varepsilon_{ij} X_i X_j + \frac{1}{3}$$
$$\sum_{i,j,k=2}^{N} \varepsilon_{ijk} X_i X_j X_k + ... \quad [39]$$

where, again, the summations are over all combinations of the indices.

As an alternative derivation of the unified formalism, one can start with Eq. [39], which is a general polynomial expansion, and then obtain Eqs. [35] and [36] by differentiation. This demonstrates the thermodynamic consistency of Eqs. [35] and [36].

Higher-order terms were added to the Wagner formalism by Lupis and Elliot,[9] whose equations were similar to Eq. [35] except that the $(\ln \gamma_1)$ term was not included; therefore, Eqs. [4] and [7] were not satisfied. These authors used a somewhat different notation. For example, ε_{ij} was given the symbol ρ_i^j. The second-order formalism of Lupis and Elliott for a binary system is as follows:

$$\ln \gamma_2 = \ln \gamma_2^0 + \varepsilon_{22} X_2 + \rho_2^2 X_2^2 \quad [40]$$

In many compilations of interaction parameters,[10,11] one finds that ρ_2^2 is often either equal to, or approximately equal to, $(-\varepsilon_{22}/2)$. By comparing Eq. [40] with Eq. [19], it is apparent why this should be so. That is, there is really only one parameter ε_{22}, and the quadratic formalism applies.

Approximations for higher-order cross-interaction parameters

It was shown previously that the first-order "cross"-interaction parameter ε_{ij} can be estimated, to a first approximation, from the binary "self"-interaction parameters ε_{ii} and ε_{jj} by Eq. [34]. The question now arises as to how higher-order cross parameters $\varepsilon_{ijk...}$ should be estimated from binary self parameters $\varepsilon_{iii...}$. There is no unique answer to this question, although all estimation techniques should give similar results. Let us first consider some of the techniques commonly employed to estimate thermodynamic properties of ternary and multicomponent solutions from binary data and then apply these to this problem.

For a ternary system, Eq. [13] is given by the quadratic formalism when the α_{ij} parameters are constant. In general, the α_{ij} parameters are not constant but can be expanded in each binary system as polynomials:

$$a_{ij} = {}^0q_{ij} + {}^1q_{ij} X_i + {}^2q_{ij} X_i^2 + ... \quad [41]$$

or, equivalently,

$$a_{ij} = {}^0L_{ij} + {}^1L_{ij} (X_i - X_j) + {}^2L_{ij} (X_i - X_j)^2 + ... \quad [42]$$

where the constant coefficients ${}^mq_{ij}$ and ${}^mL_{ij}$ are obtained empirically by fitting binary thermodynamic data. In order now to use Eq. [13] to estimate ternary properties, a procedure is required to relate α_{ij} at a given ternary composition to its value at some composition in the binary *i-j* system. To this end, several "geometric" models, based upon regular solution theory, have been proposed. Three of these are illustrated in Figure 2. In each of these models, g^E in a ternary solution at a composition point *p* is estimated from the excess Gibbs energies in the three binary subsystems at points *a*, *b*, and *c* by the equation

$$g^E/RT = (a_{12(a)} X_1 X_2 + a_{23(b)} X_2 X_3$$
$$+ a_{31(c)} X_3 X_1) + (C_2 X_2 + C_3 X_3) \quad [43]$$

where $\alpha_{12(a)}$, $\alpha_{23(b)}$, and $\alpha_{31(c)}$ are the binary functions of Eq. [41] or [42] evaluated at points *a*, *b*, and *c*.

In the Muggianu method,[12] α_{ij} is assumed to be constant along lines of constant $(X_i - X_j)$. Hence, if α_{ij} in the binary systems is written in "Redlich–Kister" form as in Eq. [42], then Eq. [42] for each binary system can be substituted

directly into Eq. [43]. In the Kohler method,[13] α_{ij} is assumed to be constant along lines of constant ratio $X_i/(X_i + X_j)$. If one writes,

$$a_{ij} = {}^0q_{ij} + {}^1q_{ij}\ (X_i/(X_i + X_j))$$
$$+ {}^2q_{ij}\ (X_i/(X_i + X_j))^2 + ... \quad [44]$$

then the coefficients ${}^mq_{ij}$ are numerically equal to those in Eq. [41] because $X_i/(X_i + X_j) = X_i$ in the i-j binary system, and Eq. [44] for each binary system can then be substituted directly into Eq. [43]. Finally, in the Toop method,[14] α_{12} and α_{31}, written as in Eq. [41] with $X_i = X_1$, and α_{23}, written as in Eq. [44], can be substituted directly into Eq. [43].

The extension of the geometrical models to N-component systems is straightforward. Additional terms are simply added to Eq. [43].

Returning now to the question of estimating the cross parameters from the binary self parameters, let us apply the Toop method, with component 1 as the solvent, for all 1-j binary systems. That is, assume α_{1j} to be constant at constant X_1. For all other systems i-j that do not contain the solvent ($i \geq 2, j \geq 2$) set $\alpha_{ij} = 0$ as a first approximation. This gives

$$g^E/RT = \sum_{j=2}^{N} [X_1 X_j\ ({}^0q_{1j} + {}^1q_{1j}\ X_1$$
$$+ {}^2q_{1j}\ X_1^2 + ...) + C_j X_j] \quad [45]$$

By expanding Eq. [45], collecting terms, and comparing to Eq. [39], the following simple relationships are obtained for estimating the cross parameters:

$$\varepsilon_{ij} = (\varepsilon_{ii} + \varepsilon_{jj})/2 \quad [46]$$

$$\varepsilon_{ijk} = (\varepsilon_{iii} + \varepsilon_{jjj} + \varepsilon_{kkk})/3 \quad [47]$$

$$\varepsilon_{ijkl} = (\varepsilon_{iiii} + \varepsilon_{jjjj} + \varepsilon_{kkkk} + \varepsilon_{llll})/4 \ etc. \quad [48]$$

For example,

$$\varepsilon_{223} = \varepsilon_{232} = \varepsilon_{322} = (2\varepsilon_{222} + \varepsilon_{333})/3 \quad [49]$$

Using the Muggianu model rather than the Toop model gives equations that are similar to Eqs. [46] through [48] but not as simple. The Kohler method cannot be used directly because this model involves ratios of mole fractions which are not equivalent to a simple polynomial expression as in Eq. [39]. Hence, it is proposed that Eqs. [46] through [48] be used for estimation purposes.

As discussed in the subsection to Section II–B, Eqs. [46] through [48] should only be used if, in fact, the solute-solute interactions can reasonably be assumed to be weak.

Finally, suppose that one wishes to estimate cross parameters in a ternary solution, where component 1 is the solvent, and that one possesses experimental data for the binary system 2-3. In general, these data are of limited value in this regard, because interactions between components 2 and 3 in a binary solution containing only components 2 and 3 can be very different from interactions between components 2 and 3 in dilute solution in a solvent 1. If all three components are chemically similar (all metals, for example), then it is probably justified to approximate ε_{23} from Eqs. [29] and [30] as

$$\varepsilon_{23} = (\varepsilon_{22} + \varepsilon_{33})/2 + a_{23} \quad [50]$$

with α_{23} as a constant. However, there is little justification for expanding α_{23} as a polynomial as in Eq. [41] or [42], and an average value over the 2-3 binary should suffice.

Of course, if estimations of the thermodynamic properties of an N-component system are being made over a wide composition range such that no single component can be considered to be the solvent, then one should not use the unified interaction parameter formalism at all. In such cases, one of the geometric models of Figure 2 might be used. See, for example, references 15 through 17. In this case, an argument in favor of the Kohler and Toop models over the Muggianu model is given in Section V.

III. INTERACTION PARAMETER FORMALISM WITH MOLAR RATIOS

Another means of rendering the interaction parameter formalism consistent with the Gibbs–Duham Eq. [4] and with Eq. [7] is to replace the mole fractions X_i in the expansions by the molar ratios $y_i = X_i/X_1$ (where 1 = solvent).

In the general case,

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{N} \varepsilon_{ij} y_j + \sum_{j,k=2}^{N} \varepsilon_{ijk} y_j y_k + ... \quad (i \geq 2) \quad [51]$$

$$\ln \gamma_1 = -\frac{1}{2} \sum_{j,k=2}^{N} \varepsilon_{jk} y_j y_k - \frac{2}{3} \sum_{j,k,l=2}^{N} \varepsilon_{jkl} y_j y_k y_l - ... \quad [52]$$

Equations [51] and [52] are very similar to Eqs. [35] and [36], with the important exception that the ($\ln \gamma_1$) terms of Eq. [35] do not appear in Eq. [51]. It can easily be shown that Eqs. [51] and [52] satisfy Eqs. [4] and [7]. Furthermore, the very simple relationships of Eq. [37] can also be shown to apply.

The advantage of using molar ratios in graphical integrations of the Gibbs–Duhem equation was recognized very early,[18,19] and the application to the case of first-order interaction parameters was pointed out by Schuhmann.[20] However, Eqs. [37], [51], and [52] for the general case have not been given previously. Similar expansions are used in the well-known Pitzer equation[21] for aqueous solutions. Here, the composition variables are the molalities $m_i = (y_i/y_1) (1000/M_1)$, where M_1 is the molecular weight of the solvent.

An advantage of the interaction parameter formalism with molar ratios is that Eqs. [51] and [52] can be written with weight ratios (m_i/m_1) in place of the molar ratios y_i, because weight ratios vary directly as molar ratios: $(m_i/m_1) = y_i(M_i/M_1)$, where (M_i/M_1) is the ratio of molecular weights. It is only necessary to multiply each interaction parameter by a constant. This conversion is not so simple when mole fractions are used as in Eqs. [35] and [36], because weight fractions do not vary directly as mole fractions.

The disadvantage of the molar ratio representation is that it is not consistent with the quadratic formalism, and so, for simple substitutional solutions at least, it is less likely to provide as good a fit to experimental data and to extrapolate as well as do Eqs. [35] and [36].

Nonmetallic Solutes in a Metallic Solvent

However, as pointed out by Schuhmann,[20] the molar ratio Eqs. [51] and [52] can provide a better representation

of the data in certain cases such as solutions of nonmetallic solutes in a metallic solvent, provided that a different definition of γ_i is adopted.

Defining an ideal solution as one in which $a_i = X_i$ implies a random distribution of all species 1, 2, 3, ... on one set of equivalent lattice sites. The activity coefficient defined as in Eq. [2] can thus account for the excess enthalpy and for the nonconfigurational entropy but can only account well for small excess configurational entropy effects (i.e., for small departures from a random substitutional distribution.)

As an example, Schuhmann[20] showed that the excess thermodynamic properties of relatively dilute solutions of n_X moles of a nonmetallic solute X (such as O, S, and C) in n_{Fe} moles of Fe solvent can be well represented by a model in which Fe and "FeX" are the components. One mole of solution contains n_X moles of "FeX" and ($n_{Fe} - n_X$) moles of "unassociated" Fe, so that

$$a_{FeX} = \gamma'_{FeX} \frac{n_X}{n_X + (n_{Fe} - n_X)} = \gamma'_{FeX}\, y_X \qquad [53]$$

$$a_{Fe} = \gamma'_{Fe} \frac{n_{Fe} - n_X}{n_X + (n_{Fe} - n_X)} \qquad [54]$$

Applying the quadratic formalism as in Eqs. [19] and [20] gives

$$\ln \gamma'_{FeX} = \ln \gamma^0_{FeX} + \varepsilon_{22} \left(y_X - \frac{1}{2} y_X^2\right) \qquad [55]$$

$$\ln \gamma'_{Fe} = -(\varepsilon_{22}/2)\, y_X^2 \qquad [56]$$

However,

$$a_X = K \frac{a_{FeX}}{a_{Fe}} = K \frac{\gamma'_{FeX}}{\gamma'_{Fe}} \frac{n_X}{(n_{Fe} - n_X)} \qquad [57]$$

Hence,

$$a_X = \gamma'_X \frac{n_X}{(n_{Fe} - n_X)} \qquad [58]$$

If one substitutes $\gamma'_X = K(\gamma'_{FeX}/\gamma'_{Fe})$ into Eqs. [55] and [56], the quadratic terms cancel, giving

$$\ln \gamma'_X = \ln (\gamma^0_X)' + \varepsilon_{22}\, y_X \qquad [59]$$

That is, a linear formalism in terms of y_X is predicted as long as the activity coefficient is defined by Eq. [58] and not by Eq. [2].

This is not meant to imply the existence of FeX "molecules" in solution. If the solute, for example carbon, forms an interstitial solution, then the same Eqs. [53] through [59] apply, because distributing n_X X atoms and ($n_{Fe} - n_X$) vacancies randomly over n_{Fe} equivalent interstitial sites obviously gives the same configurational entropy as distributing n_X "FeX" species and n_{Fe} Fe atoms over n_{Fe} equivalent sites. Although Schuhmann used this argument for both carbon and sulfur as solutes in Fe, it is probably more realistic to consider S as a substitutional solute in molten Fe. Nevertheless, Eqs. [53] through [59] can still be shown to apply if we assume short-range ordering such that Fe and S occupy equivalent sites but S-S nearest-neighbor pairs are prohibited. In this case, the configurational entropy is given by distributing (Zn_S) nearest-neighbor Fe-S pairs

and $[(Z/2)(n_{Fe} + n_S) - Zn_S] = (Z/2)(n_{Fe} - n_S)$ nearest-neighbor Fe-Fe pairs over $(Z/2)(n_{Fe} + n_S)$ "bond sites," where Z is the coordination number. If the Ising approximation is applied,[22] this can be shown to give the same expression for the configurational entropy as in the case of a solution of Fe and "FeX" species.

Schuhmann[20] extended Eqs. [53] through [59] to the case of two nonmetallic solutes in a metallic solvent. It is easy to show in general that the linear formalism in terms of y_i, Eqs. [51] and [52], is predicted by the model for any number of nonmetallic solutes.

It may also be predicted that the molar ratio formalism, as is used in the Pitzer equations, should apply well to aqueous solutions in which ionic solutes are surrounded by a solvation shell of water molecules, because this is similar to an interstitial solution or to an ordered solution in which solute-solute nearest-neighbor pairs are prohibited. However, in this case, γ_i should be defined similarly to Eq. [58], and this is not usually the case in the Pitzer equations.

It should be stressed that there is no thermodynamic reason for preferring Eqs. [35] and [36] in the case of metallic solutes and Eqs. [51] and [52] in the case of nonmetallic solutes, because both formalisms are thermodynamically consistent. However, the former will more likely yield a better fit to experimental data, with fewer coefficients and a higher probability of extrapolating well, in the case of metallic solutes, while the latter will more likely be better for nonmetallic solutes.

Usually, of course, a solution will contain both metallic and nonmetallic solutes. In this case, it is recommended that the mole fraction unified formalism be used, Eqs. [35] and [36], and that the association of solutes as discussed in Section IV be taken into account.

IV. ASSOCIATION OF SOLUTES—TEMPERATURE DEPENDENCE OF PARAMETERS

As was pointed out in the subsection to Section III, a definition of γ_i as in Eq. [2] for all solutes implies an approximately random distribution of species 1, 2, 3, ... on equivalent sites. Simple series expansions for $\ln \gamma_i$ cannot therefore be expected to yield satisfactory results when there are large deviations from a random distribution.

An important case in point is a liquid solution of a nonmetallic solute X and a relatively reactive metallic solute M in a less reactive metallic solvent (e.g., Al and O in Fe). In this case, there is a strong tendency to form associated molecules MX.

As an example, activities of sulfur have been measured[23,24,25] at several temperatures from 400 °C to 1000 °C and over a range of compositions in liquid solutions of S and Cu in Pb solvent. If these data are represented by a first-order interaction parameter formalism as in Eqs. [31] through [33], then it is necessary[26] for ε_{CuS} to have an extremely large temperature dependence. If, as is usually done, one writes

$$RT\varepsilon = AT - B \qquad [60]$$
$$\varepsilon = A/R - B/RT \qquad [61]$$

then the entropic term, (B/R), required to fit the data is 526 J/mol K,[24,26] which is two orders of magnitude larger than
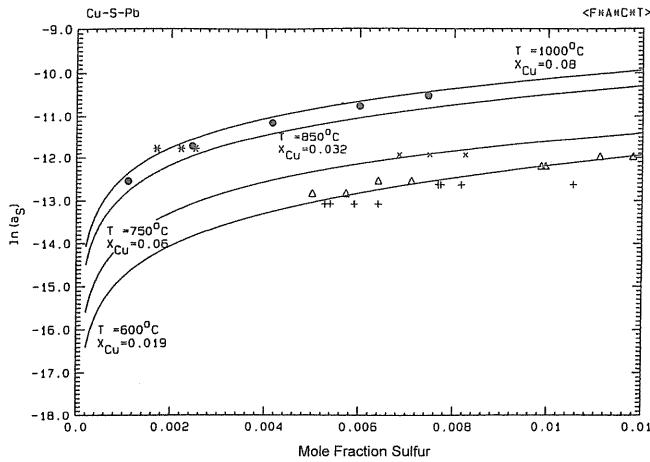
Fig. 3—Activity of sulfur (liquid standard state) in liquid Pb-Cu-S solutions. Curves are calculated with $\Delta G° = -62{,}500$ J/mol for Reaction [62]. $\triangle$ (Ref. 23); $+$, X, and $*$ (Ref. 24); and $\circledcirc$ (Ref. 25).
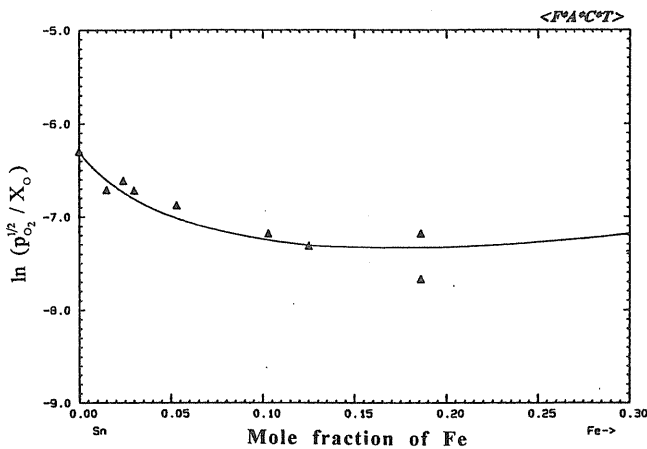

Fig. 4—Ln $(p_{O_2}^{1/2}/X_O)$ at 1300 °C, where X_O is the total solubility of oxygen under a pressure p_{O_2} in liquid Sn-Fe-O solutions calculated[28] by assuming association as in Eq. [68]. Points are from Ref. 27.
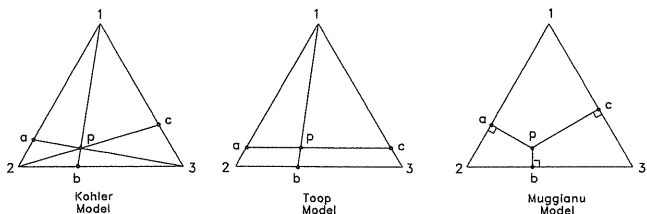

Fig. 5—The three geometric models of Fig. 2 when the composition point p is close to the 2-3 binary system.

is physically reasonable. This result indicates that the assumptions of the model are incorrect.

Let us assume instead that Cu and S atoms are associated to form CuS molecules:

$$\underline{Cu} + \underline{S} = \underline{CuS} \qquad [62]$$

so that there are now three solute species: CuS, unassociated Cu, and unassociated S. If n_S and n_{Cu} are the overall number of moles of S and Cu in solution, then

$$n_S^! = n_S - n_{CuS}^! \qquad [63]$$

$$n_{Cu}^! = n_{Cu} - n_{CuS}^! \qquad [64]$$

where $n_S^!$, $n_{Cu}^!$, and $n_{CuS}^!$ are the numbers of moles of unassociated S and Cu and of CuS associates. Mole fractions may be defined as

$$X_i^! = n_i^!/(n_S^! + n_{Cu}^! + n_{CuS}^!) \qquad [65]$$

and the unified interaction parameter Eq. [35] for ln γ_i (i = Cu, S, CuS) is written in terms of these mole fractions. From a critical evaluation of data for the Pb-S and Pb-Cu binary solutions, the following binary parameters were obtained:[26]

$$\ln \gamma_S^0 = -0.7074 - 4918/T$$

$$\varepsilon_{SS} = 1.4147 - 5218/T$$

$$\varepsilon_{SSS} = 22{,}580/T \qquad [66]$$

$$\ln \gamma_{Cu}^0 = -0.3879 + 3065/T$$

$$\varepsilon_{CuCu} = 0.7758 - 6130/T$$

All the data[23,24,25] for the ternary Pb-Cu-S solutions were then represented[26] by selecting $\Delta G°$ of Reaction [62] to be $-62{,}500$ J/mol (where the standard states were chosen as pure liquid Cu, S, and "CuS").

That is,

$$K = (X_{CuS}^!/X_{Cu}^! X_S^!)(\gamma_{CuS}/\gamma_{Cu} \gamma_S) \qquad [67]$$
$$= \exp (-62{,}500/RT)$$

As can be seen in Figure 3, all the data are well represented with this one temperature-independent parameter. No ternary interaction parameters were required. That is, ε_{SCu}, $\varepsilon_{Cu(CuS)}$, $\varepsilon_{S(CuS)}$, and $\varepsilon_{(CuS)(CuS)}$ were all set to zero.

As a second example, the effect of Fe additions upon the solubility of oxygen in molten Sn was studied at 1300 °C.[27] Results are shown in Figure 4. If only Fe and O species are considered, then a curve of this shape can only be reproduced through the use of several cross parameters ε_{OFe}, ε_{OFeFe}, etc. A simpler result is obtained by assuming association according to

$$\underline{Fe} + \underline{O} = \underline{FeO} \qquad [68]$$

With $\ln \gamma_{Fe}^0$, ε_{FeFe}, and ε_{FeFeFe} taken from a critical evaluation of data for Sn-Fe solutions,[28] and with $\Delta G°$ chosen as $-42{,}760$ J/mol for Reaction [68] (relative to liquid Fe, liquid "FeO", and O at infinite dilution as standard states), the data are well fitted with only this one parameter, as can be seen in Figure 4.[28] The interaction parameters ε_{OO}, ε_{OFe}, $\varepsilon_{Fe(FeO)}$, $\varepsilon_{O(FeO)}$, and $\varepsilon_{(FeO)(FeO)}$ were all set to zero.

Bouchard and Bale[29,30] had similar success in representing data in molten Fe by assuming "AlO" and "CaO" associates.

Generally, if there are strong interactions between two solutes i and j, then a temperature dependence for ε_{ij} as in Eq. [61] is invalid, and association of solutes should be explicitly taken into account.

V. DILUTE SOLUTIONS OF A SOLUTE IN A BINARY SOLVENT

For nondilute solutions in which no single component can be considered to be the solvent, it was recommended in the subsection to section II–C that one of the geometric models of Figure 2 might be used. At least in the case of a dilute solution of a solute (component 1) in a binary solvent (components 2, 3), the Toop and Kohler models are

to be preferred, as can be seen with reference to Figure 5. When the ternary composition point is close to the 2-3 binary system, then the Toop and Kohler models estimate excess properties at the dilute ternary composition p from values for dilute solutions of 1 in 2 (point a) and dilute solutions of 1 in 3 (point c). In contrast, the Muggianu model uses binary values much further from the dilute range. The Muggianu model is thus less likely to provide a good estimate. This may be taken as an argument for preferring the Kohler or Toop model over the Muggianu model in general.

A more sophisticated model of dilute solution behavior is supplied by the coordination cluster theory[31,32,33] of which the Toop model is a very simple limiting case. For the dissolution of a dilute solute C in a binary solvent A-B, the theory considers the formation of $(Z + 1)$ different "coordination clusters" by the reaction

$$C + (Z - i) A + iB = C (A_{Z-i}B_i) \qquad 0 \le i \le Z \quad [69]$$
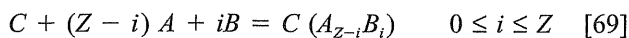
where Z is the coordination number. In this way, the nonrandom configurational entropy is taken into account. When the solution is also dilute in B, then $C(A_{Z-1} B)$ clusters predominate, and the coordination cluster theory reduces closely to the association model of Section IV. Blander pointed out, on the basis of coordination cluster theory, that the usual practice of expressing the temperature dependence of cross-interaction parameters by Eq. [61] can be invalid.

VI. CONCLUSIONS

The several attempts to extend the interaction parameter formalism to higher-order polynomials and to render it thermodynamically consistent at finite concentrations have given rise to much confusion and complexity. The problem is best resolved through extension of Darken's quadratic formalism, which has a sound theoretical foundation. This leads to the general and simple equations of the unified interaction parameter formalism, which reduces to the original Wagner formalism at infinite dilution.

The first-order equations proposed by Hajra et al.[7] for ternary systems, while thermodynamically consistent, are not based upon a theoretical model, and so are less likely to provide a good representation of experimental data or to extrapolate well. Furthermore, these equations are complex and not easily generalizable to higher-order terms and to N-component systems. The proposed equations of Srikanth and Jacob[8] are not consistent with the necessary thermodynamic relationship of Eq. [7].

Very simple general relationships [46] through [48] have been derived for estimating higher-order cross parameters from binary parameters in a first approximation.

The interaction parameter formalism can also be rendered thermodynamically consistent at finite concentrations by replacing mole fractions by molar ratios (X_i/X_1). General equations to any order for N-component systems are given. In general, these equations will not provide as good a representation of data, nor will they extrapolate as well, as the equations of the unified formalism in terms of the mole fractions. However, if the activity coefficients are properly redefined, as shown by Schuhmann,[20] then the molar ratio formalism may be better for solutions with only interstitial solutes. It has been shown in the present article that this

should also be true for ordered substitutional solutions, such as solutions of S or O in liquid Fe, and for aqueous solutions. Also, the molar ratio formalism lends itself better to the use of weight fractions.

For solutions of a reactive metal and a nonmetal in a metallic solvent (such as Al and O in molten Fe), the formation of complex species such as "AlO" must be explicitly taken into account; otherwise, an unreasonably large temperature dependence of the cross-interaction parameters will result. In such cases of strong solute-solute interaction, the usual practice of expressing the parameters as linear functions of $(1/T)$ is invalid.

It has also been shown that for more concentrated solutions, the use of the Kohler or Toop interpolation model for predicting multicomponent thermodynamic properties from binary data is to be preferred over the use of the Muggianu model, which is widespread.

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