Thermodynamic Consistency of the Interaction Parameter Formalism

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The apparent contradiction between the exact nature of the interaction parameter formalism as presented by Lupis and Elliott and the inconsistencies discussed recently by Pelton and Bale arise from the truncation of the Maclaurin series in the latter treatment. The truncation removes the exactness of the expression for the logarithm of the activity coefficient of a solute in a multi-component system. The integrals are therefore path dependent. Formulae for integration along paths of constant X_i or X_i/X_j are presented. The expression for ln γ_{solvent} given by Pelton and Bale is valid only in the limit that the mole fraction of solvent tends to one. The truncation also destroys the general relations between interaction parameters derived by Lupis and Elliott. For each specific choice of parameters special relationships are obtained between interaction parameters.

I. INTRODUCTION

FREE energy interaction parameters are related to the coefficients of the Maclaurin series for logarithm of the activity coefficient of a solute in a multicomponent system. The formalism is mathematically exact if the series is not truncated as in treatment of Lupis and Elliott.[1] However, higher order interaction parameters are rarely available for systems of practical interest. Moreover, the measurement of the interaction coefficients beyond second order requires accuracies of measurement which are difficult to obtain in practice. It is therefore often necessary to calculate activity coefficients of solutes at finite concentrations using only the first or second order interaction parameters. The purpose of this communication is to show that the truncated Maclaurin series expansion is not exact and can therefore be integrated only along chosen paths. The general relations between interaction parameters derived by Lupis and Elliott[1] are also invalid when the Maclaurin series is truncated. For each mode of truncation special relationships are obtained. Pelton and Bale[2] have recently shown that the expression for logarithm of the activity coefficient of a solute in a multicomponent system in terms of first order interaction parameters is thermodynamically inconsistent. They have indicated that the expression can be made consistent by adding a term for ln γ_{solvent}. Their expression for ln γ_{solvent}, however, is valid only for the limit that the mole fraction of solvent tends to unity. At finite concentrations of solute the expression for ln γ_{solvent} is shown to be dependent upon the path of integration, when the Maclaurin series for the logarithm of activity coefficient is truncated. Expressions for ln γ_{solvent} are derived for paths of constant X_i/X_j or X_i.

II. EXACTNESS OF EQUATION AND THERMODYNAMIC CONSISTENCY

From the fundamental definition, the Gibbs free energy, G, is a state function and hence its differential is exact. In a mathematical sense the necessary and sufficient condition for exactness is given by Maxwell's relation:

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial n_j}\right) = \frac{\partial}{\partial n_j}\left(\frac{\partial G}{\partial n_i}\right) \qquad [1]$$

for all values of i and j, where n_i and n_j are the number of moles of components i and j in a multicomponent solution. Equation [1] can be modified and rewritten in terms of the partial property as[2]

$$\frac{\partial \ln \gamma_i}{\partial n_j} = \frac{\partial \ln \gamma_j}{\partial n_i} \qquad [2]$$

from which it follows that (Appendix I)

$$\frac{\partial \ln \gamma_j}{\partial X_i} - \sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_j}{\partial X_k} = \frac{\partial \ln \gamma_i}{\partial X_j} - \sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_i}{\partial X_k} \qquad [3]$$

where X_i indicates the mole fraction of component i.

Any power series expansion chosen to represent the logarithm of the activity coefficient should conform to Eq. [3] and approach at infinite dilution Raoult's law for the solvent and Henry's law for each solute. Noncompliance of any formalism to relationship [3] implies that dG is inexact, which is thermodynamically inconsistent.

Having expressed the partial property of the solutes as a power series expansion of composition, the solvent property is then deduced by integrating the Gibbs-Duhem equation for an m-component system.

$$(1 - X_2 - X_3 - \cdots - X_m)d \ln \gamma_{\text{solvent}} + X_2 d \ln \gamma_2 + \ldots\ldots + X_m d \ln \gamma_m = 0 \qquad [4]$$

The subscripts $2, 3 \ldots . m$ denote the solutes and 1 represents the solvent.

If the exactness criterion is not satisfied, then Eq. [4] does not possess a definite integral for ln γ_{solvent} and can be integrated only along a chosen path in an m-dimensional space, but the integral will in general depend on the path of integration.

III. INFINITE SERIES REPRESENTATION OF ln γ

It is conventional to express the partial thermodynamic properties of solutes in dilute multicomponent solutions as

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a function of composition through a Maclaurin infinite series expansion. The partial excess free energy can be accordingly expressed as

$$\mathrm{R}T \ln \gamma_i = \mathrm{R}T \sum_{n_2=0}^{\propto} \cdots \sum_{n_j=0}^{\propto} \cdots \sum_{n_m=0}^{\propto} J^{(i)}_{n_2 \ldots n_j \ldots n_m} \cdot X_2^{n_2} \ldots X_j^{n_j} \ldots X_m^{n_m} \qquad [5a]$$

where

$$J^{(i)}_{n_2 \ldots n_j \ldots n_m} = \frac{1}{n_2! \ldots n_j! \ldots n_m!} \frac{\partial^{n_2 + \ldots + n_j + \ldots + n_m} \ln \gamma_i}{\partial X_2^{n_2} \ldots . \partial X_j^{n_j} \ldots . \partial X_m^{n_m}} \qquad [5b]$$

The coefficient $J^{(i)}_{n_2 \ldots n_j \ldots n_m}$ is termed interaction parameter of order $\Sigma_{j=2}^{m} n_j$.

Lupis and Elliott[1] assume the existence of a Maclaurin infinite series for the logarithm of the activity coefficient of solvent also and derive reciprocal relationships between the interaction parameters of the solute and solvent through the Gibbs-Duhem equation. The general relationship is given by,

$$J^{(i)}_{n_2 . . n_j . . n_m} = J^{(1)}_{n_2 . . n_j . . n_m} - \frac{n_i + 1}{\sum_{j=2}^{m} n_j} J^{(1)}_{n_2 . . n_i + 1 . . n_m} \qquad [6a]$$

As shown in Appendix II, an algebraic manipulation of Eq. [6a] leads to:

$$(n_i + 1) J^{(j)}_{n_2 . . n_i + 1 . . n_m} - (n_j + 1) J^{(i)}_{n_2 . . n_j + 1 . . n_m} = \frac{1}{\sum_{j=2}^{m} n_j} \left(J^{(j)}_{n_2 . . n_i . . n_m} - J^{(i)}_{n_2 . . n_j . . n_m} \right) \qquad [6b]$$

Expression [6b] shows the interrelationship between the interaction parameters of solutes. As shown in Appendices III and IV, the formalism of Lupis and Elliott[1] satisfies the condition for exactness and the Gibbs-Duhem equation.

IV. CONSEQUENCES OF POWER SERIES TRUNCATION

Very often higher order interaction parameters are not available for systems of practical interest and precise measurement of the interaction coefficients beyond second order must await major improvement in high temperature experimental techniques. Hence frequently the partial properties of solutes are expressed only in terms of the first order interaction parameters, *i.e.*, Maclaurin series truncated to first order.

$$\ln \gamma_i = \ln \gamma_i^\circ + \varepsilon_i^2 X_2 + \varepsilon_i^3 X_3 \ldots\ldots + \varepsilon_i^m X_m \qquad (i = 2, \ldots . m) \qquad [7]$$

The first order interaction parameter formalism was first proposed by Wagner[3] and extensively used by Chipman.[4] Sometimes a second order interaction parameter formalism is chosen to represent the logarithm of the activity coefficient of solutes.[5]

$$\ln \gamma_i = \ln \gamma_i^\circ + \sum_{j=2}^{m} \varepsilon_i^j X_j + \sum_{j=2}^{m} \rho_i^j X_j^2 + \sum_{j=2}^{m} \sum_{k>j}^{m} \rho_i^{jk} X_j X_k \qquad [8]$$

Equations [7] and [8] do not satisfy Eq. [3] and so both the first order and second order interaction parameter formalisms are thermodynamically inconsistent except at infinite dilution, *i.e.*, $X_{\text{solvent}} \rightarrow 1$, as discussed by Pelton and Bale.[2] Any truncation of the infinite series expansion of $\ln \gamma_{\text{solute}}$ renders Eq. [4] inexact at finite solute concentrations. Also, upon truncation of the Maclaurin infinite series, the general reciprocal relationships derived by Lupis and Elliott[1] become invalid and one obtains a set of special relationships between interaction parameters for each specific choice of parameters.

As an example, consider a ternary system and a second order Maclaurin series expansion for the solutes as well as solvent. The reciprocal relationships between interaction parameters can be derived through the Gibbs-Duhem equation. A second order Maclaurin series expansion for $\ln \gamma_2$ and $\ln \gamma_3$ where subscripts 2 and 3 denote solutes yields:

$$\ln \gamma_2 = \ln \gamma_2^\circ + \varepsilon_2^2 X_2 + \varepsilon_2^3 X_3 + \rho_2^2 X_2^2 + \rho_2^3 X_3^2 + \rho_2^{23} X_2 X_3 \qquad [9]$$

$$\ln \gamma_3 = \ln \gamma_3^\circ + \varepsilon_3^2 X_2 + \varepsilon_3^3 X_3 + \rho_3^2 X_2^2 + \rho_3^3 X_3^2 + \rho_3^{23} X_2 X_3 \qquad [10]$$

Similarly,

$$\ln \gamma_{\text{solvent}} = J^1_{00} + J^1_{01} X_3 + J^1_{02} X_3^2 + J^1_{10} X_2 + J^1_{11} X_2 X_3 + J^1_{20} X_2^2 \qquad [11]$$

The Gibbs-Duhem equation for a ternary system, after some modification, can be written as

$$(1 - X_2 - X_3) \frac{\partial \ln \gamma_{\text{solvent}}}{\partial X_i} + X_2 \frac{\partial \ln \gamma_2}{\partial X_i} + X_3 \frac{\partial \ln \gamma_3}{\partial X_i} = 0 \qquad (i = 2, 3) \qquad [12]$$

Differentiating expressions [9], [10], and [11] with respect to X_2 and substitution into [12] yields

$$J^1_{10} + X_2(2J^1_{20} - J^1_{10} + \varepsilon_2^2) + X_3(J^1_{11} - J^1_{10} + \varepsilon_3^2) + X_2 X_3(\rho_2^{23} + 2\rho_3^2 - J^1_{11} - 2J^1_{20}) + X_2^2(2\rho_2^2 - 2J^1_{20}) + X_3^2(\rho_3^{23} - J^1_{11}) = 0 \qquad [13]$$

Since X_2 and X_3 are independent variables, each term in Eq. [13] is null and hence the following relationships result:

$$J^1_{10} = 0; \qquad J^1_{20} = -\frac{1}{2} \varepsilon_2^2 = \rho_2^2; \qquad J^1_{11} = -\varepsilon_3^2 = \rho_3^{23}$$

$$\rho_2^{23} + 2\rho_3^2 = \rho_3^{23} + 2\rho_2^2 = -\varepsilon_3^2 - \varepsilon_2^2 \qquad [14]$$

Similarly, differentiation with respect to X_3 and application of Gibbs-Duhem equation yields the relationship

$$J_{01}^{1} = 0; \qquad J_{02}^{1} = -\frac{1}{2}\varepsilon_3^3 = \rho_3^3; \qquad J_{11}^{1} = -\varepsilon_2^3 = \rho_2^{23}$$

$$\rho_3^{23} + 2\rho_2^3 = 2\rho_3^3 + \rho_2^{23} = -\varepsilon_2^3 - \varepsilon_3^3 \qquad [15]$$

Equations [14] and [15] are different from the general relationships derived by Lupis[5] for a ternary system. If the expressions for ln γ_2 and ln γ_3 are approximated by a first order interaction parameter formalism and if a Maclaurin series expansion is assumed to exist for ln γ_{solvent}, application of a similar procedure results in:

$$\varepsilon_2^2 = \varepsilon_2^3 = \varepsilon_3^2 = \varepsilon_3^3 = 0$$

which is absurd, a result of the inexactness of the first order representation. The convention adopted here for superscripts and subscripts is the same as that of Lupis and Elliott.[1]

Recently Pelton and Bale[2] have indicated that thermodynamic consistency can be achieved by adding a term for ln γ_{solvent} in the expression for ln γ_i, where i is the solute. They have derived expressions for ln γ_{solvent} by solving the Gibbs-Duhem equation for a first and higher order interaction parameter formalism for ln γ_i. Their expression for ln γ_{solvent}, however, is valid only for the limit that the mole fraction of solvent tends to unity.

Differentiation of Eq. [7] yields:

$$d \ln \gamma_i = \sum_{j=2}^{m} \varepsilon_i^j \, dX_j \qquad [16]$$

At $X_{\text{solvent}} \rightarrow 1$, the Gibbs-Duhem relation takes the form

$$d \ln \gamma_{\text{solvent}} + \sum_{i=2}^{m} X_i \, d \ln \gamma_i = 0 \qquad [17]$$

Combining Eqs. [16] and [17] and after some modification

$$d \ln \gamma_{\text{solvent}} + \sum_{j=2}^{m} \varepsilon_j^j X_j \, dX_j + \sum_{i=2}^{m} \sum_{j>i}^{m} \varepsilon_i^j d(X_i X_j) = 0 \qquad [18]$$

where $\varepsilon_i^j = \varepsilon_j^i$. Integration of [18] yields an expression for ln γ_{solvent} at the limit $X_{\text{solvent}} \rightarrow 1$

$$\ln \gamma_{\text{solvent}} = -\frac{1}{2} \sum_{i=2}^{m} \sum_{j=2}^{m} \varepsilon_i^j X_i X_j \qquad [19]$$

Similarly, it can be shown that with a second order interaction parameter formalism for ln γ_i (i = solute) and at the limit $X_{\text{solvent}} \rightarrow 1$

$$\ln \gamma_{\text{solvent}} = -\frac{1}{2} \sum_{i=2}^{m} \sum_{j=2}^{m} \varepsilon_i^j X_i X_j - \frac{2}{3}\left(\sum_{i=2}^{m} \rho_i^i X_i^3 + \sum_{i=2}^{m} \sum_{j=2}^{m} \sum_{k \neq i}^{m} \rho_i^{jk} X_i X_j X_k \right) \qquad [20]$$

For binary systems even with a truncated Maclaurin series approximation for ln γ_i, a precise expression for ln γ_{solvent} can be derived through the Gibbs-Duhem equation, given by

$$\ln \gamma_{\text{solvent}} = \varepsilon_2^2[\ln(1 - X_2) + X_2] + 2\rho_2^2\left[\ln(1 - X_2) + X_2 + \frac{X_2^2}{2}\right] + 3\tau_2^2\left[\ln(1 - X_2) + X_2 + \frac{X_2^2}{2} + \frac{X_2^3}{3}\right] + \ldots \qquad [21]$$

where ε_2^2, ρ_2^2, and τ_2^2 are the first, second, and third order free energy interaction parameters, respectively. Hence there is no justification for including a term for ln γ_{solvent} in an expression for ln γ_i in a binary.

V. PATH DEPENDENT INTEGRALS FOR ln γ_{SOLVENT}

The truncated Maclaurin series for the solutes is inexact at finite concentrations and hence ln γ_{solvent} is dependent upon the path of integration.

A. *Path* $X_i/X_j = K_{ij}$

For simplicity an expression for ln γ_{solvent} will be derived initially for a ternary system and later generalized to a multicomponent system.

Along the path $X_2/X_3 = K_{23}$ (Figure 1(a)) the Gibbs-Duhem equation can be written as

$$[1 - X_3(K_{23} + 1)]d \ln \gamma_{\text{solvent}} + K_{23} X_3 d \ln \gamma_2 + X_3 d \ln \gamma_3 = 0 \qquad [22]$$

If a first order Maclaurin series expansion is considered for the logarithm of the activity coefficient of solutes:

$$\ln \gamma_2 = \ln \gamma_2^{\circ} + \varepsilon_2^2 X_2 + \varepsilon_2^3 X_3 \qquad [23a]$$

$$\ln \gamma_3 = \ln \gamma_3^{\circ} + \varepsilon_3^2 X_2 + \varepsilon_3^3 X_3 \qquad [23b]$$

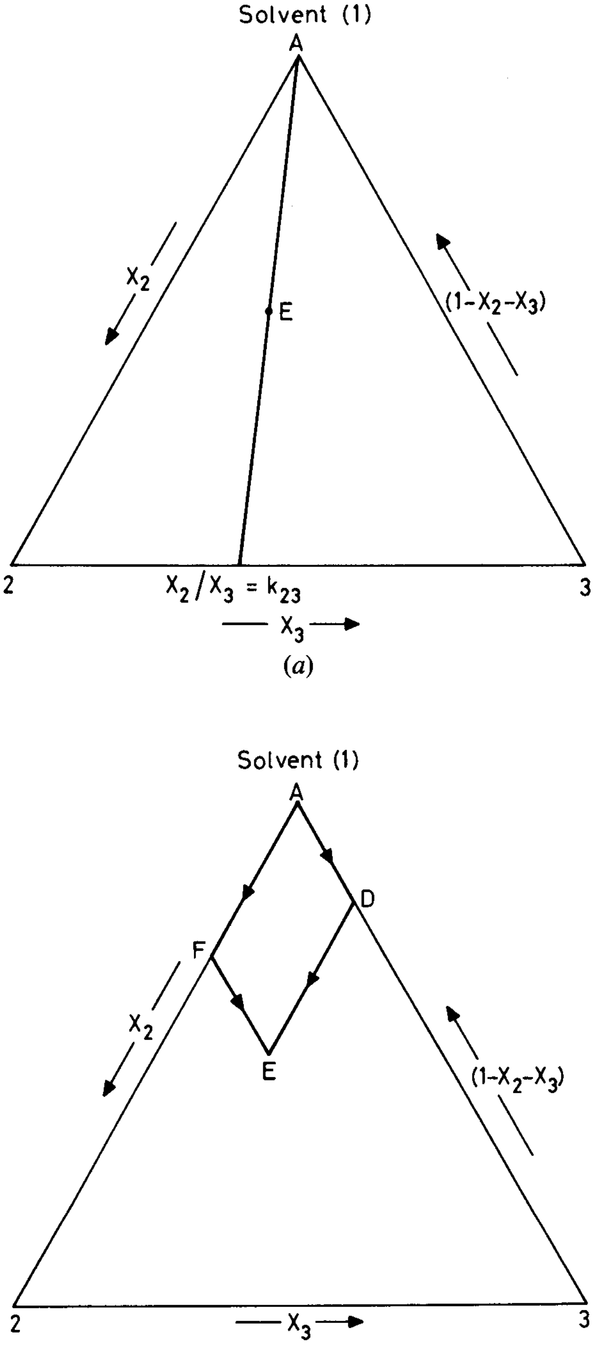
and these expressions are differentiated along the path $X_2/X_3 = K_{23}$ and substituted into Eq. [22], one obtains:

$$\frac{d \ln \gamma_{\text{solvent}}}{dX_3} = \frac{-K_{23} X_3[\varepsilon_2^2 K_{23} + \varepsilon_2^3] - X_3[\varepsilon_3^2 K_{23} + \varepsilon_3^3]}{[1 - X_3(K_{23} + 1)]} \qquad [24]$$

Integrating Eq. [24] along the path $X_2/X_3 = K_{23}$ between the limits A (pure solvent) and an arbitrary point E (Figure 1(a)), an expression for ln γ_{solvent} is derived as

$$\ln \gamma_{\text{solvent}} = \left[\frac{\varepsilon_2^2 X_2^2 + \varepsilon_2^3 X_2 X_3 + \varepsilon_3^2 X_2 X_3 + \varepsilon_3^3 X_3^2}{(X_2 + X_3)^2}\right] \cdot [(X_2 + X_3) + \ln\{1 - (X_2 + X_3)\}] \qquad [25]$$

Similarly, if a second order Maclaurin series expansion is considered for ln γ_{solute}, it can be shown that along the path



(*a*)

(*b*)

Fig. 1—Paths of integration in a ternary system. (*a*) Path of constant X_2/X_3; (*b*) paths of constant X_i.

$$X_2/X_3 = K_{23}$$

$$\ln \gamma_{\text{solvent}} = \left[\frac{\varepsilon_2^2 X_2^2 + \varepsilon_2^3 X_2 X_3 + \varepsilon_3^2 X_2 X_3 + \varepsilon_3^3 X_3^2}{(X_2 + X_3)^2}\right] \cdot [(X_2 + X_3) + \ln\{1 - (X_2 + X_3)\}]$$
$$+ 2\left[\frac{X_2^3\rho_2^2 + X_2 X_3^2 \rho_2^3 + X_2^2 X_3 \rho_2^{23} + X_2^2 X_3 \rho_3^2 + X_2 X_3^2 \rho_3^{23} + X_3^3 \rho_3^3}{(X_2 + X_3)^3}\right]$$
$$\left[\ln\{1 - (X_2 + X_3)\} + (X_2 + X_3) + \frac{(X_2 + X_3)^2}{2}\right] \quad [26]$$

At infinite dilution, approximating the logarithmic term by a truncated power series expansion, Eqs. [25] and [26] reduce to the form given by Eqs. [19] and [20], respectively, for ternary systems ($m = 3$). For a multicomponent system, an expression for $\ln \gamma_{\text{solvent}}$ along the path $X_j/X_k = K_{jk}$, with first order Maclaurin series approximation for $\ln \gamma_i$ is given by

$$\ln \gamma_{\text{solvent}} = \sum_{i=2}^{m} \sum_{j=2}^{m} \varepsilon_i^j X_i X_j \left[\frac{\ln\left(1 - \sum_{i=2}^{m} X_i\right) + \sum_{i=2}^{m} X_i}{\left(\sum_{i=2}^{m} X_i\right)^2}\right] \quad [27]$$

and with second order Maclaurin series approximation for $\ln \gamma_i$ by

$$\ln \gamma_{\text{solvent}} = \sum_{i=2}^{m} \sum_{j=2}^{m} \varepsilon_i^j X_i X_j \left[\frac{\ln\left(1 - \sum_{i=2}^{m} X_i\right) + \sum_{i=2}^{m} X_i}{\left(\sum_{i=2}^{m} X_i\right)^2}\right]$$
$$+ 2\sum_{i=2}^{m} \rho_i^i X_i^3 + 2\sum_{i=2}^{m} \sum_{j=2}^{m} \sum_{\substack{k \neq i \\ k=2}}^{m} \rho_i^{jk} X_i X_j X_k$$
$$\cdot \left[\frac{\ln\left(1 - \sum_{i=2}^{m} X_i\right) + \sum_{i=2}^{m} X_i + \frac{1}{2}\left(\sum_{i=2}^{m} X_i\right)^2}{\left(\sum_{i=2}^{m} X_i\right)^3}\right] \quad [28]$$

At infinite dilution, Eqs. [27] and [28] reduce to Eqs. [19] and [20], respectively, and are identical to those derived by Pelton and Bale.[2]

B. *Path of Constant X_i*

Analysis of a multicomponent system along paths $X_i = K_i$ is complex and hence only a ternary system is considered (Figure 1(b)). Along the path *AD*, $X_2 = 0$ and the Gibbs-Duhem equation reduces to,

$$(1 - X_3)d \ln \gamma_{\text{solvent}} + X_3 d \ln \gamma_3 = 0 \quad [29]$$

Differentiating Eq. [23] along the path $X_2 = 0$ and combining with [29] yields:

$$\left(\frac{d \ln \gamma_{\text{solvent}}}{dX_3}\right)_{X_2=0} = -\frac{X_3 \varepsilon_3^3}{(1 - X_3)} \quad [30]$$

Integrating Eq. [30] between the limits *A* to *D* gives:

$$[\ln \gamma_{\text{solvent}}]_{X_2=0} = \varepsilon_3^3[\ln(1 - X_3) + X_3] \quad [31]$$

Along *DE*, $X_3 = K_3$ and the Gibbs-Duhem equation takes the form

$$(1 - X_2 - K_3)d \ln \gamma_{\text{solvent}} + X_2 d \ln \gamma_2 + K_3 d \ln \gamma_3 = 0 \quad [32]$$

Differentiating Eq. [23] along $X_3 = K_3$ and substituting into [31] yields:

$$\left(\frac{d \ln \gamma_{\text{solvent}}}{dX_2}\right)_{X_3=K_3} = \frac{-\varepsilon_2^2 X_2 - K_3 \varepsilon_3^2}{(1 - X_2 - K_3)} \quad [33]$$

Integrating Eq. [33] between the limits $X_2 = 0$ at *D* to $X_2 = X_2$ at *E*

$$[\ln \gamma_{\mathrm{solvent}}]_E = \varepsilon_3^3 X_3 + \varepsilon_2^2 X_2 + (\varepsilon_3^3 - \varepsilon_2^2 + X_3\varepsilon_2^2 - X_3\varepsilon_3^2)\ln(1 - X_3) + (\varepsilon_2^2 - X_3\varepsilon_2^2 + X_3\varepsilon_3^2)\ln(1 - X_2 - X_3) \qquad [34]$$

Similarly, if we consider the path *AFE* it can be shown that

$$[\ln \gamma_{\mathrm{solvent}}]_E = \varepsilon_3^3 X_3 + \varepsilon_2^2 X_2 + (\varepsilon_2^2 - X_2\varepsilon_2^3 - \varepsilon_3^3 + X_2\varepsilon_3^3)\ln(1 - X_2) + (X_2\varepsilon_2^3 + \varepsilon_3^3 - X_2\varepsilon_3^3)\ln(1 - X_2 - X_3) \qquad [35]$$

VI. EXAMPLE: SYSTEM Ni-Fe-Cr AT 1873 K

Activities of all components for Ni-Fe-Cr alloys at 1873 K have been measured by a Knudsen effusion–mass spectrometry and analysis of condensed vapors by Gilby and St. Pierre.[6] The first order interaction parameters for Fe- and Ni-base alloys were deduced by these investigators. The function $\ln \gamma_{\mathrm{Ni}}$ was calculated employing Eqs. [25], [34], and [35] in the range $0.5 < X_{\mathrm{Ni}} < 1.0$ at several compositions along the paths $X_{\mathrm{Fe}}/X_{\mathrm{Cr}}$ = constant, X_{Fe} = constant, and X_{Cr} = constant using interaction parameters of Gilby and St. Pierre.[6] The value of $\ln \gamma_{\mathrm{Ni}}$ was also calculated using Eq. [19] which is identical with the equation proposed by Pelton and Bale.[2] The calculated values for $\ln \gamma_{\mathrm{Ni}}$ along various paths are shown in Table I, along with the experimental data.

It is seen that integration along paths using interaction parameters given by Gilby and St. Pierre[6] gives values for $\ln \gamma_{\mathrm{solvent}}$ in closer agreement with experimental data than Eq. [19]. It is also observed that the difference in the logarithm of the activity coefficient of the solvent, derived along different paths, is not very significant. A closer conformity to the experimental $\ln \gamma_{\mathrm{solvent}}$ may be achieved by adopting a second order interaction parameter formalism for $\ln \gamma_i$, followed by integration along the various paths.

VII. CONCLUSIONS

The general interaction parameter formalism presented by Lupis and Elliott[1] is thermodynamically consistent. Truncation of the Maclaurin series removes the exactness of the equations for logarithm of the activity coefficient of the solutes. The activity coefficient of the solvent derived by integration of Gibbs-Duhem equation will therefore depend on path of integration. Formulae have been derived for calculating the activity coefficient of the solvent along defined paths. The expression given recently by Pelton and Bale[2] for $\ln \gamma_{\mathrm{solvent}}$ is valid only in the limit that the mole fraction of solvent tends to one. The general relationships between interaction parameters derived by Lupis and Elliott[1] based on infinite series are also invalid when only the first and second order terms are employed. For some modes of truncation special relationships have been derived. It is shown that the expression for the activity coefficient of the solute employing only first order free energy interaction parameters leads to relationships between parameters that are difficult to accept from a conceptual point of view.

APPENDIX I

Thermodynamic requirement for exactness of *dG*

From [2] one obtains

$$\left(\frac{\partial \ln \gamma_j}{\partial n_i}\right)_{n_1..n_j..n_m} = \left(\frac{\partial \ln \gamma_i}{\partial n_j}\right)_{n_1..n_i..n_m} \qquad [A1]$$

Expressing the mole fraction X_i as,

$$X_i = n_i/(n_1 + n_2 + \cdots + n_m) \qquad [A2]$$

and differentiation with respect to n_i's yields,

$$\frac{\partial X_j}{\partial n_i} = \frac{-X_j}{n}; \quad \frac{\partial X_i}{\partial n_i} = \frac{(1 - X_i)}{n}; \quad \frac{\partial X_i}{\partial n_j} = \frac{-X_i}{n}; \quad \frac{\partial X_j}{\partial n_j} = \frac{(1 - X_j)}{n} \qquad [A3]$$

Table I. Comparison between Computation and Experimental Values for $\ln \gamma_{\mathrm{Ni}}$ (Ni = Solvent)

$\varepsilon^{\mathrm{Fe}}_{\mathrm{Fe}} = 1.92$(6); $\varepsilon^{\mathrm{Cr}}_{\mathrm{Cr}} = 1.85$(6); $\varepsilon^{\mathrm{Fe}}_{\mathrm{Cr}} = 2.19$(6)

			$\ln \gamma_{\mathrm{Ni}}$				
Composition			Path of Integration			Eq. [19] $X_{\mathrm{Ni}} \to 1$ Approx.	Experiment(6)
X_{Cr}	X_{Fe}	X_{Ni}	$X_{\mathrm{Fe}}/X_{\mathrm{Cr}} = K$	$X_{\mathrm{Cr}} = K$	$X_{\mathrm{Fe}} = K$		
0.05	0.2620	0.6880	−0.1234	−0.1232	−0.1238	−0.0969	−0.1385
0.05	0.1560	0.7490	−0.0497	−0.0497	−0.0498	−0.0428	−0.0517
0.05	0.0988	0.8512	−0.0250	−0.0250	−0.0251	−0.0225	−0.0432
0.05	0.0528	0.8972	−0.0116	−0.0116	−0.0116	−0.0108	−0.0135
0.10	0.2080	0.6920	−0.1222	−0.1223	−0.1226	−0.0963	−0.1561
0.10	0.1570	0.7430	−0.0816	−0.0817	−0.0818	−0.0673	−0.0842
0.10	0.1050	0.7950	−0.0498	−0.0499	−0.0498	−0.0428	−0.0650
0.10	0.0530	0.8470	−0.0263	−0.0263	−0.0263	−0.0236	−0.0348
0.20	0.2060	0.5940	−0.2341	−0.2350	−0.2346	−0.1680	−0.2341
0.20	0.1030	0.6970	−0.1166	−0.1171	−0.1165	−0.0923	−0.1399
0.20	0.0545	0.7455	−0.0771	−0.0775	−0.0770	−0.0637	−0.1030
0.30	0.1040	0.5960	−0.2253	−0.2270	−0.2248	−0.1620	−0.2504
0.30	0.0541	0.6459	−0.1610	−0.1619	−0.1607	−0.1216	−0.2340

where

$$n = n_1 + n_2 + \cdots\cdots + n_m \qquad \text{[A4]}$$

Now,

$$\begin{aligned}\frac{\partial \ln \gamma_j}{\partial n_i} = {} & \frac{\partial \ln \gamma_j}{\partial X_2}\left(\frac{\partial X_2}{\partial n_i}\right)_{n_1..n_j..n_m} + \ldots \\ & + \frac{\partial \ln \gamma_j}{\partial X_i}\left(\frac{\partial X_i}{\partial n_i}\right)_{n_1..n_j..n_m} + \ldots \\ & + \frac{\partial \ln \gamma_j}{\partial X_m}\left(\frac{\partial X_m}{\partial n_i}\right)_{n_1..n_j..n_m} \qquad \text{[A5]}\end{aligned}$$

Combining [A5] with [A3],

$$\begin{aligned}\frac{\partial \ln \gamma_j}{\partial n_i} = \frac{1}{n}\Bigg[& -\frac{\partial \ln \gamma_j}{\partial X_2}X_2 - \cdots + \frac{\partial \ln \gamma_j}{\partial X_i}(1 - X_i) \\ & - \cdots - \frac{\partial \ln \gamma_j}{\partial X_m}X_m \Bigg] \qquad \text{[A6]}\end{aligned}$$

Similarly,

$$\begin{aligned}\frac{\partial \ln \gamma_i}{\partial n_j} = \frac{1}{n}\Bigg[& -\frac{\partial \ln \gamma_i}{\partial X_2}X_2 - \cdots + \frac{\partial \ln \gamma_i}{\partial X_j}(1 - X_j) \\ & - \cdots - \frac{\partial \ln \gamma_i}{\partial X_m}X_m \Bigg] \qquad \text{[A7]}\end{aligned}$$

Substituting [A6] and [A7] into [A1]:

$$\frac{\partial \ln \gamma_j}{\partial X_i} - \sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_j}{\partial X_k} = \frac{\partial \ln \gamma_i}{\partial X_j} - \sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_i}{\partial X_k}$$

APPENDIX II

Interrelation between the interaction parameters of solutes

We have from Eq. [5]

$$J^{(i)}_{n_2..n_i..n_m} = J^{(1)}_{n_2..n_i..n_m} - \left[(n_i + 1)\Big/\sum_{j=2}^{m} n_j\right] J^{(1)}_{n_2..n_i+1..n_m} \qquad \text{[A8]}$$

Therefore,

$$\begin{aligned}J^{(i)}_{n_2..n_j+1..n_m} = {} & J^{(1)}_{n_2..n_j+1..n_m} \\ & - \left[(n_i + 1)\Big/\sum_{j=2}^{m} n_j + 1\right] J^{(1)}_{n_2..n_i+1,n_j+1..n_m} \qquad \text{[A9]}\end{aligned}$$

Similarly,

$$\begin{aligned}J^{(j)}_{n_2..n_i+1..n_m} = {} & J^{(1)}_{n_2..n_i+1..n_m} \\ & - \left[(n_j + 1)\Big/\sum_{j=2}^{m} n_j + 1\right] J^{(1)}_{n_2..n_i+1,n_j+1..n_m} \qquad \text{[A10]}\end{aligned}$$

Multiplying [A9] by $(n_j + 1)$ and [A10] by $(n_i + 1)$ and subtracting one from the other,

$$\begin{aligned}& (n_i + 1)J^{(j)}_{n_2..n_i+1..n_m} - \\ & (n_j + 1)J^{(i)}_{n_2..n_j+1..n_m} = (n_i + 1)J^{(1)}_{n_2..n_i+1..n_m} \\ & \qquad - (n_j + 1)J^{(1)}_{n_2..n_j+1..n_m} \qquad \text{[A11]}\end{aligned}$$

Now,

$$J^{(j)}_{n_2..n_i..n_m} = J^{(1)}_{n_2..n_i..n_m} - \left[(n_j + 1)\Big/\sum_{j=2}^{m} n_j\right] J^{(1)}_{n_2..n_j+1..n_m} \qquad \text{[A12]}$$

Subtracting [A8] from [A12] and substituting [A11] into the resultant equation, one obtains,

$$\begin{aligned}& (n_i + 1)J^{(j)}_{n_2..n_i+1..n_m} - \\ & (n_j + 1)J^{(i)}_{n_2..n_j+1..n_m} = \frac{1}{\sum_{j=2}^{m} n_j}\left[J^{(j)}_{n_2..n_j..n_m} - J^{(i)}_{n_2..n_j..n_m}\right] \qquad \text{[A13]}\end{aligned}$$

APPENDIX III

Conformity of the formalism of
Lupis and Elliott to Maxwell's relation

Equation [5a] gives

$$\ln \gamma_i = \sum_{n_2=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \sum_{n_m=0}^{\infty} J^{(i)}_{n_2..n_j..n_m} X_2^{n_2} \ldots X_j^{n_j} \ldots X_m^{n_m} \qquad \text{[A14]}$$

$$\begin{aligned}\frac{\partial \ln \gamma_i}{\partial X_j} = {} & \sum_{n_2=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \sum_{n_m=0}^{\infty} J^{(i)}_{n_2..n_j..n_m} \\ & \cdot n_j X_2^{n_2} \ldots X_j^{n_j-1} \ldots X_m^{n_m} \qquad \text{[A15]}\end{aligned}$$

$$\begin{aligned}\frac{\partial \ln \gamma_j}{\partial X_i} = {} & \sum_{n_2=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \sum_{n_m=0}^{\infty} J^{(j)}_{n_2..n_j..n_m} \\ & \cdot n_i X_2^{n_2} \ldots X_i^{n_i-1} \ldots X_m^{n_m} \qquad \text{[A16]}\end{aligned}$$

$$\begin{aligned}\sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_i}{\partial X_k} = {} & \sum_{k=2}^{m} \sum_{n_2=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \sum_{n_m=0}^{\infty} J^{(i)}_{n_2..n_j..n_m} \\ & \cdot n_k X_2^{n_2} \ldots X_k^{n_k} \ldots X_m^{n_m} \qquad \text{[A17]}\end{aligned}$$

$$\begin{aligned}\sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_j}{\partial X_k} = {} & \sum_{k=2}^{m} \sum_{n_2=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \sum_{n_m=0}^{\infty} J^{(j)}_{n_2..n_j..n_m} \\ & \cdot n_k X_2^{n_2} \ldots X_k^{n_k} \ldots X_m^{n_m} \qquad \text{[A18]}\end{aligned}$$

The coefficient of the general term $X_2^{n_2} \ldots X_i^{n_i} \ldots X_m^{n_m}$ in the expression,

$$\frac{\partial \ln \gamma_j}{\partial X_i} - \frac{\partial \ln \gamma_i}{\partial X_j} + \sum_{k=2}^{m} X_k \left[\frac{\partial \ln \gamma_i}{\partial X_k} - \frac{\partial \ln \gamma_j}{\partial X_k}\right] \qquad \text{[A19]}$$

is,

$$\begin{aligned}& \left[(n_i + 1)J^{(j)}_{n_2..n_i+1..n_m} - (n_j + 1)J^{(i)}_{n_2..n_j+1..n_m}\right] \\ & \qquad + \sum_{k=2}^{m} n_k\left[J^{(i)}_{n_2..n_j..n_m} - J^{(j)}_{n_2..n_j..n_m}\right] \qquad \text{[A20]}\end{aligned}$$

Subtracting [A12] from [A8] we have,

$$\begin{aligned}\sum_{k=2}^{m} n_k\left[J^{(i)}_{n_2..n_j..n_m} - J^{(j)}_{n_2..n_j..n_m}\right] = {} & (n_j + 1)J^{(1)}_{n_2..n_j+1..n_m} \\ & - (n_i + 1)J^{(1)}_{n_2..n_i+1..n_m} \qquad \text{[A21]}\end{aligned}$$

Substituting [A11] and [A21] into [A20]

$$[(n_i + 1)J^{(j)}_{n_2 \ldots n_i+1 \ldots n_m} - (n_j + 1)J^{(i)}_{n_2 \ldots n_j+1 \ldots n_m}] + \sum_{k=2}^{m} n_k[J^{(i)}_{n_2 \ldots n_j \ldots n_m} - J^{(j)}_{n_2 \ldots n_j \ldots n_m}] = 0 \qquad \text{[A22]}$$

Hence each coefficient of the general term in expression [A19] is null which implies that,

$$\frac{\partial \ln \gamma_j}{\partial X_i} - \frac{\partial \ln \gamma_i}{\partial X_j} + \sum_{k=2}^{m} X_k \left[\frac{\partial \ln \gamma_i}{\partial X_k} - \frac{\partial \ln \gamma_j}{\partial X_k}\right] = 0$$

APPENDIX IV

Conformity of the formalism of Lupis and Elliott to the Gibbs-Duhem equation

The coefficient of the general term $X_2^{n_2} \ldots X_i^{n_i} \ldots X_m^{n_m}$ in the Gibbs-Duhem equation,

$$\frac{\partial \ln \gamma_1}{\partial X_j} + \sum_{i=2}^{m} X_i \left[\frac{\partial \ln \gamma_i}{\partial X_j} - \frac{\partial \ln \gamma_j}{\partial X_j}\right] = 0 \text{ is}$$

$$(n_j + 1)J^{(1)}_{n_2 \ldots n_j+1 \ldots n_m} + \sum_{i=2}^{m} [J^{(i)}_{n_2 \ldots n_i-1, n_j+1 \ldots n_m} - J^{(1)}_{n_2 \ldots n_i-1, n_j+1 \ldots n_m}](n_j + 1) \qquad \text{[A23]}$$

The reciprocal relationship [5] after some modification can be written as,

$$J^{(i)}_{n_2 \ldots n_i-1, n_j+1 \ldots n_m} = J^{(1)}_{n_2 \ldots n_i-1, n_j+1 \ldots n_m} - \left[n_i \Big/ \sum_{j=2}^{m} n_j\right] J^{(1)}_{n_2 \ldots n_i, n_j+1 \ldots n_m} \qquad \text{[A24]}$$

Substituting [A24] into [A23] we get,

$$(n_j + 1)J^{(1)}_{n_2 \ldots n_j+1 \ldots n_m} + \sum_{i=2}^{m} [J^{(i)}_{n_2 \ldots n_i-1, n_j+1 \ldots n_m} - J^{(1)}_{n_2 \ldots n_i-1, n_j+1 \ldots n_m}](n_j + 1) = 0 \qquad \text{[A25]}$$

Hence the coefficient of the general term in the Gibbs-Duhem expression is null, which implies that

$$\frac{\partial \ln \gamma_1}{\partial X_j} + \sum_{i=2}^{m} X_i \left[\frac{\partial \ln \gamma_i}{\partial X_j} - \frac{\partial \ln \gamma_j}{\partial X_j}\right] = 0$$

i.e., Gibbs-Duhem relation is satisfied.

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