The Uniqueness of a Correction to Interaction Parameter Formalism in a Thermodynamically Consistent Manner

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Polynomial representation of partial excess Gibbs energy (*i.e.*, activity coefficient) in multicomponent dilute solution has been widely used after Wagner. Although Wagner's Interaction Parameter Formalism has been known to be only strictly valid at infinite dilute concentration, it has been used often, even at finite concentration, due to its mathematical simplicity. Nevertheless, several attempts have been made to correct the formalism to be thermodynamically consistent at finite concentration. Among those, Unified Interaction Parameter Formalism proposed by Pelton and Bale, which may be considered as an extension of Darken's quadratic formalism, has obtained much attention. However, there have been much confusion and debate about the way of the correction. Recently, a thermodynamic analysis was reported that there are infinite numbers of ways to correct Wagner's formalism to be thermodynamically consistent, which may prevent one from using the Unified Interaction Parameter Formalism with confidence. In the present article, the correction to the Wagner's formalism is discussed by revisiting Darken's condition of the thermodynamic consistency. It is shown that the correction to the Wagner's formalism can be made uniquely. It is pointed out that to ensure the thermodynamic consistency among the activity coefficients of all components, Gibbs–Duhem relation and Maxwell relation among all components including solvent–solute, must be obeyed. Derived expressions for activity coefficients of all components by path-independent integration are also shown to be the same as those obtained by differentiating a corresponding integral excess partial Gibbs energy.

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I. INTRODUCTION

THERMODYNAMIC properties of a multicomponent dilute solution such as molten steel, copper, manganese are most well practically characterized by partial excess Gibbs energies of solutes: in other words, activity coefficients of solutes. For practical applications, Wagner proposed a Taylor series expansion for the partial excess Gibbs energy, and it has been most widely used in the metallurgical community.[1] Although this formalism is strictly valid only at infinite dilution, thus thermodynamically inconsistent at a finite concentration as discussed by Darken,[2,3] the formalism has been still used at finite concentrations. Depending on the system used, however, the formalism can cause significant errors.

Darken corrected the Wagner's formalism to be thermodynamically consistent at finite concentration, but it has not been well appreciated. In 1986, Pelton and Bale proposed a modified form of the Wagner's formalism,[4] which has been further discussed in their subsequent articles.[5,6] The basic idea of their modification is a correction to the Wagner's formalism by adding activity coefficient of solvent to activity coefficients of all solutes. This makes the Gibbs–Duhem relation for the activity coefficients among the solvent and all the solutes be obeyed, even at finite concentration. They also stated that Maxwell's relation for partial excess Gibbs energy should also be respected.[4–6] Their proposed formalism exactly reduces to Wagner's formalism at infinite dilution, to Darken's quadratic formalism at finite concentration, and also could be reduced to Lupis and Elliott's formalism[7] as well as that of Margules.[8] They named it as a Unified Interaction Parameter Formalism (UIPF), and the formalism has been successfully applied to multicomponent metallic solutions.[9–13]

Some other approaches also have been proposed to make the Wagner's formalism be thermodynamically consistent.[14–18] Srikanth and Jacob[14] attempted to keep the original expression of Wagner for the activity

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coefficient of solute, while the activity coefficient of solvent can be obtained by *path-dependent* integration of the Gibbs–Duhem equation. This is due to the thermodynamic inconsistency of the original expression of Wagner's formalism. Hajra and coworkers suggested using the activity coefficients of solutes derived from a Maclaurin infinite series of integral excess Gibbs energy.[15–17] While the approaches by Srikanth and Jacob[14] and Hajra *et al.*[15–17] keep the original expression of Wagner for the activity coefficient of solute, the proposal by Darken,[2,3] Pelton and Bale[4–6] uses corrected forms of the activity coefficient of solutes. All these approaches proposed one to consider the activity coefficient of solvent to represent thermodynamic consistency between all components through the Gibbs–Duhem equation, which was not considered by Wagner. There has also been a debate that the activity coefficient of solvent satisfying the Gibbs–Duhem relation can be obtained, not in a unique way, but in an infinite number of ways.[18] This would make one to hesitate to have a confidence in the value calculated by the UIPF.[19] Somewhat different approaches are also available in which the activity coefficient of non-metallic solute was formulated as a function of the composition of a metallic solvent of two-component.[20–23]

In the present article, it will be shown that the activity coefficient of solvent can be obtained uniquely, for a given polynomial expression for the activity coefficient of solute, in a thermodynamically consistent manner. To make this discussion more clear, the corrections made previously are briefly reviewed and it will be pointed out what should be explicitly considered to have the thermodynamic consistency. Two approaches will be shown to obtain expression of the activity coefficient of the solvent in a ternary solution: (1) integrating differential equations containing activity coefficients of solutes and (2) differentiating an integral excess Gibbs energy. Similar approaches are expanded for a multicomponent solution, and it will be shown that the same conclusion is valid in general. This discussion will provide a solid background for the use of such formalism with a confidence. As long as the expression of the activity coefficient of solute has a sound theoretical foundation, and the activity coefficient of solvent can be obtained in a unique and thermodynamically consistent way based on the activity coefficients of solutes, the obtained activity coefficient of solvent should have its own physical meaning.

The present analysis has been carried out under constant temperature and constant pressure condition in most cases. Temperature dependence of the activity coefficient is briefly discussed in Section IV

II. THERMODYNAMIC CONSISTENCY OF INTERACTION PARAMETER FORMALISM

Let us consider an N-component solution 1–2–3–···–N where 1 is a solvent and the others are solutes. According to Wagner's formalism, the activity coefficient of any solute i (γ_i) is expressed as:

$$\ln(\gamma_i/\gamma_i^\circ) = \sum_{j=2}^{N} \epsilon_{ij} X_j \qquad (i = 2, 3, \ldots, N) \qquad [1]$$

where γ_i°, ϵ_{ij}, and X_j are the Henrian activity coefficient of solute i, a first-order interaction parameter between solutes i and j (following the notation after Pelton and Bale[4]), and mole fraction of solute j, respectively. In addition, the following reciprocity relation was proposed:

$$\epsilon_{ij} = \epsilon_{ji} \qquad [2]$$

when X_1 approaches to 1.[1] This has been extended to include second-order terms by Lupis and Elliott[7]:

$$\ln(\gamma_i/\gamma_i^\circ) = \sum_{j=2}^{N} \epsilon_{ij} X_j + \sum_{j=2}^{N} \rho_i^j X_j^2 + \sum_{j,k=2}^{N} \rho_i^{j,k} X_j X_k \qquad [3]$$

where ρ_i^j, $\rho_i^{j,k}$ are the second-order interaction parameters.

A. *Darken: Quadratic Formalism*

For a ternary 1–2–3 solution, Darken pointed out that application of Eq. [1] is only valid at infinite dilution ($X_1 \rightarrow 1$), and generally, it is not thermodynamically consistent at finite concentration.[3] He proposed that any formalism should satisfy the following condition of thermodynamic consistency between the solutes 2 and 3:

$$(1 - X_3)\frac{\partial \ln \gamma_2}{\partial X_3} + X_3 \frac{\partial \ln \gamma_3}{\partial X_3} = X_2 \frac{\partial \ln \gamma_2}{\partial X_2} + (1 - X_2)\frac{\partial \ln \gamma_3}{\partial X_2} \qquad [4]$$

In addition, Raoult's law and Henry's law must be obeyed by the solvent and the solutes, respectively, as limiting conditions at infinite dilution. Then, by analyzing several binary and ternary systems, he proposed a quadratic formalism to represent activity coefficients of solutes:

$$\ln(\gamma_2/\gamma_2^\circ) = \epsilon_{22} X_2 + \epsilon_{23} X_3 - \frac{1}{2}\epsilon_{22} X_2^2 - \frac{1}{2}\epsilon_{33} X_3^2 - \epsilon_{23} X_2 X_3 \qquad [5]$$

$$\ln(\gamma_3/\gamma_3^\circ) = \epsilon_{32} X_2 + \epsilon_{33} X_3 - \frac{1}{2}\epsilon_{22} X_2^2 - \frac{1}{2}\epsilon_{33} X_3^2 - \epsilon_{23} X_2 X_3 \qquad [6]$$

Mathematical forms of the Eqs. [5] and [6] are very similar to the Eq. [3], and it reduces to Eq. [1] at infinite dilution. He had shown that $\epsilon_{23} = \epsilon_{32}$. He also considered the activity coefficient of *the solvent* to be[3]:

$$\ln \gamma_1 = -\frac{1}{2}\epsilon_{22} X_2^2 - \frac{1}{2}\epsilon_{33} X_3^2 - \epsilon_{23} X_2 X_3 \qquad [7]$$

The formalism eliminates the thermodynamic inconsistency of Wagner's formalism even at finite concentration *via* Gibbs–Duhem equation at constant T and P:

$$X_1 d\ln\gamma_1 + X_2 d\ln\gamma_2 + X_3 d\ln\gamma_3 = 0 \qquad [8]$$

Therefore, it was considered that the Eqs. [4] and [8] are to be obeyed in the development of an activity coefficient equation in a ternary solution.

In this approach, as seen in the name of the formalism, the quadratic term of composition is considered.

B. *Pelton and Bale: Unified Interaction Parameter Formalism*

The Darken's formalism applied for several ternary solutions has been generalized and extended into a multicomponent solution by Pelton and Bale.[4–6] They proposed the following form of γ_i for solutes and γ_1 for solvent:

$$\ln(\gamma_i/\gamma_i^\circ) = \ln\gamma_1 + \sum_{j=2}^{N}\epsilon_{ij}X_j + \sum_{j,k=2}^{N}\epsilon_{ijk}X_jX_k + \sum_{\substack{j,k,l\\=2}}^{N}\epsilon_{ijkl}X_jX_kX_l + \ldots \qquad [9]$$

$$\ln\gamma_1 = -\frac{1}{2}\sum_{j,k=2}^{N}\epsilon_{jk}X_jX_k - \frac{2}{3}\sum_{\substack{j,k,l\\=2}}^{N}\epsilon_{jkl}X_jX_kX_l - \frac{3}{4}\sum_{\substack{j,k,l,m\\=2}}^{N}\epsilon_{jklm}X_jX_kX_lX_m + \ldots \qquad [10]$$

where they found that $\epsilon_{ij} = \epsilon_{ji}$, $\epsilon_{ijk} = \epsilon_{jik} = \epsilon_{kij} = \ldots$, and so on. If only first-order interaction parameters are considered by setting all higher-order parameters ϵ_{ijk}, ϵ_{ijkl}, *etc.* zero, the above equations are reduced to:

$$\ln(\gamma_i/\gamma_i^\circ) = \ln\gamma_1 + \sum_{j=2}^{N}\epsilon_{ij}X_j \qquad (i = 2, 3, \ldots, N) \qquad [11]$$

$$\ln\gamma_1 = -\frac{1}{2}\sum_{j,k=2}^{N}\epsilon_{jk}X_jX_k \qquad [12]$$

Equations [11] and [12] are identical to Darken's formalism for a ternary case (Eqs. [5] to [7]). Pelton and Bale noticed that the last three terms of the Eqs. [5] and [6] are identical to those in Eq. [7]. They added the $\ln\gamma_1$ to the original form of $\ln\gamma_i$ for all solutes (Eq. [1]) as a *corrective function*. This results in an obedience of the Gibbs–Duhem relation in the multicomponent solution at constant T and P:

$$\sum_{i=1}^{N} X_i d\ln\gamma_i = X_1 d\ln\gamma_1 + X_2 d\ln\gamma_2 + \cdots + X_N d\ln\gamma_N = 0 \qquad [13]$$

and of the following thermodynamic relationship which is equivalent to Darken's condition of thermodynamic consistency (See Appendix A):

$$\frac{\partial \ln\gamma_j}{\partial n_i} = \frac{\partial \ln\gamma_i}{\partial n_j} \qquad [14]$$

where n_i is the number of moles of component i. The formalism has been successfully applied several metal solutions.[9–12] The formalism keeps the simple form of Wagner's formalism, and it should be stressed that the formalism can utilize already well-tabulated interaction parameters for the Wagner's formalism.[24]

C. *Srikanth and Jacob: Path-Dependent Integration*

Srikanth and Jacob considered the Eqs. [1] and [3] as truncations of the Maclaurin infinite series (Taylor series at zero concentration).[14] Upon the truncation, the activity coefficients of solutes are thermodynamically inconsistent, except at infinite dilution. Therefore, they pointed out that the interaction parameters ($\epsilon_{ij}, \rho_i^{j,k}$) should satisfy special relationships to be thermodynamically consistent through the Eq. [4]. Moreover, as the $\ln\gamma_i$'s are inexact due to the truncation, the $\ln\gamma_1$, which may be obtained by the integration of the Gibbs–Duhem equation (Eq. [13]), does depend upon the *path of integration*. In this way, they obtained expressions of the $\ln\gamma_1$ per chosen integration paths, while they kept the original expression for the $\ln\gamma_i$ to be Eq. [1] for the first-order case.

Their approach keeps the original mathematical form of Wagner's formalism for solutes without adding any corrective function, although they are thermodynamically inconsistent except at infinite dilution. However, it was possible to obtain $\ln\gamma_1$ to be consistent with the Gibbs–Duhem equation (Eq. [13]) because of the path-dependent integration. For example, if first-order interaction parameters are considered for solute 2 and 3 in a 1–2–3 solution from the Eq. [1]:

$$\ln(\gamma_2/\gamma_2^{\circ}) = \epsilon_{22}X_2 + \epsilon_{23}X_3 \qquad [15]$$

$$\ln(\gamma_3/\gamma_3^{\circ}) = \epsilon_{23}X_2 + \epsilon_{33}X_3 \qquad [16]$$

along the path $X_2/X_3 = K_{23}$, where K_{23} is a constant, they obtained:

$$\ln\gamma_1 = \left[\frac{\epsilon_{22}X_2^2 + 2\epsilon_{23}X_2X_3 + \epsilon_{33}X_3^2}{(X_2+X_3)^2}\right][(X_2+X_3) + \ln(1-(X_2+X_3))] \qquad [17]$$

through the integration of Eq. [8].

Upon the paths taken for the integration, there could be many numbers of the expression for the $\ln\gamma_1$. This is due to the thermodynamic inconsistency of the Eqs. [15] and [16]. Although the Gibbs–Duhem relation is satisfied, the thermodynamic consistency equation (Eq. [4]) is not obeyed except at infinite dilute concentration. It is noted that regardless of the way of integration to get the $\ln\gamma_1$, it is a prerequisite to have the thermodynamically consistent expression of $\ln\gamma_i$ for all solutes i.

D. *Malakhov: Corrective Function*

Malakhov raised an issue regarding a uniqueness of the expression for $\ln\gamma_1$, even though $\ln\gamma_2$ and $\ln\gamma_3$ obey the condition of thermodynamic consistency (Eq. [4]).[18] In his analysis for a ternary 1–2–3 solution, he defined a corrective function $\varphi(X_2, X_3)$ to be added to inexact forms of $\ln\gamma_2$ and $\ln\gamma_3$ (Eqs. [15] and [16]), so the following revised forms are considered:

$$\ln(\gamma_2/\gamma_2^{\circ}) = \epsilon_{22}X_2 + \epsilon_{23}X_3 + \varphi_2 \qquad [18]$$

$$\ln(\gamma_3/\gamma_3^{\circ}) = \epsilon_{23}X_2 + \epsilon_{33}X_3 + \varphi_3 \qquad [19]$$

to satisfy the Eq. [4] for the thermodynamic consistency:

$$(1-X_3)\epsilon_{23} + X_3\epsilon_{33} + \frac{\partial\varphi_2}{\partial X_3} = X_2\epsilon_{22} + (1-X_2)\epsilon_{23} + \frac{\partial\varphi_3}{\partial X_2} \qquad [20]$$

As long as the final form of activity coefficients of components are to be expressed as a polynomial function, the corrective functions φ_2 and φ_3 must be a form of the quadratic polynomial: $\varphi_2 = \alpha_{22}X_2^2 + \alpha_{23}X_2X_3 + \alpha_{33}X_3^2$ and $\varphi_3 = \beta_{22}X_2^2 + \beta_{23}X_2X_3 + \beta_{33}X_3^2$, where all α_{ij}'s and β_{ij}'s are constant according to the form of the Eq. [20]. Inserting φ_2 and φ_3 into the Eq. [20] and setting all coefficients of terms involving the independent variables X_2 and X_3 to be zero, the following conditions are obtained:

$$\alpha_{ij} = \beta_{ij} \qquad (i,j = 2,3) \qquad [21]$$

yielding $\varphi_2 = \varphi_3$. Therefore, the corrective function must be identical for the two solutes ($\varphi_2 = \varphi_3 = \varphi$), and hereafter it is denoted as φ*. Furthermore, it is also obtained:

$$2\alpha_{22} - \alpha_{23} = \epsilon_{23} - \epsilon_{22} \qquad [22]$$

$$2\alpha_{33} - \alpha_{23} = \epsilon_{23} - \epsilon_{33} \qquad [23]$$

Malakhov pointed out that three variables ($\alpha_{22}, \alpha_{23}, \alpha_{33}$) with two equations Eqs. [22] and [23] result in an infinite number of sets for the α_{22}, α_{23}, and α_{33}, so does for the corrective function φ. If one chooses

$$\alpha_{22} = -\frac{1}{2}\epsilon_{22}, \quad \alpha_{33} = -\frac{1}{2}\epsilon_{33}, \quad \alpha_{23} = -\epsilon_{23} \qquad [24]$$

thus,

$$\varphi = -\frac{1}{2}\epsilon_{22}X_2^2 - \epsilon_{23}X_2X_3 - \frac{1}{2}\epsilon_{33}X_3^2 \qquad [25]$$

then the form of φ becomes identical to the $\ln\gamma_1$ in Eq. [7], and the Eqs. [18] and [19] become identical to the Eqs. [5] and [6]. *Via* the Gibbs–Duhem integration, the obtained $\ln\gamma_1$ will be the same as the Eq. [7], as well as the φ shown in the Eq. [25].

On the other hand, other choices for the α_{22}, α_{23}, and α_{33} satisfying the Eqs. [22] and [23] (thus satisfying the thermodynamic consistency through the Eq. [20]) may be considered. The other form of φ than the Eq. [25] may have the following form[18]:

$$\varphi = \frac{\epsilon_{23} - \epsilon_{22}}{2}X_2^2 + \frac{\epsilon_{23} - \epsilon_{33}}{2}X_3^2 \qquad [26]$$

This alternative form of φ is inserted into Eqs. [18] and [19], then carrying out the Gibbs–Duhem integration, at least numerically or through a special path as was done by Srikanth and Jacob,[14] will result in a different form of $\ln\gamma_1$. Nevertheless, this other choice still satisfies the thermodynamic consistency of Eq. [20] and the Gibbs–Duhem relation (Eq. [13]), both. Based on this reasoning, Malakhov claimed that limitless numbers of such corrective functions can be generated, thus any correction may not be used with high confidence.[18] Instead of using this formalism with non-unique correction, he suggested using a modern CALPHAD-type approach where the activity coefficient (partial excess Gibbs energy) can be derived from an integral excess Gibbs energy by differentiating it.

This analysis is in line with the correction to Wagner's formalism previously done by Darken,[2,3] and Pelton and Bale.[4–6] However, in the following section, it will be shown that there is one and only one expression for

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*Although Malakhov added the same φ to Eqs. [18] and [19] in his analysis without clear reasoning,[18] it is shown in the present article that φ_2 and φ_3 must be the same.

the activity coefficient of solvent for given polynomial expressions of activity coefficients of solutes by revisiting the condition for the thermodynamic consistency proposed by Darken.[3] Examples will be shown by a ternary case, but it will be further shown to be valid in a multicomponent solution.

III. CORRECTION TO MAKE INTERACTION PARAMETER FORMALISM BE THERMODYNAMICALLY CONSISTENT

In the discussions and debate made in previous publications regarding thermodynamic consistency of polynomial representations for the activity coefficient of components,[2–6,14,18] two criteria have been employed: Gibbs–Duhem relationship (Eq. [8]) and Darken's condition of thermodynamic consistency (Eq. [4]) for solutes in a ternary solution (1–2–3 where 1 is a solvent). Although

1. both corrective functions φ in Eq. [25] and in Eq. [26] make the $\ln\gamma_2$ (Eq. [18]) and $\ln\gamma_3$ (Eq. [19]) satisfy the condition of thermodynamic consistency (Eq. [4]), and
2. $\ln\gamma_1$ is subsequently obtained in such a way that the Gibbs–Duhem relation is obeyed through integration,

it is not clear whether the condition of thermodynamic consistency is also obeyed *between solute (2 and 3) and solvent (1)*. As the Gibbs–Duhem relation concerns all components including the solvent, the condition of thermodynamic consistency must also concern the relation between solutes and the solvent, not just between a solute and the other solute.

A. *Thermodynamic Consistency in a Ternary System: From Partial Excess Gibbs Energy*

Applying Eq. [14] for solvent 1 and solute 2 in the ternary 1–2–3 solution, the following relationship is obtained:

$$\frac{\partial\ln\gamma_1}{\partial n_2}=\frac{\partial\ln\gamma_2}{\partial n_1} \qquad [27]$$

Taking X_2 and X_3 as independent variables, and using the following derivatives,

$$\begin{aligned}&\frac{\partial X_2}{\partial n_1}=\frac{\partial(n_2/n)}{\partial n_1}=\frac{-n_2}{n^2}=-\frac{X_2}{n}\\&\frac{\partial X_2}{\partial n_2}=\cdots=\frac{1-X_2}{n},\quad\frac{\partial X_3}{\partial n_1}=-\frac{X_3}{n},\quad\frac{\partial X_3}{\partial n_2}=-\frac{X_3}{n}\end{aligned} \qquad [28]$$

where n is the total number of moles of all components in the solution, so $n=n_1+n_2+n_3$ in this example. Using the above equations, it is obtained:

$$\begin{aligned}\frac{\partial\ln\gamma_1}{\partial n_2}&=\frac{\partial\ln\gamma_1}{\partial X_2}\left(\frac{\partial X_2}{\partial n_2}\right)+\frac{\partial\ln\gamma_1}{\partial X_3}\left(\frac{\partial X_3}{\partial n_2}\right)\\&=\frac{1}{n}\left[\frac{\partial\ln\gamma_1}{\partial X_2}(1-X_2)+\frac{\partial\ln\gamma_1}{\partial X_3}(-X_3)\right]\end{aligned} \qquad [29]$$

Similarly,

$$\frac{\partial\ln\gamma_2}{\partial n_1}=\frac{1}{n}\left[\frac{\partial\ln\gamma_2}{\partial X_2}(-X_2)+\frac{\partial\ln\gamma_2}{\partial X_3}(-X_3)\right] \qquad [30]$$

Therefore, according to the Eq. [27], the following equation is obtained which represents the conditions of thermodynamic consistency between two components (solvent 1 and solute 2) in the 1–2–3 solution:

$$\frac{\partial\ln\gamma_1}{\partial X_2}-X_2\frac{\partial\ln\gamma_1}{\partial X_2}-X_3\frac{\partial\ln\gamma_1}{\partial X_3}=-X_2\frac{\partial\ln\gamma_2}{\partial X_2}-X_3\frac{\partial\ln\gamma_2}{\partial X_3} \qquad [31]$$

Following a similar procedure, the thermodynamic consistency condition for solvent 1 and the other solute 3 is obtained as:

$$\frac{\partial\ln\gamma_1}{\partial X_3}-X_2\frac{\partial\ln\gamma_1}{\partial X_2}-X_3\frac{\partial\ln\gamma_1}{\partial X_3}=-X_2\frac{\partial\ln\gamma_3}{\partial X_2}-X_3\frac{\partial\ln\gamma_3}{\partial X_3} \qquad [32]$$

Any polynomial representation for activity coefficients of solvent and solutes must obey the above conditions (Eqs. [31] and [32]), apart from the Eq. [4]. To correct the original Wagner's formalism to be thermodynamically consistent, a corrective function φ is added to the $\ln\gamma_2$ and $\ln\gamma_3$ as seen in Eqs. [18] and [19]. Inserting these equations into Eqs. [31] and [32] gives:

$$\begin{aligned}&(1-X_2)\frac{\partial\ln\gamma_1}{\partial X_2}-X_3\frac{\partial\ln\gamma_1}{\partial X_3}\\&\quad=-X_2\left(\epsilon_{22}+\frac{\partial\varphi}{\partial X_2}\right)-X_3\left(\epsilon_{23}+\frac{\partial\varphi}{\partial X_3}\right)\end{aligned} \qquad [33]$$

$$\begin{aligned}&(1-X_3)\frac{\partial\ln\gamma_1}{\partial X_3}-X_2\frac{\partial\ln\gamma_1}{\partial X_2}\\&\quad=-X_2\left(\epsilon_{23}+\frac{\partial\varphi}{\partial X_2}\right)-X_3\left(\epsilon_{33}+\frac{\partial\varphi}{\partial X_3}\right)\end{aligned} \qquad [34]$$

From Eqs. [33] and [34], it is obtained:

$$\frac{\partial\ln\gamma_1}{\partial X_2}-\frac{\partial\ln\gamma_1}{\partial X_3}=(\epsilon_{23}-\epsilon_{22})X_2+(\epsilon_{33}-\epsilon_{23})X_3 \qquad [35]$$

Then, it can be easily shown that:

$$\ln\gamma_1=-\frac{1}{2}\epsilon_{22}X_2^2-\epsilon_{23}X_2X_3-\frac{1}{2}\epsilon_{33}X_3^2 \qquad [36]$$

which satisfies the above condition and Raoult's law at infinite dilution. Therefore, the $\ln\gamma_1$ has been obtained, no matter what the corrective function φ is.

Inserting the $\ln\gamma_1$ and $\varphi = \alpha_{22}X_2^2 + \alpha_{23}X_2X_3 + \alpha_{33}X_3^2$ into Eqs. [33] or [34] yields:

$$\varphi = -\frac{1}{2}\epsilon_{22}X_2^2 - \epsilon_{23}X_2X_3 - \frac{1}{2}\epsilon_{33}X_3^2 \qquad [37]$$

Therefore, the derived $\ln\gamma_1$ is indeed identical to the corrective function φ, and to the expression proposed by Darken (Eq. [7]) and by Pelton and Bale (Eq. [12]) for the ternary case. It is evident that the expression for the $\ln\gamma_1$ in the Eq. [36] also obeys the Gibbs–Duhem relation along with $\ln\gamma_2$ and $\ln\gamma_3$ corrected by φ (Eq. [37]). Therefore, the $\ln\gamma_1$ and the corrective function φ have been obtained as:

- the corrective function φ is identical to the $\ln\gamma_1$
- $\ln\gamma_1$, $\ln\gamma_2$, and $\ln\gamma_3$ obey the Gibbs–Duhem relation (Eq. [8])
- $\ln\gamma_1$, $\ln\gamma_2$, and $\ln\gamma_3$ obey the thermodynamic consistency Eqs. [4], [31], and [32].

The Eqs. [31] and [32] are additional requirements to fulfill the thermodynamic consistency, which have not been explicitly described previously. Regardless of the choice of φ, the $\ln\gamma_1$ is determined from the form of $\ln\gamma_2$ and $\ln\gamma_3$ before the correction, through the condition of thermodynamic consistency. Other choices are thermodynamically inconsistent at finite concentration.

B. *Alternative Proof in the Ternary System: From Integral Excess Gibbs Energy*

Following the approach proposed by Bale and Pelton,[5,6] the above proof can be made more clearly and simply by deriving all partial excess Gibbs energies from a corresponding integral excess Gibbs energy. Suppose an integral molar excess Gibbs energy of the ternary solution is given as a general quadratic polynomial function of composition:

$$g^{ex} = X_1X_2\omega_{12} + X_2X_3\omega_{23} + X_1X_3\omega_{13} + C_2X_2 + C_3X_3 \qquad [38]$$

where ω_{12}, ω_{23}, ω_{13}, C_2, and C_3 are constants and C_2 and C_3 may not be zero because the equation is valid in the solvent-rich region.[2,6] This expression may be rationalized by a regular solution theory.[6] By replacing $X_1 = 1 - X_2 - X_3$, partial excess Gibbs energies can be obtained by the following relationship:

$$g_i^{ex} = \left.\frac{\partial(n \times g^{ex})}{\partial n_i}\right)_{n_j \neq n_i} = \mathrm{R}T\ln\gamma_i \qquad [39]$$

where $n \times g^{ex}$ is the total excess Gibbs energy in J. Differentiating the integral excess Gibbs energy gives

$$\ln\gamma_1 = [\omega_{12}X_2^2 + \omega_{13}X_3^2 + (\omega_{12} + \omega_{13} - \omega_{23})X_2X_3]/\mathrm{R}T \qquad [40]$$

$$\begin{aligned}\ln\gamma_2 = {} & [\omega_{12}X_2^2 + \omega_{13}X_3^2 + (\omega_{12} + \omega_{13} - \omega_{23})X_2X_3 - 2\omega_{12}X_2 \\ & + (\omega_{23} - \omega_{12} - \omega_{13})X_3 + \omega_{12} + C_2]/\mathrm{R}T\end{aligned} \qquad [41]$$

$$\begin{aligned}\ln\gamma_3 = {} & [\omega_{12}X_2^2 + \omega_{13}X_3^2 + (\omega_{12} + \omega_{13} - \omega_{23})X_2X_3 - 2\omega_{13}X_3 \\ & + (\omega_{23} - \omega_{12} - \omega_{13})X_2 + \omega_{13} + C_3]/\mathrm{R}T\end{aligned} \qquad [42]$$

By setting:

$$[\omega_{12} + C_2]/\mathrm{R}T = \ln\gamma_2^\circ \qquad [43]$$

$$[\omega_{13} + C_3]/\mathrm{R}T = \ln\gamma_3^\circ \qquad [44]$$

$$[-2\omega_{12}]/\mathrm{R}T = \epsilon_{22} \qquad [45]$$

$$[-2\omega_{13}]/\mathrm{R}T = \epsilon_{33} \qquad [46]$$

$$[\omega_{23} - \omega_{12} - \omega_{13}]/\mathrm{R}T = \epsilon_{23} \qquad [47]$$

the above Eqs. [40] to [42] change to:

$$\ln\gamma_1 = -\frac{1}{2}\epsilon_{22}X_2^2 - \frac{1}{2}\epsilon_{33}X_3^2 - \epsilon_{23}X_2X_3 \qquad [48]$$

$$\begin{aligned}\ln\gamma_2 &= \ln\gamma_2^\circ + \epsilon_{22}X_2 + \epsilon_{23}X_3 - \frac{1}{2}\epsilon_{22}X_2^2 - \frac{1}{2}\epsilon_{33}X_3^2 - \epsilon_{23}X_2X_3 \\ &= \ln\gamma_2^\circ + \epsilon_{22}X_2 + \epsilon_{23}X_3 + \varphi\end{aligned} \qquad [49]$$

$$\begin{aligned}\ln\gamma_3 &= \ln\gamma_3^\circ + \epsilon_{33}X_3 + \epsilon_{23}X_2 - \frac{1}{2}\epsilon_{22}X_2^2 - \frac{1}{2}\epsilon_{33}X_3^2 - \epsilon_{23}X_2X_3 \\ &= \ln\gamma_3^\circ + \epsilon_{33}X_3 + \epsilon_{23}X_2 + \varphi\end{aligned} \qquad [50]$$

It is seen that:

- the corrective function φ is identical for both $\ln\gamma_2$ and $\ln\gamma_3$
- the corrective function φ in the above example is the same as the $\ln\gamma_1$
- $\ln\gamma_1$ obtained in the Eq. [48] is the same as the Eq. [36]

Therefore, it can be concluded that the $\ln\gamma_1$ can be obtained in a unique form per given polynomial form of an integral excess Gibbs energy or partial excess Gibbs energies of solutes (activity coefficients of solutes), no matter how it has been obtained (differentiation or integration), as long as the activity coefficient of solute is thermodynamically consistent. The $\ln \gamma_1$ does not depend on the form of corrective function nor path of integration. Moreover, the corrective function to the activity coefficient of solutes should be the same as the activity coefficient of the solvent. This ensures all mandatory requirements of thermodynamic principles: Maxwell relations (Eqs. [4], [31], and [32]), and Gibbs–Duhem equation (Eq. [8]).

C. *Multicomponent System*

Darken's condition of thermodynamic consistency between two solutes was shown by himself for a ternary case (Eq. [4]),[3] and it has been extended to a multicomponent solution by Srikanth and Jacob for a relation of activity coefficients between two solutes.[14] As was shown in Sections. III–A and III–B for the ternary case, to examine the condition between solvent and solute in a multicomponent solution 1–2–· · ·–N where 1 is a solvent, the equation for the condition of thermodynamic consistency is revised in the present study in more general form (See Appendix A):

$$\sum_{k=2}^{N}(\delta_{ik}-X_k)\frac{\partial \ln \gamma_j}{\partial X_k}=\sum_{k=2}^{N}(\delta_{jk}-X_k)\frac{\partial \ln \gamma_i}{\partial X_k} \qquad [51]$$

where i and j are 1 (solvent), 2, …, N. If $N=3$, $i=2$ and $j=3$, then the above equation reduces to the original Darken's equation (Eq. [4]). If $i\neq 1$ and $j\neq 1$, then the above equation reduces to the equation derived by Srikanth and Jacob.[14] For the present analysis, if $i=1$ and $j\neq 1$, then

$$-\sum_{k=2}^{N}X_k\frac{\partial \ln \gamma_j}{\partial X_k}=\frac{\partial \ln \gamma_1}{\partial X_j}-\sum_{k=2}^{N}X_k\frac{\partial \ln \gamma_1}{\partial X_k} \qquad [52]$$

showing the condition of thermodynamic consistency between the solvent 1 and a solute j.

A corrective function $\varphi(X_2, X_3, \ldots, X_N)$ is defined, and added to *incorrect* $\ln \gamma_j$ of first-order formalism that:

$$\ln(\gamma_j/\gamma_j^{\circ})=\sum_{k=2}^{N}\epsilon_{jk}X_k+\varphi \qquad [53]$$

$$\frac{\partial \ln \gamma_j}{\partial X_i}=\epsilon_{ji}+\frac{\partial \varphi}{\partial X_i} \qquad [54]$$

Inserting the Eqs. [54] into [52] yields:

$$\frac{\partial \ln \gamma_1}{\partial X_j}-\sum_{k=2}^{N}X_k\frac{\partial \ln \gamma_1}{\partial X_k}=-\sum_{k=2}^{N}X_k\left(\epsilon_{jk}+\frac{\partial \varphi}{\partial X_k}\right) \qquad (j=2,3,\ldots,N) \qquad [55]$$

Considering a similar equation, replacing j by i, and subtracting one from the other, one obtains:

$$\frac{\partial \ln \gamma_1}{\partial X_i}-\frac{\partial \ln \gamma_1}{\partial X_j}=\sum_{k=2}^{N}(\epsilon_{jk}-\epsilon_{ik})X_k \qquad (i,j=2,3,\ldots,N) \qquad [56]$$

From the form of the above equation, $\ln \gamma_1$ should have a formula

$$\ln \gamma_1=\sum_{k=2}^{N}a_{kk}X_k^2+\sum_{\substack{k,l=2\\k\neq l}}^{N}b_{kl}X_kX_l+\sum_{k=2}^{N}c_kX_k \qquad [57]$$

Using the Eq. [56], it can be shown as (See Appendix B):

$$\ln \gamma_1=-\frac{1}{2}\sum_{j,k=2}^{N}\epsilon_{jk}X_jX_k \qquad [58]$$

which is identical to the $\ln \gamma_1$ proposed by Pelton and Bale[4–6] (Eq. [12]). Therefore, the $\ln \gamma_1$ can be uniquely defined, no matter how the φ is defined. And the corrective function φ can be uniquely obtained through the Gibbs–Duhem equation along with all $\ln \gamma_i$'s, which is indeed identical to the $\ln \gamma_1$.

Expansion to include higher-order interaction parameters ($\epsilon_{ijk}, \epsilon_{ijkl}$, *etc.*) are straightforward.

IV. DISCUSSION

In general, partial properties can be obtained by differentiating an expression of the corresponding integral property, as was shown in Section III–B. By this process, the partial properties can be made in an unique way, and this assures thermodynamic consistency. Therefore, it may be said that there are an infinite number of ways of expressing the partial properties of a solution in a thermodynamically consistent way, for each *infinite number of expressions for the integral property*. However, calling these "correction" to Wagner's formalism is a stretch since most of them would not resemble Wagner's formalism at all. The mathematical expression for the integral property should be based on a reasonable solution model. The quadratic formalism, with polynomial expansions to cubic and higher-order terms, satisfies this criterion since it is based on regular solution theory. Wagner's formalism is based on the quadratic formalism, but is not thermodynamically consistent except in very dilute solutions. The UIPF can be derived from the regular solution theory as the basis but corrects the thermodynamic inconsistency in non-dilute solutions while reducing to Wagner's formalism at infinite dilution.

The present thermodynamic consistency analysis has been applied to the composition dependence of the activity coefficients of all the components. Since the activity coefficient of a component i in a logarithm scale is obtained by a partial differential of the total excess Gibbs energy by the amount of the component i (see Eq. [39]), partial differentials by the amount of different components yield different excess partial Gibbs energies and corresponding activity coefficients. Nevertheless, these must satisfy the Gibbs–Duehm relation (Eq. [13]) and the thermodynamic consistency equation (Eq. [51]) by the Maxwell relation. This ensures the uniqueness of the correction to the Wagner's interaction parameter formalism.

Temperature dependence of the activity coefficients of components may be also sought in view of the thermodynamic consistency. It may be tested by applying the Gibbs–Duhem relation under constant pressure (but not under constant temperature) and the Maxwell relation in the following ways:

$$\sum_{i=1}^{N} X_i dg_i + sdT = 0 \tag{59}$$

where s is the molar entropy of the solution and,

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right) \tag{60}$$

However, since the partial differential to T does not yield any different expression per each component i, these relations do not provide some useful relationship, contrary to the present analysis for the composition dependence of the activity coefficient.

Temperature dependence of parameters in the UIPF, for example, $\ln\gamma_2^\circ$, $\ln\gamma_3^\circ$, ϵ_{22}, ϵ_{33}, and ϵ_{23} in a ternary 1–2–3 system, depend on the temperature dependence of interaction energies (ω_{12}, ω_{23}, and ω_{13})) and that of C_2 and C_3, as can be seen in the Eq. [38]. By inspecting the Eqs. [43] through [47], it is evident that there is no interrelationship among the temperature dependence of the parameters, in general. This means, if the formalism is intended to be used only in the solvent-rich region, thereby none of C_2 and C_3 is zero, the temperature dependence of the five parameters is independent of each other. However, if the formalism is to be valid over the whole concentration range, therefore $C_2 = C_3 = 0$, then, the following relationship should be held:

$$\epsilon_{22} = -2\ln\gamma_2^\circ \tag{61}$$

$$\epsilon_{33} = -2\ln\gamma_3^\circ \tag{62}$$

$$\epsilon_{23} = \frac{\omega_{23}}{RT} - \ln\gamma_2^\circ - \ln\gamma_3^\circ \tag{63}$$

which was already well-known relationship.[3,25] Accordingly, temperature dependence among the parameters (Henrian activity coefficients and interaction parameters) should satisfy similar relations which are simply obtained by the partial differential of the above equations (Eqs. [61] through [63]). This is valid when the solution behaves as the regular solution. If the solution's behavior is interpreted by the quasichemical theory, different relations between Henrian activity coefficients and interaction parameters are found.[25]

By a choice of the temperature dependence of the ω_{ij}'s and C_i's in Eq. [38], the temperature dependence of Henrian activity coefficients and interaction parameters are determined. While a linear dependence has been most widely accepted (*i.e.*, $\omega_{ij} = \eta_{ij} - \sigma_{ij}T$), a number of different approaches are also available.[26–28]

V. CONCLUSION

Condition of thermodynamic consistency for the representation of excess partial Gibbs energy of multicomponent solution has been discussed, in particular in the course of correction to the Wagner's formalism. Apart from the Gibbs–Duhem relation and Darken's condition of thermodynamic consistency for solutes, it has been stressed that a similar condition should also be obeyed between solvent and solute. A general condition of thermodynamic consistency has been derived in the present study.

A recent issue raised for the possibility of non-unique correction to Wagner's formalism was analyzed.[18] It has been shown in the present article that the correction can be made in a unique way for given functional form of the activity coefficient of solutes ($\ln\gamma_i$, $i = 2, 3, \ldots, N$) regardless of the way of the correction. The corrective function $\varphi(X_2, X_3, \ldots, X_N)$, as well as the activity coefficient of solvent ($\ln\gamma_1$) can be uniquely defined through the Gibbs–Duhem relation and the general condition of thermodynamic consistency. It ensures the use of UIPF with a confidence for multicomponent dilute solution. Temperature dependence of the interaction parameters (ϵ_{ij}) and Henrian activity coefficients ($\ln\gamma_i^\circ$) was discussed, although it depends on temperature dependence of interaction energies (ω_{ij}).

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APPENDICES

APPENDIX A

Extension of Darken's Thermodynamic Consistency into Multicomponent Solution including Solvent

As Gibbs energy, G, is a state function, and its differential is exact, the Maxwell's relation is obeyed:

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial n_j}\right) = \frac{\partial}{\partial n_j}\left(\frac{\partial G}{\partial n_i}\right) \qquad \text{[A1]}$$

where n_i, n_j are the number of moles of components i and j, and

$$G = \sum_{i=1}^{N} n_i g_i^{\circ} + \mathrm{R}T\left(\sum_{i=1}^{N} n_i \ln X_i + \sum_{i=1}^{N} n_i \ln \gamma_i\right) \qquad \text{[A2]}$$

and

$$\begin{aligned} X_i &= \frac{n_i}{\sum_{j=1}^{N} n_j} = \frac{n_i}{n} \\ \text{where } n &= \sum_{j=1}^{N} n_j \qquad (i = 1, 2, \ldots, N) \end{aligned} \qquad \text{[A3]}$$

By differentiating G with respect to n_j, while all other $n_i (i \neq j)$ are kept constant,

$$\frac{\partial G}{\partial n_j} = g_j^{\circ} + \mathrm{R}T\left(\ln X_j + \ln \gamma_j + \sum_{k=1}^{N} n_k \frac{\partial \ln \gamma_k}{\partial n_j}\right) \qquad \text{[A4]}$$

The last term in the Eq. [A4] is zero due to the Gibbs–Duhem relation. From the above,

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial n_j}\right) = \mathrm{R}T\left(\frac{\partial \ln \gamma_j}{\partial n_i} - \frac{1}{n}\right) \qquad \text{[A5]}$$

Similarly,

$$\frac{\partial}{\partial n_j}\left(\frac{\partial G}{\partial n_i}\right) = \mathrm{R}T\left(\frac{\partial \ln \gamma_i}{\partial n_j} - \frac{1}{n}\right) \qquad \text{[A6]}$$

Therefore, the following relationship between activity coefficients of components i and j are obtained:

$$\frac{\partial \ln \gamma_j}{\partial n_i} = \frac{\partial \ln \gamma_i}{\partial n_j} \qquad \text{[A7]}$$

which is the same as the Eq. [14]. Taking all X_i's except for X_1 as independent variables, and using the following derivatives of X_k with respect to n_i,

$$\begin{aligned} \frac{\partial X_k}{\partial n_i} &= \frac{\partial (n_k/n)}{\partial n_i} = \frac{\delta_{ik} n - n_k}{n^2} \\ &= \frac{\delta_{ik} - X_k}{n} \qquad (i, k = 1, 2, \ldots, N) \end{aligned} \qquad \text{[A8]}$$

the above equation is expressed as:

$$\begin{aligned} \frac{\partial \ln \gamma_j}{\partial n_i} &= \sum_{k=2}^{N} \frac{\partial \ln \gamma_j}{\partial X_k}\left(\frac{\partial X_k}{\partial n_i}\right) \\ &= \sum_{k=2}^{N} \frac{\partial \ln \gamma_j}{\partial X_k}\left(\frac{\delta_{ik} - X_k}{n}\right) \end{aligned} \qquad \text{[A9]}$$

Similarly,

$$\frac{\partial \ln \gamma_i}{\partial n_j} = \sum_{k=2}^{N} \frac{\partial \ln \gamma_i}{\partial X_k}\left(\frac{\delta_{jk} - X_k}{n}\right) \qquad \text{[A10]}$$

Therefore, the following equation is obtained which represents the conditions of thermodynamic consistency between two components (i and j) in N-component system, including solvent ($i = 1$ or $j = 1$) and solute ($i, j \neq 1$):

$$\sum_{k=2}^{N} (\delta_{ik} - X_k) \frac{\partial \ln \gamma_j}{\partial X_k} = \sum_{k=2}^{N} (\delta_{jk} - X_k) \frac{\partial \ln \gamma_i}{\partial X_k} \qquad \text{[A11]}$$

APPENDIX B

Derivation of $\ln \gamma_1$ in Multicomponent Solution

From the Eq. [57],

$$\frac{\partial \ln \gamma_1}{\partial X_i} = 2a_{ii} X_i + 2 \sum_{\substack{k=2 \\ k \neq i}}^{N} b_{ik} X_k + c_i \qquad \text{[B1]}$$

$$\frac{\partial \ln \gamma_1}{\partial X_j} = 2a_{jj} X_j + 2 \sum_{\substack{k=2 \\ k \neq j}}^{N} b_{jk} X_k + c_j \qquad \text{[B2]}$$

Then,

$$\begin{aligned} &\frac{\partial \ln \gamma_1}{\partial X_i} - \frac{\partial \ln \gamma_1}{\partial X_j} \\ &\quad = (2a_{ii} - 2b_{ji}) X_i + (2b_{ij} - 2a_{jj}) X_j + \sum_{\substack{k=2 \\ k \neq i,j}} 2b_{ik} X_k \\ &\quad - \sum_{\substack{k=2 \\ k \neq i,j}} 2b_{jk} X_k + c_i - c_j \end{aligned} \qquad \text{[B3]}$$

$$\begin{aligned} &= \sum_{\substack{k=2 \\ k \neq i,j}} (2b_{ik} - 2b_{jk}) X_k + (2a_{ii} - 2b_{ji}) X_i + (2b_{ij} - 2a_{jj}) X_j \\ &\quad + c_i - c_j \end{aligned} \qquad \text{[B4]}$$

Therefore by comparison with the Eq. [56],

$$2a_{ii} - 2b_{ji} = \epsilon_{ji} - \epsilon_{ii} \qquad \text{[B5]}$$

$$2b_{ij} - 2a_{jj} = \epsilon_{jj} - \epsilon_{ij} \qquad \text{[B6]}$$

$$2b_{ik} - 2b_{jk} = \epsilon_{jk} - \epsilon_{ik} \qquad [\mathrm{B7}]$$

$$c_i - c_j = 0 \qquad [\mathrm{B8}]$$

According to Raoult's law ($\frac{\partial \ln \gamma_1}{\partial X_i} \rightarrow 0$ when $X_i, X_j \rightarrow 0$), it can be shown that $c_i = c_j = 0$. Furthermore, by inspection, $a_{ii} = -\frac{1}{2}\epsilon_{ii}$, $a_{jj} = -\frac{1}{2}\epsilon_{jj}$, $b_{ij} = b_{ji} = -\frac{1}{2}\epsilon_{ij}$, *etc*. Therefore,

$$\ln \gamma_1 = -\frac{1}{2}\sum_{k=2}^{N} \epsilon_{kk} X_k^2 - \frac{1}{2}\sum_{\substack{k,l=2 \\ k \neq l}}^{N} \epsilon_{kl} X_k X_l \qquad [\mathrm{B9}]$$

$$= -\frac{1}{2}\sum_{j,k=2}^{N} \epsilon_{jk} X_j X_k \qquad [\mathrm{B10}]$$

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