Discussion of "Thermodynamic Consistency of the Interaction Parameter Formalism"*

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Srikanth and Jacob[1] stated that the general relations between interaction parameters derived by Lupis and Elliott[2] are subject to errors due to improper truncations of the Maclaurin series by the latter. It will be proven in this note that the relations of Lupis and Elliott remain generally valid, while the relations derived by Srikanth and Jacob are valid only for regular solutions. Indeed, it will be demonstrated that both relations are equivalent insofar as ternary regular solutions are concerned.

For ternary solutions of the system 1-2-3 where the component 1 is the major solvent, Lupis and Elliott[2] derived the following relation:

$$L = \rho_2^{2,3} + \varepsilon_2^3 - 2\rho_3^2 - \varepsilon_2^2 = 0 \qquad [1]$$

In contrast, for the activity coefficients of solutes that can be expressed by the Wagnerian first order and Lupisian second order interaction parameters, Srikanth and Jacob derived the following relations (their Eq. [14]):

$$J_1 = \rho_2^{2,3} + 2\rho_3^2 + \varepsilon_3^2 + \varepsilon_2^2 = 0 \qquad [2]$$

$$J_2 = \rho_3^{2,3} + 2\rho_2^2 + \varepsilon_3^2 + \varepsilon_2^2 = 0 \qquad [3]$$

$$J_3 = \rho_2^{2,3} + 2\rho_3^2 - \rho_3^{2,3} - 2\rho_2^2 = 0 \qquad [4]$$

Equations [2], [3], and [4] appear so different from Eq. [1] that Srikanth and Jacob concluded that Eq. [1] is not a general relation. They derived Eqs. [2], [3], and [4] by truncating third and higher terms in series expansions, as expressed by their Eqs. [9] and [10]. Since such a truncation is the necessary condition for ternary regular solutions, the present discussion may be begun with the redefinition of a ternary regular assembly, as will be done below.

The concepts of regular solutions are based on random atomic distribution for entropy and nearest neighbor bond energies for internal energy of mixing. A ternary substitutional regular solution consisting of N_1 atoms of metal 1, N_2 atoms of metal 2, and N_3 atoms of metal 3 can be defined most elegantly by use of the Grand Partition Function (GPF), as shown in Table I. All the thermodynamic properties of a regular solution, such as activities, activity coefficients, interaction parameters, and their temperature dependence, can be derived from this sole equation, Eq. [1.1], Table I. When this regular assembly is in thermal equilibrium, it satisfies the following conditions:[3,4]

$$\frac{\partial \ln \Xi^\circ}{\partial N_1} = 0; \qquad \frac{\partial \ln \Xi^\circ}{\partial N_2} = 0; \qquad \frac{\partial \ln \Xi^\circ}{\partial N_3} = 0 \qquad [5]$$

When the Raoultian standarization is applied, these three relations become the expression of the Raoultian activity coefficient of each constituent, as shown by Eqs. [1.3], [1.4], and [1.5], Table I. These three relations are valid for all binary and ternary compositions from concentrated to infinitely dilute solutions.

It may be of interest to prove here that Eqs. [1.3], [1.4], and [1.5] satisfy the Gibbs-Duhem relation, as shown in Table II. This is quite natural since the three equations are all derived originally by differentiating partially one single function, GPF. Nonetheless, this confirmation is important in that the GPF method henceforth annihilates the need for the Gibbs-Duhem integrations which may bring in unnecessary complications due to its path dependency or inevitable introduction of integration constant. By Wagner's definition of interaction parameters,[5] ln γ_2 is treated as a function of x_2 and x_3, or the atomic fractions of two solutes. The Taylor series expansion can also be made by looking upon ln γ_2 as a function of x_1 and x_2, or that of x_1 and x_3, which are called non-Wagnerian in this note. They are all valid mathematically. For regular solutions, they can be expressed analytically, as shown in Table III. Partial differentiation of these analytical expressions readily yields

Table I. Grand Partition Function for Ternary Regular Solutions and Its Conditions for Equilibrium

$$\Xi = \sum_{N_1}\sum_{N_2}\sum_{N_3} \frac{(N_1 + N_2 + N_3)!}{N_1!N_2!N_3!} (q_1\lambda_1)^{N_1}(q_2\lambda_2)^{N_2}(q_3\lambda_3)^{N_3} \exp\left[\frac{-1}{\mathrm{k}T}\frac{1}{N_1 + N_2 + N_3}(w_{12}N_1N_2 + w_{23}N_2N_3 + w_{31}N_3N_1)\right] \qquad [1.1]$$

$$\begin{aligned}\ln \Xi^\circ = {} & (N_1 + N_2 + N_3)\ln(N_1 + N_2 + N_3) - N_1 \ln N_1 - N_2 \ln N_2 - N_3 \ln N_3 + N_1 \ln q_1\lambda_1 + N_2 \ln q_2\lambda_2 + N_3 \ln q_3\lambda_3 \\ & - \frac{1}{\mathrm{k}T}\frac{1}{N_1 + N_2 + N_3}(w_{12}N_1N_2 + w_{23}N_2N_3 + w_{31}N_3N_1)\end{aligned} \qquad [1.2]$$

$$\frac{\partial \ln \Xi^\circ}{\partial N_1} = 0\text{: } \ln\frac{q_1\lambda_1}{x_1} = (1 - x_1)(V_{12}x_2 + V_{31}x_3) - V_{23}x_2x_3 = \ln \gamma_1 \qquad [1.3]$$

$$\frac{\partial \ln \Xi^\circ}{\partial N_2} = 0\text{: } \ln\frac{q_2\lambda_2}{x_2} = (1 - x_2)(V_{23}x_3 + V_{12}x_1) - V_{31}x_3x_1 = \ln \gamma_2 \qquad [1.4]$$

$$\frac{\partial \ln \Xi^\circ}{\partial N_3} = 0\text{: } \ln\frac{q_3\lambda_3}{x_3} = (1 - x_3)(V_{31}x_1 + V_{23}x_2) - V_{12}x_1x_2 = \ln \gamma_3 \qquad [1.5]$$

where Ξ° = maximum term in Ξ; $x_i = N_i/(N_1 + N_2 + N_3)$; $V_{ij} = w_{ij}/\mathrm{k}T$

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the Wagnerian and non-Wagnerian interaction parameters, as summarized in Tables IV and V.

When these values are substituted in the Taylor series expansion for ln γ_2, for example, it can be proven that the original regularity expressions can fully be restored by Wagnerian ε's and Lupisian ρ's alone without any remainder of higher order in the infinite series, as shown in Table VI. Conversely, the truncation of third and higher order terms in the infinite series, as was done by Srikanth and Jacob in their Eqs. [9] and [10], signifies that the ternary activity coefficient has then been approximated by the regular solution model. The Eqs. [9] and [10] of Srikanth and Jacob may be withstood by solutions other than regular, but Eq. [1.1] still remains valid as a sufficient condition, thus affecting no argument here.

While Lupis-Elliott's Eq. [1] was derived for any ternary solutions, those of Srikanth and Jacob were derived, perhaps unintentionally but in essence, for regular solutions when they chose only the first and second order terms. Let us substitute the values given in Tables IV and V in Eqs. [1] through [4]:

Table II. Ternary Regular Solutions and Gibbs-Duhem Equation

$$\ln \gamma_1 = (1 - x_1)\,(V_{12}x_2 + V_{31}x_3) - V_{23}x_2x_3 \qquad [2.1]$$

$$\ln \gamma_2 = (1 - x_2)\,(V_{23}x_3 + V_{12}x_1) - V_{31}x_3x_1 \qquad [2.2]$$

$$\ln \gamma_3 = (1 - x_3)\,(V_{31}x_1 + V_{23}x_2) - V_{12}x_1x_2 \qquad [2.3]$$

$$x_1\left(\frac{d \ln \gamma_1}{dx_1}\right) = x_1\left\{-V_{12}x_2 - V_{31}x_3 + \left(\frac{dx_2}{dx_1}\right)[V_{12}(1 - x_1) - V_{23}x_3] + \left(\frac{dx_3}{dx_1}\right)[V_{31}\,(1 - x_1) - V_{23}x_2]\right\} \qquad [2.4]$$

$$x_2\left(\frac{d \ln \gamma_2}{dx_1}\right) = x_2\left\{V_{12}(1 - x_2) - V_{31}x_3 + \left(\frac{dx_2}{dx_1}\right)[-V_{12}x_1 - V_{23}x_3] + \left(\frac{dx_3}{dx_1}\right)[V_{23}(1 - x_2) - V_{31}x_1]\right\} \qquad [2.5]$$

$$x_3\left(\frac{d \ln \gamma_3}{dx_1}\right) = x_3\left\{V_{31}(1 - x_3) - V_{12}x_2 + \left(\frac{dx_2}{dx_1}\right)[V_{23}(1 - x_3) - V_{12}x_1] + \left(\frac{dx_3}{dx_1}\right)[-V_{31}x_1 - V_{23}x_2]\right\} \qquad [2.6]$$

$$x_1\,d \ln \gamma_1 + x_2\,d \ln \gamma_2 + x_3\,d \ln \gamma_3 = dx_1\left[x_1\left(\frac{d \ln \gamma_1}{dx_1}\right) + x_2\left(\frac{d \ln \gamma_2}{dx_1}\right) + x_3\left(\frac{d \ln \gamma_3}{dx_1}\right)\right] = 0 \qquad [2.7]$$

Table III. Wagnerian and Non-Wagnerian Expressions for Activity Coefficients of Solutes in Ternary Regular Solutions

Wagnerian: $\ln \gamma_2(x_2, x_3) = V_{12}(1 - x_2 - x_3)\;(1 - x_2) + V_{23}x_3(1 - x_2) - V_{31}x_3(1 - x_2 - x_3)$ [3.1]

Wagnerian: $\ln \gamma_3(x_2, x_3) = -V_{12}x_2(1 - x_2 - x_3) + V_{23}x_2(1 - x_3) + V_{31}(1 - x_3)\,(1 - x_2 - x_3)$ [3.2]

Non-Wagnerian: $\ln \gamma_2(x_1, x_2) = V_{12}x_1(1 - x_2) + V_{23}(1 - x_2)\,(1 - x_1 - x_2) - V_{31}x_1(1 - x_1 - x_2)$ [3.3]

Non-Wagnerian: $\ln \gamma_3(x_1, x_2) = -V_{12}x_1x_2 + V_{23}x_2(x_1 + x_2) + V_{31}x_1(x_1 + x_2)$ [3.4]

Non-Wagnerian: $\ln \gamma_2(x_3, x_1) = V_{12}x_1(x_3 + x_1) + V_{23}x_3(x_3 + x_1) - V_{31}x_3x_1$ [3.5]

Non-Wagnerian: $\ln \gamma_3(x_3, x_1) = -V_{12}x_1(1 - x_1 - x_3) + V_{23}(1 - x_3)\,(1 - x_1 - x_3) + V_{31}x_1(1 - x_3)$ [3.6]

Table IV. Partial Derivatives of ln γ_2 for Ternary Regular Solutions

Function	Wagnerian ln $\gamma_2(x_2, x_3)$	Non-Wagnerian ln $\gamma_2(x_1, x_2)$	Non-Wagnerian ln $\gamma_2(x_3, x_1)$
Condition	$x_2 \to 0$; $x_3 \to 0$	$x_1 \to 1$; $x_2 \to 0$	$x_3 \to 0$; $x_1 \to 1$
ln γ_2°	V_{12}	V_{12}	V_{12}
$\partial \ln \gamma_2/\partial x_1$	—	$V_{12} - V_{23} + V_{31}$	$2V_{12}$
$\partial \ln \gamma_2/\partial x_2$	$-2V_{12} = \varepsilon_2^2$	$-V_{12} - V_{23} + V_{31}$	—
$\partial \ln \gamma_2/\partial x_3$	$-V_{12} + V_{23} - V_{31} = \varepsilon_2^3$	—	$V_{12} + V_{23} - V_{31}$
$\partial^2 \ln \gamma_2/\partial x_1^2$	—	$2V_{31}$	$2V_{12}$
$\partial^2 \ln \gamma_2/\partial x_2^2$	$2V_{12} = 2\rho_2^2$	$2V_{23}$	—
$\partial^2 \ln \gamma_2/\partial x_3^2$	$2V_{31} = 2\rho_2^3$	—	$2V_{23}$
$\partial^2 \ln \gamma_2/(\partial x_1 \partial x_2)$	—	$-V_{12} + V_{23} + V_{31}$	—
$\partial^2 \ln \gamma_2/(\partial x_2 \partial x_3)$	$V_{12} - V_{23} + V_{31} = \rho_2^{2,3}$	—	—
$\partial^2 \ln \gamma_2/(\partial x_3 \partial x_1)$	—	—	$V_{12} + V_{23} - V_{31}$

Table V. Partial Derivatives of ln γ_3 for Ternary Regular Solutions

Function	Wagnerian ln $\gamma_3(x_2, x_3)$	Non-Wagnerian ln $\gamma_3(x_1, x_2)$	Non-Wagnerian ln $\gamma_3(x_3, x_1)$
Condition	$x_2 \rightarrow 0; \quad x_3 \rightarrow 0$	$x_1 \rightarrow 1; \quad x_2 \rightarrow 0$	$x_3 \rightarrow 0; \quad x_1 \rightarrow 1$
$\ln \gamma_3^\circ$	V_{31}	V_{31}	V_{31}
$\partial \ln \gamma_3/\partial x_1$	—	$2V_{31}$	$V_{12} - V_{23} + V_{31}$
$\partial \ln \gamma_3/\partial x_2$	$-V_{12} + V_{23} - V_{31} = \varepsilon_3^2$	$-V_{12} + V_{23} + V_{31}$	—
$\partial \ln \gamma_3/\partial x_3$	$-2V_{31} = \varepsilon_3^3$	—	$V_{12} - V_{23} - V_{31}$
$\partial^2 \ln \gamma_3/\partial x_1^2$	—	$2V_{31}$	$2V_{12}$
$\partial^2 \ln \gamma_3/\partial x_2^2$	$2V_{12} = 2\rho_3^2$	$2V_{23}$	—
$\partial^2 \ln \gamma_3/\partial x_3^2$	$2V_{31} = 2\rho_3^3$	—	$2V_{23}$
$\partial^2 \ln \gamma_3/(\partial x_1 \partial x_2)$	—	$-V_{12} + V_{23} + V_{31}$	—
$\partial^2 \ln \gamma_3/(\partial x_2 \partial x_3)$	$V_{12} - V_{23} + V_{31} = \rho_3^{2,3}$	—	—
$\partial^2 \ln \gamma_3/(\partial x_3 \partial x_1)$	—	—	$V_{12} + V_{23} - V_{31}$

$$\begin{aligned} L &= \rho_2^{2,3} + \varepsilon_2^3 - 2\rho_3^2 - \varepsilon_2^2 \\ &= (V_{12} - V_{23} + V_{31}) + (-V_{12} + V_{23} - V_{31}) \\ &\quad - 2V_{12} - (-2V_{12}) = 0 \end{aligned} \qquad [6]$$

$$\begin{aligned} J_1 &= \rho_2^{2,3} + 2\rho_3^2 + \varepsilon_3^2 + \varepsilon_2^2 \\ &= (V_{12} - V_{23} + V_{31}) + 2V_{12} \\ &\quad + (-V_{12} + V_{23} - V_{31}) - 2V_{12} = 0 \end{aligned} \qquad [7]$$

$$\begin{aligned} J_2 &= \rho_3^{2,3} + 2\rho_2^2 + \varepsilon_3^2 + \varepsilon_2^2 \\ &= (V_{12} - V_{23} + V_{31}) + 2V_{12} \\ &\quad + (-V_{12} + V_{23} - V_{31}) - 2V_{12} = 0 \end{aligned} \qquad [8]$$

$$\begin{aligned} J_3 &= \rho_2^{2,3} + 2\rho_3^2 - \rho_3^{2,3} - 2\rho_2^2 \\ &= (V_{12} - V_{23} + V_{31}) + 2V_{12} \\ &\quad - (V_{12} - V_{23} + V_{31}) - 2V_{12} = 0 \end{aligned} \qquad [9]$$

Table VI. Wagnerian and Non-Wagnerian Series Expansions for ln γ_2 in Ternary Regular Solutions

General:

$$\ln \gamma_2(\text{gen}) = V_{12}x_1(1 - x_2) + V_{23}x_3(1 - x_2) - V_{31}x_3x_1 \qquad [6.1]$$

Wagnerian:

$$\ln \gamma_2(x_2, x_3) = V_{12}(1 - x_2 - x_3)\,(1 - x_2) + V_{23}x_3(1 - x_2) - V_{31}x_3(1 - x_2 - x_3) \qquad [6.2]$$

$$\begin{aligned} \ln \gamma_2(x_2, x_3) = {} & [\ln \gamma_2^\circ]_A + x_2\left[\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{x_3}\right]_A + x_3\left[\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)_{x_2}\right]_A + \frac{1}{2}x_2^2\left[\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2^2}\right)_{x_3}\right]_A \\ & + \frac{1}{2}x_3^2\left[\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3^2}\right)_{x_2}\right]_A + x_2x_3\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_3}\right)_A = \ln \gamma_2(\text{gen}) \end{aligned} \qquad [6.3]$$

Non-Wagnerian:

$$\ln \gamma_2(x_1, x_2) = V_{12}x_1(1 - x_2) + V_{23}(1 - x_2)\,(1 - x_1 - x_2) - V_{31}x_1(1 - x_1 - x_2) \qquad [6.4]$$

$$\begin{aligned} \ln \gamma_2(x_1, x_2) = {} & [\ln \gamma_2^\circ]_B + (x_1 - 1)\left[\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{x_2}\right]_B + x_2\left[\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{x_1}\right]_B + \frac{1}{2}(x_1 - 1)^2\left[\left(\frac{\partial^2 \ln \gamma_2}{\partial x_1^2}\right)_{x_2}\right]_B \\ & + \frac{1}{2}x_2^2\left[\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2^2}\right)_{x_1}\right]_B + (x_1 - 1)x_2\left(\frac{\partial^2 \ln \gamma_2}{\partial x_1 \partial x_2}\right)_B = \ln \gamma_2(\text{gen}) \end{aligned} \qquad [6.5]$$

Non-Wagnerian:

$$\ln \gamma_2(x_3, x_1) = V_{12}x_1(x_3 + x_1) + V_{23}x_3(x_3 + x_1) - V_{31}x_3x_1 \qquad [6.6]$$

$$\begin{aligned} \ln \gamma_2(x_3, x_1) = {} & [\ln \gamma_2^\circ]_C + (x_1 - 1)\left[\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{x_3}\right]_C + x_3\left[\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)_{x_1}\right]_C + \frac{1}{2}(x_1 - 1)^2\left[\left(\frac{\partial^2 \ln \gamma_2}{\partial x_1^2}\right)_{x_3}\right]_C \\ & + \frac{1}{2}x_3^2\left[\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3^2}\right)_{x_1}\right]_C + (x_1 - 1)x_3\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3 \partial x_1}\right)_C = \ln \gamma_2(\text{gen}) \end{aligned} \qquad [6.7]$$

Notes: (1) The subscripts A, B, and C refer to the conditions $A(x_2 \rightarrow 0;\ x_3 \rightarrow 0)$, $B(x_1 \rightarrow 1;\ x_2 \rightarrow 0)$, and $C(x_1 \rightarrow 1;\ x_3 \rightarrow 0)$, respectively. (2) The actual values of partial derivatives are given in Table IV.

Surprisingly, Eqs. [1] through [4], which appeared so different that Srikanth and Jacob were induced to denounce the generality of the Lupis-Elliott equation, are all equivalent so long as regular solutions are concerned. Owing to the fact that Srikanth and Jacob assumed unintentionally the ternary regularity, Eqs. [2], [3], and [4] become invalid in dealing with solutions other than regular. On the other hand, the Lupis-Elliott equation should be considered of general validity for all regular or nonregular solutions.

Not only the integration for the activity coefficient of solvent, as discussed by Srikanth and Jacob, but the definition itself of interaction parameters also depends on path in ternary solutions, as restated correctly by Sukiennik and Olesinski.[6] This fact can be put in evidence most demonstratively by the GPF method. For example, directly from Table IV, we have

$$\left[\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)_{x_1}\right]_{x_1 \to 1, x_3 \to 0} = V_{12} + V_{23} - V_{31} \qquad [10]$$

$$\left[\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)_{x_2}\right]_{x_2 \to 0, x_3 \to 0} = -V_{12} + V_{23} - V_{31} \qquad [11]$$

Equations [10] and [11] clearly indicate that the partial derivative along the path of x_1 = const converges to a value different from that along the path of x_2 = const. Although Srikanth and Jacob used only the Wagnerian terms, namely their Eq. [23], the present Eqs. [10] and [11] are derived based on more rigorous expressions including both Wagnerian and Lupisian terms, as done earlier by Srikanth and Jacob in their Eqs. [9] and [10], for which the activity coefficient of solvent has already been given by Eq. [1.3] without any integration. This tremendous simplicity is a merit of the GPF method which obliterates all integrating operations from solution theories. Equation [1.3] does not depend on path, being valid for all compositions, dilute or concentrated, binary or ternary. It may be suggested that the activity coefficient of solvent is best assessed by regularity approximation, or Eq. [1.3], even if the solutes may not behave exactly regularly.

In reference to Eqs. [10] and [11], it is of great importance to note that in a ternary solution 1-2-3 where the component 1 is the dominant solvent, the condition of ($x_{\text{solvent}} \to 1$), or ($x_1 \to 1$, $x_3 \to 0$), is not the same as that of ($x_2 \to 0$, $x_3 \to 0$). Thus, the GPF formalism for regular solutions lends support to Srikanth and Jacob when they meant that some previous researchers and authors were misled due to the overlooking of the path dependence of interaction parameters. Incidentally, Wagner's original definition[5] clearly designates the condition of ($x_2 \to 0$, $x_3 \to 0$) with categorical rejection of the other conditions such as ($x_1 \to 1$, $x_3 \to 0$), ($x_1 \to 1$, $x_2 \to 0$), and (x_2/x_3 = const, $x_1 \to 1$).

NOMENCLATURE

E_{ij}	pairwise single bond energy between i and j
k	Boltzmann constant
N_i	number of atoms of metal i
q_i	vibrational partition function of atom i
T	temperature in Kelvin
V_{ij}	$= w_{ij}/\text{k}T$
w_{ij}	$= z[E_{ij} - 0.5(E_{ii} + E_{jj})]$
x_i	atomic fraction of atom i
z	number of nearest neighbor atoms
ε	Wagnerian interaction parameter, Tables IV and V
γ	Raoultian activity coefficient
λ_i	absolute activity of component i
Ξ	grand partition function (GPF)
ρ	Lupisian interaction parameter, Tables IV and V.

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REFERENCES

1. S. Srikanth and K.T. Jacob: *Metall. Trans. B*, 1988, vol. 19B, pp. 269-75.
2. C.H.P. Lupis and J.F. Elliott: *Acta Metall.*, 1966, vol. 14, pp. 529-38.
3. R. Fowler and E.A. Guggenheim: *Statistical Thermodynamics*, Cambridge University Press, London, 1965.
4. M. Nagamori: *Metall. Review of MMIJ*, 1986, vol. 3, no. 3, pp. 26-41.
5. C. Wagner: *Thermodynamics of Alloys*, Addison-Wesley Pub. Co., Reading, MA, 1952, p. 51.
6. M.Z. Sukiennik and R.W. Olesinski: *Metall. Trans. B*, 1984, vol. 15B, pp. 677-80.

Authors' Reply

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Nagamori's discussion of our paper on the thermodynamic consistency of the interaction parameter formalism[1] is based on an incomplete understanding of several aspects of our analysis. Further, Nagamori restricts his attention to ternary regular solutions, whereas the thrust of our paper is on the representation of thermodynamic data for dilute multicomponent solutions in general. Most multicomponent solutions encountered in metal processing are nonregular, although Darken's quadratic formalism[2,3] may be obeyed in the terminal regions, especially in weakly interacting systems.

Thermodynamic treatment of ternary and higher order regular solutions is well established in the literature[4,5,6] and does not require reformulation on the basis of the grand partition function. When the integral mixing properties are defined, the partials derived therefrom obviously satisfy Gibbs-Duhem equation. This does not require further demonstration for ternary regular solutions. The interaction parameter representation was formulated for partial properties; therefore, its thermodynamic consistency has to be explored with respect to both the relations of Maxwell and Gibbs-Duhem, as done in our paper.