Communication

Correct Expressions of Enthalpy of Mixing and Excess Entropy from MIVM and Their Simplified Forms

DONG-PING TAO

In this work, the author pointed out that empirically to compare the molecular interaction volume model (MIVM) with thermodynamic definition of excess Gibbs energy would result in the incorrect expressions of enthalpy of mixing and excess entropy. The correct expressions of molar and partial molar enthalpies of mixing and excess entropies from the MIVM are consistent thermodynamically and are suggested for replacing their past incorrect ones. The simplification of $Z_i = Z = 10$ is verified to be feasible by the average errors of fitting in the binary liquid alloys M-P (M = Cr, Fe, and Mn) and of predicting in the ternary liquid alloys Fe-Cr-P and Fe-Mn-P by using two coordination numbers of phosphorus $Z_P = 3.04$ and $Z_P = 8.96$. Further, their simplified forms are proposed for predicting easily thermodynamic properties of a multicomponent liquid system and are preliminarily tested to be coordinated mutually in the binary liquid alloys Au-Cu, Cd-Zn, Ca-Zn, and Ni-Pb.

DOI: 10.1007/s11663-015-0460-5

At present, thermodynamic models still are important methods to solve problems relating to thermodynamic properties of liquid alloys and silicate melts, such as chemical interaction in Cu-Zr melts,[1] interfacial energies in the fcc Au-Ni, liquid Ga-Pb, and liquid Al-Bi,[2] mixing functions in binary silicate and aluminate melts,[3] element partitioning between plagioclase and melt,[4] and so forth. Especially, the molecular interaction volume model (MIVM)[5] has been successfully applied to some practical systems.[6–10] But in the model calculation it is often difficult to find out the coordination numbers and molar volumes of some components in liquid state, such as P, C, Ta, TiO_2, V_2O_5, Cu_2S, FeS, NaCl, $MgCl_2$, $CaSiO_3$, and so on. This would hinder application of the MIVM to many practical systems. For this reason, the author tried to simplify the MIVM reasonably. In its simplification process, however, the incorrect expressions thermodynamically were found in its molar enthalpy of mixing and excess entropy.[11–14] So it is necessary to correct them in public.

For a C-component system, the molar excess Gibbs energy G_m^E of the MIVM[5] can be expressed as

$$\frac{G_m^E}{RT} = \sum_{i=1}^{C} x_i \ln \frac{V_{mi}}{\sum_{j=1}^{C} x_j V_{mj} B_{ji}} - \frac{1}{2} \sum_{i=1}^{C} Z_i x_i \left(\frac{\sum_{j=1}^{C} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j B_{ji}} \right), \quad [1]$$

where R(J/mol K) is the gas constant, T(K) is the absolute temperature, C is the component number, x_i, V_{mi}(cm^3/mol), and Z_i are the molar fraction, molar volume, and coordination number of component i, respectively, and B_{ji} and B_{ij} are the pair potential parameters of the i–j binary system which are defined as

$$B_{ji} = \exp[-N_A(\varepsilon_{ji} - \varepsilon_{ii})/RT] \quad B_{ij} = \exp[-N_A(\varepsilon_{ij} - \varepsilon_{jj})/RT], \quad [2]$$

where ε_{ii} (J) is the i–i pair potential energy and N_A (1/mol) is the Avogadro constant. It can be seen that the temperature dependence of the MIVM is determined by Eq. [2], that is, if both $\theta_{ji} = N_A(\varepsilon_{ji} - \varepsilon_{ii})/R$ and $\theta_{ij} = N_A(\varepsilon_{ij} - \varepsilon_{jj})/R$ are constant, the binary parameters B_{ji} and B_{ij} gradually approach unity as temperature increases. It indicates that the non-ideality of solutions will diminish at high temperatures. This case of the MIVM is consistent with the tendency described by the rule of Lupis and Elliott (LE rule) which was reformulated and rationalized by Kaptay[15] (LE rule: "Real solid, liquid and gaseous solutions (and pure gases) gradually approach the state of an ideal solution (perfect gas) as temperature increases at any fixed pressure and composition."). At limited temperatures, if real solutions want to approach the state of an ideal solution, then the necessary conditions from the MIVM are as follows: all of B_{ji} are equal to a same constant and all of V_{mi} are equal to a same constant.

In Eq. [1], the first term involving molar volumes represents a contribution of entropy to the non-ideality and the second term involving coordination numbers represents a contribution of enthalpy to the non-ideality. Especially, when all of the pair potential energy are equal to a same constant or $B_{ji} = B_{ij} = 1$, Eq. [1] would

---

DONG-PING TAO, Professor, is with the Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, P.R. China. Contact e-mail: dongpingt@aliyun.com

Manuscript submitted January 11, 2015.

be reduced to the famous Flory–Huggins equation[16]: $G_{\mathrm{m}}^{\mathrm{E}} = RT\left[\sum_{i=1}^{C} x_i \ln(\phi_i/x_i)\right]$, where $\phi_i = x_i V_{\mathrm{m}i}/V_{\mathrm{m}}$ is the volume fraction of component i and $V_{\mathrm{m}} = \sum_{j=1}^{C} x_j V_{\mathrm{m}j}$ is the molar volume of the system. It means that the MIVM could be equivalent to the contribution of excess entropy of the system or $G_{\mathrm{m}}^{\mathrm{E}} = -TS_{\mathrm{m}}^{\mathrm{E}}$ under this condition. However, the incorrect expressions of molar enthalpy of mixing $\Delta H_{\mathrm{m}}^{\mathrm{M}}$ and the molar excess entropy $S_{\mathrm{m}}^{\mathrm{E}}$ from the MIVM were originated from comparing the $G_{\mathrm{m}}^{\mathrm{E}}$ of Eq. [1] with its thermodynamic definition: $G_{\mathrm{m}}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E}} - TS_{\mathrm{m}}^{\mathrm{E}} = \Delta H_{\mathrm{m}}^{\mathrm{M}} - TS_{\mathrm{m}}^{\mathrm{E}}$, that is[11–14]

$$\Delta H_{\mathrm{m}}^{\mathrm{M}} = -\frac{RT}{2}\sum_{i=1}^{C} Z_i x_i \left(\frac{\sum_{j=1}^{C} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j B_{ji}}\right) \qquad [3]$$

$$S_{\mathrm{m}}^{\mathrm{E}} = -R\sum_{i=1}^{C} x_i \ln \frac{V_{\mathrm{m}i}}{\sum_{j=1}^{C} x_j V_{\mathrm{m}j} B_{ji}}. \qquad [4]$$

Both of them cannot satisfy the thermodynamic partial derivatives of $G_{\mathrm{m}}^{\mathrm{E}}$:

$$\left(\frac{\partial (G_{\mathrm{m}}^{\mathrm{E}}/T)}{\partial T}\right)_{P,x} = -\frac{\Delta H_{\mathrm{m}}^{\mathrm{M}}}{T^2} \qquad [5]$$

$$\left(\frac{\partial G_{\mathrm{m}}^{\mathrm{E}}}{\partial T}\right)_{P,x} = -S_{\mathrm{m}}^{\mathrm{E}} \text{ or } S_{\mathrm{m}}^{\mathrm{E}} = \left(\Delta H_{\mathrm{m}}^{\mathrm{M}} - G_{\mathrm{m}}^{\mathrm{E}}\right)/T, \qquad [6]$$

where the subscripts P and x represent the pressure and composition of the system, respectively. So, substituting Eq. [1] into Eqs. [5] and [6], the correct expressions of $\Delta H_{\mathrm{m}}^{\mathrm{M}}$ and $S_{\mathrm{m}}^{\mathrm{E}}$ can be derived as follows: for the i–j binary system, its $G_{\mathrm{m}}^{\mathrm{E}}$ can be written from Eq. [1] as

$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = x_i \ln\left(\frac{V_{\mathrm{m}i}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}}\right) + x_j \ln\left(\frac{V_{\mathrm{m}j}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}}\right) - \frac{x_i x_j}{2}\left(\frac{Z_i B_{ji} \ln B_{ji}}{x_i + x_j B_{ji}} + \frac{Z_j B_{ij} \ln B_{ij}}{x_j + x_i B_{ij}}\right). \qquad [7]$$

Here assume that the Z_i and Z_j in Eq. [7] $\theta_{ji} = N_{\mathrm{A}}(\varepsilon_{ji} - \varepsilon_{ii})/R$ and $\theta_{ij} = N_{\mathrm{A}}(\varepsilon_{ij} - \varepsilon_{jj})/R$ in Eq. [2] are independent of temperature, and one can obtain the partial derivatives $(\partial B_{ji}/\partial T)_P = -(1/T)B_{ji} \ln B_{ji}$ and $(\partial B_{ij}/\partial T)_P = -(1/T)B_{ij} \ln B_{ij}$. Then, substituting Eq. [7] into Eq. [5], the $\Delta H_{\mathrm{m}}^{\mathrm{M}}$ of the 1–2 binary system can be derived as

$$\begin{aligned}\frac{\Delta H_{\mathrm{m}}^{\mathrm{M}}}{RT} &= \frac{1}{2}\left\{Z_1 x_1\left[\left(\frac{x_2 B_{21} \ln B_{21}}{x_1 + x_2 B_{21}}\right)^2 - \frac{(1+\ln B_{21}) x_2 B_{21} \ln B_{21}}{x_1 + x_2 B_{21}}\right] + Z_2 x_2\left[\left(\frac{x_1 B_{12} \ln B_{12}}{x_1 B_{12} + x_2}\right)^2 - \frac{(1+\ln B_{12}) x_1 B_{12} \ln B_{12}}{x_1 B_{12} + x_2}\right]\right\} \\ &\quad - \frac{x_1 x_2 V_{\mathrm{m}2} B_{21} \ln B_{21}}{x_1 V_{\mathrm{m}1} + x_2 V_{\mathrm{m}2} B_{21}} - \frac{x_2 x_1 V_{\mathrm{m}1} B_{12} \ln B_{12}}{x_1 V_{\mathrm{m}1} B_{12} + x_2 V_{\mathrm{m}2}}.\end{aligned} \qquad [8]$$

Extending the binary 1–2 to the C-component system, one can obtain its $\Delta H_{\mathrm{m}}^{\mathrm{M}}$:

$$\begin{aligned}\frac{\Delta H_{\mathrm{m}}^{\mathrm{M}}}{RT} &= \frac{1}{2}\sum_{i=1}^{C} Z_i x_i \times \left[\left(\frac{\sum_{j=1}^{C} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j B_{ji}}\right)^2 - \frac{\sum_{j=1}^{C} (1+\ln B_{ji}) x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j B_{ji}}\right] \\ &\quad - \sum_{i=1}^{C} x_i \left(\frac{\sum_{j=1}^{C} x_j V_{\mathrm{m}j} B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j V_{\mathrm{m}j} B_{ji}}\right).\end{aligned} \qquad [9]$$

Similarly, the $S_{\mathrm{m}}^{\mathrm{E}}$ expressions of the 1–2 binary and C-component systems can also be derived, respectively, as

$$\begin{aligned}\frac{S_{\mathrm{m}}^{\mathrm{E}}}{RT} &= \frac{1}{2}\left\{Z_1 x_1\left[\left(\frac{x_2 B_{21} \ln B_{21}}{x_1 + x_2 B_{21}}\right)^2 - \frac{x_2 B_{21} (\ln B_{21})^2}{x_1 + x_2 B_{21}}\right] + Z_2 x_2\left[\left(\frac{x_1 B_{12} \ln B_{12}}{x_1 B_{12} + x_2}\right)^2 - \frac{x_1 B_{12} (\ln B_{12})^2}{x_1 B_{12} + x_2}\right]\right\}, \\ &\quad - x_1\left(\ln\frac{V_{\mathrm{m}1}}{x_1 V_{\mathrm{m}1} + x_2 V_{\mathrm{m}2} B_{21}} + \frac{x_2 V_{\mathrm{m}2} B_{21} \ln B_{21}}{x_1 V_{\mathrm{m}1} + x_2 V_{\mathrm{m}2} B_{21}}\right) \\ &\quad - x_2\left(\ln\frac{V_{\mathrm{m}2}}{x_1 V_{\mathrm{m}1} B_{12} + x_2 V_{\mathrm{m}2}} + \frac{x_1 V_{\mathrm{m}1} B_{12} \ln B_{12}}{x_1 V_{\mathrm{m}1} B_{12} + x_2 V_{\mathrm{m}2}}\right)\end{aligned} \qquad [10]$$

$$\begin{aligned}\frac{S_{\mathrm{m}}^{\mathrm{E}}}{R} &= \frac{1}{2}\sum_{i=1}^{C} Z_i x_i \left[\left(\frac{\sum_{j=1}^{C} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j B_{ji}}\right)^2 - \frac{\sum_{j=1}^{C} x_j B_{ji} (\ln B_{ji})^2}{\sum_{j=1}^{C} x_j B_{ji}}\right] \\ &\quad - \sum_{i=1}^{C} x_i \left(\ln\frac{V_{\mathrm{m}i}}{\sum_{j=1}^{C} x_j V_{\mathrm{m}j} B_{ji}} + \frac{\sum_{j=1}^{C} x_j V_{\mathrm{m}j} B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j V_{\mathrm{m}j} B_{ji}}\right).\end{aligned} \qquad [11]$$

Then, based on the classical thermodynamic relations between partial molar quantity and molar quantity

$$\frac{\overline{G}_i^{\mathrm{E}}}{RT} = \ln\gamma_i = \frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} + \left(\frac{\partial(G_{\mathrm{m}}^{\mathrm{E}}/RT)}{\partial x_i}\right)_{T,P,x[i,C]} - \sum_{l=1}^{C-1} x_l \left(\frac{\partial(G_{\mathrm{m}}^{\mathrm{E}}/RT)}{\partial x_l}\right)_{T,P,x[l,C]} \qquad [12]$$

$$\frac{\Delta\overline{H}_i}{RT} = \frac{\Delta H_{\mathrm{m}}^{\mathrm{M}}}{RT} + \left(\frac{\partial(\Delta H_{\mathrm{m}}^{\mathrm{M}}/RT)}{\partial x_i}\right)_{T,P,x[i,C]} - \sum_{l=1}^{C-1} x_l \left(\frac{\partial(\Delta H_{\mathrm{m}}^{\mathrm{M}}/RT)}{\partial x_l}\right)_{T,P,x[l,C]}, \qquad [13]$$

where $\overline{G}_i^{\mathrm{E}}$ and $\Delta\overline{H}_i$ are the partial molar excess Gibbs energy and the partial molar enthalpy of mixing of component i, respectively, the subscript symbol $x[l, C]$ represents that x_l and x_C are two variables of the partial derivative and $x_C = 1 - \sum_{l=1}^{C-1} x_l$ is a subordinate variable which needs special attention in the deducing processes of the partial derivatives in Eqs. [12] and [13].

Substituting Eq. [7] into Eq. [12], the expressions of $\ln\gamma_i$ for the 1–2 binary system can be, respectively, derived as

$$\ln\gamma_1 = 1 + \ln\frac{V_{\mathrm{m}1}}{x_1V_{\mathrm{m}1} + x_2V_{\mathrm{m}2}B_{21}} - \frac{x_1V_{\mathrm{m}1}}{x_1V_{\mathrm{m}1} + x_2V_{\mathrm{m}2}B_{21}} - \frac{x_2V_{\mathrm{m}1}B_{12}}{x_1V_{\mathrm{m}1}B_{12} + x_2V_{\mathrm{m}2}} - \frac{x_2^2}{2}\left(\frac{Z_1B_{21}^2\ln B_{21}}{(x_1 + x_2B_{21})^2} + \frac{Z_2B_{12}\ln B_{12}}{(x_1B_{12} + x_2)^2}\right), \qquad [14]$$

$$\ln\gamma_2 = 1 + \ln\frac{V_{\mathrm{m}2}}{x_1V_{\mathrm{m}1}B_{12} + x_2V_{\mathrm{m}2}} - \frac{x_1V_{\mathrm{m}2}B_{21}}{x_1V_{\mathrm{m}1} + x_2V_{\mathrm{m}2}B_{21}} - \frac{x_2V_{\mathrm{m}2}}{x_1V_{\mathrm{m}1}B_{12} + x_2V_{\mathrm{m}2}} - \frac{x_1^2}{2}\left(\frac{Z_2B_{12}^2\ln B_{12}}{(x_1B_{12} + x_2)^2} + \frac{Z_1B_{21}\ln B_{21}}{(x_1 + x_2B_{21})^2}\right). \qquad [15]$$

Both Eqs. [14] and [15] are consistent with the Gibbs–Duhem equation $x_1d\ln\gamma_1 + x_2d\ln\gamma_2 = 0$.

Extending the binary 1–2 to the C-component system, one can obtain the $\ln\gamma_i$ of component i:

$$\ln\gamma_i = 1 + \ln\frac{V_{\mathrm{m}i}}{\sum_{j=1}^{C} x_jV_{\mathrm{m}j}B_{ji}} - \sum_{j=1}^{C}\frac{x_jV_{\mathrm{m}i}B_{ij}}{\sum_{t=1}^{C} x_tV_{\mathrm{m}t}B_{tj}} - \frac{1}{2}\left[\frac{Z_i\sum_{j=1}^{C} x_jB_{ji}\ln B_{ji}}{\sum_{t=1}^{C} x_tB_{ti}} + \sum_{j=1}^{C}\frac{Z_jx_jB_{ij}}{\sum_{t=1}^{C} x_tB_{tj}}\left(\ln B_{ij} - \frac{\sum_{t=1}^{C} x_tB_{tj}\ln B_{tj}}{\sum_{t=1}^{C} x_tB_{tj}}\right)\right]. \qquad [16]$$

And substituting Eq. [8] into Eq. [13], the expressions of $\Delta\overline{H}_i/RT$ for the 1–2 binary system can be, respectively, derived as

$$\begin{aligned}\frac{\Delta\overline{H}_1}{RT} = {} & \frac{Z_1}{2}\left[\left(\frac{x_2B_{21}\ln B_{21}}{x_1 + x_2B_{21}}\right)^2 - \frac{(1 + \ln B_{21})x_2B_{21}\ln B_{21}}{x_1 + x_2B_{21}}\right] - \frac{x_2V_{\mathrm{m}2}B_{21}\ln B_{21}}{x_1V_{\mathrm{m}1} + x_2V_{\mathrm{m}2}B_{21}} \\ & + \frac{Z_1x_1x_2}{2}\left[\begin{array}{l} -\dfrac{2x_2(B_{21}\ln B_{21})^2}{(x_1 + x_2B_{21})^2} - \dfrac{2(1 - B_{21})(x_2B_{21}\ln B_{21})^2}{(x_1 + x_2B_{21})^3} \\ + \dfrac{(1 + \ln B_{21})B_{21}\ln B_{21}}{x_1 + x_2B_{21}} + \dfrac{(1 - B_{21})(1 + \ln B_{21})x_2B_{21}\ln B_{21}}{(x_1 + x_2B_{21})^2} \end{array}\right] \\ & + \frac{Z_2x_2^2}{2}\left[\begin{array}{l} \dfrac{2x_1(B_{12}\ln B_{12})^2}{(x_1B_{12} + x_2)^2} - \dfrac{2(B_{12} - 1)(x_1B_{12}\ln B_{12})^2}{(x_1B_{12} + x_2)^3} \\ - \dfrac{(1 + \ln B_{12})B_{12}\ln B_{12}}{x_1B_{12} + x_2} + \dfrac{(B_{12} - 1)(1 + \ln B_{12})x_1B_{12}\ln B_{12}}{(x_1B_{12} + x_2)^2} \end{array}\right] \\ & + x_1x_2\left[\frac{V_{\mathrm{m}2}B_{21}\ln B_{21}}{x_1V_{\mathrm{m}1} + x_2V_{\mathrm{m}2}B_{21}} + \frac{(V_{\mathrm{m}1} - V_{\mathrm{m}2}B_{21})x_2V_{\mathrm{m}2}B_{21}\ln B_{21}}{(x_1V_{\mathrm{m}1} + x_2V_{\mathrm{m}2}B_{21})^2}\right] \\ & - x_2^2\left[\frac{V_{\mathrm{m}1}B_{12}\ln B_{12}}{x_1V_{\mathrm{m}1}B_{12} + x_2V_{\mathrm{m}2}} - \frac{(V_{\mathrm{m}1}B_{12} - V_{\mathrm{m}2})x_1V_{\mathrm{m}1}B_{12}\ln B_{12}}{(x_1V_{\mathrm{m}1}B_{12} + x_2V_{\mathrm{m}2})^2}\right],\end{aligned} \qquad [17]$$

$$
\begin{aligned}
\frac{\Delta\overline{H}_2}{RT} = {} & \frac{Z_2}{2}\left[\left(\frac{x_1B_{12}\ln B_{12}}{x_1B_{12}+x_2}\right)^2-\frac{(1+\ln B_{12})x_1B_{12}\ln B_{12}}{x_1B_{12}+x_2}\right]-\frac{x_1V_{\mathrm{m}1}B_{12}\ln B_{12}}{x_1V_{\mathrm{m}1}B_{12}+x_2V_{\mathrm{m}2}} \\
& +\frac{Z_1x_1^2}{2}\left[\frac{2x_2(B_{21}\ln B_{21})^2}{(x_1+x_2B_{21})^2}-\frac{2(B_{21}-1)(x_2B_{21}\ln B_{21})^2}{(x_1+x_2B_{21})^3}-\frac{(1+\ln B_{21})B_{21}\ln B_{21}}{x_1+x_2B_{21}}+\frac{(B_{21}-1)(1+\ln B_{21})x_2B_{21}\ln B_{21}}{(x_1+x_2B_{21})^2}\right] \\
& +\frac{Z_2x_1x_2}{2}\left[\begin{array}{l} -\dfrac{2x_1(B_{12}\ln B_{12})^2}{(x_1B_{12}+x_2)^2}+\dfrac{2(B_{12}-1)(x_1B_{12}\ln B_{12})^2}{(x_1B_{12}+x_2)^3} \\ +\dfrac{(1+\ln B_{12})B_{12}\ln B_{12}}{x_1B_{12}+x_2}-\dfrac{(B_{12}-1)(1+\ln B_{12})x_1B_{12}\ln B_{12}}{(x_1B_{12}+x_2)^2} \end{array}\right]. \\
& +x_1^2\left[\frac{V_{\mathrm{m}2}B_{21}\ln B_{21}}{x_1V_{\mathrm{m}1}+x_2V_{\mathrm{m}2}B_{21}}-\frac{(V_{\mathrm{m}2}B_{21}-V_{\mathrm{m}1})x_2V_{\mathrm{m}2}B_{21}\ln B_{21}}{(x_1V_{\mathrm{m}1}+x_2V_{\mathrm{m}2}B_{21})^2}\right] \\
& +x_1x_2\left[\frac{V_{\mathrm{m}1}B_{12}\ln B_{12}}{x_1V_{\mathrm{m}1}B_{12}+x_2V_{\mathrm{m}2}}+\frac{(V_{\mathrm{m}2}-V_{\mathrm{m}1}B_{12})x_1V_{\mathrm{m}1}B_{12}\ln B_{12}}{(x_1V_{\mathrm{m}1}B_{12}+x_2V_{\mathrm{m}2})^2}\right]
\end{aligned}
\tag{18}
$$

Both Eqs. [17] and [18] are consistent with the Gibbs–Duhem equation $x_1d\Delta\overline{H}_1+x_2d\Delta\overline{H}_2=0$.

Similarly, extending the binary 1–2 to the C-component system, one can obtain the $\Delta\overline{H}_i/RT$ of component i:

$$
\begin{aligned}
\frac{\Delta\overline{H}_i}{RT} = {} & \frac{Z_i}{2}\left[\left(\frac{\sum_{j=1}^{C}x_jB_{ji}\ln B_{ji}}{\sum_{j=1}^{C}x_jB_{ji}}\right)^2-\frac{\sum_{j=1}^{C}(1+\ln B_{ji})x_jB_{ji}\ln B_{ji}}{\sum_{j=1}^{C}x_jB_{ji}}\right]-\frac{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{ji}\ln B_{ji}}{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{ji}} \\
& +\frac{1}{2}\sum_{t=1}^{C}Z_tx_t\left[\begin{array}{l} \dfrac{2\sum_{j=1}^{C}x_jB_{jt}\ln B_{jt}}{\left(\sum_{j=1}^{C}x_jB_{jt}\right)^2}\left(B_{it}\ln B_{it}-\sum_{j=1}^{C}x_jB_{jt}\ln B_{jt}-\dfrac{\left(B_{it}-\sum_{j=1}^{C}x_jB_{jt}\right)\sum_{j=1}^{C}x_jB_{jt}\ln B_{jt}}{\sum_{j=1}^{C}x_jB_{jt}}\right) \\ -\dfrac{(1+\ln B_{it})B_{it}\ln B_{it}-\sum_{j=1}^{C}x_j(1+\ln B_{jt})B_{jt}\ln B_{jt}}{\left(\sum_{j=1}^{C}x_jB_{jt}\right)^2}+\dfrac{\left(B_{it}-\sum_{j=1}^{C}x_jB_{jt}\right)\sum_{j=1}^{C}(1+\ln B_{jt})x_jB_{jt}\ln B_{jt}}{\left(\sum_{j=1}^{C}x_jB_{jt}\right)^3} \end{array}\right]. \\
& -\sum_{t=1}^{C}x_t\left(\frac{V_{\mathrm{m}i}B_{it}\ln B_{it}-\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}\ln B_{jt}}{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}}-\frac{\left(V_{\mathrm{m}i}B_{it}-\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}\right)\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}\ln B_{jt}}{\left(\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}\right)^2}\right)
\end{aligned}
\tag{19}
$$

Here, note that the partial derivative in Eq. [13] for the binary 1–2 system is

$$\left(\frac{\partial(\Delta H_{\mathrm{m}}^{\mathrm{M}}/RT)}{\partial x_1}\right)_{T,P,x[1,2]} = \frac{1}{2}\left\{\begin{array}{l} Z_1\left[\left(\frac{x_2B_{21}\ln B_{21}}{x_1+x_2B_{21}}\right)^2-\frac{(1+\ln B_{21})x_2B_{21}\ln B_{21}}{x_1+x_2B_{21}}\right] \\ -Z_2\left[\left(\frac{x_1B_{12}\ln B_{12}}{x_1B_{12}+x_2}\right)^2-\frac{(1+\ln B_{12})x_1B_{12}\ln B_{12}}{x_1B_{12}+x_2}\right] \\ +Z_1x_1\left[-\frac{2x_2(B_{21}\ln B_{21})^2}{(x_1+x_2B_{21})^3}+\frac{(1+\ln B_{21})B_{21}\ln B_{21}}{(x_1+x_2B_{21})^2}\right] \\ +Z_2x_2\left[\frac{2x_1(B_{12}\ln B_{12})^2}{(x_1B_{12}+x_2)^3}+\frac{(1+\ln B_{12})B_{12}\ln B_{12}}{(x_1B_{12}+x_2)^2}\right] \end{array}\right\}$$
$$-\left(\frac{x_2V_{\mathrm{m}2}B_{21}\ln B_{21}}{x_1V_{\mathrm{m}1}+x_2V_{\mathrm{m}2}B_{21}}-\frac{x_1V_{\mathrm{m}1}B_{12}\ln B_{12}}{x_1V_{\mathrm{m}1}B_{12}+x_2V_{\mathrm{m}2}}\right)$$
$$+x_1\left[\frac{V_{\mathrm{m}2}B_{21}\ln B_{21}}{x_1V_{\mathrm{m}1}+x_2V_{\mathrm{m}2}B_{21}}+\frac{(V_{\mathrm{m}1}-V_{\mathrm{m}2}B_{21})x_2V_{\mathrm{m}2}B_{21}\ln B_{21}}{(x_1V_{\mathrm{m}1}+x_2V_{\mathrm{m}2}B_{21})^2}\right]$$
$$-x_2\left[\frac{V_{\mathrm{m}1}B_{12}\ln B_{12}}{x_1V_{\mathrm{m}1}B_{12}+x_2V_{\mathrm{m}2}}-\frac{(V_{\mathrm{m}1}B_{12}-V_{\mathrm{m}2})x_1V_{\mathrm{m}1}B_{12}\ln B_{12}}{(x_1V_{\mathrm{m}1}B_{12}+x_2V_{\mathrm{m}2})^2}\right]. \qquad [20]$$

Similarly, extending the binary 1–2 to the *C*-component system, one can obtain the first partial derivative of component *i* in Eq. [13] as follows:

$$\left(\frac{\partial(\Delta H_{\mathrm{m}}^{\mathrm{M}}/RT)}{\partial x_i}\right)_{T,P,x[i,C]}$$
$$= \frac{1}{2}\left\{\begin{array}{l} Z_i\left[\left(\frac{\sum_{j=1}^{C}x_jB_{ji}\ln B_{ji}}{\sum_{j=1}^{C}x_jB_{ji}}\right)^2-\frac{\sum_{j=1}^{C}(1+\ln B_{ji})x_jB_{ji}\ln B_{ji}}{\sum_{j=1}^{C}x_jB_{ji}}\right]-Z_C\left[\left(\frac{\sum_{j=1}^{C}x_jB_{jC}\ln B_{jC}}{\sum_{j=1}^{C}x_jB_{jC}}\right)^2-\frac{\sum_{j=1}^{C}(1+\ln B_{jC})x_jB_{jC}\ln B_{jC}}{\sum_{j=1}^{C}x_jB_{jC}}\right] \\ +\sum_{t=1}^{C}Z_tx_t\left[\frac{2\sum_{j=1}^{C}x_jB_{jt}\ln B_{jt}}{\left(\sum_{j=1}^{C}x_jB_{jt}\right)^2}\left(B_{it}\ln B_{it}-B_{Ct}\ln B_{Ct}-\frac{(B_{it}-B_{Ct})\sum_{j=1}^{C}x_jB_{jt}\ln B_{jt}}{\sum_{j=1}^{C}x_jB_{jt}}\right)-\frac{(1+\ln B_{it})B_{it}\ln B_{it}-(1+\ln B_{Ct})B_{Ct}\ln B_{Ct}}{\left(\sum_{j=1}^{C}x_jB_{jt}\right)^2}+\frac{(B_{it}-B_{Ct})\sum_{j=1}^{C}(1+\ln B_{jt})x_jB_{jt}\ln B_{jt}}{\left(\sum_{j=1}^{C}x_jB_{jt}\right)^3}\right] \end{array}\right\}.$$
$$-\left(\frac{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{ji}\ln B_{ji}}{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{ji}}-\frac{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jC}\ln B_{jC}}{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jC}}\right)$$
$$-\sum_{t=1}^{C}x_t\left(\frac{V_{\mathrm{m}i}B_{it}\ln B_{it}-V_{\mathrm{m}C}B_{Ct}\ln B_{Ct}}{\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}}-\frac{(V_{\mathrm{m}i}B_{it}-V_{\mathrm{m}C}B_{Ct})\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}\ln B_{jt}}{\left(\sum_{j=1}^{C}x_jV_{\mathrm{m}j}B_{jt}\right)^2}\right) \qquad [21]$$

And the second partial derivative $\left(\frac{\partial(\Delta H_{\mathrm{m}}^{\mathrm{M}}/RT)}{\partial x_l}\right)_{T,P,x[l,C]}$ is same as in Eq. [21] in which the subscript *i* is replaced by the subscript *l* correspondingly. It can be seen that Eqs. [17] through [21] are complex, especially the last one, but they are correct indeed for the MIVM thermodynamically.

Similarly, the partial molar excess entropy of the MIVM can be also derived from Eq. [22]:

$$\overline{S}_i^{\mathrm{E}} = S_{\mathrm{m}}^{\mathrm{E}} + \left(\frac{\partial S_{\mathrm{m}}^{\mathrm{E}}}{\partial x_i}\right)_{T,P,x[i,C]} - \sum_{l=1}^{C-1} x_l \left(\frac{\partial S_{\mathrm{m}}^{\mathrm{E}}}{\partial x_l}\right)_{T,P,x[l,C]} \qquad [22]$$

$$\text{or } \overline{S}_i^{\mathrm{E}} = \frac{\Delta\overline{H}_i - \overline{G}_i^{E}}{T},$$

where $\overline{G}_i^{\mathrm{E}} = RT\ln\gamma_i$ can be obtained from Eq. [16].

Next, the author tries to simplify the MIVM reasonably. In a recent work,[11] the author used two different coordination numbers of phosphorus, $Z_{\mathrm{P}} = 3.04$ from Eq. [24] in Reference 11 and $Z_{\mathrm{P}} = 8.96$ from Eq. [26] in Reference 11, to examine how they affect the fitting accuracy of component activities in the M-P (M = Cr, Fe, and Mn) alloys[17–19] and the predicted accuracy of component activities in the Fe-Cr-P[20] in the temperature range from 1471 K to 1817 K (1198 °C to 1544 °C) and Fe-Mn-P[21] from 1302 K to 1678 K (1029 °C to 1405 °C). The results are listed in Tables I and II.

In Table I, it can be seen that the binary parameters B_{ji} and B_{ij} have different values for $Z_{\mathrm{P}} = 3.04$ and $Z_{\mathrm{P}} = 8.96$ in the same binary alloy, but the fitting errors of two component activities are close each other in the M-P (M = Cr, Fe and Mn) alloys, and the errors for $Z_{\mathrm{P}} = 8.96$ are a little smaller than those for $Z_{\mathrm{P}} = 3.04$. Here note that $S_i = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{a_{i,\mathrm{exp}} - a_{i,\mathrm{pre}}}{a_{i,\mathrm{exp}}}\right|$ is the average relative error, where $a_{i,\mathrm{exp}}$ and $a_{\mathrm{i,pre}}$ are the experimental data and the predicted values of activity of component i, respectively, and n is the number of experimental data; the binary parameters of the Ti-P at 1998 K (1725 °C) and the V-P at 1973 K (1700 °C) are supplement to their data listed in Table II in Reference 11.

In Table II, it can be seen that the average errors for $Z_{\mathrm{P}} = 3.04$ and $Z_{\mathrm{P}} = 8.96$ are close to each other by comparing the predicted values of the MIVM with the experimental data of all component activities in the ternary liquid alloys Fe-Cr-P and Fe-Mn-P, and the errors for $Z_{\mathrm{P}} = 8.96$ are a little smaller than those for $Z_{\mathrm{P}} = 3.04$ in general, which are similar to the binary M-P (M = Cr, Fe, and Mn) alloys. Here, it should be noticed that in the Fe-Mn-P, although the errors of 59 and 44 pct for P seem to be large, they are acceptable by means of comparing them with the error of 48 pct for P calculated[11] from the unified interaction parameter formalism (UIPF)[22,23] at current knowledge level.

The above results indicate that the difference of component coordination numbers, such as that (5.92) of phosphorus coordination numbers 3.04 and 8.96 in Tables I and II, would almost not affect on the accuracies of fitting and predicting component activities. It is inferred that the differences of coordination numbers in the MIVM could be neglected.

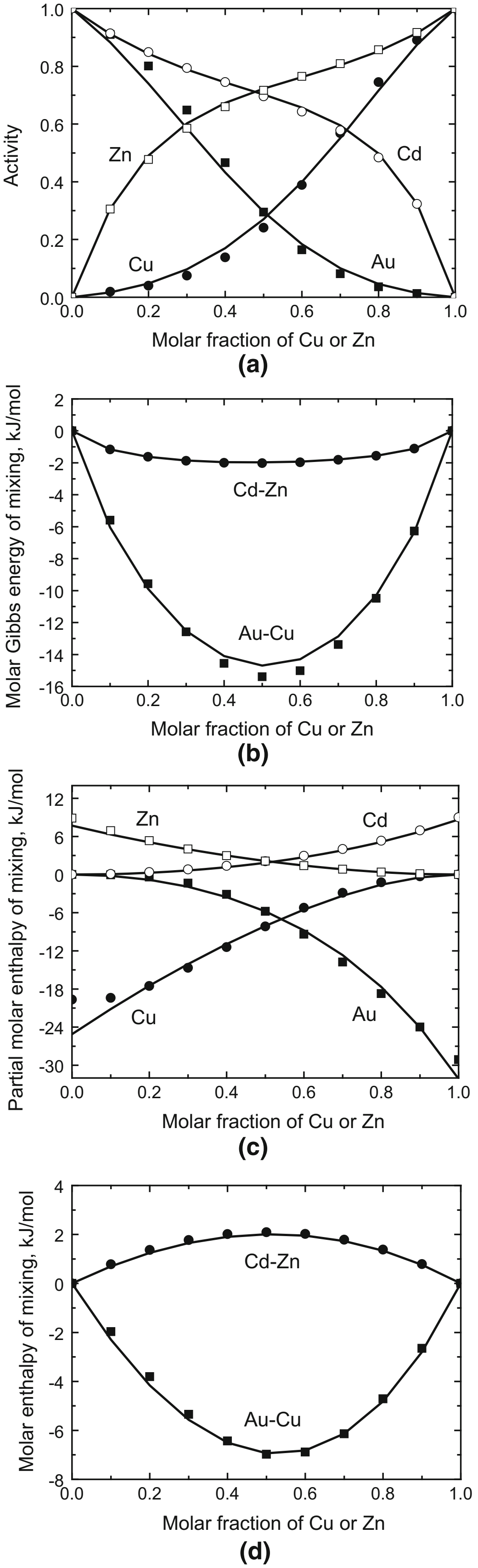
In fact, the coordination numbers of molecules have the same constant in the lattice theory of solutions and may be a value between 6 and 12 depending on the type of packing, *i.e.*, the way in which the molecules are

Table I. Fitting Errors and Binary Parameters in Binary Liquid Alloys Containing Phosphorus for $Z_{\mathrm{P}} = 3.04$ and $Z_{\mathrm{P}} = 8.96$

$i-j$	T [K (°C)]	B_{ji}	B_{ij}	θ_{ji} (K)	θ_{ij} (K)	S_i (Pct)	S_j (Pct)
$Z_{\mathrm{P}} = 3.04$							
Cr-P[17]	1800 (1527)	1.10	24.5	171.6	5758	1.4	5.1
Fe-P[18]	1809 (1536)	1.3	10	474.6	4165	8.4	46
Mn-P[19]	1600 (1327)	1.6	12.5	752.0	4041	3.5	18
Ti-P	1998 (1725)	1.74	4.988	1107	3211	—	—
V-P	1973 (1700)	1.609	3.177	938.6	2281	—	—
$Z_{\mathrm{P}} = 8.96$							
Cr-P[17]	1800 (1527)	0.95	5.33	−92.33	3012	1.1	2.2
Fe-P[18]	1809 (1536)	1.2	3.4	329.8	2214	7.5	40
Mn-P[19]	1600 (1327)	1.43	3.95	572.3	2198	2.3	10
Ti-P	1998 (1725)	1.698	2.257	1058	1626	—	—
V-P	1973 (1700)	1.383	2.474	639.8	1787	—	—

Table II. Average Errors Between Predicted Values of MIVM and Experimental Data of Component Activities in Ternary Liquid Alloys Fe-Cr-P[20] and Fe-Mn-P[21] for $Z_{\mathrm{P}} = 3.04$ and $Z_{\mathrm{P}} = 8.96$

				Average Error (Pct)	
Ternary Liquid Alloy	Temperature [K (°C)]	Component	Data	$Z_{\mathrm{P}} = 3.04$	$Z_{\mathrm{P}} = 8.96$
Fe-Cr-P[20]	1471 to 1817 (1198 to 1544)	Fe	28	5.6	5.1
		Cr	28	14	9.0
		P	28	20	18
Fe-Mn-P[21]	1302 to 1678 (1029 to 1405)	Fe	22	18	18
		Mn	22	17	19
		P	22	59	44



◀Fig. 1—In the Au-Cu at 1400 K (1127 °C) and Cd-Zn at 700 K (427 °C), comparison of fitting curves (solid line) with literature data (black or empty square and circle)[24] of (*a*) activity, (*b*) molar Gibbs energy of mixing, (*c*) partial molar enthalpy of mixing, and (*d*) molar enthalpy of mixing, standard states: pure liquid metals.

arranged in three-dimensional space; empirically, for typical liquids in ordinary conditions, Z is close to 10.[16] Therefore, one can suppose $Z_i = Z_j = Z = 10$ in the MIVM for simplifying its calculation.

On the other hand, since the difference between liquid and solid densities of a substance is often small, one can suppose that the molar volume $V_{\mathrm{m}i}$ of component i in liquid state can be replaced by its molar volume V_i in solid state.

Consequently, the molar excess Gibbs energy of the MIVM in Eq. [1] can be simplified as

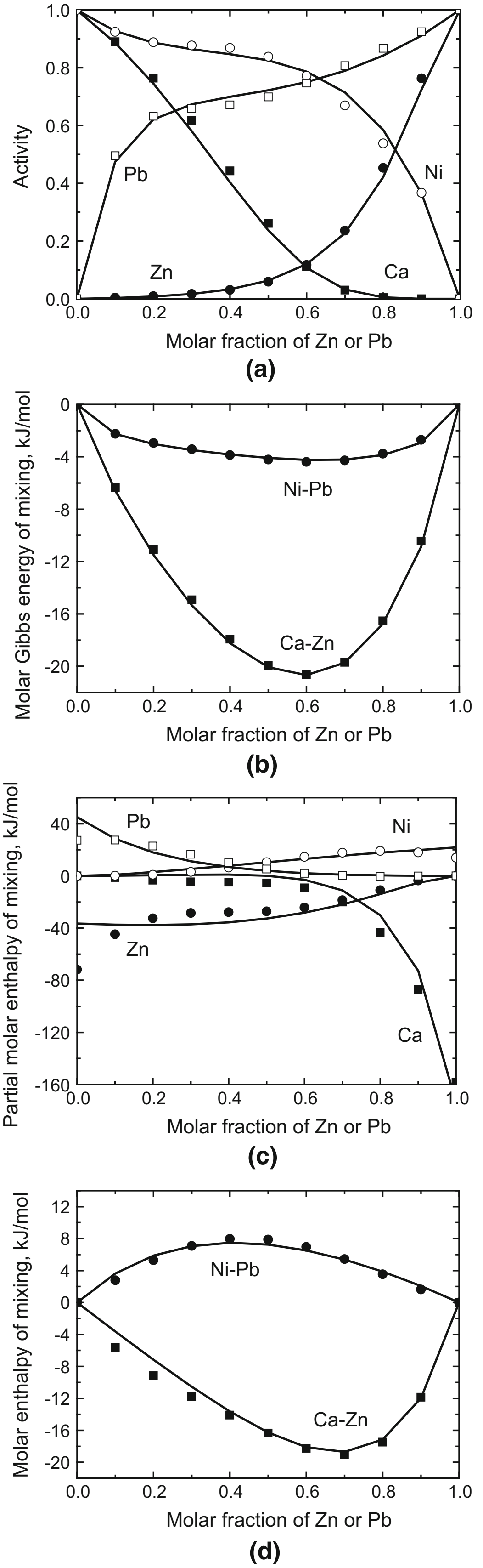
$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = \sum_{i=1}^{C} x_i \ln \frac{V_i}{\sum_{j=1}^{C} x_j V_j B_{ji}} - \frac{Z}{2} \sum_{i=1}^{C} x_i \left(\frac{\sum_{j=1}^{C} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j B_{ji}} \right) \qquad [23a]$$

$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = \sum_{i=1}^{C} x_i \ln \frac{V_i}{\sum_{j=1}^{C} x_j V_j B_{ji}} - 5 \sum_{i=1}^{C} x_i \left(\frac{\sum_{j=1}^{C} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{C} x_j B_{ji}} \right). \qquad [23b]$$

And the other expressions of the MIVM, such as Eqs. [16] and [19], can be also simplified as the similar forms in Eqs. [23a] and [23b]. It can be seen that Eq. [23b] does not explicitly involve the coordination number of pure component and so it is more convenient for use than before.

Now, let us use the simplified form of the MIVM to test the consistency of Eqs. [7], [8], [17], and [18]. Let $Z_i = Z_j = Z = 10$, $V_{\mathrm{m}i} = V_i$, and $V_{\mathrm{m}j} = V_j$ and choose the 4 binary liquid alloys Au-Cu at 1400 K (1127 °C), Cd-Zn at 700 K (427 °C), Ca-Zn at 1150 K (877 °C), and Ni-Pb at 1900 K (1627 °C)[24], which exhibit negative or positive deviation from ideality. As shown in Figures 1 and 2 and Table III, it can be seen that the fitting curves of molar quantities $\Delta G_{\mathrm{m}}^{\mathrm{M}}$ and $\Delta H_{\mathrm{m}}^{\mathrm{M}}$ are in good agreement with the literature data[24] and the former is better than the later. The average errors of the partial molar enthalpies of mixing, 94 pct for $\Delta\overline{H}_i$ and 43 pct for $\Delta\overline{H}_j$, are larger than those of the activities, 5.6 pct for a_i and 5.9 pct for a_j. But the fitting curves of $\Delta\overline{H}_i$ and $\Delta\overline{H}_j$ may be still in reasonable agreement with the literature data.[24]

The results preliminarily indicate that the correct expressions of the MIVM are mutually coordinated with the same binary parameters B_{ji} and B_{ij} in the four binary



◀Fig. 2—In the Ca-Zn at 1150 K (877 °C) and Ni-Pb at 1900 K (1627 °C), comparison of fitting curves (solid line) with literature data (black or empty square and circle)[24] of (*a*) activity, (*b*) molar Gibbs energy of mixing, (*c*) partial molar enthalpy of mixing, and (*d*) molar enthalpy of mixing, standard states: pure liquid metals.

Table III. Fitting Errors of Thermodynamic Properties and Parameters in Binary Liquid Alloys Au-Cu at 1400 K (1127 °C), Cd-Zn at 700 K (427 °C), Ca-Zn at 1150 K (877 °C), and Ni-Pb at 1900 K (1627 °C)[24]

Binary i–j	B_{ji}	B_{ij}	Z_i	Z_j	V_i (cm^3/mol)	V_j (cm^3/mol)
Au-Cu	1.127	1.244	10	10	10.21	7.12
Cd-Zn	0.862	0.892	10	10	13.01	9.21
Ca-Zn	0.72	2.19	10	10	25.86	9.21
Ni-Pb	0.923	0.681	10	10	6.60	18.27

Fitting Property	a_i	a_j	ΔG_m^M (J/mol)	$\Delta\overline{H}_i$ (J/mol)	$\Delta\overline{H}_j$ (J/mol)	ΔH_m^M (J/mol)
Au-Cu fitting error (pct)	11	12	3.4	79	14	4.5
Cd-Zn fitting error (pct)	1.2	1.2	1.3	13	2.7	5.4
Ca-Zn fitting error (pct)	7.6	7.9	2.0	80	24	8.6
Ni-Pb fitting error (pct)	2.7	2.5	2.8	204	130	11
Average error (pct)	5.6	5.9	2.4	94	43	7.4

alloys. Further systematic investigations are necessary because the good fittings in the case do not always appear. Inversely, some bad fittings are arising in the Al-Be at 1600 K (1327 °C), B-Nd at 3000 K (2727 °C), Ir-Rh at 2800 K (2527 °C), Co-In at 1800 K (1527 °C),[24] and so forth.

With regard to the strength and weakness of the MIVM, according to the experience of 15 years of working on its predictions of thermodynamic properties of liquid alloys and silicate melts, the author has empirically realized that its main points are as follows: (1) the smaller the fitting errors of the related binary systems are, the higher the predicted accuracies of the corresponding multicomponent systems are, but the necessary condition is that the binary experimental data are reliable indeed; (2) for the binary system exhibiting both positive and negative deviations from ideality, it is difficult to fit reasonably its two activity–composition curves from the positive to the negative experimentally; and (3) the MIVM itself does not show the effect of chemical interaction on the molar and partial molar excess Gibbs energies.

In conclusion, it would lead to those incorrect expressions to compare empirically the G_m^E of the MIVM with its thermodynamic definition $G_m^E = \Delta H_m^M - TS_m^E$, such as Eqs. [3] and [4]. Only based on the thermodynamic partial derivatives in Eqs. [5] and [6], the correct expressions of ΔH_m^M and $S_m{}^E$ as well as their partial molar enthalpy of mixing and excess entropy can be deduced from the MIVM in Eq. [1]. Their simplified forms are consistent thermodynamically and would be easily used to predict the thermodynamic properties of a multicomponent liquid system.

This work was financially supported by the National Natural Science Foundation of China under Grant No. 51464022.

REFERENCES

1. T.V. Kulikova, A.V. Majorova, K.Y. Shunyaev, and R.E. Ryltsev: *Physica B*, 2015, vols. 466–467, pp. 90–95.
2. G. Kaptay: *Acta Mater*., 2012, vol. 60, pp. 6804–14.
3. V.P. Glibin and P.L. King: *CALPHAD*, 2015, vol. 49, pp. 19–35.
4. R. Dohmen and J. Blundy: *Am. J. Sci*., 2014, vol. 314, pp. 1319–72.
5. D.P. Tao: *Thermochim. Acta*, 2000, vol. 363, pp. 105–13.
6. K. Liu, J.-J. Wu, K.-X. Wei, W.-H. Ma, K.-Q. Xie, S.-Y. Li, B. Yang, and Y.-N. Dai: *Vacuum*, 2015, vol. 114, pp. 6–12.
7. L.-X. Kong, B. Yang, B.-Q. Xu, and Y.-F. Li: *Metall. Mater. Trans. A*, 2014, vol. 45A, pp. 4405–11.
8. O.E. Awe and O.M. Oshakuade: *Thermochim. Acta*, 2014, vol. 589, pp. 47–55.
9. S. Poizeau and D.R. Sadoway: *J. Am. Chem. Soc*., 2013, vol. 135, pp. 8260–65.
10. J.M. Newhouse, S. Poizeau, H. Kim, B.L. Spatocco, and D.R. Sadoway: *Electrochim. Acta*, 2013, vol. 91, pp. 293–301.
11. D.P. Tao: *Metall. Mater. Trans. B*, 2014, vol. 45B, pp. 2232–46.
12. D.-P. Tao: *J. Kunming Univ. Sci. Technol*., 2004, vol. 29, pp. 15–22.
13. Z.-H. Zhou: A Master Dissertation, Kunming University of Science and Technology, March 2006.
14. H.W. Yang and D.P. Tao: *Metall. Mater. Trans. A*, 2008, vol. 39A, pp. 945–49.
15. G. Kaptay: *Metall. Mater. Trans. A*, 2012, vol. 43A, pp. 531–43.
16. J.M. Prausnitz, R.N. Lichtenthaler, and E.G.D. Azevedo: *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice-Hall Inc., Englewood Cliffs, NJ, 1999, pp. 236–94.
17. A.I. Zaitsev, N.E. Shelkova, A.D. Litvina, and B.M. Mogutnov: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 155–61.
18. A.I. Zaitsev, A.D. Litvina, N.E. Shelkova, and B.M. Mogutnov: *Thermochim. Acta*, 1998, vol. 314, pp. 307–15.
19. A.I. Zaitsev, N.E. Shelkova, A.D. Litvina, B.M. Mogutnov, and Z.V. Dobrokhotova: *J. Phase Equilib*., 1998, vol. 19, pp. 191–99.
20. A.I. Zaitsev, Z.V. Dobrokhotova, A.D. Litvina, and B.M. Mogutnov: *J. Chem. Soc. Faraday Trans*., 1995, vol. 91, pp. 703–12.
21. Y.E. Lee: *Metall. Trans. B*, 1986, vol. 17B, pp. 777–83.
22. A.D. Pelton and C.W. Bale: *Metall. Trans. A*, 1986, vol. 17A, pp. 1211–15.
23. C.W. Bale and A.D. Pelton: *Metall. Trans. A*, 1990, vol. 21A, pp. 1997–2002.
24. SGTE: *Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys*, New Series IV/19B, Landolt-Börnstein—Group IV Physical Chemistry, Springer-Verlag, New York, 2002.