

# A new model of thermodynamics of liquid mixtures and its application to liquid alloys

Dong Ping Tao\*

Mail Box 62-106, Department of Metallurgy, Kunming University of Science and Technology, Kunming 650093, Yunnan, PR China

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## Abstract

The basic feature of liquid molecules is non-random migration. The cells made up of the molecules are not the prison cages restraining themselves but are the carriers on which they are migrating. Based on this idea, new expressions for configurational partition function as well as the excess Gibbs energy of liquids and their mixtures have been derived from statistical thermodynamics. This has resulted in the establishment of a new thermodynamic model of liquid mixtures. The model has been verified to be quite convenient and reliable in predicting the thermodynamic properties of liquid alloys. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Thermodynamics; New model; Liquid mixtures; Liquid alloys

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## 1. Introduction

A great deal of binary data have been compiled in monographs such as Ref. [1], but multicomponent data is scattered over some journals and quite scarce because the determination of thermodynamic data of a multicomponent system needs not only the consummate skill of a researcher and excellent instruments but also the continuous financial support. Furthermore, there have just been numerous multicomponent systems in industrial processes. It was obviously unrealistic to measure all the data experimentally. Therefore, a unique economic and effective method to predict multicomponent systems from theories or from thermodynamic models which depend on less experimental data is required.

The thermodynamic models suggested so far cannot make accurate prediction for multicomponent liquid alloys over a wide range of concentration [2], e.g. the

Pelton–Flengas’s or P–F model [3] requires fitting many model parameters which have unclear physical meaning and thus its predicting ability is very limited; a linear chemical–physical theory model [4] gives a good fit to binary liquid alloys, but it is difficult to extend it to ternary systems; Fan–Zhou’s model [5] is only suitable for a dilute metals solution; Wilson’s model [6] cannot be used for liquid–liquid partial miscible systems and their model parameters lack physical understanding. The purpose of this work, therefore, is to derive new expressions of configurational partition function of liquids and their mixtures based on the basic feature of liquid molecular movements and to establish a new thermodynamic model of liquid mixtures.

## 2. The new expressions of configurational partition function of liquids and their mixtures

The new expression of configurational partition function was obtained from the physical sense

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\*Tel.: +86-0871-5116730.

of liquid molecular movements in that liquid molecules are not like gas molecules which are in continuous irregular motion and not like solid ones which are vibrating continuously at one site but are migrating non-randomly from one cell to another. In fact, the magnitude of the self-diffusion coefficient  $D$  of liquid molecules is usually  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , and the distance the molecules move per second is about  $10^{-3} \text{ cm}$  which is an estimate of  $\sqrt{Dt}$ . This distance is about  $10^5$  times the size of a molecular cell  $10^{-8} \text{ cm}$ . It can be seen that the hypothesis that liquid molecules are almost in cells all the time contradicts the basic feature of them moving at least in a time interval of seconds. This shows that the molecular cells are not the prison cages which restrain them but are the carriers in which they are migrating. According to statistical thermodynamics, therefore, the partition function of the pure matter  $i$  is

$$Q_i = \frac{Q_{pi}}{N_i! A_i^{3N_i}} \quad (1)$$

where  $A_i^{3N_i}$ ,  $N_i$  and  $Q_{pi}$  are the partition function of molecular kinetic energy, the molecular number and the configurational partition function of the pure matter  $i$ , respectively. The last term can usually be expressed as

$$Q_{pi} = \int_{V_i} \dots \int \exp\left(-\frac{E_{pi}}{kT}\right) dx_{N_i} dy_{N_i} dz_{N_i} \quad (2)$$

where  $V_i$  is the volume, and  $E_{pi}$  the potential energy. This may be chosen as

$$E_{pi} = \frac{1}{2} Z_i N_i \varepsilon_{ii} \quad (3)$$

where  $Z_i$  is the nearest molecule or first coordination number and  $\varepsilon_{ii}$  is the  $i$ - $i$  pair-potential energy. Substituting Eq. (3) into Eq. (2) and considering the basic feature of the liquid molecular motion as mentioned above, Eq. (2) can be simplified to

$$Q_{pi} = \left[ \int_{\pm\infty} \int \int \exp\left(-\frac{Z_i \varepsilon_{ii}}{2kT}\right) dx dy dz \right]^{N_i} \\ = \left(\frac{V_i}{N_i}\right)^{N_i} \exp\left(-\frac{Z_i N_i \varepsilon_{ii}}{2kT}\right) \quad (4)$$

Similarly, the partition function and the configura-

tional partition function of the pure matter  $j$  are, respectively,

$$Q_j = \frac{Q_{pj}}{N_j! A_j^{3N_j}} \quad (5)$$

$$Q_{pj} = \left(\frac{V_j}{N_j}\right)^{N_j} \exp\left(-\frac{Z_j N_j \varepsilon_{jj}}{2kT}\right) \quad (6)$$

where the symbols have the same meaning as those of the pure matter  $i$ . The partition function and the configurational partition function of a binary liquid mixture  $i$ - $j$  are, respectively,

$$Q = \frac{Q_p}{N_i! A_i^{3N_i} N_j! A_j^{3N_j}} \quad (7)$$

$$Q_p = \int_V \dots \int \exp\left(-\frac{\varepsilon_p}{kT}\right) \\ \times (dx_1 dy_1 dz_1 \dots dx_{N_i} dy_{N_i} dz_{N_i}) \\ \times (dx_1 dy_1 dz_1 \dots dx_{N_j} dy_{N_j} dz_{N_j}) \\ = \left[ \int_{\pm\infty} \int \int \exp\left(-\frac{\varepsilon_p}{kT}\right) dx_i dy_i dz_i \right]^{N_i} \\ \times \left[ \int_{\pm\infty} \int \int \exp\left(-\frac{\varepsilon_p}{kT}\right) dx_j dy_j dz_j \right]^{N_j} \\ = \left[ \int_{\pm\infty} \int \int \exp\left(-\frac{\varepsilon_p}{kT}\right) dx dy dz \right]^N \\ = \left(\frac{V}{N}\right)^N \exp\left(-\frac{N\varepsilon_p}{kT}\right) \quad (8)$$

where  $V$  and  $N$  are the volume and molecular number of the mixture, respectively, and  $\varepsilon_p$  is the mixing potential energy function of the molecules  $i$  and  $j$ .

### 3. A new expression of excess Gibbs energy of liquid mixtures

According to the relation between Gibbs energy and partition function

$$G = kT \left[ V \left( \frac{\partial \ln Q}{\partial V} \right)_T - \ln Q \right] \quad (9)$$

one can get the Gibbs energy of a binary mixture  $i$ – $j$ :

$$G = kT \left[ N - N \ln \left( \frac{V}{N} \right) + \frac{N\varepsilon_p}{kT} + \ln(N_i! A_i^{3N_i} N_j! A_j^{3N_j}) \right] \quad (10)$$

as well as the Gibbs energies of the pure matters  $i$  and  $j$ , respectively:

$$G_i = kT \left[ N_i - N_i \ln \left( \frac{V_i}{N_i} \right) + \frac{Z_i N_i \varepsilon_{ii}}{2kT} + \ln(N_i! A_i^{3N_i}) \right] \quad (11)$$

$$G_j = kT \left[ N_j - N_j \ln \left( \frac{V_j}{N_j} \right) + \frac{Z_j N_j \varepsilon_{jj}}{2kT} + \ln(N_j! A_j^{3N_j}) \right] \quad (12)$$

Thus the new expression of the excess Gibbs energy of mixture  $i$ – $j$  is

$$\begin{aligned} G^E &= \Delta G^M - \Delta G^{\text{idM}} = (G - G^\circ) - (G_i + G_j - G^\circ) \\ &= G - G_i - G_j = kT \left[ N_i \ln \left( \frac{V_i}{N_i} \right) + N_j \ln \left( \frac{V_j}{N_j} \right) \right. \\ &\quad \left. - N \ln \left( \frac{V}{N} \right) + \frac{2N\varepsilon_p - Z_i N_i \varepsilon_{ii} - Z_j N_j \varepsilon_{jj}}{2kT} \right] \\ &= RT \left[ n_i \ln \left( \frac{V_i}{x_i V} \right) + n_j \ln \left( \frac{V_j}{x_j V} \right) \right. \\ &\quad \left. + \frac{2n\varepsilon_p - Z_i n_i \varepsilon_{ii} - Z_j n_j \varepsilon_{jj}}{2kT} \right] \\ &= nRT \left[ x_i \ln \left( \frac{V_{mi}}{V_m} \right) + x_j \ln \left( \frac{V_{mj}}{V_m} \right) \right. \\ &\quad \left. + \frac{2\varepsilon_p - Z_i x_i \varepsilon_{ii} - Z_j x_j \varepsilon_{jj}}{2kT} \right] \\ &= nRT \left[ x_i \ln \left( \frac{\Phi_i}{x_i} \right) + x_j \ln \left( \frac{\Phi_j}{x_j} \right) + \frac{\Delta\varepsilon_p}{2kT} \right] \quad (13) \end{aligned}$$

where  $\Delta G^M$ ,  $\Delta G^{\text{idM}}$  and  $G^\circ$  are the real Gibbs energy of mixing, the ideal Gibbs energy of mixing and the standard Gibbs energy of mixing  $i$ – $j$ ,  $n_i$ ,  $n_j$  and  $n$  are the number of moles of  $i$  and  $j$  and the mixture  $i$ – $j$ ,  $x_i$  and  $x_j$  the molar fractions of  $i$  and  $j$ , and  $V_{mi}$ ,  $V_{mj}$  and  $V_m$  the molar volumes of  $i$  and  $j$  and the mixture  $i$ – $j$ , respectively;  $\Phi_i = x_i V_{mi}/V_m$  and  $\Phi_j = x_j V_{mj}/V_m$  are the molar volume fractions of components  $i$  and  $j$  in the mixture  $i$ – $j$ , respectively; and the excess potential energy function of the mixture  $i$ – $j$  is

$$\Delta\varepsilon_p = 2\varepsilon_p - Z_i x_i \varepsilon_{ii} - Z_j x_j \varepsilon_{jj} \quad (14)$$

If  $\Delta\varepsilon_p = 0$ , then Eq. (13) may be reduced to

$$G^E = nRT \left[ x_i \ln \left( \frac{\Phi_i}{x_i} \right) + x_j \ln \left( \frac{\Phi_j}{x_j} \right) \right] \quad (15)$$

which is the well-known Flory–Huggins equation [2].

Suppose that in the liquid mixture  $i$ – $j$ , there are two types of molecular cells in which the central molecules  $i$  and  $j$  reside, respectively. Then the local coordination numbers of the cell  $i$  are  $Z_{ii}$  and  $Z_{ji}$  that are defined as the numbers of molecules  $i$  and  $j$  surrounding the central molecule  $i$ . The local coordination numbers of the cell  $j$  are  $Z_{jj}$  and  $Z_{ij}$  that are defined as the numbers of molecules  $j$  and  $i$  surrounding the central molecule  $j$ . They are also proportional to their corresponding Boltzmann's factors, i.e.

$$Z_{ii} = x_i \exp \left( -\frac{\varepsilon_{ii}}{kT} \right), \quad Z_{ji} = x_j \exp \left( -\frac{\varepsilon_{ji}}{kT} \right) \quad (16)$$

$$Z_{jj} = x_j \exp \left( -\frac{\varepsilon_{jj}}{kT} \right), \quad Z_{ij} = x_i \exp \left( -\frac{\varepsilon_{ij}}{kT} \right) \quad (17)$$

Based on the above considerations, the local molecular fractions of the molecules  $i$  and  $j$  surrounding a central molecule  $i$  can be defined, respectively, as

$$\begin{aligned} x_{ii} &= \frac{Z_{ii}}{Z_{ii} + Z_{ji}} = \frac{x_i}{x_i + x_j B_{ji}}, \\ x_{ji} &= \frac{Z_{ji}}{Z_{ii} + Z_{ji}} = \frac{x_j B_{ji}}{x_i + x_j B_{ji}} \end{aligned} \quad (18)$$

and the local molecular fractions of the molecules  $j$  and  $i$  surrounding a central molecule  $j$  can be, respectively, defined as

$$\begin{aligned} x_{jj} &= \frac{Z_{jj}}{Z_{ij} + Z_{jj}} = \frac{x_j}{x_j + x_i B_{ij}}, \\ x_{ij} &= \frac{Z_{ij}}{Z_{ij} + Z_{jj}} = \frac{x_i B_{ij}}{x_j + x_i B_{ij}} \end{aligned} \quad (19)$$

where the pair-potential energy interaction parameters  $B_{ji}$  and  $B_{ij}$  are defined, respectively, as

$$B_{ji} = \exp \left( -\frac{\varepsilon_{ji} - \varepsilon_{ii}}{kT} \right), \quad B_{ij} = \exp \left( -\frac{\varepsilon_{ij} - \varepsilon_{jj}}{kT} \right) \quad (20)$$

Obviously, Eqs. (18) and (19) satisfy the normalization conditions

$$x_{ii} + x_{ji} = 1, \quad x_{jj} + x_{ij} = 1 \quad (21)$$

Therefore, the local volume fractions of the molecules

$i$  and  $j$  in the mixture  $i$ – $j$  can be expressed as

$$\zeta_i = \frac{x_{ii}V_{mi}}{x_{ii}V_{mi} + x_{ji}V_{mj}} = \frac{x_iV_{mi}}{x_iV_{mi} + x_jV_{mj}B_{ji}} \quad (22)$$

$$\zeta_j = \frac{x_{jj}V_{mj}}{x_{jj}V_{mj} + x_{ij}V_{mi}} = \frac{x_jV_{mj}}{x_jV_{mj} + x_iV_{mi}B_{ij}} \quad (23)$$

According to the two-liquid theory [2], the mixing potential energy function  $\varepsilon_p$  of the molecules  $i$  and  $j$  can be chosen as

$$\varepsilon_p = \frac{1}{2} [Z_i x_i (x_{ii} \varepsilon_{ii} + x_{ji} \varepsilon_{ji}) + Z_j x_j (x_{jj} \varepsilon_{jj} + x_{ij} \varepsilon_{ij})] \quad (24)$$

Substituting Eq. (24) into (13) in which  $\Phi_i$  and  $\Phi_j$  are replaced by  $\zeta_i$  and  $\zeta_j$ , one can achieve a new model of the molar excess Gibbs energy  $G_m^E$  of the liquid mixture  $i$ – $j$ :

$$\begin{aligned} \frac{G_m^E}{RT} = & x_i \ln \left( \frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} \right) \\ & + x_j \ln \left( \frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) \\ & - \frac{x_i x_j}{2} \left( \frac{Z_i B_{ji} \ln B_{ji}}{x_i + x_j B_{ji}} + \frac{Z_j B_{ij} \ln B_{ij}}{x_j + x_i B_{ij}} \right) \end{aligned} \quad (25)$$

as well as new expressions of activity coefficients of the components  $i$  and  $j$ , respectively:

$$\begin{aligned} \ln \gamma_i = & \ln \left( \frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} \right) \\ & + x_j \left( \frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ij}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) \\ & - \frac{x_j^2}{2} \left[ \frac{Z_i B_{ji}^2 \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_j B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2} \right] \end{aligned} \quad (26)$$

$$\begin{aligned} \ln \gamma_j = & \ln \left( \frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) \\ & - x_i \left( \frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ij}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) \\ & - \frac{x_i^2}{2} \left[ \frac{Z_j B_{ij}^2 \ln B_{ij}}{(x_j + x_i B_{ij})^2} + \frac{Z_i B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2} \right] \end{aligned} \quad (27)$$

Extending Eq. (25) to a multicomponent mixture, its molar excess Gibbs energy can be generalized as

$$\begin{aligned} \frac{G_m^E}{RT} = & \sum_{i=1}^n x_i \ln \frac{V_{mi}}{\sum_{j=1}^n x_j V_{mj} B_{ji}} \\ & - \frac{1}{2} \sum_{i=1}^n Z_i x_i \left( \frac{\sum_{j=1}^n x_j B_{ji} \ln B_{ji}}{\sum_{k=1}^n x_k B_{ki}} \right) \end{aligned} \quad (28)$$

and the expression of activity coefficient of any component  $i$  is

$$\begin{aligned} \ln \gamma_i = & 1 + \ln \frac{V_{mi}}{\sum_{j=1}^n x_j V_{mj} B_{ji}} - \sum_{k=1}^n \frac{x_k V_{mi} B_{ik}}{\sum_{j=1}^n x_j V_{mj} B_{jk}} \\ & - \frac{1}{2} \left[ \frac{Z_i \sum_{j=1}^n x_j B_{ji} \ln B_{ji}}{\sum_{l=1}^n x_l B_{li}} + \sum_{j=1}^n \frac{Z_j x_j B_{ij}}{\sum_{l=1}^n x_l B_{lj}} \right] \\ & \times \left( \ln B_{ij} - \frac{\sum_{l=1}^n x_l B_{lj} \ln B_{lj}}{\sum_{l=1}^n x_l B_{lj}} \right) \end{aligned} \quad (29)$$

#### 4. Prediction on the thermodynamic properties of liquid alloys with the new model

It is necessary to determine the coordination numbers of liquid metals before applying the new model to liquid alloys. For the liquid metal  $i$ , the coordination can be defined as [7]

$$Z_i = 2 \int_{r_{0i}}^{r_{mi}} 4\pi r^2 \rho_i g_i(r, T) dr \quad (30)$$

where  $\rho_i = N_i/V_i$  and  $g_i(r, T)$  are the molecular number density and the radial distribution function,  $r_{0i}$  and  $r_{mi}$  the beginning and first peak values of radial distance near its melting point, respectively. Since the coordination decreases exponentially with temperature,  $g_i(r, T)$  may be represented as

$$g_i(r, T) = g_i(r) \exp \left( \frac{\alpha \Delta H_{mi}}{RT} \right) \quad (31)$$

where  $\alpha = 2/Z_c$  is a constant and  $Z_c = 12$  is the close-packed coordination, and  $\Delta H_{mi}$  the melting enthalpy. Suppose that first peak of the radial distribution function  $g_i(r)$  at  $T$  K approaches a normal distribution, and then when  $r = r_{mi}$ , it should be

$$g_i(r_{mi}) = \frac{r_{mi}}{(r_{mi} - r_{0i}) \sqrt{2\pi}} \quad (32)$$

Thus substituting Eqs. (31) and (32) into Eq. (30) and integrating it, one can obtain the equation of coordination number of a liquid metal

$$Z_i = \frac{2\sqrt{2\pi}}{3} \left( \frac{r_{mi}^3 - r_{0i}^3}{r_{mi} - r_{0i}} \right) \rho_i r_{mi} \exp \left( \frac{2\Delta H_{mi}}{ZRT} \right) \quad (33)$$

The activities of the components of the ternary liquid alloys Cd–Bi–Pb(773 K) [8] and Cd–Bi–

Table 1  
The related parameters of the components

<i>i</i>	$r_{0i}$ ( $10^{-8}$ cm)	$r_{mi}$ ( $10^{-8}$ cm)	$\Delta H_{mi}$ (kJ/mol)	$V_{mi}$ ( $\text{cm}^3/\text{mol}$ )
Cd	2.54	3.00	6.109	$14.00[1 + 1.50 \times 10^{-4}(T - 594)]$
Pb	2.76	3.26	5.104	$19.42[1 + 1.24 \times 10^{-4}(T - 600)]$
Bi	2.78	3.34	10.878	$20.80[1 + 1.17 \times 10^{-4}(T - 544)]$
Sn	2.68	3.14	7.196	$17.00[1 + 0.87 \times 10^{-4}(T - 505)]$

Sn(773 K) [9] and the quaternary liquid alloys Cd–Bi–Pb–Sn(773 K) [10] were chosen to check Eq. (29) since the data are well known to be reliable. In order to determine the required binary parameters  $B_{ji}$  and  $B_{ij}$ , the thermodynamic properties of the Cd–Bi, Cd–Pb, Cd–Sn, Bi–Pb, Bi–Sn [1] and Pb–Sn [11] liquid alloys and the related parameters [7] of their components must have been found out for the model as shown in Table 1.

When  $x_i$  or  $x_j$  approaches zero, the infinite dilution activity coefficients  $\gamma_i^\infty$  and  $\gamma_j^\infty$  are derived from Eqs. (26) and (27), respectively:

$$\ln \gamma_i^\infty = 1 - \ln \left( \frac{V_{mj} B_{ji}}{V_{mi}} \right) - \frac{V_{mi} B_{ij}}{V_{mj}} - \frac{1}{2} (Z_i \ln B_{ji} + Z_j B_{ij} \ln B_{ij}) \quad (34)$$

$$\ln \gamma_j^\infty = 1 - \ln \left( \frac{V_{mi} B_{ij}}{V_{mj}} \right) - \frac{V_{mj} B_{ji}}{V_{mi}} - \frac{1}{2} (Z_i \ln B_{ij} + Z_i B_{ji} \ln B_{ji}) \quad (35)$$

The parameter  $B_{ij}$  is solved by connecting Eqs. (34) and (35):

$$B_{ij} = e^B \quad (36)$$

$$B = \frac{2}{2 + Z_j} \left( 1 - \ln r_j^\infty - \ln \frac{V_i}{V_j} - \frac{V_j B_{ji}}{V_i} - \frac{1}{2} Z_i B_{ji} \ln B_{ji} \right) \quad (37)$$

Let a function and its derivative be, respectively,

$$f(B_{ji}) = \left( 1 + \frac{Z_i}{2} \right) \ln B_{ji} + \left( \frac{V_i}{V_j} + \frac{Z_j B}{2} \right) e^B + \ln \left( \frac{V_j}{V_i} \right) + \ln \gamma_i^\infty - 1 \quad (38)$$

$$f'(B_{ji}) = \frac{1 + Z_i/2}{B_{ji}} + \left( \frac{V_i}{V_j} + \frac{Z_j}{2} + B \right) B' e^B \quad (39)$$

$$B' = -\frac{2}{2 + Z_j} \left( \frac{V_j}{V_i} + \frac{Z_i \ln B_{ji}}{2} + \frac{Z_i}{2} \right) \quad (40)$$

According to the Newton formulae,

$$B_{ji(n+1)} = B_{ji(n)} - \frac{f[B_{ji(n)}]}{f'[B_{ji(n)}]} \quad (41)$$

The initial values of  $B_{ji}$  and  $B_{ij}$  can be obtained from the data of  $\gamma_i^\infty$  and  $\gamma_j^\infty$  through computing repeatedly ( $n + 1$ ) times until  $|B_{ji(n)} - B_{ji(n+1)}| \leq 10^{-8}$ . By substituting the values into Eqs. (26) and (27), the final values of  $B_{ji}$  and  $B_{ij}$  are determined by making the average fitting deviation  $S_{i,orj} = \pm \left\{ \sum_{i,orj=1}^n [a_{i,orj(\text{exp})} - a_{i,orj(\text{cal})}]^2 / n \right\}^{1/2}$  less than  $(\pm 0.007-0.02)$

Table 2  
The values of  $B_{ji}$ ,  $B_{ij}$ ,  $S$  and  $S^*$  of the binary liquid alloys  $i-j$  at 773 K

$i-j$	$T$ (K)	$B_{ji}$	$B_{ij}$	$\pm S_i$	$\pm S_j$	$\pm S_i^*$	$\pm S_j^*$	$(\varepsilon_{ji} - \varepsilon_{ii})/k$ (K)	$(\varepsilon_{ij} - \varepsilon_{jj})/k$ (K)
Cd–Bi	773	0.471	1.634	0.0086	0.0060	0.01	0.01	581.57	–379.54
Bi–Pb	700	1.152	1.071	0.0043	0.0030	0.007	0.007	–99.05	–48.01
	773	1.137	1.064						
Cd–Pb	773	0.900	0.720	0.0032	0.0028	0.01	0.01	81.27	253.72
Bi–Sn	600	1.153	0.789	0.0076	0.0075	0.02	0.02	–85.57	142.15
	773	1.117	0.832						
Cd–Sn	773	0.893	0.956	0.0048	0.0047	0.01	0.01	87.87	34.85
Pb–Sn	773	0.895	0.878 <sup>a</sup>	–	–	–	–	85.98	100.67

<sup>a</sup> The  $B_{ji}$  and  $B_{ij}$  determined by  $\gamma_{\text{Sn}}^\infty = 2.30$  and  $r_{\text{Pb}}^\infty = 2.33$  [11].

of the experimental data as far as possible by adjusting  $B_{ji}$  and  $B_{ij}$ . On the other hand, when the values of  $B_{ji}$  and  $B_{ij}$  are known, the values of  $B_{ji}$  and  $B_{ij}$  at the required temperatures can be obtained from Eq. (20) in which the pair-potential energy interaction parameters  $(\varepsilon_{ji} - \varepsilon_{ii})/k$  and  $(\varepsilon_{ij} - \varepsilon_{jj})/k$  may be assumed to be independent of temperature, as shown in Table 2. It can be seen from the table that the values deviate less than the experimental ones, which shows that the fitting effects of the model for binary liquid alloys are excellent.

Allowing the Cd–Bi–Pb, Cd–Bi–Sn, Bi–Sn–Cd and Sn–Bi–Cd liquid alloys to be the 1–2–3 system and the Cd–Bi–Pb–Sn liquid alloys the 1–2–3–4 system, the activity coefficients of component 1 of the 1–2–3 and the 1–2–3–4 systems can be written from Eq. (29) as

Substituting the corresponding  $B_{ji}$  and  $B_{ij}$  into Eqs. (42) and (43), the activities of components of those multicomponent liquid alloys have been predicted, as shown in Tables 3–5. It can be seen from the tables that the predicted values are in good agreement with the experimental data and all the predicted deviations  $S_1$  are less than the experimental ones  $S^*$ . This shows that Eq. (29) is a convenient and reliable means of predicting the thermodynamic properties of a multicomponent solution that requires only the binary parameters and provides an important economic advantage since the amount of experimental and computing work required to represent multicomponent behavior is thereby very much reduced.

Table 5 also lists the predicted results of the P–F and Wilson models. It can be seen that P–F appears to be

$$\begin{aligned} \ln \gamma_1 = 1 + \ln & \left( \frac{V_{m1}}{x_1 V_{m1} + x_2 V_{m2} B_{21} + x_3 V_{m3} B_{31}} \right) - \frac{x_1 V_{m1}}{x_1 V_{m1} + x_2 V_{m2} B_{21} + x_3 V_{m3} B_{31}} \\ & - \frac{x_2 V_{m1} B_{12}}{x_1 V_{m1} B_{12} + x_2 V_{m2} + x_3 V_{m3} B_{32}} - \frac{x_3 V_{m1} B_{13}}{x_1 V_{m1} B_{13} + x_2 V_{m2} B_{23} + x_3 V_{m3}} - \frac{1}{2} \\ & \times \left( \frac{Z_1 (x_2 B_{21} + x_3 B_{31}) (x_2 B_{21} \ln B_{21} + x_3 B_{31} \ln B_{31})}{(x_1 + x_2 B_{21} + x_3 B_{31})^2} + \frac{Z_2 x_2 B_{12} [(x_2 + x_3 B_{32}) \ln B_{12} - x_3 B_{32} \ln B_{32}]}{(x_1 B_{12} + x_2 + x_3 B_{32})^2} \right. \\ & \left. + \frac{Z_3 x_3 B_{13} [(x_2 B_{23} + x_3) \ln B_{13} - x_2 B_{23} \ln B_{23}]}{(x_1 B_{13} + x_2 B_{23} + x_3)^2} \right) \end{aligned} \quad (42)$$

$$\begin{aligned} \ln \gamma_1 = 1 + \ln & \left( \frac{V_{m1}}{x_1 V_{m1} + x_2 V_{m2} B_{21} + x_3 V_{m3} B_{31} + x_4 V_{m4} B_{41}} \right) - \frac{x_1 V_{m1}}{x_1 V_{m1} + x_2 V_{m2} B_{21} + x_3 V_{m3} B_{31} + x_4 V_{m4} B_{41}} \\ & - \frac{x_2 V_{m1} B_{12}}{x_1 V_{m1} B_{12} + x_2 V_{m2} + x_3 V_{m3} B_{32} + x_4 V_{m4} B_{42}} - \frac{x_3 V_{m1} B_{13}}{x_1 V_{m1} B_{13} + x_2 V_{m2} B_{23} + x_3 V_{m3} + x_4 V_{m4} B_{43}} \\ & - \frac{x_4 V_{m1} B_{14}}{x_1 V_{m1} B_{14} + x_2 V_{m2} B_{24} + x_3 V_{m3} B_{34} + x_4 V_{m4}} - \frac{1}{2} \\ & \times \left( \frac{Z_1 (x_2 B_{21} + x_3 B_{31} + x_4 B_{41}) (x_2 B_{21} \ln B_{21} + x_3 B_{31} \ln B_{31} + x_4 B_{41} \ln B_{41})}{(x_1 + x_2 B_{21} + x_3 B_{31} + x_4 B_{41})^2} \right. \\ & + \frac{Z_2 x_2 B_{12} [(x_2 + x_3 B_{32} + x_4 B_{42}) \ln B_{12} - x_3 B_{32} \ln B_{32} - x_4 B_{42} \ln B_{42}]}{(x_1 B_{12} + x_2 + x_3 B_{32} + x_4 B_{42})^2} \\ & + \frac{Z_3 x_3 B_{13} [(x_2 B_{23} + x_3 + x_4 B_{43}) \ln B_{13} - x_2 B_{23} \ln B_{23} - x_4 B_{43} \ln B_{43}]}{(x_1 B_{13} + x_2 B_{23} + x_3 + x_4 B_{43})^2} \\ & \left. + \frac{Z_4 x_4 B_{14} [(x_2 B_{24} + x_3 B_{34} + x_4) \ln B_{14} - x_2 B_{24} \ln B_{24} - x_3 B_{34} \ln B_{34}]}{(x_1 B_{14} + x_2 B_{24} + x_3 B_{34} + x_4)^2} \right) \end{aligned} \quad (43)$$

Table 3

Comparison of the predicted values with the experimental data of activity of component Cd in the Cd–Bi–Pb and the Cd–Bi–Sn liquid alloys at 773 K

Cd–Bi–Pb					Cd–Bi–Sn				
$x_{Cd}$	$x_{Bi}$	$x_{Pb}$	$a_{Cd,exp}$ [8]	$a_{Cd,pre}$	$x_{Cd}$	$x_{Bi}$	$x_{Sn}$	$a_{Cd,exp}$ [9]	$a_{Cd,pre}$
0.109	0.299	0.591	0.217	0.211	0.871	0.097	0.032	0.880	0.870
0.199	0.269	0.531	0.357	0.350	0.692	0.231	0.077	0.701	0.688
0.314	0.231	0.455	0.490	0.490	0.429	0.429	0.143	0.414	0.417
0.420	0.195	0.385	0.594	0.591	0.200	0.600	0.200	0.193	0.190
0.563	0.147	0.290	0.703	0.697	0.077	0.692	0.231	0.076	0.073
0.655	0.116	0.229	0.760	0.755	0.905	0.048	0.048	0.910	0.906
0.691	0.104	0.205	0.789	0.777	0.702	0.149	0.149	0.723	0.711
0.812	0.063	0.125	0.858	0.851	0.481	0.259	0.259	0.500	0.498
0.877	0.041	0.081	0.903	0.896	0.250	0.375	0.375	0.269	0.265
0.938	0.021	0.041	0.947	0.943	0.053	0.474	0.474	0.059	0.056
0.118	0.588	0.294	0.166	0.158	0.871	0.032	0.097	0.881	0.876
0.233	0.511	0.256	0.303	0.296	0.692	0.077	0.231	0.727	0.716
0.429	0.381	0.190	0.509	0.500	0.429	0.143	0.428	0.486	0.478
0.552	0.299	0.149	0.619	0.613	0.200	0.200	0.600	0.251	0.245
0.629	0.247	0.124	0.687	0.679	0.077	0.231	0.692	0.101	0.099
0.822	0.119	0.059	0.857	0.840	–	–	–	–	–
0.950	0.033	0.017	0.956	0.952	–	–	–	–	–

$S_{Cd} = \pm 0.0065$ ,  $S_{Cd}^* = \pm 0.01$        $S_{Cd} = \pm 0.0057$ ,  $S_{Cd}^* = \pm 0.01$

the best, while Eq. (29) is better than Wilson from the predicted deviations, but actually Eq. (29) is the best, Wilson not quite so and P–F the worst because P–F model requires the experimental activities of component Cd of the three binaries Cd–Bi, Cd–Pb and Cd–Sn and the three ternaries Cd–Bi–Pb, Cd–Bi–Sn and Cd–Pb–Sn as well as the 35 measured values of activity of component Cd of the quaternary to fit the 18

multicomponent parameters which had no physical meanings [10]; and Wilson's model was not suitable for liquid–liquid partial miscible systems and its binary parameters lacked a clear physical meaning although it had been successfully applied to the prediction of thermodynamic properties of liquid alloys [12–16], molten salts [17], molten slags [18] and molten mattes [19], whereas Eq. (29) not only could

Table 4

Comparison of the predicted values with the experimental data of activity of components Bi and Sn in the Bi–Sn–Cd and Sn–Bi–Cd liquid alloys at 773 K

Bi–Sn–Cd					Sn–Bi–Cd				
$x_{Bi}$	$x_{Sn}$	$x_{Cd}$	$a_{Bi,exp}$ [9]	$a_{Bi,pre}$	$x_{Sn}$	$x_{Bi}$	$x_{Cd}$	$a_{Sn,exp}$ [9]	$a_{Sn,pre}$
0.692	0.231	0.077	0.692	0.699	0.200	0.600	0.200	0.240	0.237
0.429	0.429	0.143	0.424	0.429	0.429	0.429	0.143	0.479	0.472
0.200	0.600	0.200	0.197	0.194	0.692	0.231	0.077	0.721	0.714
0.600	0.200	0.200	0.591	0.596	0.143	0.429	0.429	0.192	0.189
0.333	0.333	0.333	0.310	0.310	0.333	0.333	0.333	0.408	0.398
0.143	0.429	0.429	0.124	0.123	0.600	0.200	0.200	0.649	0.643
0.429	0.143	0.429	0.403	0.404	0.077	0.231	0.692	0.122	0.116
0.200	0.200	0.600	0.167	0.171	0.200	0.200	0.600	0.281	0.274
0.077	0.231	0.692	0.060	0.062	0.429	0.143	0.429	0.507	0.506

$S_{Bi} = \pm 0.0028$ ,  $S_{Bi}^* = \pm 0.01$        $S_{Sn} = \pm 0.0050$ ,  $S_{Sn}^* = \pm 0.01$

Table 5

Comparison of the predicted values with the experimental data of activity of component Cd in the liquid alloys Cd–Bi–Pb–Sn at 773 K

$x_{\text{Cd}}$	$x_{\text{Bi}}$	$x_{\text{Pb}}$	$x_{\text{Sn}}$	$a_{\text{Cd}}$			
				Wilson [12]	Eq. (29)	P–F [10]	Exp. [10]
0.1000	0.1800	0.1800	0.5400	0.1414	0.1424	0.1413	0.1465
0.1998	0.1601	0.1600	0.4801	0.2703	0.2673	0.2665	0.2724
0.4000	0.1200	0.1200	0.3600	0.4860	0.4770	0.4822	0.4838
0.4999	0.1001	0.0999	0.3001	0.5768	0.5673	0.5758	0.5771
0.6000	0.0801	0.0801	0.2398	0.6611	0.6524	0.6625	0.6648
0.7000	0.0600	0.0600	0.1800	0.7417	0.7349	0.7443	0.7448
0.8000	0.0400	0.0399	0.1201	0.8222	0.8181	0.8244	0.8243
0.9001	0.0200	0.0199	0.0600	0.9067	0.9053	0.9075	0.8964
0.1001	0.1801	0.5399	0.1800	0.1933	0.1843	0.1844	0.1859
0.2002	0.1600	0.4798	0.1599	0.3432	0.3333	0.3300	0.3304
0.3001	0.1400	0.4199	0.1399	0.4615	0.4533	0.4504	0.4525
0.3999	0.1200	0.3600	0.1201	0.5577	0.5509	0.5523	0.5513
0.4999	0.1001	0.2999	0.1001	0.6388	0.6326	0.6395	0.6374
0.6002	0.0800	0.2398	0.0800	0.7105	0.7040	0.7150	0.7111
0.7000	0.0600	0.1800	0.0600	0.7767	0.7702	0.7816	0.7802
0.8001	0.0400	0.1199	0.0400	0.8424	0.8371	0.8453	0.8387
0.8999	0.0200	0.0600	0.0200	0.9133	0.9109	0.9139	0.9010
0.1007	0.2998	0.2997	0.2998	0.1480	0.1450	0.1468	0.1425
0.2002	0.2667	0.2665	0.2666	0.2789	0.2729	0.2731	0.2748
0.3002	0.2332	0.2333	0.2333	0.3943	0.3866	0.3877	0.3881
0.4000	0.2000	0.2001	0.1999	0.4956	0.4874	0.4922	0.4950
0.4999	0.1668	0.1667	0.1666	0.5863	0.5782	0.5875	0.5919
0.6001	0.1332	0.1331	0.1336	0.6697	0.6623	0.6747	0.6662
0.6997	0.1001	0.1001	0.1001	0.7485	0.7423	0.7545	0.7641
0.8000	0.0668	0.0666	0.0666	0.8269	0.8226	0.8312	0.8310
0.9001	0.0332	0.0333	0.0334	0.9086	0.9068	0.9099	0.9041
0.1001	0.5400	0.1800	0.1798	0.1179	0.1185	0.1243	0.1187
0.2001	0.4798	0.1600	0.1602	0.2334	0.2320	0.2352	0.2350
0.3000	0.4200	0.1400	0.1400	0.3433	0.3398	0.3413	0.3403
0.4001	0.3599	0.1200	0.1200	0.4472	0.4423	0.4457	0.4466
0.4999	0.3000	0.1001	0.1001	0.5450	0.5395	0.5473	0.5464
0.5999	0.2401	0.0801	0.0800	0.6381	0.6327	0.6446	0.6442
0.6999	0.1800	0.0600	0.0601	0.7279	0.7231	0.7363	0.7501
0.8500	0.0900	0.0300	0.0300	0.8604	0.8579	0.8650	0.8887
0.9193	0.0485	0.0161	0.0161	0.9229	0.9219	0.9247	0.9277

$$S_{\text{Cd}} = \pm 0.0084, \pm 0.0071, \pm 0.0065, \pm 0.01$$

characterize a multicomponent solution with only the binary parameters where physical senses were clear but also was put on the bases of statistical thermodynamics and could be used to predict the liquid–liquid immiscible systems.

## 5. Conclusions

The basic feature of the new models is of moving the liquid molecules by non-random migration. The

molecular cells are not prison cages restraining them but are the carriers of migration. The new expressions of the configurational partition function as well as the excess Gibbs energy of liquids and their mixtures have been derived from statistical thermodynamics.

The local molecular fractions and the pair-potential interaction parameters defined according to the concepts of local coordination numbers have clear physical meanings. The new model has been verified to be quite convenient and reliable by predicting the thermodynamic properties of liquid alloys.



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