ELSEVIER

Thermochimica Acta 383 (2002) 45–51

thermochimica acta

www.elsevier.com/locate/tca

Prediction of the thermodynamic properties of quaternary liquid alloys by modified coordination equation

Dong Ping Tao*, Duen Fang Li, Bin Yang

The School of Materials and Metallurgical Engineering, Kunming University of Science and Technology, Mail Box 62-106, Kunming 650093, Yunnan, PR China

Received 15 March 2001; accepted 13 June 2001

Abstract

The coordination numbers in the molecular interaction volume model (MIVM) can be calculated from common physical quantities of pure metals. A significant advantage of the model lies in its ability to predict thermodynamic properties of quaternary liquid alloys using only binary infinite dilute activity coefficients, and the predicted values are in good agreement with the experimental data of quaternary liquid alloys, which show that the model is reliable, convenient and economic.

Keywords: Thermodynamic properties; Quaternary liquid alloys; Molecular interaction volume model; Modified coordination equation

1. Introduction

The thermodynamic properties of multicomponent liquid alloys are important for understanding the process metallurgy and the metals alloying. A great deal of binary data has been so far compiled in monographs, such as Hultgren et al. [1]. But multicomponent data is scattered in journals and is quite scarce because the determination of thermodynamic data of multicomponent systems needs not only the consummate skill of a researcher and the excellent instruments but also the financial support continuously. Furthermore, there have been just numerous multicomponent systems in industrial processes. It was obviously unrealistic to get all the data experimentally. Therefore, a unique economic and effective method was to predict a multicomponent system with theories or thermodynamic models depending on less experimental data as far as possible. The purpose of this work is to apply molecular interaction volume model (MIVM) [2] to predict the thermodynamic properties of quaternary liquid alloys only using the corresponding binary infinite dilute activity coefficients and the coordination numbers of the constituent elements in liquid alloys.

2. Molecular interaction volume model

The MIVM was obtained in the physical sense 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 constantly at one site but are migrating non-randomly from one cell to another. The molar excess Gibbs energy G_m^E of the liquid

* Corresponding author. Tel.: +86-871-511-6730.

0040-6031/02/$ – see front matter
PII: S0040-6031(01)00655-4

mixture *i–j*

$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = x_i \ln\left(\frac{V_{\mathrm{m}i}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}}\right) + x_j \ln\left(\frac{V_{\mathrm{m}j}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}}\right) - \frac{x_i x_j}{2} \times \left(\frac{Z_i B_{ji} \ln B_{ji}}{x_i + x_j B_{ji}} + \frac{Z_j B_{ij} \ln B_{ij}}{x_j + x_i B_{ij}}\right) \quad (1)$$

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

$$\ln \gamma_i = \ln\left(\frac{V_{\mathrm{m}i}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}}\right) + x_j \left(\frac{V_{\mathrm{m}j} B_{ji}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}} - \frac{V_{\mathrm{m}i} B_{ij}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}}\right) - \frac{x_j^2}{2}\left(\frac{Z_i B_{ji}^2 \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_j B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2}\right) \quad (2)$$

$$\ln \gamma_j = \ln\left(\frac{V_{\mathrm{m}j}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}}\right) - x_i \left(\frac{V_{\mathrm{m}j} B_{ji}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}} - \frac{V_{\mathrm{m}i} B_{ij}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}}\right) - \frac{x_i^2}{2}\left(\frac{Z_j B_{ij}^2 \ln B_{ij}}{(x_j + x_i B_{ij})^2} + \frac{Z_i B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2}\right) \quad (3)$$

Extending Eq. (1) to a multicomponent mixture, its molar excess Gibbs energy can be generalized as

$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = \sum_{i=1}^{n} x_i \ln \frac{V_{\mathrm{m}i}}{\sum_{j=1}^{n} x_j V_{\mathrm{m}j} B_{ji}} - \frac{1}{2}\sum_{i=1}^{n} Z_i x_i \left(\frac{\sum_{j=1}^{n} x_j B_{ji} \ln B_{ji}}{\sum_{k=1}^{n} x_k B_{ki}}\right) \quad (4)$$

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

$$\ln \gamma_i = 1 + \ln \frac{V_{\mathrm{m}i}}{\sum_{j=1}^{n} x_j V_{\mathrm{m}j} B_{ji}} - \sum_{k=1}^{n} \frac{x_k V_{\mathrm{m}i} B_{ik}}{\sum_{j=1}^{n} x_j V_{\mathrm{m}j} B_{jk}} - \frac{1}{2}\left(\frac{Z_i \sum_{j=1}^{n} x_j B_{ji} \ln B_{ji}}{\sum_{l=1}^{n} x_l B_{li}} + \sum_{j=1}^{n} \frac{Z_j x_j B_{ij}}{\sum_{l=1}^{n} x_l B_{lj}} \times \left(\ln B_{ij} - \frac{\sum_{t=1}^{n} x_t B_{tj} \ln B_{tj}}{\sum_{l=1}^{n} x_l B_{lj}}\right)\right) \quad (5)$$

where Z_i and Z_j are the nearest molecule or first coordination numbers, x_i and x_j the molar fractions, $V_{\mathrm{m}i}$ and $V_{\mathrm{m}j}$ the molar volumes of the matters *i* and *j*, respectively; and the pair-potential energy interaction parameters B_{ji} and B_{ij} are defined as, respectively

$$B_{ji} = \exp\left[\frac{-(\varepsilon_{ji} - \varepsilon_{ii})}{kT}\right], \quad B_{ij} = \exp\left[-\frac{(\varepsilon_{ij} - \varepsilon_{jj})}{kT}\right] \quad (6)$$

where ε_{ii}, ε_{jj} and ε_{ji} are the *i–i*, *j–j* and *i–j* pair-potential energies, and $\varepsilon_{ji} = \varepsilon_{ij}$, and k the Boltzmann constant and T is the absolute temperature.

3. Modified coordination equation

It is necessary to determine the coordination numbers of liquid metals by applying MIVM to liquid alloys. For the liquid metal *i*, its coordination can be defined as [3]

$$Z_i = 2\int_{r_{0i}}^{r_{\mathrm{m}i}} 4\pi r^2 \rho_i g_i(r, T)\, \mathrm{d}r \quad (7)$$

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 $r_{\mathrm{m}i}$ the beginning and first peak values of radial distance near its melting point, respectively. Since the coordination exponentially decreases with temperature, $g_i(r, T)$ may be represented as

$$g_i(r, T) = g_i(r) \exp\left(\frac{\alpha \Delta H_{\mathrm{m}i}}{RT}\right) \quad (8)$$

where $\alpha = 1/Z_{\mathrm{c}}$ is a constant and $Z_{\mathrm{c}} = 12$ is a close-packed coordination, and $\Delta H_{\mathrm{m}i}$ 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 $r = r_{\mathrm{m}i}$, it should be

$$g_i(r_{\mathrm{m}i}) = \frac{r_{\mathrm{m}i}}{(r_{\mathrm{m}i} - r_{0i})\sqrt{2\pi}} \quad (9)$$

Thus, substituting Eqs. (8) and (9) into Eq. (7) and integrating it, one can obtain the equation of coordination number of a liquid metal

$$Z_i = \frac{2\sqrt{2\pi}}{3}\left(\frac{r_{\mathrm{m}i}^3 - r_{0i}^3}{r_{\mathrm{m}i} - r_{0i}}\right)\rho_i r_{\mathrm{m}i} \exp\left(\frac{\Delta H_{\mathrm{m}i}}{Z_{\mathrm{c}} RT}\right) \quad (10)$$

Suppose that the atoms of liquid metals are physical particles and the r_{0i} is the distance of closest approach

of the atoms, σ_i, and r_{mi} is the average distance of the atoms at T (K), d_i, approximately, i.e. the former can be fined out from a textbook of crystal chemistry [5] and the later can be calculated from Eq. (11)

$$d_i = 2 \times 10^{-8} \left(\frac{3V_{mi}}{0.6022 \times 4\pi} \right)^{1/3} \tag{11}$$

Thus, Eq. (10) becomes

$$Z_i = \frac{2\sqrt{2\pi}}{3} \left(\frac{d_i^3 - \sigma_i^3}{d_i - \sigma_i} \right) \rho_i d_i \exp\left(\frac{\Delta H_{mi}}{Z_c RT} \right) \tag{12}$$

4. Prediction on thermodynamic properties of quaternary liquid alloys

For a binary mixture *i–j*, the partial molar excess Gibbs energy of component *i* is

$$\overline{G}_i^E = \overline{H}_i^E - T\overline{S}_i^E = RT \ln \gamma_i \tag{13}$$

where $\overline{H}_i^E$ and $\overline{S}_i^E$ are the partial molar excess enthalpy and entropy of component *i*. When $x_i \to 0$, Eq. (13) becomes

$$\ln \gamma_i^\infty = \frac{\overline{H}_i^{E\infty}}{RT} - \frac{\overline{S}_i^{E\infty}}{R} \tag{14}$$

Suppose that the partial molar infinite dilute excess enthalpy $\overline{H}_i^{E\infty}$ and entropy $\overline{S}_i^{E\infty}$ of component *i* are independent of temperature. Then Eq. (14) may be [4]

$$\ln \gamma_i^\infty = \frac{a}{T} + b \tag{15}$$

where $a = \overline{H}_i^{E\infty}/R$ and $b = -\overline{S}_i^{E\infty}/R$. Notice that $\overline{H}_i^{E\infty}$ equals the partial molar infinite dilute mixing enthalpy of component *i*, $\Delta\overline{H}_i^{M\infty}$. Based on the Eq. (15) one can estimate the infinite dilute activity coefficient γ_i^∞ at any temperature from the known $\Delta\overline{H}_i^{M\infty}$ and $\overline{S}_i^{E\infty}$.

Then the activities of components of the quaternary liquid alloys Cd–Bi–Pb–Sn (773 K) [6], Zn–Sn–Cd–Pb (877 K) [7] and Zn–Sn–Cd–Bi (877 K) [8] may be chosen to check Eqs. (5) and (12) because those data were well known to be reliable. In order to determine the required binary parameters B_{ji} and B_{ij}, the some parameters of pure metals and the infinite dilute thermodynamic properties of binary liquid alloys must have been found out for the model as shown in Tables 1 and 2, respectively.

When x_i or x_j approaches zero, the infinite dilution activity coefficients γ_i^∞ and γ_j^∞ are derived from Eqs. (2) and (3), respectively

$$\ln \gamma_i^\infty = 1 - \ln\left(\frac{V_{mj} B_{ji}}{V_{mi}} \right) - \frac{V_{mi} B_{ij}}{V_{mj}} - \frac{1}{2}(Z_i \ln B_{ji} + Z_j B_{ij} \ln B_{ij}) \tag{16}$$

$$\ln \gamma_j^\infty = 1 - \ln\left(\frac{V_{mi} B_{ij}}{V_{mj}} \right) - \frac{V_{mj} B_{ji}}{V_{mi}} - \frac{1}{2}(Z_j \ln B_{ij} + Z_i B_{ji} \ln B_{ji}) \tag{17}$$

The parameter B_{ij} is solved by connecting Eqs. (16) and (17)

$$B_{ij} = \exp(B) \tag{18}$$

$$B = \frac{2}{2 + Z_j} \left(1 - \ln \gamma_j^\infty - \ln \frac{V_i}{V_j} - \frac{V_j B_{ji}}{V_i} - \frac{1}{2} Z_i B_{ji} \ln B_{ji} \right) \tag{19}$$

Let a function and its derivative be, respectively

$$f(B_{ji}) = \left(\frac{1 + Z_i}{2} \right) \ln B_{ji} + \left(\frac{V_i}{V_j} + \frac{Z_j B}{2} \right) \times \exp(B) + \ln\left(\frac{V_j}{V_i} \right) + \ln \gamma_i^\infty - 1 \tag{20}$$

Table 1
Some parameters of the pure metals

i	σ_i [5] (10^{-8} cm)	ΔH_{mi} (kJ/mol)	V_{mi} [3] (cm^3/mol)
Bi	3.10	10.878	$20.80[1 + 1.17 \times 10^{-4}(T - 544)]$
Cd	2.96	6.109	$14.00[1 + 1.50 \times 10^{-4}(T - 594)]$
Pb	3.48	5.104	$19.42[1 + 1.24 \times 10^{-4}(T - 600)]$
Sn	2.80	7.196	$17.00[1 + 0.87 \times 10^{-4}(T - 505)]$
Zn	2.66	7.364	$9.94[1 + 1.50 \times 10^{-4}(T - 693)]$

Table 2
The infinite dilute thermodynamic properties of the related binary liquid alloys [1]

i–j	T (K)	$\Delta\overline{H}_i^{M\infty}$ (kJ mol^{-1})	$\overline{S}_i^{E\infty}$ (JK^{-1} mol^{-1})	$\Delta\overline{H}_j^{M\infty}$ (kJ mol^{-1})	$\overline{S}_j^{E\infty}$ (JK^{-1} mol^{-1})
Bi–Cd	773	8.368	9.540	2.824	3.653
Bi–Pb	700	−3.489	0.950	−3.460	1.393
Bi–Sn	600	4.184	−1.837	4.184	−0.523
Bi–Zn	873	26.150	0.958	13.577	6.925
Cd–Pb	773	9.326	1.950	15.899	6.849
Cd–Sn	773	6.577	4.502	9.351	6.644
Cd–Zn	800	8.828	−0.795	8.786	1.046
Pb–Sn	1050	5.690	−1.117	6.276	−9.979
Pb–Zn	923	23.012	−4.531	20.083	4.531
Sn–Zn	750	22.761	17.703	8.661	5.971

$$f'(B_{ji}) = \left(\frac{(1+Z_i)/2}{B_{ji}}\right) + \left(\frac{V_i}{V_j} + \frac{Z_j}{2}(1+B)\right) B' \exp(B) \tag{21}$$

$$B' = -\frac{2}{2+Z_j}\left(\frac{V_j}{V_i} + \frac{Z_i \ln B_{ji}}{2} + \frac{Z_i}{2}\right) \tag{22}$$

According to the Newton formulas, here

$$B_{ji(n+1)} = B_{ji(n)} - \frac{f[B_{ji(n)}]}{f'[B_{ji(n)}]} \tag{23}$$

The values of B_{ji} and B_{ij} can be obtained from the given data of γ_i^∞ and γ_j^∞ through computing repeatedly $(n+1)$ times until $|B_{ji(n)} - B_{ji(n+1)}| \le 10^{-8}$, as shown in Table 3.

Letting the Cd–Bi–Pb–Sn, Zn–Sn–Cd–Pb and Zn–Sn–Cd–Bi liquid alloys be the 1–2–3–4 system, the activity coefficients of the component 1 of the 1–2–3–4 systems can be written from Eq. (5), respectively

$$\begin{aligned}
\ln\gamma_1 = {} & 1 + \ln\left(\frac{V_{m1}}{x_1V_{m1} + x_2V_{m2}B_{21} + x_3V_{m3}B_{31} + x_4V_{m4}B_{41}}\right) - \frac{x_1V_{m1}}{x_1V_{m1} + x_2V_{m2}B_{21} + x_3V_{m3}B_{31} + x_4V_{m4}B_{41}} \\
& - \frac{x_2V_{m1}B_{12}}{x_1V_{m1}B_{12} + x_2V_{m2} + x_3V_{m3}B_{32} + x_4V_{m4}B_{42}} - \frac{x_3V_{m1}B_{13}}{x_1V_{m1}B_{13} + x_2V_{m2}B_{23} + x_3V_{m3} + x_4V_{m4}B_{43}} \\
& - \frac{x_4V_{m1}B_{14}}{x_1V_{m1}B_{14} + x_2V_{m2}B_{24} + x_3V_{m3}B_{34} + x_4V_{m4}} \\
& - \frac{1}{2}\left(\frac{Z_1(x_2B_{21} + x_3B_{31} + x_4B_{41})(x_2B_{21}\ln B_{21} + x_3B_{31}\ln B_{31} + x_4B_{41}\ln B_{41})}{(x_1 + x_2B_{21} + x_3B_{31} + x_4B_{41})^2}\right. \\
& + \frac{Z_2x_2B_{12}[(x_2 + x_3B_{32} + x_4B_{42})\ln B_{12} - x_3B_{32}\ln B_{32} - x_4B_{42}\ln B_{42}]}{(x_1B_{12} + x_2 + x_3B_{32} + x_4B_{42})^2} \\
& + \frac{Z_3x_3B_{13}[(x_2B_{23} + x_3 + x_4B_{43})\ln B_{13} - x_2B_{23}\ln B_{23} - x_4B_{43}\ln B_{43}]}{(x_1B_{13} + x_2B_{23} + x_3 + x_4B_{43})^2} \\
& \left. + \frac{Z_4x_4B_{14}[(x_2B_{24} + x_3B_{34} + x_4)\ln B_{14} - x_2B_{24}\ln B_{24} - x_3B_{34}\ln B_{34}]}{(x_1B_{14} + x_2B_{24} + x_3B_{34} + x_4)^2}\right)
\end{aligned} \tag{24}$$

Substituting the corresponding B_{ji} and B_{ij} into Eq. (24), the activities of components of those liquid quaternary alloys have been predicted, as shown in Tables 4–6. It can be seen from the Tables that the predicted values are in good agreement with the experimental data and all the predicting average relative errors $S_1 = (100/n)\sum|(a_{1,\mathrm{exp}} - a_{1,\mathrm{pre}})/a_{1,\mathrm{exp}}|$ are acceptable, which show that MIVM and the modified coordination equation are quite convenient and reliable for predicting the thermodynamic properties of a quaternary liquid alloys that requires only the binary infinite dilute data

Table 3
The values of γ_i^{∞}, γ_j^{∞}, B_{ji} and B_{ij} of the binary liquid alloys *i–j* at the required temperatures

i–j	*T* (K)	γ_i^{∞}	γ_j^{∞}	B_{ji}	B_{ij}
Bi–Cd	773	1.167	1.000	0.7211	1.2359
Bi–Pb	773	0.518	0.494	0.5274	1.6017
Bi–Sn	773	1.331	1.137	0.7438	1.2237
Cd–Pb	773	3.376	5.208	0.9814	0.7474
Cd–Sn	773	1.619	1.927	1.0639	0.8120
Pb–Sn	773	2.773	8.819	1.1645	0.5341
Bi–Cd	877	1.000	0.949	0.7744	1.2017
Bi–Pb	877	0.553	0.526	0.5433	1.5708
Bi–Sn	877	1.321	1.128	0.7409	1.2260
Bi–Zn	877	32.180	2.799	0.4142	1.1101
Cd–Pb	877	2.843	3.885	0.9835	0.7847
Cd–Sn	877	1.435	1.621	1.0688	0.8352
Cd–Zn	877	3.693	2.943	0.8165	0.9462
Pb–Sn	877	2.495	7.855	1.1889	0.5282
Pb–Zn	877	40.500	9.114	0.5512	0.8773
Sn–Zn	877	3.231	1.526	0.6008	1.1796

Table 4
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[a]

x_{Cd}	x_{Bi}	x_{Pb}	x_{Sn}	$a_{Cd,exp}$ [6]	$a_{Cd,pre}$
0.1000	0.1800	0.1800	0.5400	0.147	0.140
0.1998	0.1601	0.1600	0.4801	0.272	0.267
0.2999	0.1401	0.1400	0.4200	0.238	0.382
0.4000	0.1200	0.1200	0.3600	0.484	0.486
0.4999	0.1001	0.0999	0.3001	0.577	0.580
0.6000	0.0801	0.0801	0.2398	0.665	0.667
0.7000	0.0600	0.0600	0.1800	0.745	0.748
0.8000	0.0400	0.0399	0.1201	0.824	0.826
0.9001	0.0200	0.0199	0.0600	0.896	0.908
0.1001	0.1801	0.5399	0.1800	0.186	0.168
0.2002	0.1600	0.4798	0.1599	0.330	0.316
0.3001	0.1400	0.4199	0.1399	0.452	0.443
0.3999	0.1200	0.3600	0.1201	0.551	0.551
0.4999	0.1001	0.2999	0.1001	0.637	0.642
0.6002	0.0800	0.2398	0.0800	0.711	0.718
0.7000	0.0600	0.1800	0.0600	0.780	0.784
0.8001	0.0400	0.1199	0.0400	0.839	0.847
0.8999	0.0200	0.0600	0.0200	0.901	0.915
0.1007	0.2998	0.2997	0.2998	0.142	0.144
0.2002	0.2667	0.2665	0.2666	0.275	0.274
0.3002	0.2332	0.2333	0.2333	0.388	0.393
0.4000	0.2000	0.2001	0.1999	0.495	0.500
0.4999	0.1668	0.1667	0.1666	0.592	0.596
0.6001	0.1332	0.1331	0.1336	0.666	0.681
0.6997	0.1001	0.1001	0.1001	0.764	0.759
0.8000	0.0668	0.0666	0.0666	0.831	0.834
0.9001	0.0332	0.0333	0.0334	0.904	0.911
0.1001	0.5400	0.1800	0.1798	0.119	0.127
0.2001	0.4798	0.1600	0.1602	0.235	0.248
0.3000	0.4200	0.1400	0.1400	0.340	0.363
0.4001	0.3599	0.1200	0.1200	0.447	0.470
0.4999	0.3000	0.1001	0.1001	0.546	0.570
0.5999	0.2401	0.0801	0.0800	0.644	0.661
0.6999	0.1800	0.0600	0.0601	0.750	0.746
0.7500	0.1500	0.0500	0.0500	0.805	0.787
0.8500	0.0900	0.0300	0.0300	0.889	0.868
0.9000	0.0599	0.0201	0.0200	0.923	0.909
0.9193	0.0485	0.0161	0.0161	0.928	0.926

[a] $S_{Cd} = \pm 3.63\%$.

Table 5
Comparison of the predicted values with the experimental data of activity of component Zn in the liquid alloys Zn–Sn–Cd–Pb at 877 K[a]

x_{Zn}	x_{Sn}	x_{Cd}	x_{Pb}	$a_{Zn,exp}$ [7]	$a_{Zn,pre}$
0.100	0.100	0.100	0.700	0.476	0.447
0.100	0.100	0.200	0.600	0.411	0.401
0.100	0.100	0.300	0.500	0.363	0.360
0.100	0.100	0.400	0.400	0.306	0.325
0.100	0.100	0.700	0.100	0.239	0.245
0.100	0.200	0.100	0.600	0.372	0.359
0.100	0.200	0.200	0.500	0.324	0.327
0.100	0.200	0.300	0.400	0.294	0.298
0.100	0.200	0.400	0.300	0.261	0.272
0.100	0.200	0.600	0.100	0.197	0.228
0.100	0.300	0.100	0.500	0.298	0.300
0.100	0.300	0.200	0.400	0.270	0.276
0.100	0.300	0.300	0.300	0.242	0.253
0.100	0.300	0.500	0.100	0.208	0.214
0.094	0.403	0.100	0.403	0.249	0.244
0.090	0.405	0.202	0.303	0.210	0.216
0.100	0.400	0.300	0.200	0.212	0.219
0.100	0.400	0.400	0.100	0.191	0.202
0.100	0.500	0.100	0.300	0.204	0.225
0.100	0.500	0.200	0.200	0.196	0.208
0.100	0.500	0.300	0.100	0.176	0.192
0.100	0.601	0.099	0.200	0.191	0.198
0.100	0.600	0.200	0.100	0.175	0.183
0.100	0.700	0.100	0.100	0.176	0.172
0.200	0.100	0.100	0.600	0.719	0.693
0.200	0.100	0.200	0.500	0.631	0.621
0.200	0.100	0.300	0.400	0.541	0.559
0.200	0.100	0.400	0.300	0.500	0.505
0.199	0.101	0.599	0.101	0.406	0.419
0.200	0.200	0.100	0.500	0.592	0.571

Table 5 (*Continued*)

x_{Zn}	x_{Sn}	x_{Cd}	x_{Pb}	$a_{Zn,exp}$ [7]	$a_{Zn,pre}$
0.200	0.200	0.200	0.400	0.527	0.520
0.200	0.200	0.300	0.300	0.466	0.474
0.200	0.200	0.500	0.100	0.389	0.398
0.200	0.300	0.100	0.400	0.496	0.488
0.200	0.300	0.200	0.300	0.447	0.448
0.200	0.300	0.300	0.200	0.405	0.411
0.200	0.300	0.400	0.100	0.371	0.379
0.200	0.400	0.100	0.300	0.428	0.427
0.200	0.400	0.200	0.200	0.388	0.393
0.200	0.400	0.300	0.100	0.354	0.363
0.200	0.500	0.100	0.200	0.377	0.378
0.200	0.500	0.200	0.100	0.346	0.349
0.200	0.600	0.100	0.100	0.336	0.337
0.300	0.100	0.100	0.500	0.830	0.814
0.300	0.100	0.200	0.400	0.742	0.730
0.300	0.100	0.300	0.300	0.657	0.659
0.309	0.099	0.493	0.099	0.549	0.558
0.300	0.200	0.100	0.400	0.700	0.688
0.300	0.200	0.200	0.300	0.623	0.627
0.300	0.200	0.300	0.200	0.568	0.573
0.300	0.200	0.400	0.100	0.508	0.526
0.300	0.300	0.100	0.300	0.600	0.601
0.299	0.301	0.200	0.200	0.541	0.550
0.300	0.300	0.300	0.100	0.495	0.508
0.300	0.400	0.100	0.200	0.533	0.534
0.300	0.400	0.200	0.100	0.487	0.493
0.300	0.500	0.100	0.100	0.470	0.480
0.400	0.100	0.100	0.400	0.845	0.859
0.400	0.100	0.200	0.300	0.779	0.774
0.400	0.100	0.300	0.200	0.701	0.702
0.400	0.100	0.400	0.100	0.642	0.644
0.399	0.200	0.100	0.301	0.761	0.745
0.400	0.200	0.200	0.200	0.687	0.681
0.400	0.200	0.300	0.100	0.627	0.626
0.400	0.300	0.100	0.200	0.669	0.651
0.406	0.305	0.187	0.102	0.611	0.619
0.400	0.400	0.100	0.100	0.501	0.602
0.499	0.100	0.100	0.301	0.867	0.864
0.500	0.100	0.200	0.200	0.786	0.783
0.500	0.100	0.300	0.100	0.710	0.718
0.500	0.200	0.100	0.200	0.772	0.769
0.500	0.200	0.200	0.100	0.704	0.707
0.500	0.300	0.100	0.100	0.700	0.701
0.600	0.100	0.100	0.200	0.856	0.851
0.600	0.100	0.200	0.100	0.784	0.781

[a] $S_{Zn} = \pm 2.46\%$.

and provides an important economic advantage since the amount of experimental and computing work required to represent quaternary behavior is thereby very much reduced.

Table 6
Comparison of the predicted values with the experimental data of activity of component Zn in the liquid alloys Zn–Sn–Cd–Bi at 877 K[a]

x_{Zn}	x_{Sn}	x_{Cd}	x_{Bi}	$a_{Zn,exp}$ [8]	$a_{Zn,pre}$
0.100	0.100	0.100	0.700	0.233	0.262
0.100	0.100	0.200	0.600	0.235	0.264
0.100	0.100	0.300	0.500	0.240	0.260
0.100	0.100	0.400	0.400	0.246	0.262
0.100	0.100	0.700	0.100	0.234	0.240
0.100	0.200	0.100	0.600	0.224	0.246
0.100	0.200	0.200	0.500	0.222	0.247
0.100	0.200	0.300	0.400	0.229	0.244
0.100	0.200	0.400	0.300	0.219	0.240
0.100	0.200	0.600	0.100	0.218	0.223
0.100	0.300	0.100	0.500	0.212	0.231
0.100	0.300	0.200	0.400	0.239	0.229
0.100	0.300	0.300	0.300	0.210	0.225
0.100	0.300	0.500	0.100	0.199	0.209
0.100	0.400	0.100	0.400	0.200	0.216
0.100	0.400	0.200	0.300	0.199	0.212
0.100	0.400	0.300	0.200	0.194	0.206
0.100	0.400	0.400	0.100	0.189	0.198
0.100	0.500	0.100	0.300	0.184	0.200
0.100	0.500	0.200	0.200	0.200	0.195
0.100	0.500	0.300	0.100	0.178	0.187
0.095	0.619	0.095	0.191	0.163	0.175
0.100	0.600	0.200	0.100	0.171	0.179
0.100	0.700	0.100	0.100	0.163	0.170
0.200	0.100	0.100	0.600	0.434	0.486
0.200	0.100	0.200	0.500	0.434	0.481
0.200	0.100	0.300	0.400	0.439	0.471
0.200	0.100	0.400	0.300	0.440	0.457
0.200	0.100	0.600	0.100	0.408	0.417
0.200	0.200	0.100	0.500	0.413	0.454
0.200	0.200	0.200	0.400	0.411	0.446
0.200	0.200	0.300	0.300	0.410	0.433
0.200	0.200	0.500	0.100	0.379	0.394
0.200	0.300	0.100	0.400	0.387	0.423
0.200	0.300	0.200	0.300	0.377	0.411
0.200	0.300	0.300	0.200	0.376	0.395
0.200	0.300	0.400	0.100	0.361	0.375
0.200	0.400	0.100	0.300	0.365	0.391
0.200	0.400	0.200	0.200	0.357	0.377
0.200	0.400	0.300	0.100	0.342	0.358
0.200	0.500	0.100	0.200	0.348	0.360
0.200	0.500	0.200	0.100	0.334	0.343
0.200	0.600	0.100	0.100	0.323	0.331
0.300	0.100	0.100	0.500	0.598	0.661
0.300	0.100	0.200	0.400	0.593	0.642
0.300	0.100	0.300	0.300	0.594	0.617
0.300	0.100	0.500	0.100	0.538	0.550
0.300	0.200	0.100	0.400	0.561	0.614
0.300	0.200	0.200	0.300	0.543	0.590
0.300	0.200	0.300	0.200	0.540	0.561
0.300	0.200	0.400	0.100	0.514	0.527

Table 6 (*Continued*)

x_{Zn}	x_{Sn}	x_{Cd}	x_{Bi}	$a_{Zn,exp}$ [8]	$a_{Zn,pre}$
0.300	0.300	0.100	0.300	0.527	0.567
0.299	0.301	0.200	0.200	0.498	0.540
0.300	0.300	0.300	0.100	0.493	0.507
0.300	0.400	0.100	0.200	0.461	0.521
0.300	0.400	0.200	0.100	0.456	0.491
0.300	0.500	0.100	0.100	0.470	0.476
0.400	0.100	0.100	0.400	0.715	0.783
0.400	0.100	0.200	0.300	0.707	0.745
0.400	0.100	0.300	0.200	0.681	0.701
0.400	0.100	0.400	0.100	0.644	0.653
0.400	0.200	0.100	0.300	0.672	0.721
0.400	0.200	0.200	0.200	0.651	0.680
0.400	0.200	0.300	0.100	0.619	0.632
0.400	0.300	0.100	0.200	0.584	0.661
0.400	0.300	0.200	0.100	0.597	0.616
0.400	0.400	0.100	0.100	0.582	0.603
0.500	0.100	0.100	0.300	0.800	0.851
0.500	0.100	0.200	0.200	0.763	0.794
0.500	0.100	0.300	0.100	0.721	0.734
0.500	0.200	0.100	0.200	0.744	0.778
0.507	0.197	0.197	0.099	0.702	0.725
0.500	0.300	0.100	0.100	0.692	0.709
0.600	0.100	0.100	0.200	0.838	0.871
0.600	0.100	0.200	0.100	0.791	0.801

[a] $S_{Zn} = \pm 6.08\%$.

5. Conclusions

The coordination numbers in the molecular interaction volume model can be calculated from common physical quantities of pure metals. A significant advantage of the model lies in its ability to predict the thermodynamic properties of quaternary liquid alloys using only binary infinite dilute activity coefficients, and the predicted values are in good agreement with the experimental data of quaternary liquid alloys, which show that the model is reliable, convenient and economic.

References

[1] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Geiser, K.K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, Ohio, 1973.
[2] D.P. Tao, Thermochim. Acta 363 (2000) 105.
[3] T. Iida, R.I.L. Guthrie, The Physical Properties of Liquid Metals, Clarendon Press, Oxford, 1988, p. 19.
[4] D.P. Tao, Nonferrous Met. (Q.) (in Chinese) 45 (1993) 59.
[5] R.C. Evans, An Introduction to Crystal Chemistry, Cambridge University Press, London, 1976, p. 87.
[6] W.T. Thompson, A. Leung, D.G. Hurkot, Can. Metall. Q. 12 (1975) 421.
[7] W. Ptak, Z. Moser, Trans. Metall. Soc. AIME 242 (1968) 558.
[8] W. Ptak, Z. Moser, J. Electrochem. Soc. 119 (1972) 843.