Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 408 (2003) 67–74
thermochimica acta
www.elsevier.com/locate/tca

Prediction of the thermodynamic properties of binary continuous solid solutions by infinite dilute activity coefficients

Dong Ping Tao*

The School of Materials and Metallurgical Engineering, Kunming University of Science and Technology, P.O. Box 62-106, Kunming 650093, Yannan Province, PR China

Received 18 July 2002; received in revised form 19 May 2003; accepted 29 May 2003

Abstract

A new thermodynamic model based on the free volume theory and the lattice model was proposed for solid solutions. A significant advantage of the model lies in its ability to predict the thermodynamic properties of solid solutions using only the binary infinite dilute activity coefficients and the predicted values are in good agreement with their experimental data. This shows that the model with a good physical basis is reliable, convenient and economic.

Keywords: Thermodynamic properties; New model; Solid solutions; Prediction

1. Introduction

The main aim of solutions thermodynamics for model researches is to predict all thermodynamic properties of a multicomponent system using less experimental data as possible, especially only the physical and chemical properties of pure matters and molecular or atomic parameters. The theory of van Laar [1] assumed that the volumetric properties of the pure fluids and the mixture are given by the van der Waals equation and predicts that the nonideality of a solution rises with increasing difference in the critical pressures of the components which is contrary to experiment [2]. This work shows that the molecular interaction volume model [3–5] may be applied to solid solutions after some essential modifications.

2. A new thermodynamic model

Solid atoms are vibrating constantly at one site. In fact, the magnitude of self-diffusion coefficient D of solid atoms is usually about $10^{-10}\,\mathrm{cm^2\,s^{-1}}$ near the melting point of a metal, and the distance the atoms jump per second, d, is about 10^{-11} cm that is an estimate of $d^2 = (D/\nu_0)\exp(\varepsilon/kT)$ when the atomic vibration frequency, ν_0, is about $10^{12}\,\mathrm{s^{-1}}$ and the interstitial atomic potential barrier, ε, is about the average vibration energy of kT. This distance is about 10^3 times less than the size of an atomic cell 10^{-8} cm. It can be seen that the hypothesis that solid atoms are almost in atomic cells all the time is consistent with the basic feature of them motioning at least in a time interval of seconds. According to statistical thermodynamics, therefore, the partition function of the pure solid i is

$$Q_i = Q_{\mathrm{T}i} Q_{\mathrm{p}i} \tag{1}$$

where $Q_{\mathrm{T}i}$ and $Q_{\mathrm{p}i}$ are the partition function of atomic kinetic energy and the configurational partition func-

---

* Tel.: +86-871-511-6730.
E-mail address: dongpingt@yahoo.com.cn (D.P. Tao).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00320-4

tion of the pure solid i respectively, and the last one can be usually expressed as

$$Q_{\mathrm{p}i}=\int_{V_i}\cdots\int \exp\left(-\frac{E_{\mathrm{p}i}}{kT}\right)\mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1\cdots\mathrm{d}x_{N_i}\times\mathrm{d}y_{N_i}\,\mathrm{d}z_{N_i} \qquad (2)$$

where V_i is the volume, $E_{\mathrm{p}i}$ the potential energy, and N_i the atomic number of the pure solid i. The potential energy, $E_{\mathrm{p}i}$, may be chosen as

$$E_{\mathrm{p}i}=\tfrac{1}{2}Z_iN_i\varepsilon_{ii} \qquad (3)$$

where Z_i is the nearest molecules or first coordination number and ε_{ii} is the $i-i$ pair-potential energy. Substituting Eq. (3) into Eq. (2) and considering the basic motion feature of solid atoms above mentioned, then based on the free volume theory and the lattice model [6], Eq. (2) can be simplified as

$$\begin{aligned}Q_{pi}&=\left[\iiint_{\pm\infty}\exp\left(-\frac{Z_i\varepsilon_{ii}}{2kT}\right)\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\right]^{N_i}\\&=\left[\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\varphi\int_{\sigma_i/2}^{r_i}r^2\exp\left(-\frac{Z_i\varepsilon_{ii}}{2kT}\right)\mathrm{d}r\right]^{N_i}\\&=\left(\frac{V_i-V_{i0}}{N_i}\right)^{N_i}\exp\left(-\frac{Z_iN_i\varepsilon_{ii}}{2kT}\right)\end{aligned} \qquad (4)$$

where r_i is the average radius of atomic cells, σ_i is the hard spherical diameter of atoms and V_{i0} is the hard spherical volume of the pure solid i.

Similarly, the partition function and the configurational partition function of the pure solid j are, respectively,

$$Q_j=Q_{\mathrm{T}j}Q_{\mathrm{p}j} \qquad (5)$$

$$Q_{\mathrm{p}j}=\left(\frac{V_j-V_{j0}}{N_j}\right)^{N_j}\exp\left(-\frac{Z_jN_j\varepsilon_{jj}}{2kT}\right) \qquad (6)$$

where the meanings of the symbols are same as those of the pure solid i. The partition functions of the real and the ideal solid solutions of a binary system $i-j$ are, respectively

$$Q=gQ_{\mathrm{T}i}Q_{\mathrm{T}j}Q_{\mathrm{p}},\qquad Q^{\mathrm{id}}=gQ_{\mathrm{T}i}Q_{\mathrm{p}i}Q_{\mathrm{T}j}Q_{\mathrm{p}j} \qquad (7)$$

where g is the combinatorial factor, equal to the number of ways of arranging N_i atoms of pure solid i and N_j atoms of pure solid j on a lattice with a total of (N_i+N_j) sites. To avoid the difficulty of deriving nonrandom combinatorial factor and to stress the free volume variation, here has to hypothesize a completely random mixing of i and j, i.e. a mixture where all possible arrangements of the atoms on the lattice are equally probable, $g=(N_i+N_j)!/(N_i!N_j!)$. The configurational partition function of a binary solid solution $i-j$ is

$$\begin{aligned}Q_{\mathrm{p}}&=\int_V\cdots\int\exp\left(-\frac{\varepsilon_{\mathrm{p}}}{kT}\right)(\mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1\cdots\mathrm{d}x_{N_i}\\&\quad\times\mathrm{d}y_{N_i}\,\mathrm{d}z_{N_i})(\mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1\cdots\mathrm{d}x_{N_j}\,\mathrm{d}y_{N_j}\,\mathrm{d}z_{N_j})\\&=\left[\iiint_{\pm\infty}\exp\left(-\frac{\varepsilon_{\mathrm{p}}}{kT}\right)\mathrm{d}x_i\,\mathrm{d}y_i\,\mathrm{d}z_i\right]^{N_i}\\&\quad\times\left[\iiint_{\pm\infty}\exp\left(-\frac{\varepsilon_{\mathrm{p}}}{kT}\right)\mathrm{d}x_j\,\mathrm{d}y_j\,\mathrm{d}z_j\right]^{N_j}\\&=\left[\iiint_{\pm\infty}\exp\left(-\frac{\varepsilon_{\mathrm{p}}}{kT}\right)\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\right]^{N}\\&=\left(\frac{V-V_0}{N}\right)^{N}\exp\left(-\frac{N\varepsilon_{\mathrm{p}}}{kT}\right)\end{aligned} \qquad (8)$$

where V, V_0 and N are the volume, hard spherical volume and atomic number of the mixture respectively, and ε_{p} is the mixing potential energy function of the atoms i and j.

According to the relation between Gibbs energy and partition function

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

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

$$G=kT\left[\frac{NV}{V-V_0}-N\ln\left(\frac{V-V_0}{N}\right)+\frac{N\varepsilon_{\mathrm{p}}}{kT}-\ln(gQ_{\mathrm{T}i}Q_{\mathrm{T}j})\right] \qquad (10)$$

as well as the Gibbs energies of the pure solids i and j, respectively

$$G_i=kT\left[\frac{N_iV_i}{V_i-V_{i0}}-N_i\ln\left(\frac{V_i-V_{i0}}{N_i}\right)+\frac{Z_iN_i\varepsilon_{ii}}{kT}-\ln(Q_{\mathrm{T}i})\right] \qquad (11)$$

$$G_j = kT\left[\frac{N_jV_j}{V_j - V_{j0}} - N_j \ln\left(\frac{V_j - V_{j0}}{N_j}\right) + \frac{Z_jN_j\varepsilon_{jj}}{kT} - \ln(Q_{\mathrm{T}j})\right] \tag{12}$$

Thus, a new expression of the excess Gibbs energy of the mixture $i - j$ can be achieved as

$$\begin{aligned}
G^{\mathrm{E}} &= \Delta G^{\mathrm{M}} - \Delta G^{\mathrm{idM}} \\
&= (G - G^{\circ}) - (G^{\mathrm{id}} - G^{\circ}) = G - G^{\mathrm{id}} \\
&= kT\left[\frac{NV}{V - V_0}\frac{N_iV_i}{V_i - V_{i0}} - \frac{N_jV_j}{V_j - V_{j0}}\right. \\
&\quad - N\ln\left(\frac{V - V_0}{N}\right) + N_i \ln\left(\frac{V_i - V_{i0}}{N_i}\right) \\
&\quad + N_j \ln\left(\frac{V_j - V_{j0}}{N_j}\right) \\
&\quad \left. + \frac{N}{2kT}\left(2\varepsilon_{\mathrm{p}} - \frac{Z_iN_i\varepsilon_{ii}}{N} - \frac{Z_jN_j\varepsilon_{jj}}{N}\right)\right] \\
&= nRT\left[\frac{V_m}{V_m - V_{m0}} - \frac{x_iV_{mi}}{V_{mi} - V_{mi0}} - \frac{x_jV_{mj}}{V_{mj} - V_{mj0}}\right. \\
&\quad + x_i \ln\left(\frac{V_{mi} - V_{mi0}}{V_m - V_{m0}}\right) + x_j \ln\left(\frac{V_{mj} - V_{mj0}}{V_m - V_{m0}}\right) \\
&\quad \left. + \frac{2\varepsilon_{\mathrm{p}} - Z_ix_i\varepsilon_{ii} - Z_jx_j\varepsilon_{jj}}{2kT}\right]
\end{aligned} \tag{13}$$

where ΔG^{M}, ΔG^{idM} and G° are the real mixing Gibbs energy, ideal mixing Gibbs energy and standard Gibbs energy of the mixture $i - j$, and n is the molar number of the mixture $i - j$, x_i and x_j the molar fractions of the solids i and j, and $V_{\mathrm{m}i}$, $V_{\mathrm{m}j}$ and V_{m} the molar volumes of the solids i and j and the mixture $i - j$, respectively. The space numbers in the solids i and j and the mixture $i - j$, i.e. a reciprocal of space ratio between the molar space volume and the molar volume of a solid, may be defined as, respectively

$$\lambda_i = \frac{V_{\mathrm{m}i}}{V_{\mathrm{m}i} - V_{\mathrm{m}i0}}, \quad \lambda_j = \frac{V_{\mathrm{m}j}}{V_{\mathrm{m}j} - V_{\mathrm{m}j0}}, \quad \lambda = \frac{V_{\mathrm{m}}}{V_{\mathrm{m}} - V_{\mathrm{m}0}} \tag{14}$$

The space fractions of the solids i and j in the mixture $i - j$ may be defined as, respectively

$$\varphi_i = \frac{x_i(V_{\mathrm{m}i} - V_{\mathrm{m}i0})}{V_{\mathrm{m}} - V_{\mathrm{m}0}}, \quad \varphi_j = \frac{x_j(V_{\mathrm{m}j} - V_{\mathrm{m}j0})}{V_{\mathrm{m}} - V_{\mathrm{m}0}} \tag{15}$$

and the excess potential energy function of the mixture $i - j$ is

$$\Delta\varepsilon_{\mathrm{p}} = 2\varepsilon_{\mathrm{p}} - Z_ix_i\varepsilon_{ii} - Z_jx_j\varepsilon_{jj} \tag{16}$$

Thus substituting Eqs. (14) through (16) into Eq. (13), it becomes

$$G^{\mathrm{E}} = nRT\left[\lambda - x_i\lambda_i - x_j\lambda_j + x_i \ln\left(\frac{\varphi_i}{x_i}\right) + x_j \ln\left(\frac{\varphi_j}{x_j}\right) + \frac{\Delta\varepsilon_{\mathrm{p}}}{2kT}\right] \tag{17}$$

Suppose that in the solid solutions $i - j$ there are two types of atomic cells in which the central atoms 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 atoms i and j of surrounding the central atom i, and the local coordination numbers of the cell j are Z_{jj} and Z_{ij} that are defined as the numbers of atoms j and i of surrounding the central atom j, which are proportional to their corresponding Boltzmann's factors, i.e.

$$Z_{ii} = x_i \exp\left(-\frac{\varepsilon_{ii}}{kT}\right), \quad Z_{ji} = x_j \exp\left(-\frac{\varepsilon_{ji}}{kT}\right) \tag{18}$$

$$Z_{jj} = x_j \exp\left(-\frac{\varepsilon_{jj}}{kT}\right), \quad Z_{ij} = x_i \exp\left(-\frac{\varepsilon_{ij}}{kT}\right) \tag{19}$$

Based on the earlier considerations, the local atomic fractions of the atoms i and j surrounding a central atom i can be, respectively, defined as

$$\begin{aligned}
x_{ii} &= \frac{Z_{ii}}{Z_{ii} + Z_{ji}} = \frac{x_i}{x_i + x_jB_{ji}}, \\
x_{ji} &= \frac{Z_{ji}}{Z_{ii} + Z_{ji}} = \frac{x_jB_{ji}}{x_i + x_jB_{ji}}
\end{aligned} \tag{20}$$

and the local atomic fractions of the atoms j and i surrounding a central atom j can be, respectively, defined as

$$\begin{aligned}
x_{jj} &= \frac{Z_{jj}}{Z_{jj} + Z_{ij}} = \frac{x_j}{x_j + x_iB_{ij}}, \\
x_{ij} &= \frac{Z_{ij}}{Z_{jj} + Z_{ij}} = \frac{x_iB_{ij}}{x_j + x_iB_{ij}}
\end{aligned} \tag{21}$$

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

$$B_{ji} = \exp\left[-\frac{(\varepsilon_{ji} - \varepsilon_{ii})}{kT}\right], \quad B_{ij} = \exp\left[-\frac{(\varepsilon_{ij} - \varepsilon_{jj})}{kT}\right] \tag{22}$$

Obviously Eqs. (20) and (21) can satisfy the normalization conditions

$$x_{ii}+x_{ji}=1,\quad x_{jj}+x_{ij}=1 \tag{23}$$

Therefore, the local space fractions of the atoms i and j in the mixture $i-j$ can be expressed as

$$\zeta_i=\frac{x_{ii}V_{si}}{x_{ii}V_{si}+x_{ji}V_{sj}}=\frac{x_iV_{si}}{x_iV_{si}+x_jV_{sj}B_{ji}} \tag{24}$$

$$\zeta_j=\frac{x_{jj}V_{sj}}{x_{jj}V_{sj}+x_{ij}V_{si}}=\frac{x_jV_{sj}}{x_jV_{sj}+x_iV_{si}B_{ij}} \tag{25}$$

where $V_{si}=V_{mi}-V_{mi0}$ and $V_{sj}=V_{mj}-V_{mj0}$ are the molar space of pure solids i and j. For the two types of atomic cells, the mixing potential energy function ε_p of the atoms i and j can be chosen as

$$\varepsilon_p=\tfrac{1}{2}[Z_ix_i(x_{ii}\varepsilon_{ii}+x_{ji}\varepsilon_{ji})+Z_jx_j(x_{jj}\varepsilon_{jj}+x_{ij}\varepsilon_{ij})] \tag{26}$$

The space number in the mixture $i-j$ can be chosen as

$$\lambda=x_i(x_{ii}\lambda_i+x_{ji}\lambda_j)+x_j(x_{jj}\lambda_j+x_{ij}\lambda_i) \tag{27}$$

Then substituting Eqs. (24) through (26) into Eq. (17) in which φ_i and φ_j are replaced by ζ_i and ζ_j, one can achieve a new model of the molar excess Gibbs energy G_m^E of the solid solutions $i-j$

$$\begin{aligned}\frac{G_m^E}{RT}&=x_i\ln\left(\frac{V_{si}}{x_iV_{si}+x_jV_{sj}B_{ji}}\right)\\&\quad+x_j\ln\left(\frac{V_{sj}}{x_jV_{sj}+x_iV_{si}B_{ij}}\right)\\&\quad+\frac{x_ix_j}{2}\left(\frac{B_{ji}[2(\lambda_j-\lambda_i)-Z_i\ln B_{ji}]}{x_i+x_jB_{ji}}\right.\\&\quad\left.+\frac{B_{ij}[2(\lambda_i-\lambda_j)-Z_j\ln B_{ij}]}{x_j+x_iB_{ij}}\right)\end{aligned} \tag{28}$$

Then, from a standard thermodynamic formula:

$$\begin{aligned}\overline{G}_i^E&=RT\ln\gamma_i=G_m^E+\delta\left(\frac{\partial G_m^E}{\partial x_i}\right)_{T,P,x[i,k]}\\&\quad-\sum_{j=1}^{k-1}x_j\left(\frac{\partial G_m^E}{\partial x_j}\right)_{T,P,x[j,k]}\end{aligned}$$

under the conditions of $i\neq k$, $\delta=1$; and $i=k$, $\delta=0$; the new expressions of activity coefficients of the components i and j can be deduced as, respectively

$$\begin{aligned}\ln\gamma_i&=\ln\left(\frac{V_{si}}{x_iV_{si}+x_jV_{sj}B_{ji}}\right)\\&\quad+x_j\left(\frac{V_{sj}B_{ji}}{x_iV_{si}+x_jV_{sj}B_{ji}}-\frac{V_{si}B_{ij}}{x_jV_{sj}+x_iV_{si}B_{ij}}\right)\\&\quad+\frac{x_j^2}{2}\left(\frac{B_{ji}^2[2(\lambda_j-\lambda_i)-Z_i\ln B_{ji}]}{(x_i+x_jB_{ji})^2}\right.\\&\quad\left.+\frac{B_{ij}[2(\lambda_i-\lambda_j)-Z_j\ln B_{ij}]}{(x_j+x_iB_{ij})^2}\right)\end{aligned} \tag{29}$$

$$\begin{aligned}\ln\gamma_j&=\ln\left(\frac{V_{sj}}{x_jV_{sj}+x_iV_{si}B_{ij}}\right)\\&\quad-x_i\left(\frac{V_{sj}B_{ji}}{x_iV_{si}+x_jV_{sj}B_{ji}}-\frac{V_{si}B_{ij}}{x_jV_{sj}+x_iV_{si}B_{ij}}\right)\\&\quad+\frac{x_i^2}{2}\left(\frac{B_{ij}^2[2(\lambda_i-\lambda_j)-Z_j\ln B_{ij}]}{(x_j+x_iB_{ij})^2}\right.\\&\quad\left.+\frac{B_{ji}[2(\lambda_j-\lambda_i)-Z_i\ln B_{ji}]}{(x_i+x_jB_{ji})^2}\right)\end{aligned} \tag{30}$$

Thus, the new model naturally combines the excess entropy and excess enthalpy of a solution by means of new expressions of the configurational partition functions of solids and their mixtures derived from statistical thermodynamics, which is approximate to actual solutions, that is $S^E\neq 0$ ($V^E\neq 0$) and $H^E\neq 0$ due to Eq. (9).

3. Prediction of the thermodynamic properties of binary continuous solid solutions

The activity cefficients of components of the binary solid alloys Ag–Au, Au–Ni, Cd–Mg, Cu–Ni, Cu–Pt, Fe–Ir, Fe–Mn, Fe–Pd, Fe–V and Ni–Pt at some temperatures [7] may be chosen to check Eqs. (29) and (30). In order to determine the required binary parameters B_{ji} and B_{ji}, the infinite dilute activity coefficients of the those binary solid alloys and the related parameters of their components must have been found out for the model as shown in Tables 1 and 2, where $\sigma_i/2$ is the hard spherical radius which may be assumed to be equal to the atomic radius of corresponding to 12-coordination [8], $V_{m0i}=(4\pi/3)(\sigma_i/2)^3$ and V_{mi}

Table 1
The related parameters of some components

i	$\sigma_i/2$ (10^{-8} cm)	V_{m0i} (cm^3/mol)	V_{mi} (cm^3/mol)
Ag	1.445	7.611	10.30
Au	1.442	7.564	10.20
Cd	1.568	9.725	13.10
Cu	1.278	5.265	7.10
Fe	1.274	5.216	7.10
Ir	1.357	6.303	8.54
Mn	1.254	4.974	7.39
Ni	1.246	4.880	6.60
Pt	1.387	6.731	9.10
V	1.346	6.151	8.35

is experimental.The B_{ji} and B_{ij} can be determined by the procedure as follows. When x_i or x_j approaches zero, the infinite dilution activity coefficients γ_i^∞ and γ_j^∞ are derived from Eqs. (29) and (30), respectively

$$\begin{aligned}\ln\gamma_i^\infty &= 1-\ln\left(\frac{V_{sj}B_{ji}}{V_{si}}\right)-\frac{V_{si}B_{ij}}{V_{sj}}\\ &\quad+\frac{1}{2}[2(\lambda_j-\lambda_i)-Z_i\ln B_{ji}]\\ &\quad+\frac{1}{2}[2(\lambda_i-\lambda_j)-Z_j\ln B_{ij}] \qquad (31)\end{aligned}$$

$$\begin{aligned}\ln\gamma_j^\infty &= 1-\ln\left(\frac{V_{si}B_{ij}}{V_{sj}}\right)-\frac{V_{sj}B_{ji}}{V_{si}}\\ &\quad+\frac{1}{2}[2(\lambda_i-\lambda_j)-Z_j\ln B_{ij}]\\ &\quad+\frac{1}{2}[2(\lambda_j-\lambda_i)-Z_i\ln B_{ji}] \qquad (32)\end{aligned}$$

The parameter B_{ij} is solved by connecting Eqs. (31) and (32)

$$B_{ij}=\exp(B) \qquad (33)$$

Table 2
The values of γ_i^∞, γ_j^∞ [7], B_{ji}, and B_{ij} of the binary solid alloys $i-j$

$i-j$	T (K)	γ_i^∞	γ_j^∞	B_{ji}	B_{ij}
Ag–Au	800	0.158	0.094	1.3085	0.9947
Au–Ni	1150	10.215	5.151	0.7167	0.9869
Cd–Mg	543	0.035	0.036	1.2252	1.2534
Cr–Mo	1471	3.644	6.245	1.0307	0.7414
Cu–Ni	973	5.898	3.285	0.7167	1.0764
Cu–Pt	1350	0.048	0.008	1.5607	0.9836
Fe–Ir	1473	0.025	0.010	1.4292	1.1599
Fe–Mn	1450	1.764	1.542	0.7705	1.1863
Fe–V	1600	0.129	0.045	1.4407	0.9218
Ni–Pt	1625	0.126	0.048	1.3902	0.9575

$$\begin{aligned}B&=\frac{2}{2+Z_j}\left(1-\ln\frac{V_{si}\gamma_j^\infty}{V_{sj}}-\frac{V_{sj}B_{ji}}{V_{si}}+\lambda_i-\lambda_j\right.\\ &\quad\left.+\frac{B_{ji}}{2}[2(\lambda_j-\lambda_i)-Z_i\ln B_{ji}]\right) \qquad (34)\end{aligned}$$

Let a function and its derivative be, respectively

$$\begin{aligned}f(B_{ji})&=\ln\gamma_i^\infty-1+\ln\left(\frac{V_{sj}B_{ji}}{V_{si}}\right)\\ &\quad-\frac{1}{2}[2(\lambda_j-\lambda_i)-Z_i\ln B_{ji}]\\ &\quad+\left(\frac{V_{si}}{V_{sj}}-\frac{1}{2}[2(\lambda_i-\lambda_j)-Z_jB]\right)\exp(B) \qquad (35)\end{aligned}$$

$$\begin{aligned}f'(B_{ji})&=\frac{2+Z_i}{2B_{ji}}+\left(\frac{V_{si}}{V_{sj}}-(\lambda_i-\lambda_j)+\frac{Z_j}{2}(1+B)\right)\\ &\quad\times B'\exp(B) \qquad (36)\end{aligned}$$

$$B'=-\frac{2}{2+Z_j}\left(\frac{V_{sj}}{V_{si}}+\frac{Z_i}{2}(1+\ln B_{ji})-(\lambda_j-\lambda_i)\right) \qquad (37)$$

According to the Newton formulas, here has

$$B_{ji(n+1)}=B_{ji(n)}-\frac{f[B_{ji(n)}]}{f'[B_{ji(n)}]} \qquad (38)$$

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 $|B_{ji(n)}-B_{ji(n+1)}|\le 10^{-6}$ by Eqs. (33) through (38) in which $Z_i=Z_j=12$.

Substituting the corresponding B_{ji} and B_{ij} in Table 2 into Eqs. (29) and (30), the predicted values of activity of both components in the solid solutions can be obtained, as shown in Tables 3 through 12. It can be seen that the predicted average deviations compared with the experimental data, $S_i=\pm\left[\sum(a_{i,\mathrm{exp}}-a_{i,\mathrm{pre}})^2/n\right]^{1/2}$, are less than the experimental deviations or approximate to that, S_i^*. This shows that the new model is quite convenient and reliable for predicting the thermodynamic properties of binary continuous solid solutions that requires only the binary infinite dilute activity coefficients.

Table 3
Comparison of the predicted values with the experimental data of activity of both components in the Ag–Au solid alloys at 800 K

x_{Ag}	$a_{Ag,pre}$	$a_{Ag,exp}$	$a_{Au,pre}$	$a_{Au,exp}$
0.100	0.021	0.021	0.887	0.887
0.200	0.055	0.054	0.751	0.753
0.300	0.107	0.104	0.603	0.604
0.400	0.180	0.177	0.455	0.454
0.500	0.280	0.277	0.318	0.315
0.600	0.406	0.404	0.201	0.198
0.700	0.555	0.555	0.112	0.110
0.800	0.718	0.719	0.052	0.050
0.900	0.875	0.875	0.016	0.016
	$S_{Ag} = \pm 0.0018$		$S_{Au} = \pm 0.0018$	
	$S^{*}_{Ag} = \pm 0.025$		$S^{*}_{Ag} = \pm 0.035$	

Table 4
Comparison of the predicted values with the experimental data of activity of both components in the Au–Ni solid alloys at 1150 K

x_{Au}	$a_{Au,pre}$	$a_{Au,exp}$	$a_{Ni,pre}$	$a_{Ni,exp}$
0.100	0.563	0.557	0.928	0.929
0.200	0.705	0.673	0.895	0.902
0.300	0.734	0.683	0.884	0.898
0.400	0.737	0.693	0.882	0.891
0.500	0.743	0.717	0.876	0.866
0.600	0.761	0.754	0.851	0.813
0.700	0.794	0.799	0.785	0.737
0.800	0.843	0.848	0.651	0.607
0.900	0.911	0.914	0.408	0.388
	$S_{Au} = \pm 0.0268$		$S_{Ni} = \pm 0.0268$	
	$S^{*}_{Au} = \pm 0.025$		$S^{*}_{Ni} = \pm 0.035$	

Table 5
Comparison of the predicted values with the experimental data of activity of both components in the Cd–Mg solid alloys at 543 K

x_{Cd}	$a_{Cd,pre}$	$a_{Cd,exp}$	$a_{Mg,pre}$	$a_{Mg,exp}$
0.100	0.007	0.004	0.869	0.889
0.200	0.024	0.012	0.698	0.737
0.300	0.060	0.031	0.517	0.541
0.400	0.123	0.076	0.352	0.333
0.500	0.220	0.172	0.218	0.171
0.600	0.354	0.332	0.122	0.077
0.700	0.519	0.539	0.060	0.031
0.800	0.700	0.739	0.024	0.012
0.900	0.870	0.891	0.007	0.004
	$S_{Cd} = \pm 0.0304$		$S_{Mg} = \pm 0.0300$	
	$S^{*}_{Cd} = \pm 0.01$		$S^{*}_{Mg} = \pm 0.01$	

Table 6
Comparison of the predicted values with the experimental data of activity of both components in the Cr–Mo solid alloys at 1471 K

x_{Cr}	$a_{Cr,pre}$	$a_{Cr,exp}$	$a_{Mo,pre}$	$a_{Mo,exp}$
0.100	0.304	0.290	0.909	0.911
0.200	0.510	0.474	0.834	0.839
0.300	0.644	0.600	0.773	0.777
0.400	0.728	0.683	0.724	0.725
0.500	0.781	0.744	0.685	0.677
0.600	0.814	0.792	0.650	0.626
0.700	0.842	0.838	0.611	0.564
0.800	0.874	0.879	0.544	0.487
0.900	0.922	0.926	0.393	0.357
	$S_{Cr} = \pm 00287$		$S_{mo} = \pm 0.0289$	
	$S^{*}_{Cr} = \pm 0.025$		$S^{*}_{Mo} = \pm 0.025$	

Table 7
Comparison of the predicted values with the experimental data of activity of both components in the Cu–Ni solid alloys at 973 K

x_{Cu}	$a_{Cu,pre}$	$a_{Cu,exp}$	$a_{Ni,pre}$	$a_{Ni,exp}$
0.100	0.371	0.369	0.922	0.922
0.200	0.516	0.506	0.873	0.876
0.300	0.584	0.566	0.839	0.844
0.400	0.627	0.610	0.808	0.811
0.500	0.666	0.659	0.768	0.761
0.600	0.711	0.713	0.709	0.690
0.700	0.764	0.767	0.618	0.601
0.800	0.829	0.832	0.481	0.469
0.900	0.908	0.908	0.281	0.277
	$S_{cu} = \pm 0.0093$		$S_{Ni} = \pm 0.0101$	
	$S^{*}_{Cu} = \pm 0.03$		$S^{*}_{Ni} = \pm 0.04$	

Table 8
Comparison of the predicted values with the experimental data of activity of both components in the Cu–Pt solid alloys at 1350 K

x_{Cu}	$a_{Cu,pre}$	$a_{Cu,exp}$	$a_{Pt,pre}$	$a_{Pt,exp}$
0.100	0.007	0.008	0.882	0.877
0.200	0.021	0.025	0.732	0.721
0.300	0.046	0.053	0.563	0.561
0.400	0.088	0.095	0.394	0.410
0.500	0.159	0.163	0.243	0.263
0.600	0.268	0.266	0.128	0.144
0.700	0.425	0.416	0.054	0.062
0.800	0.626	0.616	0.017	0.019
0.900	0.841	0.836	0.003	0.003
	$S_{Cu} = \pm 0.0062$		$S_{Pt} = \pm 0.0111$	
	$S^{*}_{Cu} = \pm 0.01$		$S^{*}_{Pt} = \pm 0.01$	

Table 9
Comparison of the predicted values with the experimental data of activity of both components in the Fe–Ir solid alloys at 1473 K

x_{Fe}	$a_{Fe,pre}$	$a_{Fe,exp}$	$a_{Fe,pre}$	$a_{Fe,exp}$
0.100	0.005	0.004	0.872	0.878
0.200	0.016	0.012	0.702	0.720
0.300	0.040	0.030	0.517	0.541
0.400	0.085	0.062	0.344	0.362
0.500	0.163	0.122	0.203	0.207
0.600	0.282	0.232	0.104	0.095
0.700	0.447	0.427	0.044	0.030
0.800	0.648	0.674	0.014	0.008
0.900	0.851	0.870	0.003	0.002
	$S_{Fe} = \pm 0.0265$		$S_{Ir} = \pm 0.0133$	
	$S^*_{Fe} = \pm 0.008$		$S^*_{Ir} = \pm 0.009$	

Table 10
Comparison of the predicted values with the experimental data of activity of both components in the Fe–Mn solid alloys at 1450 K

x_{Fe}	$a_{Fe,pre}$	$a_{Fe,exp}$	$a_{Mn,pre}$	$a_{Mn,exp}$
0.100	0.154	0.152	0.906	0.907
0.200	0.276	0.272	0.821	0.822
0.300	0.378	0.375	0.740	0.740
0.400	0.470	0.469	0.659	0.656
0.500	0.556	0.557	0.575	0.570
0.600	0.640	0.641	0.484	0.480
0.700	0.725	0.726	0.383	0.381
0.800	0.812	0.812	0.271	0.270
0.900	0.903	0.903	0.144	0.144
	$S_{Fe} = \pm 0.0019$		$S_{Mn} = \pm 0.0024$	
	$S^*_{Fe} = \pm 0.019$		$S^*_{Mn} = \pm 0.0020$	

Table 11
Comparison of the predicted values with the experimental data of activity of both components in the Fe–V solid alloys at 1600 K

x_{Fe}	$a_{Fe,pre}$	$a_{Fe,exp}$	$a_{V,pre}$	$a_{V,exp}$
0.100	0.017	0.018	0.887	0.884
0.200	0.044	0.049	0.752	0.745
0.300	0.086	0.095	0.602	0.597
0.400	0.148	0.160	0.449	0.450
0.500	0.237	0.249	0.306	0.314
0.600	0.357	0.370	0.185	0.195
0.700	0.510	0.516	0.095	0.103
0.800	0.686	0.687	0.039	0.043
0.900	0.863	0.861	0.010	0.012
	$S_{Fe} = \pm 0.0081$		$S_{V} = \pm 0.0061$	
	$S^*_{Fe} = \pm 0.01$		$S^*_{V} = \pm 0.01$	

Table 12
Comparison of the predicted values with the experimental data of activity of both components in the Ni–Pt solid alloys at 1625 K

x_{Ni}	$a_{Ni,pre}$	$a_{Ni,exp}$	$a_{Pt,pre}$	$a_{Pt,exp}$
0.100	0.017	0.016	0.887	0.888
0.200	0.044	0.042	0.750	0.753
0.300	0.087	0.082	0.599	0.601
0.400	0.150	0.144	0.446	0.444
0.500	0.240	0.235	0.303	0.298
0.600	0.362	0.358	0.184	0.177
0.700	0.514	0.515	0.095	0.090
0.800	0.689	0.693	0.039	0.037
0.900	0.864	0.867	0.011	0.010
	$S_{Ni} = \pm 0.0037$		$S_{Pt} = \pm 0.0037$	
	$S^*_{Ni} = \pm 0.011$		$S^*_{Pt} = \pm 0.014$	

4. Conclusion

A new thermodynamic model based on the free volume theory and the lattice model was proposed for solid solutions. The space numbers in the solids i and j and the mixture $i - j$, and the space fractions and the local space fractions of the solids i and j in the mixture $i - j$ were defined, respectively. A significant advantage of the model lies in its ability to predict the thermodynamic properties of binary continuous solid solutions using only the binary infinite dilute activity coefficients. The predicted values with the model are in good agreement with those experimental data. This shows that the model is reliable, convenient and economic and has a good physical basis.

Acknowledgements

Financial support from The Joint Fund of National Natural Science Foundation of China and Baoshan Steel Complex of Shanghai under Grant no. 50274039 is gratefully acknowledged.

References

[1] J.J. van Laar, Z. Physik Chem. 72 (1910) 723.

[2] J. M. Prausnitz, R.N. Lichtenthaler, E.G.D. Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, Second ed., Prentice-Hall, Englewood Cliffs, NJ, 1986, p. 276.

[3] D.P. Tao, Thermochim. Acta 363 (2000) 105.

[4] D.P. Tao, Metall. Mater. Trans. B 32B (2001) 1205.
[5] D.P. Tao, B. Yang, D.F. Li, Fluid Phase Equilibria 193 (2002) 167.
[6] A. Munster, Statistical Thermodynamics, vol. II, Academic Press, New York, 1974, p. 328, 641.
[7] 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.
[8] R. Ferro, A. Saccone, Structure of Solids, in: V. Gerold (Ed.), VCH Verlagasgesellschaft, Weinheim, 1993, p. 194.