Modeling activity and interaction coefficients of components of multicomponent alloy melts: An example of iron melt

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Abstract: As a popular thermodynamic calculation method for binary alloys, Miedema's model has been applied in many fields. Chou's Model, a new generation of geometric model for ternary and multicomponent alloy systems, overcomes the intrinsic theoretical defects (including symmetric and asymmetric) existing in some original geometric models. Here, by means of combining Miedema's model and Chou's model as well as including the consideration of the excess entropy we attempted to build the new thermodynamic model to evaluate thermodynamic properties of ternary and multicomponent alloying systems in terms of the physical parameters (molar volume, electronegativity, electronic density and melting point) of constituents. Moreover, the activity and interaction coefficients of a wide of components in iron melt have been discussed in details.

Key words: Miedema's model, Chou's model, Ternary alloy, Free volume theory, Excess entropy

1. Introduction

As the fundamental physical parameters, thermodynamic parameters of alloy systems are not only important for the development of new techniques but also for the optimization of industrial process in many fields, such as metallurgy, materials, casting and welding, and so on. It is well-known that most particle systems are non-ideal alloy melt in the field metallurgy. Therefore, to describe accurately the thermodynamic parameters of alloy melts, it is necessary to replace the so-called concept of concentration with the activity [1]. In fact, the activity coefficient can be measured by experiments, such as vapor pressure methods, electromotive force measurements, and formation calorimetry techniques et al[2]. However, due to complexity and lack of accuracy, the results obtained by high temperature experiments quite often differ highly to some extent, resulting in the waste of time-consuming and expensive experimental processes and materials. Due to the difficulty in high temperature experiments, it's thus desirable to develop theoretical methods to evaluate thermodynamic properties for metallurgical melts.

Given the fact that thermodynamic behaviors in the actual alloy melts are highly complicated [3], numerous theoretical and empirical models have been proposed to estimate thermodynamic properties (regular solution model[4], Miedema's model[5], Wilson's model[6], Toop Model, and Chou's model[7-8], etc.) off alloy melts during the last few decades. Each model has its own pros and cons. For instance, due to self-deficiency, the regular solution model[4] is only limited to the alloy with similar atomic volume and molecular structure. In particular, to solve the original Toop and other models' symmetric and asymmetric defects, Chou [7,8] have proposed successfully a new ternary alloy model (called Chou's model). This geometric model introduced a concept of "similarity criterion" with an aim of reducing the impacts of artificial effects. In the meanwhile, Chou's model still provides the useful solution[7,8] to solve the intrinsic problem by reducing the traditional ternary models to their corresponding binary ones.

It is clear that the Chou’s geometric model indeed establishes a bridge between binary and ternary (or multicomponent) systems. However, the description of ternary (or multicomponent) alloy systems has to be dependent on the successful description of the thermodynamic properties of binary alloys. Fortunately, there have been many attempts in the past to establish valid theoretical models to predict the enthalpies of formation of binary compounds. The earliest attempt was by Hume-Rothery *et. al*, who proposed empirical rules to predict the formation of alloys by considering the atomic size, electrochemical, and valence electron factors of constituent elements. In the early 1950s, Darken and Gurry constructed a two-dimensional map using the atomic size and electronegativity as the intrinsic parameters to predict the formation of solid solutions. In the early 1970s, Phillips *et al.* proposed a relationship for the enthalpies of formation of the covalent compounds using the ionization energy as a parameter. In the mid-1970s, Miedema *et al.* proposed a semi-empirical model to calculate the enthalpies of formation for binary transition-metal alloys based on the molar volume, electronegativity, and electronic density of constituent elements. Among these models, the Miedema's model is the most prevalent one and has been applied extensively, although the predicted values are often inaccurate. The validity of Miedema’s theory has led to numerous applications in solid solution, formation of amorphous alloy, alloy surface energy, vacancy formation energy, and Calphad, and so on.

In this work, based on binary Miedema’s model and Chou’s model for multicomponent systems, we attempted to derive the theoretical formula for a series of thermodynamic properties in coupling with excess entropy introduced by free volume theory. In particular, in combinations of with several basic thermodynamic relations, we derived the activity coefficient of a solute at infinite dilution solution, $\ln\gamma^0$ and an activity interaction coefficient ε_i^j in liquid iron-base systems. The obtained results are also compared with available experimental data.

2.1 Enthalpies of formation for binary systems

Through Miedema’s model, we can calculate enthalpies of formation as follows [5]:

$$\Delta H_{ij} = f_{ij}\frac{x_i\left[1+\mu_i x_j\left(\phi_i-\phi_j\right)\right]x_j\left[1+\mu_j x_i\left(\phi_j-\phi_i\right)\right]}{x_iV_i^{2/3}\left[1+\mu_i x_j\left(\phi_i-\phi_j\right)\right]+x_jV_j^{2/3}\left[1+\mu_j x_i\left(\phi_j-\phi_i\right)\right]} \qquad (1)$$

$$f_{ij}=\frac{2pV_i^{2/3}V_j^{2/3}\left\{q/p\left[\left(n_{Ws}^{1/3}\right)_i-\left(n_{Ws}^{1/3}\right)_j\right]^2-\left(\phi_i-\phi_j\right)^2-a(r/p)\right\}}{\left(n_{WS}^{1/3}\right)_i^{-1}+\left(n_{Ws}^{1/3}\right)_j^{-1}}$$

where p, q, μ, a, r/p –empirical constants; n_{WS} – the boundary electron density of the Wigner-Seitz cell; V – molar Volume; ϕ – electronegativity. For solid alloys a=1, liquid alloys a=0.73.

2.2 Gibbs free energy

Based on the enthalpies of formation specified in Eq. (1) and after the introduction of the excess entropy terms (excess vibrational entropy and excess configuration entropy), the excess Gibbs free energy can be further derived as a function of temperatures. Because the basic physical picture of the free volume theory assumes that each atom in a liquid metal vibrates harmonically in a cell comprised by its nearest-neighboring atoms [9], the excess vibrational entropy ΔS_{VIB}^{E} and excess configuration entropy ΔS_{CONF}^{E} can be further derived as follows,

$$\Delta S_{CONF}^{E} = \Delta H_{ij} / \left(2T\right) + \left(R/4\right)\left[1 - 4\Delta H_{ij} / \left(RT\right)\right]^{1/2} - R/4 \tag{2}$$

$$\Delta S_{VIB}^{E} = 3/2 R x_j x_i \left[\frac{\left(L_{ii} - L_{jj}\right)^2}{L_{ii} L_{jj}} + 2 - \frac{\left(U_{ii} + U_{jj}\right)^2}{2 U_{ii} U_{jj}} \right] + \frac{3}{4} R^2 T \frac{\left(U_{ii} + U_{jj}\right)}{U_{ii} U_{jj}} \left[1 - \left(1 - \frac{4\Delta H_{ij}}{RT} \right)^{1/2} \right] \tag{3}$$

Combined with the following relations:

$$\Delta G_{ij}^{E} = \Delta H_{ij} - T \Delta S_{ij}^{E} \tag{4}$$

$$\Delta S_{ij}^{E} = \Delta S_{CONF}^{E} + \Delta S_{VIB}^{E} \tag{5}$$

From Eqs (1) – (5), we can get the excess gibbs free energy[10]:

$$\Delta G_{ij}^{E} = \frac{\Delta H_{ij}}{2} - \frac{3}{2} B_{ij} RT x_i x_j - A_{ij} T \left[\left(1 - \frac{4\Delta H_{ij}}{RT} \right)^{1/2} - 1 \right] \tag{6}$$

where:

$$A_{ij} = R/4 + 3/4 \cdot R^2 T \left(U_{ii} + U_{jj}\right) / (U_{ii} U_{jj})$$

$$B_{ij} = \left(L_{ii} - L_{jj}\right)^2 / (L_{ii} L_{jj}) + 2 - (U_{ii} + U_{jj})^2 / (2 U_{ii} U_{jj})$$

$L_{ii} = 1/2(\sqrt{2} V_i / N_0)^{1/3}$ (i can be substituted by j)

$$U_{ii} = -685 \cdot \beta_i^2 T_{m,i}$$

where N_0 –Avogadro constant; $T_{m,i}$ – melting point of component i; V_i – the molar volume of component i; β_i – the frequency factor, in general $\beta_i = 0.5$ [11]. From the above equations Eq. (1) to Eq. (6), for any binary system the temperature and concentration dependent Gibbs free energies can be estimated just after knowing four basic physical parameters: moral volume (V), electronic densitie (n_{WS}), electronegativity (ϕ), and the melting point (T_m) of the constituents in binary alloys.

2.3 Chou' s model[7-8]

Combining the excess Gibbs free energies from Eqs (1 to 6) for binary systems to the well-known Chou's geometric model, the excess Gibbs free energy of a i-j-k system ΔG^E can be obtained from the three related excess energy free energies of binary systems, namely, ΔG_{ij}^E for i-j system, ΔG_{jk}^E for j-k system, and ΔG_{ki}^E for k-i system:

$$\Delta G^E = \frac{x_i x_j \Delta G_{ij}^E}{\left(x_i + x_k \xi_{ij}\right)\left(x_j + x_k \xi_{ji}\right)} + \frac{x_j x_k \Delta G_{jk}^E}{\left(x_j + x_i \xi_{jk}\right)\left(x_k + x_i \xi_{kj}\right)} + \frac{x_k x_i \Delta G_{ki}^E}{\left(x_k + x_j \xi_{ki}\right)\left(x_i + x_j \xi_{ik}\right)} \tag{7}$$

where x_i, x_j, x_k -the molar fraction of i, j, k in i-j,j-k,k-i systems; ξ_{ij}, ξ_{jk}, ξ_{ki} - the similarity criterions in different systems.

$$\left.\begin{array}{l} \xi_{ij} = \dfrac{\eta_i}{\eta_i + \eta_j}, \xi_{ji} = \dfrac{\eta_j}{\eta_i + \eta_j} \\ \xi_{jk} = \dfrac{\eta_j}{\eta_k + \eta_j}, \xi_{kj} = \dfrac{\eta_k}{\eta_k + \eta_j} \\ \xi_{\mathrm{ki}} = \dfrac{\eta_k}{\eta_k + \eta_i}, \xi_{ik} = \dfrac{\eta_i}{\eta_i + \eta_k} \end{array}\right\} \tag{8}$$

Here, the sum of squared deviations of η_i, η_j, and η_k can be obtained by the following relations

$$\left.\begin{array}{l} \eta_i = \int_0^1 \left(\Delta G_{ij}^E - \Delta G_{ki}^E\right)^2 dx_i \\ \eta_j = \int_0^1 \left(\Delta G_{jk}^E - \Delta G_{ij}^E\right)^2 dx_j \\ \eta_k = \int_0^1 \left(\Delta G_{ki}^E - \Delta G_{jk}^E\right)^2 dx_k \end{array}\right\} \tag{9}$$

2.4 Activity coefficients of ternary system

In a ternary system, i-j-k, the mole fractions of elements i, j, and k are denoted by x_i, x_j, x_k. If k is considered as a solvent and i and j as solutes, the following relations exist at a certain temperature T;

$$RT \ln \gamma_i = \Delta G^E + \frac{\partial \Delta G^E}{\partial x_i} - \sum_{m=i,j,k} x_m \frac{\partial \Delta G^E}{\partial x_m} \tag{10}$$

When $x_j=0$，$x_k \to 1$, we obtain the activity coefficient of a solute at infinite dilution solution:

$$\Delta G_{ij}^{E} = 0, \Delta G_{jk}^{E} = 0 \qquad （11）$$

Simplify Eq(7), we obtain:

$$\Delta G^{E} = \frac{x_i x_j \Delta G_{ik}^{E}}{\left(x_k + \xi_{ki} x_j\right)\left(x_i + \xi_{ik} x_j\right)} \qquad (12)$$

The activity coefficient of a solute at infinite dilution solution, $\ln \gamma_i^0$ can be obtained by following relation:

$$\ln \gamma_i^0 = \frac{1}{RT}\left(\Delta G^{E} + \frac{\partial \Delta G^{E}}{\partial x_i}\right)_{x_j \to 0, x_k \to 1} \qquad (13)$$

As x_j=0，x_k→1,

$$\Delta G^{E} = \Delta G_{ik}^{E} \to 0 \qquad (14)$$

$$\left.\frac{\partial \Delta G^{E}}{\partial x_i}\right|_{x_j=0,\, x_k \to 1} = \frac{1}{RT}\left[\left(\frac{1}{2} + \frac{2A_{ik}}{R}\right)\frac{\partial \Delta H_{ik}}{\partial x_i} - \frac{3}{2} B_{ik} RT\right] \qquad (15)$$

Combining Eqs (1), (14), and (15), we obtain,

$$\ln \gamma_i^0 = \frac{1}{RT}\left[\frac{f_{ik}\left[1 + \mu_i\left(\varphi_i - \varphi_k\right)\right]}{V_K^{2/3}}\left(\frac{1}{2} + \frac{2A_{ik}}{R}\right) - \frac{3}{2} B_{ik} RT\right] \qquad (16)$$

2.5 Interaction parameters of i-j-k system

In the ternary system i-j-k, the relation for partial molar excess free energy are presented as[12],

$$\begin{aligned}
\overline{G}_i^{E} &= \Delta G^{E} - x_i \frac{\partial \Delta G^{E}}{\partial x_j} + \left(1 - x_j\right)\frac{\partial \Delta G^{E}}{\partial x_j} \\
\overline{G}_j^{E} &= \Delta G^{E} - x_j \frac{\partial \Delta G^{E}}{\partial x_i} + \left(1 - x_j\right)\frac{\partial G^{E}}{\partial x_j} \\
\overline{G}_k^{E} &= \Delta G^{E} - x_i \frac{\partial \Delta G^{E}}{\partial x_i} + x_j \frac{\partial \Delta G^{E}}{\partial x_j}
\end{aligned} \qquad (17)$$

And by the definition of Wagner, we obtain ε_i^i and ε_i^j [13]:

$$\varepsilon_i^i = \frac{1}{RT}\left(\frac{\partial^2 \Delta G^E}{\partial x_i^2}\right)_{x_k \to 1} \tag{18}$$

$$\varepsilon_i^j = \frac{1}{RT}\left(\frac{\partial^2 \Delta G^E}{\partial x_j \partial x_i}\right)_{x_k \to 1} \tag{19}$$

Combine Eqs (6), (15), (18), (19):

$$\begin{aligned}\varepsilon_i^i &= \frac{1}{RT}\left\{\frac{\partial}{\partial x_i}\left[\left(\frac{\partial \Delta H_{ik}}{\partial x_i}\right)_{x_k \to 1}\left(1/2+\frac{2A_{ik}}{R}\right)-\frac{3}{2}B_{ik}RT\right]\right\} \\ &= \frac{1}{RT}\left(\frac{\partial^2 \Delta H_{ik}}{\partial x_i^2}\right)_{x_k \to 1}\left(\frac{1}{2}+\frac{2A_{ik}}{R}\right)\end{aligned} \tag{20}$$

$$\begin{aligned}\varepsilon_i^j = {} & \frac{1}{\xi_{ij}\xi_{ji}RT} f_{ij}\left\{\frac{1}{V^{2/3}\left[1+\mu_i\left(\varphi_i-\varphi_j\right)\right]}+\frac{1}{V^{2/3}\left[1+\mu_j\left(\varphi_j-\varphi_i\right)\right]}\right\}^{-1} \\ & -\frac{1}{RT} f_{ik}V_i^{2/3}\left\{\xi_{ki}+\mu_i\left(\varphi_i-\varphi_k\right)+\xi_{ik}\left[1+\mu_i\left(\varphi_i-\varphi_k\right)\right]^2\frac{V_i^{2/3}}{V_k^{2/3}}\right\}\cdot \\ & \left(\frac{1}{2}+\frac{2A_{ik}}{R}\right)-\frac{1}{RT} f_{jk}V_j^{2/3}\left\{\xi_{kj}+\mu_j\left(\varphi_j-\varphi_k\right)+\xi_{jk}\left[1+\mu_j\left(\varphi_j-\varphi_k\right)\right]^2\frac{V_j^{2/3}}{V_k^{2/3}}\right\}\cdot\left(\frac{1}{2}+\frac{2A_{jk}}{R}\right)\end{aligned} \tag{21}$$

where

$$\frac{\partial^2 \Delta H_{ik}}{\partial x_i^2}_{x_k \to 1} = -2 f_{ik}V_i^{2/3}\left\{\mu_i\left(\varphi_i-\varphi_k\right)+\left[1+\mu_i\left(\varphi_i-\varphi_k\right)\right]^2\frac{V_i^{2/3}}{V_k^{2/3}}\right\}$$

3. Results and discussion

In terms of Eqs (16) and (21), the active coefficient of $\ln\gamma_i^0$ and interaction coefficients of ε_i^j of elements in liquid iron-base alloys are calculated in Tables 1 and 2. Furthermore, the calculated results are compared with available experimental data[15] and theoretical values from literature (14). Those results calculated within the model are found to be reasonably close to available experimental values, seeming to have a better agreement than those in Ref. (14). The reason can be attributed to the success inclusion of excess entropies in this work.

3.1 Activity coefficients of a solute at infinite dilution $\ln \gamma_i^0$

Table 1 the comparison of the Calculation and Experiment Values of $\ln \gamma_i^0$ in Iron-Base Alloys at 1873K

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Y
Cal. ln γ_i^0	-2.95	-3.99	-1.58	-0.26	0.05	0	-0.12	-0.33	-0.49
Cal.Ref. [14]	-3.4	-4.7	-1.88	-0.37	0.06	0	-0.14	-0.39	-0.38
Exp[15]	-	-4.71	-2.3	0.0	0.36	0	-0.6	-0.42	-1.08
Element	Zr	Nb	Mo	Tc	Ru	Rh	Pd	La	Ce
Cal.ln γ_i^0	-6.48	-3.72	-0.26	-0.63	-0.91	-1.20	-1.02	1.12	-2.25
Cal.Ref. [14]	-7.56	-4.48	-0.55	-0.84	-1.26	-1.47	-1.57	0.87	0.23
Exp[15]	-3.30	-1.61	-0.36	-	-	-	-	2.22	-1.14
Element	Pr	Nd	Pm	Sm	Eu	Ho	Er	Yb	Lu
Cal.ln γ_i^0	-0.34	-3.08	-3.71	-3.49	-3.3	-3.68	-4.26	-3.82	-4.78
Cal.Ref. [14]	0.23	0.23	-0.68	-0.38	-0.38	-0.66	-1.48	-1.45	-2.25
Exp[15]	-	-1.75	-	-	-	-	-	-	-
Element	Hf	Ta	W	Re	Os	Ir	Pt	Th	U
Cal.ln γ_i^0	-1.17	2.66	6.34	1.94	5.12	11.39	15.95	15.23	15.91
Cal.Ref. [14]	-6.23	-4.28	-0.01	-0.09	-1.11	-2.44	-3.73	-3.68	-3.53
Exp[15]	-	-	-	-	-	-	-	-	-
Element	Pu	Cu	Ag	Au	Li	Na	K	Rb	Cs
Cal.ln γ_i^0	-1.17	2.66	6.34	1.94	5.12	11.39	15.95	15.23	15.91
Cal.Ref. [14]	-1.83	3.20	7.85	2.36	6.02	17.69	27.63	30.44	8.22
Exp[15]	-	2.15	5.30	-	-		-	-	-
Element	Ca	Sr	Ba	Zn	Cd	Hg	B	Al	Ga
Cal.ln γ_i^0	4.89	7.74	8.42	1.09	4.05	5.42	-5.16	-2.22	0.0087
Cal.Ref. [14]	8.22	12.19	13.60	0.92	4.91	14.16	-6.07	-3.05	-0.51
Exp[15]	-	-	-	-	-	-	-	-0.32	-
Element	In	Tl	C	Si	Ge	Sn	Pb	P	As
Cal.ln γ_i^0	4.85	7.86	-6.78	-3.52	-0.72	2.96	7.91	-2.82	-3.37
Cal.Ref. [14]	6.07	10.22	-8.18	-4.81	-0.90	3.58	10.29	-11.07	-4.36
Exp[15]	-	-	-	-6.63	-	1.25	6.73	-	-

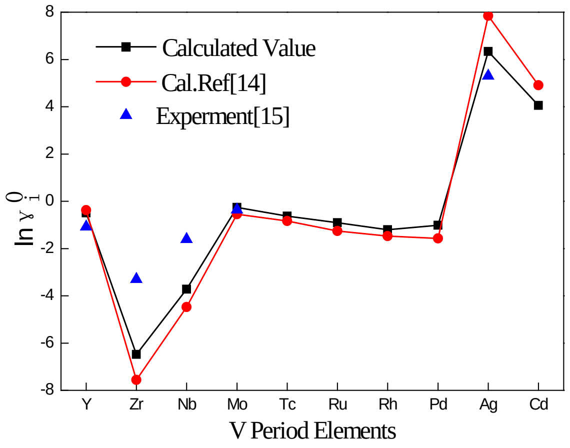

Fig 1 $\ln\gamma^0$ of V period transition elements in in liquid iron at 1873K

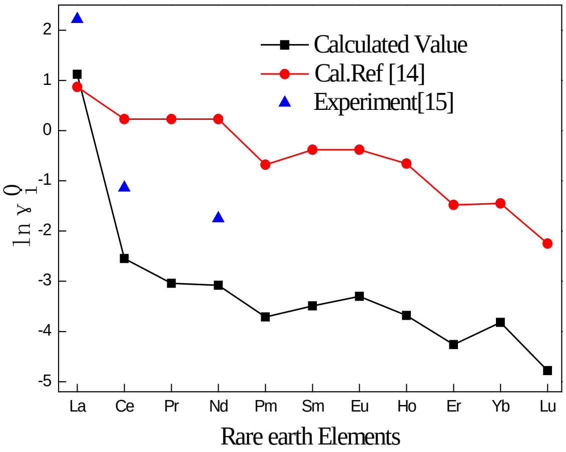

Fig 2 $\ln\gamma^0$ of rare earth transition liquid iron at 1873K

We further compared the calculated values with available experimental data and previously theoretical values [14] in Figs. 1 and 2. It has been noted that the obtained results by including the term of excess entropy shows a better agreement with the experimental data than those values reported in Ref. [14]. In fact, the results reported in Ref. [14] did not include the excess entropy term. In addition, note that, if the properties of element I are similar to those of Fe, our currently obtained results are highly similar to those reported in Ref. [14] as evidenced in Table 1. For instance, it has been demonstrated that the basic parameters of Mn are highly similar to those of Fe. Therefore, we currently obtained $\ln\gamma_{Mn}^0$ =0.05, which is in nice agreement with the reported value of 0.06 in Ref. [14]. Again for Ni, its parameter is highly close to those of Fe. Hence, it has been noted that the obtained $\ln\gamma_{Ni}^0$ =-0.33 is highly close to $\ln\gamma_{Ni}^0$ =-0.39 in Ref. (14), as well as to the experimental data of -0.42. In contrast, if element i is quite different from Fe, then the discrepancy is large. Taking an example, those parameters of Pb is quite different from those of Fe. Therefore, we see that $\ln\gamma_{Pb}^0$ =7.91 is significantly smaller than the reported value of 12.29 in Ref. (14). Apparently, the former is much closer to the experimental value 6.73. From table 1, we conclude that it's reasonable to consider the excess entropy if the difference between components in the system is intrinsically larger.

3.2 Interaction coefficient ε_i^j

Table 2 compiles the interaction parameters of $\varepsilon_C^j, \varepsilon_{Si}^j, \varepsilon_{Mn}^j, \varepsilon_P^j, \varepsilon_N^j$ in the iron-base alloys at 1873K. We also compared the experimental data, derived values from this work and from Ref. [14] in Figs. 3 and 4 for Fe-N-j system and Fe-C-j systems, respectively. It has been seen that in fig 3, the large discrepancies between our results and those from literature (14) have been observed and, importantly, ε_N^N , ε_N^P is more close to experimental data than the results in Ref. (14). Nevertheless, ε_N^{As} , ε_N^{Sb} , ε_N^{Bi} are in good agreement with the reported values in literatures. This is mainly because the metallic properties of As, Sb, and Bi increase. In comparison with N and P, the properties of these elements are much more similar with Fe. Because non-metal elements such as N and P are different from Fe, the interaction force of their alloys would be highly strong. The origins can be ascribed not only to the large differences in their atomic radius but also to the intrinsic electronic difference. Definitely, the substantial difference results in the change of entropy. Therefore, the entropies have to be considered for these systems, in particular, for the cases of non-metal and metal alloy melts.

Table 2 Compaison between calculation and experimental data of interaction parameters in liquid iron-base alloys at 1873K

j	$\varepsilon_{\mathrm{C}}^{j}$		$\varepsilon_{\mathrm{P}}^{j}$		$\varepsilon_{\mathrm{N}}^{j}$		$\varepsilon_{\mathrm{Mn}}^{j}$		$\varepsilon_{\mathrm{Si}}^{j}$	
	Cal	Exp [16]	Cal	Exp [16]	Cal	Exp [16]	Cal	Exp [16]	Cal	Exp [16]
Ag	-4.3	12	-15.4	-	-7.3	-	-5.1	-	-7	-
Al	5.3	5.3	8.3	4.7	3.2	1.6	-3.1	-	6.37	7.0
As	8.3	-	15	-	13	-	-4.3	-	17	-
B	13.2	12	20	1.5	20	5.0	-1.9	-0.89	10.3	9.5
Ba	-25	-	-29	-	-47	-	-3.6	-	-27	-
Bi	-3.3	-	2.7	-	-7.0	-	-14	-	-0.72	-
C	13.8	13	19.5	7.0	32	7.2	-4.7	-1.9	7.4	9.8
Ca	-17.6	-16	-16	-	-37	-	-2.9	-	-14	-11
Ce	-20	-59	-15.4	-	-40	-515	-1.32	21	-10.3	-
Co	1.93	1.8	1.32	0.92	2.2	2.9	-1.07	-0.93	-0.94	-
Cr	-3.7	-4.9	-3.2	-3.8	-3.7	-9.8	0.89	0.90	-0.73	0.034
Cu	-1.6	4.0	0.98	-9.3	-3.2	2.2	-2.3	-	-0.95	3.6
Hf	-14	-	-10	-	-26	-280	3.5	3.4	-2.3	-
La	-27	-59	-11.3	-	-40	-515	-3.4	63	-2.0	-
Mg	-3.2	8.2	-2.75	-	-25	-	-4.7	-	-3.2	-
Mn	-5.6	-1.9	-5.4	-7.2	-10	-4.5	-0.14	0.016	-4.1	-3.3
Mo	-7.2	-6.1	-1.92	-0.32	-3	-5.1	2.3	1.1	0.92	-
N	2.8	7.2	10.9	8.0	15	0.75	-6.3	-4.5	10.3	-6.1
Nb	-10.7	-23	-4.7	-5.3	-15	-27	4.7	2.1	1.2	-0.66
Ni	2.2	2.4	2.1	0.68	4.0	1.6	-1.8	-1.8	1.32	1.2
P	21	7.0	24	7.3	18	8.0	-5.3	-7.2	16	12
Pb	5.6	5.7	4.53	6.7	-9.3	-	-17	-5.2	-1.9	6.1
Pt	5.9	-	6.3	-	10	-	-3.6	-	0.75	-
Sb	3.4	6.2	7.5	-	1.9	3.2	-8.4	-	4.5	-
Si	10.73	9.7	16	12	8.3	6.1	-2.9	-3.3	13	12
Sn	6.73	9.7	6.2	5.0	-1.6	2.3	-7.3	-	7.4	7.1
Sr	-27	-	-13	-	-39	-	-4.2	-	-30	-
Ta	-69	-	-3.7	-	-20	-39	3.9	-0.38	0.89	27
Ti	-12	-31	-7.4	-7.2	-24	-118	3.2	-9.7	-3.2	240
V	-7.4	-6.1	-4.9	-4.9	-19	-26	1.42	1.3	9.4	5.3
W	-10.8	-6.5	-0.88	-20	-2.7	-3.8	2.4	3.1	1.0	-
Zn	2.5	-	7.2	-	-0.19	-	-3.6	-	3.8	-
Zr	-18	-	-19.3	-	-27	236	3.4	3.0	-4	-

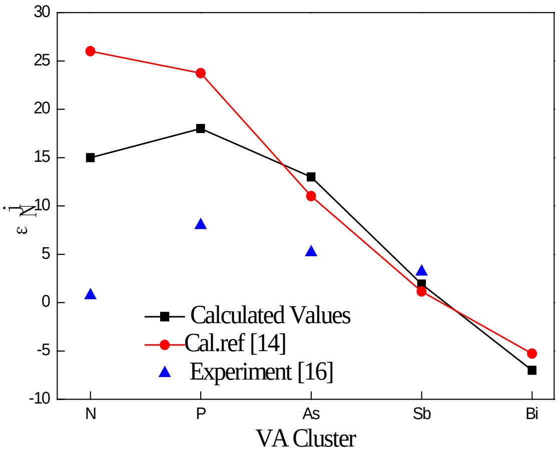

Fig 3 ε_N^j of VA cluster elements in liquid Iron at 1873K.

4. Conclusions

On the basis of Chou's model and Miedema's mode as well as the excess entropy, we have established a new model to predict the thermodynamic properties of the metal solution. The formulas for calculating the excess Gibbs free energy ΔG_{ij}^E , the activity coefficients of a solute at infinite dilution, $\ln \gamma_i^0$, as well as interaction parameters , ε_i^i *and* ε_i^j , in alloy melts have been proposed. The results indicate that the excess entropy need to be considered for both dilution solution and regular solution for alloy melts.

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References

[1] Guo. J. J, Liu. Y, Su.Y. Q, *Acta. Metal. Sin.*, 1999, 35（4）, p416-420.

[2] Liu. Y, Zhang. Zh. B, Cao L Sh. *Acta. Liaoning. Ind. Sin*, 2007, 27（3）, p180-182.

[3] Qin. F, Fan. T. X, Zhang. H, *J Shanghai Uni*, 2009, 43（5）, p708-712.

[4] Hildebrand J H., Scott R L. The Solubility of Nonelectrolytes .3rd Ed. Reinhold, New York, 1950.

[5] Miedema A R, De Chatel. Cohesion in Alloys Fundamentals of a Semempirical Model. *Physical*, 1988, B100, p1.

[6] Wilson. G. W. Vapor liquid equilibria XI.A new expression for the excess Gibbs Energy of mixing. *JAM. Chem. Soc*, 1964, 86(2), p127-130.

[7] Fan. P, Zhou. G. Zh. *Acta. Metal. Sin*, 1999, 35(4), p421-426.

[8] Zhen. Q, Li. W. Ch. *Acta. Metall. Sin*, 1999, 35（7）, p748-750.

[9] Tanaka. T, Goken. N. A, Morita. Z. Thermodynamics Relationship Between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys . *Z.Metallkd*, 1993, 84, p192.

[10] Chen. X. Q, Ding. X. Y. *Acta. Metall. Sin*, 2000, 36, p492.

[11] Lida. T., Guthre, R. L. L.The Physical Properties of Liquid Metals, Clarendn Press, Oxford, 1988, p125.

[12] Zhang. Sh. B, Li. D. Z. Phase Diagram Principle, Calculation and The Application in Metallurgy. Beijing, The Metallurgical Industry Press, 1986.

[13] Wanger C. Thermodynamics of Alloys. Reading. *Maschusetts:Addsion-Wesley*, 1952, p51.

[14] Ding. X. Y, Fan P. Thermodynamic Calculation for Alloys Systems. *Metall Mater Trans*, 1999, B30, p271.

[15] The Japan Society for the Promotion of Science. Steelmaking Data Souce Book. New York: Gordon and Breach Science, 1988, p375.

[16] Ding. X. Y, Fan. P. Alloy Melt Thermodynamic Model Prediction and Software Development. Shenyang: Northeastern University Press, 1998.