

# THERMODYNAMIC CALCULATION WITH MODELS FOR LIQUID COPPER<sup>①</sup>

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## ABSTRACT

The activity coefficients of a solute at infinite dilution,  $\ln\gamma_i^0$ , and interaction parameters,  $\varepsilon_i^j$  in liquid Cu at 1473 K are calculated by models. The calculation results show that the calculated values are in accordance with the experimental data on the whole. The ratios of same sign to  $\ln\gamma_i^0$  and  $\varepsilon_i^j$  reach 85% and 87.5% respectively. The main factors that affect  $\ln\gamma_i^0$  and  $\varepsilon_i^j$  are the electron density,  $n_{ws}$ , electronegativity,  $\varphi$ , and molar volume  $V$  of solute  $i$  and solvent Cu.

**Key words:** liquid Cu interaction parameter thermodynamic calculation

## 1 INTRODUCTION

The interaction parameters are one of the bases of the metallurgical thermodynamics. Since Wagner<sup>[1]</sup> put forward the concept of the interaction parameter between elements, much research works have been done and great achievements have been made. But until now, a great many interaction parameters in liquid Cu have not been measured because of experimental difficulties at high temperatures. The activity coefficients of a solute at infinite dilution,  $\ln\gamma_i^0$ , and interaction parameters,  $\varepsilon_i^j$  in liquid Cu at 1473 K are calculated by models and compared with experimental data.

## 2 CALCULATION METHODS

In ternary system,  $i-j-k$ , mole fractions of element  $i$ ,  $j$  and  $k$  are denoted by  $x_i$ ,  $x_j$ ,  $x_k$ . If  $k$  is considered as a solvent,  $i$  and  $j$  as solutes, there are the following relations by definition at  $T$ :

$$\ln\gamma_i^0 = \frac{1}{RT}(\bar{G}_i^E)_{x_i \rightarrow 1} \quad (1)$$

$$\varepsilon_i^j = \frac{1}{RT}(\frac{\partial \bar{G}_i^E}{\partial x_j})_{x_i \rightarrow 1} \quad (2)$$

$$\varepsilon_i^j = \frac{1}{RT}(\frac{\partial \bar{G}_i^E}{\partial x_j})_{x_i \rightarrow 1} \quad (3)$$

In ternary system  $i-j-k$ , the relations between partial mole excess free energy are<sup>[2]</sup>:

$$\bar{G}_i^E = G^E - x_j \frac{\partial G^E}{\partial x_j} + (1 - x_i) \frac{\partial G^E}{\partial x_i} \quad (4)$$

$$\bar{G}_j^E = G^E - x_i \frac{\partial G^E}{\partial x_i} + (1 - x_j) \frac{\partial G^E}{\partial x_j} \quad (5)$$

$$\bar{G}_k^E = G^E - x_i \frac{\partial G^E}{\partial x_i} - x_j \frac{\partial G^E}{\partial x_j} \quad (6)$$

There are different methods<sup>[3-5]</sup> adopted for predicting ternary thermodynamic properties by binary thermodynamic properties. The calculated values got by the Toop equation agree with the experimental data better than other equations<sup>[6]</sup>. The excess free energy of  $i-j-k$ , the  $G^E$  can be expressed by the Toop equation<sup>[8]</sup> from the excess free energy,  $G_{ij}^E$ ,  $G_{ik}^E$ ,  $G_{jk}^E$ , of three binary systems as:

$$G^E = \frac{x_j}{1 - x_i} G_{ij}^E(x_i, 1 - x_i) + \frac{x_k}{1 - x_k} G_{ik}^E(x_i, 1 - x_i)$$

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$$+ (x_j + x_k)^2 G_{jk}^E \left( \frac{x_j}{x_j + x_k}, \frac{x_k}{x_j + x_k} \right) \quad (7)$$

Although the deduction of the above equation is based on assuming the melt as a regular solution, this equation was well adopted in nonregular solution by Toop and other researchers<sup>[3, 7, 8]</sup>.

In binary system  $i$ - $j$  (same in  $i$ - $k$  and  $j$ - $k$ ), the relation between  $G_{ij}^E$  and  $S_{ij}$  as well as  $\Delta H_{ij}$  is:

$$G_{ij}^E = \Delta H_{ij} - TS_{ij}^E \quad (8)$$

It is difficult to determine the excess entropy  $S_{ij}^E = 0$  for the complexity in the structure of a melt at high temperatures. Therefore the assumption in which the  $S_{ij}^E$  equals zero is often adopted in phase diagram thermodynamics and good results<sup>[9, 10]</sup> were achieved. If  $S_{ij}^E$  is assumed as zero, then:

$$G_{ij}^E = \Delta H_{ij} \quad (9)$$

In  $i$ - $j$  (same in  $i$ - $k$  and  $j$ - $k$ ), formation heat can be calculated by Miedema's equation<sup>[11]</sup>. The last expression of Miedema's equation is<sup>[6]</sup>:

$$\begin{aligned} \Delta H_{ij} = & f_{ij} x_i [1 + \mu_j x_j (\varphi_i - \varphi_j)] x_j \\ & \times [1 + \mu_j x_i (\varphi_j - \varphi_i)] / \{x_i V_i^{2/3} \\ & \times [1 + \mu_i x_j (\varphi_i - \varphi_j)] + x_j V_j^{2/3} \\ & \times [1 + \mu_j x_i (\varphi_j - \varphi_i)]\} \quad (10) \end{aligned}$$

where  $f_{ij}$  is given by:

$$f_{ij} = \frac{2pV_i^{2/3}V_j^{2/3}[q/p(\Delta n_{ws}^{1/3})^2 - (\Delta\varphi)^2 - a(r/p)]}{(n_{ws}^{1/3})_i^{-1} + (n_{ws}^{1/3})_j^{-1}} \quad (10a)$$

In Eq. (10) and Eq. (10a),  $x_i$  and  $x_j$  are the mole fractions of element  $i$  and element  $j$ ;  $V_i$  and  $V_j$  are the molar volumes of  $i$  and  $j$ ;  $\Delta n_{ws}$  is the difference of electron density between  $i$  and  $j$ ;  $\Delta\varphi$  is the difference of electronegativity between  $i$  and  $j$ ;  $p$ ,  $q$ ,  $r$ ,  $\mu$ ,  $a$  are the constants and  $p/q = 9.4$ ;  $a = 0.73$  for liquid alloys and  $a = 1$  for solid solutions.

The following equations can be obtained by simultaneous equations from Eq. [1] to Eq. [10]:

$$\ln \gamma_i^0 = \frac{1}{RT} 2pV_i^{2/3} [9.4(\Delta n_{ws}^{1/3})^2 - (\Delta\varphi)^2 - a(r/p)] [1 + \mu_i(\varphi_i - \varphi_k)] / [(n_{ws}^{1/3})_i^{-1} + (n_{ws}^{1/3})_k^{-1}] \quad (11)$$

$$\begin{aligned} \varepsilon_i^j = & \frac{1}{RT} f_{ik} \{ [4\mu_i + 2\mu_k](\varphi_k - \varphi_i) - 2 - 2\mu_i\mu_k \\ & \times (\varphi_k - \varphi_i)^2 / V_i^{2/3} - 2[1 + \mu_i(\varphi_i - \varphi_k)] \\ & \times [V_i^{2/3}(1 + \mu_i(\varphi_i - \varphi_k)) + V_k^{2/3} \\ & \times (-1 + \mu_k(\varphi_k - \varphi_i))] / (V_i^{2/3})^2 \} \quad (12) \end{aligned}$$

$$\begin{aligned} \varepsilon_i^j = & \frac{1}{RT} \{ f_{ij} [1 + \mu_i(\varphi_i - \varphi_j)] / V_j^{2/3} \\ & - f_{ik} [1 + \mu_i(\varphi_i - \varphi_k)] / V_k^{2/3} \\ & - f_{jk} [1 + \mu_j(\varphi_j - \varphi_k)] / V_k^{2/3} \} \quad (13) \end{aligned}$$

where  $f_{ij}$ ,  $f_{ik}$  and  $f_{jk}$  are given by:

$$\begin{aligned} f_{ij} = & 2pV_i^{2/3}V_j^{2/3} \{ 9.4[(n_{ws}^{1/3})_j - (n_{ws}^{1/3})_i]^2 \\ & - (\varphi_j - \varphi_i)^2 - a(r/p) \} \\ & / [(n_{ws}^{1/3})_i^{-1} + (n_{ws}^{1/3})_j^{-1}] \quad (14) \end{aligned}$$

$$\begin{aligned} f_{ik} = & 2pV_i^{2/3}V_k^{2/3} \{ 9.4[(n_{ws}^{1/3})_i - (n_{ws}^{1/3})_k]^2 \\ & - (\varphi_i - \varphi_k)^2 - a(r/p) \} \\ & / [(n_{ws}^{1/3})_j^{-1} + (n_{ws}^{1/3})_k^{-1}] \quad (15) \end{aligned}$$

$$\begin{aligned} f_{jk} = & 2pV_j^{2/3}V_k^{2/3} \{ 9.4[(n_{ws}^{1/3})_j - (n_{ws}^{1/3})_k]^2 \\ & - (\varphi_j - \varphi_k)^2 - a(r/p) \} \\ & / [(n_{ws}^{1/3})_j^{-1} + (n_{ws}^{1/3})_k^{-1}] \quad (16) \end{aligned}$$

If  $k = \text{Cu}$ ,  $T = 1473 \text{ K}$ , from the above equations, it is very easy to calculate the activity coefficients of a solute at infinite dilution and interaction parameters of any elements in liquid copper.

### 3 RESULTS AND DISCUSSION

The factors affecting the  $\ln \gamma_i^0$  are the electron density,  $n_{ws}$ , electronegativity,  $\varphi$ , and molar volume  $V$  of solute  $i$  and solvent  $k$  seen from Eq. [11] combining with Eq. [15]. If  $k = \text{Cu}$ , the  $\ln \gamma_i^0$  in Cu-base alloys can be calculated out from Eq. [11]. The calculation results and the comparison with the experimental data are listed in Table 1 and part results are shown in Fig. 1 and Fig. 2.

From Table 1, the calculation values are basically in accordance with the experimental data, the ratio of same sign reaches 85%. In Table 1, the value of  $\ln \gamma_{\text{Cu}}^0$  by calculation is opposite from that by ref. [11] and the same as ref. [12] in sign.

The factors to determine the values of  $\varepsilon_i^j$  are also the  $n_{ws}$ ,  $\varphi$  and  $V$  of solute elements  $i$  and solvent  $k$ .

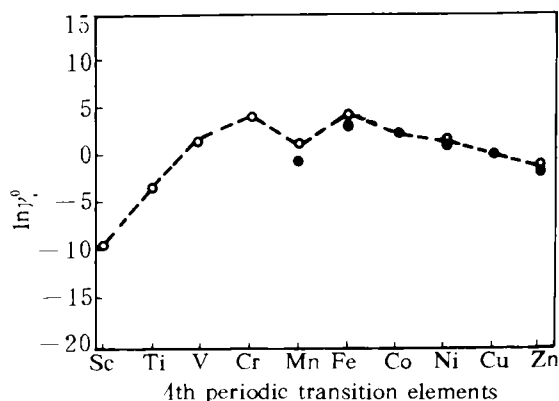
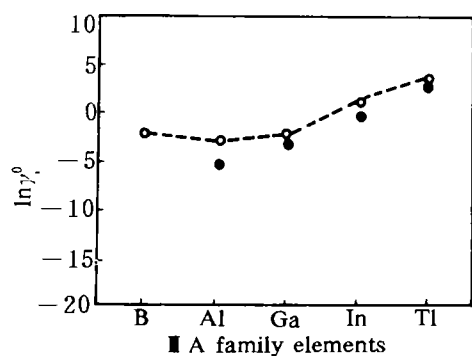


Fig. 1  $\ln \gamma_i^0$  of the 4th periodic transition elements in liquid Cu at 1473 K  
solid dots—Exp. [11]; hollow dots—Cal.

**Table 1 Comparison of  $\ln\gamma_i^0$  between calculation and experiments in liquid Cu at 1473 K**

<i>i</i>	CAL.	EXP. [12]	<i>i</i>	CAL.	EXP. [12]
Sc	-9.32		U	-2.69	
Ti	-3.22		Pu	-3.55	
V	1.69		Cu	0	0
Cr	4.11		Ag	0.79	1.17
Mn	1.23	-0.67*	Au	-3.41	-1.97
Fe	4.28	2.97	Li	-1.54	
Co	2.11		Na	6.00	
Ni	1.16	0.80	K	11.85	
Y	-9.49		Rb	13.40	
Zr	-8.93		Cs	15.04	
Nb	0.96		Ca	-5.34	-7.58
Mo	6.69		Sr	-4.22	
Tc	2.96		Ba	-4.14	
Ru	2.50		H	-3.30	
Rh	-0.88		Be	0.04	
Pd	-5.01		Mg	-1.65	-3.12
La	-9.29		Zn	-1.29	-1.92
Ce	-9.38		Cd	0.22	-0.63
Pr	-9.47		Hg	5.68	
Nd	-9.40		B	-1.91	
Pm	-9.86		Al	-2.74	-5.88
Sm	-9.53		Ga	-2.10	-3.38
Eu	-9.52		In	1.01	-0.89
Ho	-9.17		Tl	3.55	2.14
Er	-9.56		C	-5.72	
Yb	-9.40		Si	-3.25	-5.12
Lu	-9.79		Ge	-2.47	-4.71
Hf	-6.60		Sn	-0.45	-3.04
Ta	0.69		Pb	3.37	1.66
W	8.22		N	-25.56	
Re	6.61		P	-9.54	
Os	3.70		As	-4.76	-7.64
Ir	0.07		Sb	-0.82	-4.27
Pt	4.55		Bi	2.87	0.22
Th	-10.82				

\* : estimated



**Fig. 2  $\ln\gamma_i^0$  of the III A family elements in liquid Cu at 1473 K**

solid dots—Exp; hollow dots—Cal.

shown in Eq. (12) combining with Eq. [15]. If  $k = \text{Cu}$ , the  $\epsilon_i^l$  in Cu-base alloys can be calculated. The calculation results and the comparison with the experimental data are listed in Table 2 and part of the results are shown in Fig. 3 and Fig. 4.

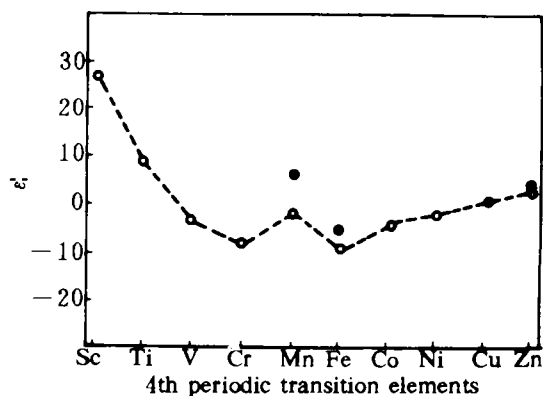
In Table 2, the ratio of same sign reaches 87.5% in the 16 data and the calculated values are the same as the experimental data in quantity order.

There are the following reasons why the calculation values are not accordant with the experimental data. (1) There exists error in the experiments; because it is very difficult to do experiments at high temperatures, different results were got for same alloy systems by different researchers. (2) The Miedema models are semi-empirical formulas. Because of the complicity in structures of liquid at high temperature, it is very difficult to predict thermodynamic data accurately. (3) The base to establish the calculation models is to assume the excess entropy in system as zero. In general, it is good to estimate the  $\ln\gamma_i^0$ ,  $\epsilon_i^l$  of elements at liquid copper with these models.

#### 4 SUMMARY

Based on the Miedema's model for calculating formation heat of binary alloys, the models to calculate the activity coefficients of a solute at infinite dilution, interaction parameters are established which can be used in liquid copper.

The values of  $\ln\gamma_i^0$  are dependent on the interaction between solute  $i$  and solvent Cu by their



**Fig. 3  $\epsilon_i^l$  of the 4th periodic transition elements in liquid Cu at 1473 K**

solid dots - Exp. [11]; hollow dots—Cal.

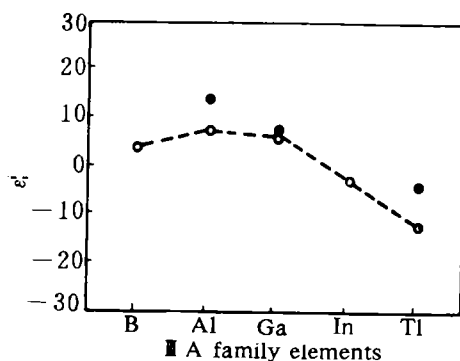
**Table 2 Comparison of  $\varepsilon_i^l$  between calculation and experiments in liquid Cu at 1473 K**

<i>i</i>	CAL.	EXP. [12]	<i>i</i>	CAL.	EXP. [12]
Sc	26.39		U	7.79	
Ti	8.01		Pu	9.65	
V	-3.71		Cu		
Cr	-8.44		Ag	-1.99	-2.5
Mn	-2.52	6	Au	9.42	3.7
Fe	-8.87	-5.7	Li	2.68	
Co	-4.26		Na	-16.37	
Ni	-2.35		K	-46.08	
Y	32.55		Rb	-58.08	
Zr	26.19		Cs	-72.90	
Nb	-2.46		Ca	18.13	20*
Mo	-16.32		Sr	16.83	
Tc	-7.17		Ba	17.68	
Ru	-5.88		H	3.42	1.0*
Rh	2.09		Be	-0.06	
Pd	12.48		Mg	4.31	9.8*
La	34.65		Zn	2.84	4
Ce	34.03		Cd	0.61	
Pr	33.44		Hg	-17.17	
Nd	32.99		B	3.28	
Pm	34.21		Al	6.65	14
Sm	32.83		Ga	5.64	7.0
Eu	32.73		In	-3.21	
Ho	30.26		Tl	-12.01	-4.8
Er	31.16		C	6.71	
Yb	30.07		Si	7.52	
Lu	31.11		Ge	6.20	13.4
Hf	19.00		Sn	1.54	10
Ta	-1.77		Pb	-12.38	-2.7
W	-20.51		N	38.23	
Re	-16.14		P	23.14	
Os	-8.88		As	13.70	
Ir	-0.16		Sb	2.93	15*
Pt	11.65		Bi	-10.97	20*
Th	39.81		* : estimated		

electron density,  $n_{ws}$ , electronegativity,  $\varphi$  and molar volume  $V$ . The calculation values agree with the experimental data on the whole. The ratio of same sign reaches 85% for Cu-base alloys.

The factors affecting  $\varepsilon_i^l$  are the electron density,  $n_{ws}$ , electronegativity,  $\varphi$  and molar volume  $V$  of solutes  $i$  and solvent Cu. By comparison, the ratio of same sign of  $\varepsilon_i^l$  for liquid copper reaches

87.5%. The values of calculation are the same as the data of experiments in quantity order.

**Fig. 4  $\varepsilon_i^l$  of the III A family elements in liquid Cu at 1473 K**

solid dots—Exp; hollow dots—Cal.

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