Journal of University of Science and Technology Beijing
Volume 9, Number 3, June 2002, Page 170

Metallurgy

Application of the annexation principle to the thermodynamic property study of ternary metallic melts In-Bi-Cu and In-Sb-Cu

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(Received 2001-10-27)

Abstract : Based on the phase diagrams, measured activities and the annexation principle, calculating models of mass action concentrations for In-Bi-Cu and In-Sb-Cu melts have been formulated. Calculated results not only agree well with practical values, but also obey the mass action law, showing that the deduced model can reflect the structural reality of given melts and that the annexation principle is applicable to these two ternary metallic melts. So long as there is one from three binary systems constituting the ternary melts, in which the activities of one component exhibit positive deviation relative to Raoultian behavior, heterogeous melts inevitably would form, so heterogeneous calculating model should be used to calculate their mass action concentrations. On the contrary, if all the binary melts are homogeneous and their activities exhibit negative deviation with respect to the Raoult's law, then the ternary melts formed from them will certainly be homogeneous,hence single phase model should be applied.

Key words: activity; mass action concentration; coexistence theory; annexation principle

After understanding of the thermodynamic properties of binary metallic melts to a certain extent [1-3], in order to apply the coexistence theory of metallic melts to practice, investigation on the thermodynamic properties of ternary metallic melts is an urgent task. Considering that the study of the binary phase diagrams relevant to two ternary systems In-Bi-Cu and In-Sb-Cu has reached identity of view [4]; the activities of every binary melts in them have been amply studied [5-10], at the same time, the activities a_{In} of two ternary systems have been also measured [11]. The above practical bases render the investigation on the thermodynamic properties of ternary metallic melts to be realizable. As a part of research works on the thermodynamic properties of ternary metallic melts, this paper aims at the formulation of the calculating models of mass action concentrations for In-Bi-Cu and In-Sb-Cu melts.

1 In-Bi-Cu melts

1.1 Bi-Cu melts

According to the phase diagram [4], there is an eutectic formed in this binary system. The activities of these melts exhibit positive nonsymmetrical deviation with respect to the Raoult's law, in accordance with the conjecture of reference [1], there should be a metastable compound Cu_2Bi_3 formed in these melts. Hence their structural units are Bi and Cu atoms as well as metastable compound Cu_2Bi_3, and they form two solutions Bi+ Cu_2Bi_3 and Cu+ Cu_2Bi_3. Assuming the composition of the melts as $b=\Sigma x_{Bi}$, $a=\Sigma x_{Cu}$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{Bi}$, $y=x_{Cu}$, $z=x_{Cu_2Bi_3}$; the mass action concentration of every structural unit as $N_1=N_{Bi}$, $N_2=N_{Cu}$, $N_3=N_{Cu_2Bi_3}$, then in the light of the mass action law, the chemical equilibrium is:

$$3Bi_{(l)}+2Cu_{(l)}=Cu_2Bi_{3(l)} \tag{1}$$

$$b=x+3z,\ a=y+2z,\ N_1=\frac{x}{b},\ N_2=\frac{y}{a},\ z=KN_1^3N_2^2 \tag{2}$$

$$N_1+3KN_1^3N_2^2/b=1,\ N_2+2K_2N_1^3N_2^2/a=1 \tag{3}$$

$$ab(2-N_1-N_2)=K(3a+2b)N_1^3N_2^2 \tag{4}$$

Equations (3) and (4) are the two phase calculating model of mass action concentrations for Bi-Cu melts, in which equation (3) is used for calculation of mass action concentrations, while equation (4) for calculation of equilibrium constants. According to the measured activities of references [6,8] and calculating by equation (4) gives $K_{Cu_2Bi_3}=0.455\,371$ at 1 200 K and $K_{Cu_2Bi_3}=0.485\,135$ at 1 408 K, consequently:

$$\lg K_{Cu_2Bi_3}=\frac{-223.362}{T}-0.155\,5 \quad (r=-1.000),$$

$$\Delta G^{\ominus}=4\,278.416+2.978\,5T,\ J\cdot mol^{-1} \tag{5}$$

Substituting equation (5) into equation (3) gives the calculated mass action concentrations compared with measured activities as shown in **figure 1**. In the figure, it is seen that the calculated and measured values not only agree considerably well, but also obey the mass

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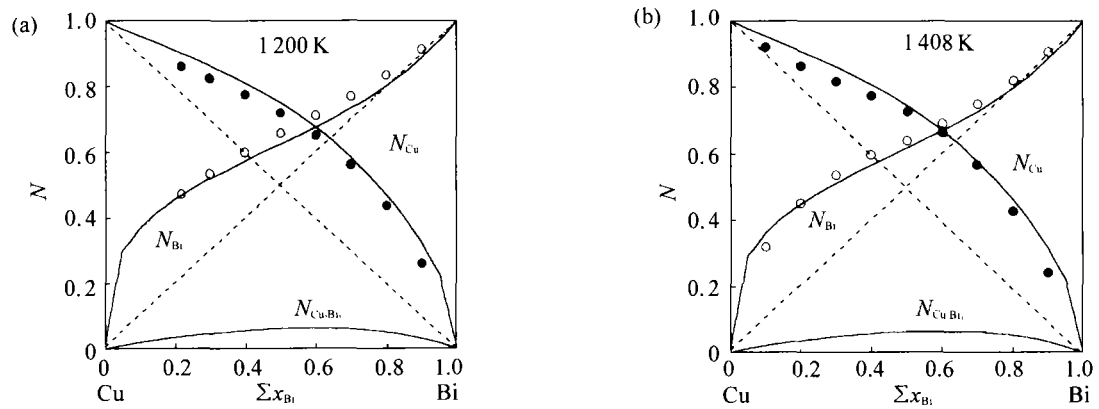

Figure 1 Comparison of calculated mass action concentrations (—) with measured activities (•,o) for Bi-Cu melts.

action law, showing that the model deduced can reflect the structural reality of these melts.

1.2 Bi-In melts

According to the phase diagram [4], there are three compounds BiIn, Bi_5In_3 and $BiIn_2$ formed in this binary system, in which BiIn and $BiIn_2$ are compounds with congruent melting point, while Bi_5In_3 is a peritectic. In accordance with reference [1], these binary melts are typical homogeneous melts. In general, their structural units are Bi and In atoms as well as compounds BiIn, Bi_5In_3 and $BiIn_2$. However, owing to the positive deviation of activities of the binary melts Bi-Cu in ternary melts In-Bi-Cu with respect to th Raoult's law, under the effect of their annexation, *i.e.*, the phase separation in these melts caused by the chemically less stable metastable compound Cu_2Bi_3, during the formation of ternary melts In-Bi-Cu, Bi-In melts would transform into two phase melts, which were otherwise studied. Here only the thermodynamic parameters obtained according to the measured activities from reference [5] are given respectively as follows:

$$\lg K_{BiIn} = \frac{363.99}{T} - 0.086\,5,$$

$$\Delta G^{\ominus} = -6\,972.069 + 1.656T,\ \mathrm{J\cdot mol^{-1}}\ (900\text{-}1\,200\ \mathrm{K}) \quad (6)$$

$$\lg K_{BiIn_2} = -\frac{99.85}{T} - 0.461\,5,$$

$$\Delta G^{\ominus} = 1\,912.584 + 8.84T,\ \mathrm{J\cdot mol^{-1}}\ (900\text{-}1\,200\ \mathrm{K}) \quad (7)$$

1.3 Cu-In melts

According to the phase diagram [6], there are compounds Cu_4In, Cu_9In_4 and Cu_2In formed in this binary system; while in accordance with reference [12], the formed compounds are Cu_4In and Cu_2In. After examination with a number of single phase calculating models, it was found that the model considering the presence of Cu_4In and Cu_2In gives the best agreement with practice. However, owing to the positive deviation of the activities of Bi-Cu melts with respect to the Raoult's law, under the effect of their annexation, during the formation of the ternary melts In-Bi-Cu, Cu-In melts would transform into two phase ones. After examination of a lot of two phase models, it was found that the model considering the presence of compounds CuIn, Cu_2In and Cu_4In gives the best agreement with practice. Hence the structural units of these melts are Cu and In atoms as well as compounds CuIn, Cu_2In and Cu_4In, and they form two solutions Cu+ CuIn +Cu_2In+ Cu_4In and In+ CuIn +Cu_2In+ Cu_4In. Assuming the composition of the melts as $b=\Sigma x_{Cu}$, $a=\Sigma x_{In}$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{Cu}$,$y=x_{In}$, $z_1=x_{CuIn}$, $z_2=x_{Cu_2In}$, $z_3=x_{Cu_4In}$; the mass action concentration of every structural unit as $N_1=N_{Cu}$, $N_2=N_{In}$, $N_3=N_{CuIn}$, $N_4=N_{Cu_2In}$, $N_5=N_{Cu_4In}$, then according to the mass action law, there are chemical equilibria:

$$Cu_{(1)} + In_{(1)} = CuIn_{(1)},\ K_1 = \frac{N_3}{N_1N_2} \quad (8)$$

$$2Cu_{(1)} + In_{(1)} = Cu_2In_{(1)},\ K_2 = \frac{N_4}{N_1^2N_2} \quad (9)$$

$$4Cu_{(1)} + In_{(1)} = Cu_4In_{(1)},\ K_3 = \frac{N_5}{N_1^4N_2} \quad (10)$$

mass balance:

$$b = x+z_1+2z_2+4z_3,\ a = y+z_1+z_2+z_3,\ N_1 = \frac{x}{b},\ N_2 = \frac{y}{a},$$

$$z_1 = K_1N_1N_2,\ z_2 = K_2N_1^2N_2,\ z_3 = K_3N_1^4N_2 \quad (11)$$

$$\begin{cases} N_1+(K_1N_1N_2+2K_2N_1^2N_2+4K_3N_1^4N_2)/b = 1 \\ N_2+(K_1N_1N_2+K_2N_1^2N_2+K_3N_1^4N_2)/a = 1 \end{cases} \quad (12)$$

$$ab(2-N_1-N_2) = K_1(a+b)N_1N_2+K_2(2a+b)N_1^2N_2+ K_3(4a+b)N_1^4N_2 \quad (13)$$

Equations (12) and (13) are the two phase calculating model of mass action concentrations for Cu-In melts, in which equation (12) is used for calculation of mass action concentrations, while equation (13) for re-

gression of equilibrium constants. According to the measured activities from references [6,7], and regressing by equation (13) gives the thermodynamic parameters respectively as follows:

$$\lg K_{\mathrm{CuIn}} = -\frac{491.655}{T} + 0.3046 \qquad (r = -1.000),$$

$$\Delta G^{\ominus} = 9417.454 - 5.835T,\ \mathrm{J \cdot mol^{-1}} \tag{14}$$

$$\lg K_{\mathrm{Cu_4In}} = \frac{852.622}{T} - 0.8334 \qquad (r = 1.000),$$

$$\Delta G^{\ominus} = -16408.253 + 15.963T,\ \mathrm{J \cdot mol^{-1}} \tag{15}$$

$$\lg K_{\mathrm{Cu_2In}} = \frac{4179.77}{T} - 3.9216 \qquad (r = 1.000),$$

$$\Delta G^{\ominus} = -80061.874 + 75.116T,\ \mathrm{J \cdot mol^{-1}} \tag{16}$$

Substituting these thermodynamic parameters into equation (12) gives the calculated mass action concentrations compared with the measured activities as shown in **figure 2**. It is seen from the figure that the calculated and measured values not only basically agree, but also obey the law of mass action, showing that the model formulated can reflect the structural reality of these melts.

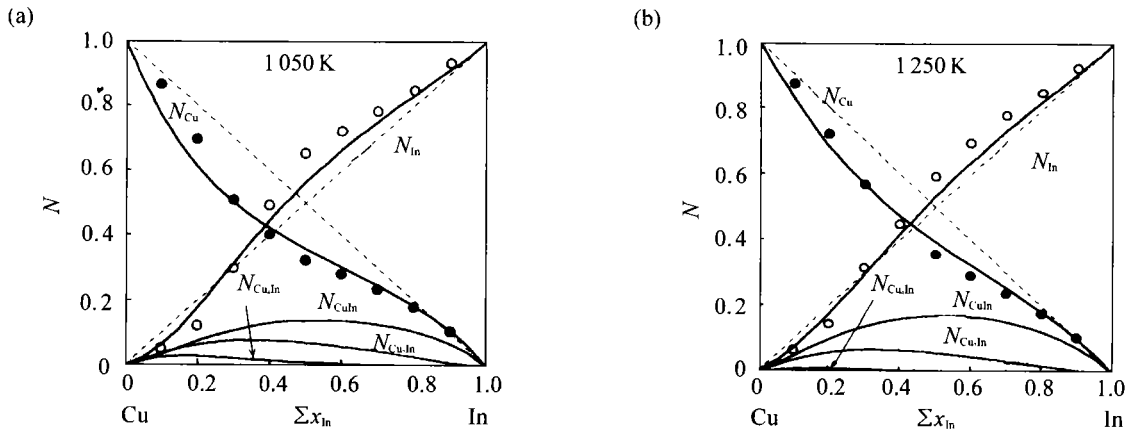

Figure 2 Comparison of calculated mass action concentrations (—) with measured activities (•, o) for Cu-In melts.

1.4 In-Bi-Cu melts

It is clear from the above discussions, that these ternary system are heterogeneous in structure, their structural units are In, Bi and Cu atoms as well as compounds BiIn, $BiIn_2$, CuIn, Cu_2In, Cu_4In and Cu_2Bi_3, and they form three solutions In+BiIn+$BiIn_2$+CuIn+Cu_2In+Cu_4In, Bi+ BiIn+ $BiIn_2$+ Cu_2Bi_3 and Cu+ CuIn+Cu_2In+ Cu_4In+ Cu_2Bi_3. Assuming the composition of the melts as $a=\sum x_{In}$, $b=\sum x_{Bi}$, $c=\sum x_{Cu}$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{In}$, $y=x_{Bi}$, $z=x_{Cu}$, $u_1=x_{BiIn}$, $u_2=x_{BiIn_2}$, $u_3=x_{CuIn}$, $u_4=x_{Cu_4In}$, $u_5=x_{Cu_2In}$, $u_6=x_{Cu_2Bi_3}$; the mass action concentration of every structural unit as $N_1=N_{In}$, $N_2=N_{Bi}$, $N_3=N_{Cu}$, $N_4=N_{BiIn}$, $N5=N_{BiIn_2}$, $N_6=N_{CuIn}$, $N_7=N_{Cu_2In}$, $N_8=N_{Cu_4In}$, $N_9=N_{Cu_2Bi_3}$, then in the light of mass action law, the chemical equilibria are:

$$\mathrm{Bi_{(l)}+In_{(l)} = BiIn_{(l)}},\ K_1 = \frac{N_4}{N_1N_2},$$

$$\Delta G^{\ominus} = -6972.069 + 1.656T,\ \mathrm{J \cdot mol^{-1}} \tag{17}$$

$$\mathrm{Bi_{(l)}+2In_{(l)} = BiIn_{2(l)}},\ K_2 = \frac{N_5}{N_1^2N_2},$$

$$\Delta G^{\ominus} = 1912.584 + 8.84T,\ \mathrm{J \cdot mol^{-1}} \tag{18}$$

$$\mathrm{Cu_{(l)}+In_{(l)} = CuIn_{(l)}},\ K_3 = \frac{N_6}{N_3N_1},$$

$$\Delta G^{\ominus} = 9417.454 - 5.835T,\ \mathrm{J \cdot mol^{-1}} \tag{19}$$

$$\mathrm{2Cu_{(l)}+In_{(l)} = Cu_2In_{(l)}},\ K_4 = \frac{N_7}{N_1N_3^2},$$

$$\Delta G^{\ominus} = -16408.253 + 15.963T,\ \mathrm{J \cdot mol^{-1}} \tag{20}$$

$$\mathrm{4Cu_{(l)}+In_{(l)} = Cu_4In_{(l)}},\ K_5 = \frac{N_8}{N_3^4N_1},$$

$$\Delta G^{\ominus} = -80061.874 + 75.116T,\ \mathrm{J \cdot mol^{-1}} \tag{21}$$

$$\mathrm{3Bi_{(l)}+2Cu_{(l)} = Cu_2Bi_{3(l)}},\ K_6 = \frac{N_9}{N_3^2N_2^3},$$

$$\Delta G^{\ominus} = 4278.416 + 2.9785T,\ \mathrm{J \cdot mol^{-1}} \tag{22}$$

mass balance is:

$$a = x + u_1 + 2u_2 + u_3 + u_4 + u_5,\ b = y + u_1 + u_2 + 3u_6,$$

$$c = z + u_3 + 2u_4 + 4u_5 + 2u_6 \tag{23}$$

$$N_1 + (K_1N_1N_2 + 2K_2N_1^2N_2 + K_3N_1N_3 + K_4N_1N_3^2 + K_5N_1N_3^4)/a = 1 \tag{24}$$

$$N_2 + (K_1N_1N_2 + K_2N_1^2N_2 + 3K_6N_2^3N_3^2)/b = 1 \tag{25}$$

$$N_3 + (K_3N_1N_3 + 2K_4N_1N_3^2 + 4K_5N_1N_3^4 + 2K_6N_2^3N_3^2)/c = 1 \tag{26}$$

Addition of equations (24)+(25)+(26) gives:

$$abc(3 - N_1 - N_2 - N_3) = c(a+b)K_1N_1N_2 + c(a+2b)K_2N_1^2N_2 + b(c+a)K_3N_1N_3 + b(c+2a)K_4N_1N_3^2 + a(c+4a)K_5N_1N_3^4 + a(2b+3c)K_6N_2^3N_3^2 \tag{27}$$

Equations (24), (25), (26) and (27) are the calculating model of mass action concentrations for In-Bi-Cu melts , in which equations (24), (25) and (26) are used for calculation of mass action concentrations, while equation (27) for regression of equilibrium constants under condition of known measured activities ($N_{In}=a_{In}$, $N_{Bi}=a_{Bi}$, $N_{Cu}=a_{Cu}$).

Using equations (24), (25) and (26) at 1 200 K the calculated mass action concentrations N_{In} are compared with the measured activities a_{In} from reference [11] as shown in **figure 3**. It can be seen in the figure, that the

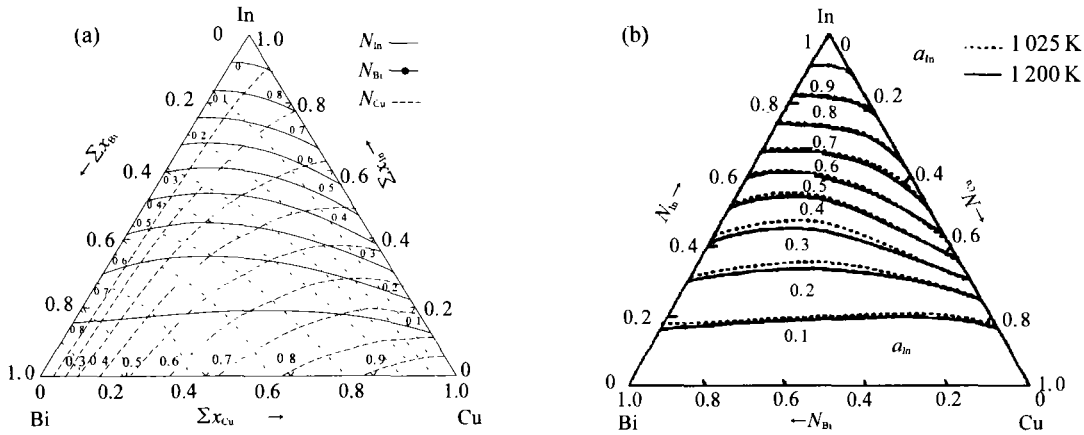

Figure 3 Comparison of calculated N_{In} and measured a_{In} for In-Bi-Cu melts at 1 200 K, (a) Calculated N_{In}; (b) measured a_{In}.

agreement between them is satisfactory, in the meantime, they obey the law of mass action, showing that the formulated model can reflect the structural characteristics of these melts. In addition, the mass action concentrations of N_{Bi} and N_{Cu} have also been evaluated by the model. However, as there aren't any corresponding measured activities to be compared with, they are given in the figure as a reference for scholars of same occupation. From the formulation of the calculating model of mass action concentrations for these melts, once again it is seen how the relation of the activity of binary melts constituting the ternary system with respect to the Raoult's law gives effect to the structure of the models; although in this ternary system binary melts Bi-In and Cu-In are all homogeneous in structure, but owing to the positive deviation of the activities of Bi-Cu melts with respect to the Raoultian behavior, under the effect of annexation, *i.e.*, the phase separation in these melts caused by the chemically less stable metastable compound Cu_2Bi_3, during the formation of ternary melts In-Bi-Cu, Bi-In and Cu-In melts had to transform into two phase melts.

2 In-Sb-Cu melts

According to the phase diagrams [4], in all binary systems constituting this ternary system, there are compounds formed with congruent melting point, hence in accordance with the classification of reference [1], they are all homogeneous melts. The model formulation for these melts begins with binary systems.

2.1 In-Sb melts

It has been discussed in reference [13] about the formation of two compounds InSb and In_3Sb in these binary melts. So the structural units of these melts are In, Sb atoms as well as compounds InSb and In_3Sb. Thus assuming the composition of the melts as $a=\Sigma x_{Sb}$, $b=\Sigma x_{In}$; the mass action concentration of every structural unit after normalization as $N_1=N_{In}$, $N_2=N_{Sb}$, $N_3=N_{InSb}$, $N_4=N_{IN,Sb}$, $\Sigma x=$ sum of all equilibrium mole fractions, then according to the mass action law, there are chemical equilibria:

$$In_{(l)}+Sb_{(l)}=InSb_{(l)},\ K_1=\frac{N_3}{N_1N_2},\ N_3=K_1N_1N_2 \tag{28}$$

$$3In_{(l)}+Sb_{(l)}=In_3Sb_{(l)},\ K_2=\frac{N_4}{N_1^3N_2},\ N_4=K_2N_1^3N_2 \tag{29}$$

Making mass balance gives:

$$N_1+N_2+K_1N_1N_2+K_2N_1^3N_2=1 \tag{30}$$

$$aN_1-bN_2+(a-b)K_1N_1N_2+(3a-b)K_2N_1^3N_2=0 \tag{31}$$

$$1-(a+1)-(1-b)N_2=K_1(a-b+1)N_1N_2+K_2(3a-b+1)N_1^3N_2 \tag{32}$$

The above mentioned equations (30), (31) and (32) are the single phase calculating model of mass action concentrations for homogeneous In-Sb melts, in which equations (30) and (31) are used for calculating the mass action concentrations, while equation (32) for regression of equilibrium constants. Using equation (32) and the measured activities from reference [9], the regressed relations K-T and $\Delta G^{\ominus}$ are given as follows:

$$\lg K_{InSb}=\frac{-472.088}{T}+0.947\,6 \qquad (r=1.000),$$

$$\Delta G^{\ominus}=9042.655-18.15T,\ J\cdot mol^{-1} \tag{33}$$

$$\lg K_{In_3Sb}=\frac{2\,446.937\,5}{T}-1.74 \qquad (r=1.000),$$

$$\Delta G^{\ominus} = -46\,870.135+33.33T,\ \mathrm{J\cdot mol^{-1}} \quad (34)$$

Substituting these thermodynamic parameters into equations (30) and (31) gives the calculated mass action concentrations compared with measured activities as shown in **figure 4**. Good agreement between calculated and measured values as well as their conformity with the law of mass action shows that the model formulated can reflect the structural characteristics of these melts.

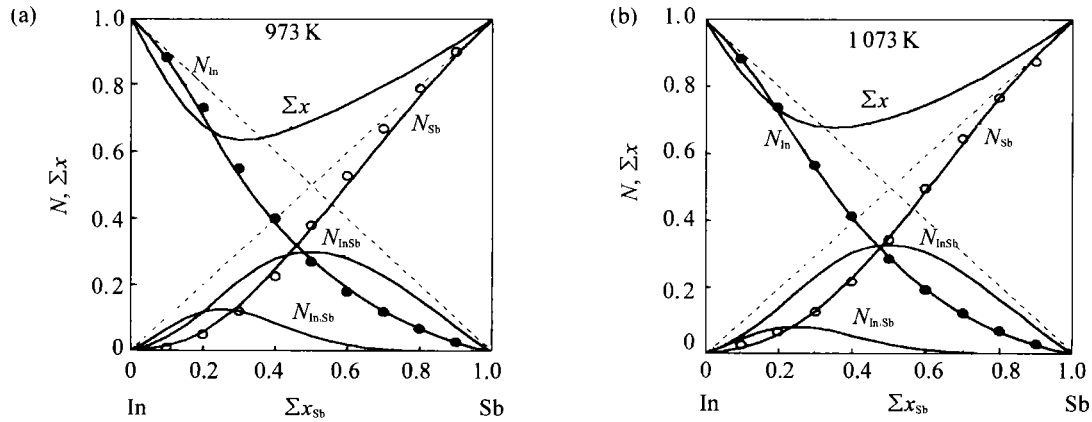

Figure 4 Comparison of calculated mass action concentrations (—) with measured activities (•, o) for In-Sb melts.

2.2 Cu-In melts

As explained in section 1.3, there are compounds Cu_2In and Cu_4In formed in this binary system. Hence, in case of homogeneous solution, the structural units of these melts are Cu and In atoms as well as compounds Cu_2In and Cu_4In. Assuming the composition of the melts as $a=\Sigma x_{Cu}$, $b=\Sigma x_{In}$; the mass action concentration of every structural unit after normalization as $N_1=N_{In}$, $N_2=N_{Cu}$, $N_3=N_{Cu_2In}$, $N_4=N_{Cu_4In}$, Σx= sum of all equilibrium mole fractions, then in the same way as2.1, the calculating model of these melts is formulated as

$$N_1+N_2+K_1N_1N_2^2+K_2N_1N_2^4=1 \quad (35)$$

$$aN_1-bN_2+(a-2b)K_2N_1N_2^4=0 \quad (36)$$

$$1-(a+1)-(1-b)N_2 = K_1(a-2b+1)N_1N_2^2+K_2(a-4b+1)N_1N_2^4 \quad (37)$$

Regressing by the use of equation (37) as well as the measured activities from references [6,7] gives the relations K-T as well as $\Delta G^{\ominus}$ as follows:

$$\lg K_{Cu_2In} = -\frac{1\,029.044\,85}{T}+0.653\,3 \quad (r=-1.000),$$

$$\Delta G^{\ominus} = 19\,710.953-12.514T,\ \mathrm{J\cdot mol^{-1}} \quad (38)$$

$$\lg K_{Cu_4In} = \frac{2\,576.397}{T}-1.638 \quad (r=1.000),$$

$$\Delta G^{\ominus} = -49\,349.89+31.377T,\ \mathrm{J\cdot mol^{-1}} \quad (39)$$

Substituting these thermodynamic parameters into equations (35) and (36) gives the calculated mass action concentrations compared with the measured activities under condition of homogeneous solution as shown in **figure 5**. It is seen from the figure that the calculated and measured values not only basically agree, but also obey the law of mass action, showing that model formulated can reflect the structural reality of these melts.

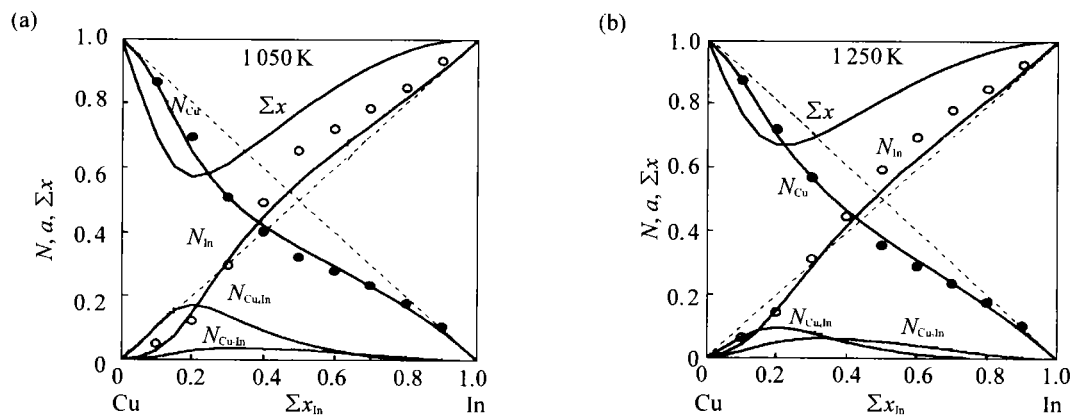

Figure 5 Comparison of calculated mass action concentrations (—) with measured activities (•, o) for Cu-In melts under condition of homogeneous solution.

2.3 Cu-Sb melts

According to the phase diagram [14], there are two compounds Cu_2Sb and Cu_3Sb formed in this binary system, the former is a peritectic, the latter a compound with congruent melting point. Hence the structural units of these melts are Cu and Sb atoms as well as compounds Cu_2Sb and Cu_3Sb. Assuming the compositions of the melts as $a=\Sigma x_{Sb}$, $b=\Sigma x_{Cu}$; the mass action concentration of every structural unit after normalization as $N_1=N_{Cu}$, $N_2=N_{Sb}$, $N_3=N_{Cu_3Sb}$, $N_4=N_{Cu_2Sb}$; Σx= sum of all equilibrium mole fractions, then in the same way as 2.1, the calculating model of these melts is formulated as

$$N_1+N_2+K_1N_1^2N_2+K_2N_1^3N_2=1 \tag{40}$$

$$aN_1-bN_2+(2a-b)K_1N_1^2N_2+(3a-b)K_2N_1^3N_2=0 \tag{41}$$

$$1-(a+1)-(1-b)N_2=K_1(2a-b+1)N_1^2N_2+K_2(3a-b+1)N_1^3N_2 \tag{42}$$

Regressing by the use of equation (42) and the measured activities a_{Cu} and a_{Sb} at 1 000 K from reference [10] gives: $K_{Cu_2Sb}=23.58$ ($\Delta G^{\ominus}=-26\,290.54\,J\cdot mol^{-1}$), $K_{Cu_3Sb}=39.067$ ($\Delta G^{\ominus}=-30\,490.50\,J\cdot mol^{-1}$). Substituting the equilibrium constants into equations (40) and (41) gives the calculated mass action concentrations compared with the measured activities as shown in **figure 6**. It can be seen from the figure that good agreement between the calculated and measured values as well as their conformity with the law of mass action show that the model formulated can reflect the structural characteristics of these melts.

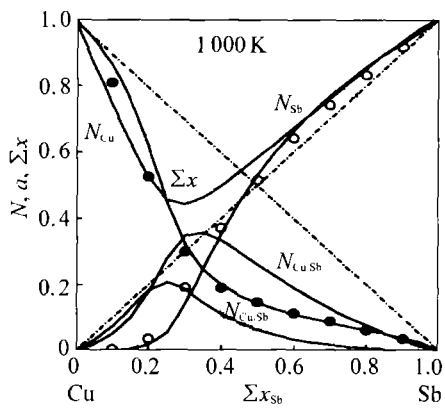

Figure 6 Comparison of calculated mass action concentrations (—) with measured activities (•, o) for Cu-Sb melts at 1 000 K.

2.4 In-Sb-Cu melts

From the discussions in sections 2.1-2.3, it is evident that three binary melts in these ternary system are all homogeneous melts, consequently, the ternary melts consisting of them are also homogeneous melts. Their structural units are In, Sb and Cu atoms as well as compounds InSb, In_3Sb, Cu_2In, Cu_4In, Cu_2Sb and Cu_3Sb. Putting the compositions of the melts as $a=\Sigma x_{In}$, $b=\Sigma x_{Sb}$, $c=\Sigma x_{Cu}$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{In}$, $y=x_{Sb}$, $z=x_{Cu}$, $u_1=x_{BiIn}$, $u_2=x_{BiIn}$, $u_3=x_{Cu_2In}$, $u_4=x_{Cu_4In}$, $u_5=x_{Cu_2Sb}$, $u_6=x_{Cu_3Sb}$; the mass action concentration of every structural unit after normalization as $N_1=N_{In}$, $N_2=N_{Sb}$, $N_3=N_{Cu}$, $N_4=N_{InSb}$, $N_5=N_{In_3Sb}$, $N_6=N_{Cu_2In}$, $N_7=N_{Cu_4In}$, $N_8=N_{Cu_2Sb}$, $N_9=N_{Cu_3Sb}$; Σx= sum of all equilibrium mole fractions, then in the light of mass action law, chemical equilibria are:

$$In_{(l)}+Sb_{(l)}=InSb_{(l)},\ K_1=\frac{N_4}{N_1N_2},\ u_1=K_1\cdot\frac{xy}{\Sigma x},$$

$$\Delta G^{\ominus}=9\,042.655-18.15T,\ J\cdot mol^{-1} \tag{43}$$

$$3In_{(l)}+Sb_{(l)}=In_3Sb_{(l)},\ K_2=\frac{N_5}{N_1^3N_2},\ u_2=K_2\frac{x^3y}{(\Sigma x)^4},$$

$$\Delta G^{\ominus}=-46\,870.135+33.33T,\ J\cdot mol^{-1} \tag{44}$$

$$2Cu_{(l)}+In_{(l)}=Cu_2In_{(l)},\ K_3=\frac{N_6}{N_3^2N_1},\ u_3=K_3\frac{xz}{(\Sigma x)^3},$$

$$\Delta G^{\ominus}=19\,710.953-12.514T,\ J\cdot mol^{-1} \tag{45}$$

$$4Cu_{(l)}+In_{(l)}=Cu_4In_{(l)},\ K_4=\frac{N_7}{N_1N_3^4},\ u_4=K_4\frac{xz^4}{(\Sigma x)^5},$$

$$\Delta G^{\ominus}=-49\,349.89+31.377T,\ J\cdot mol^{-1} \tag{46}$$

$$2Cu_{(l)}+Sb_{(l)}=Cu_2Sb_{(l)},\ K_5=\frac{N_8}{N_3^2N_2},\ u_5=K_5\frac{yz^2}{(\Sigma x)^3},$$

$$K_{Cu_2Sb}=23.58\ (\Delta G^{\ominus}=-26\,290.54\,J\cdot mol^{-1}) \tag{47}$$

$$3Cu_{(l)}+Sb_{(l)}=Cu_3Sb_{(l)},\ K_6=\frac{N_9}{N_3^3N_2},\ u_6=K_6\frac{yz^3}{(\Sigma x)^3},$$

$$K_{Cu_3Sb}=39.067\ (\Delta G^{\ominus}=-30\,490.50\,J\cdot mol^{-1}) \tag{48}$$

mass balance is:

$$a=x+u_1+3u_2+u_3+u_4 \tag{49}$$

$$b=y+u_1+u_2+u_5+u_6 \tag{50}$$

$$c=z+2u_3+4u_4+2u_5+3u_6 \tag{51}$$

mass action concentrations are:

$$N_i=\frac{x_i}{\Sigma x},\ N_j=\frac{u_j}{\Sigma x} \tag{52}$$

where x_i represents x, y and z; u_j represents u_1-u_6.

The above equations (43)-(52) are the single phase calculating model of mass action concentrations for these melts. The calculated mass action concentrations N_{In} at 1 000 K by the use of this model are compared with measured activities a_{In} as shown in **figure 7**. The agreement between calculated N_{In} and measured a_{In} as well as their conformity with the law of mass action show that the model formulated can exactly reflect the structural characteristics of these melts. In addition, the calculated mass action concentrations N_{Sb} and N_{Cu} are also listed in figure 7 (a). As there aren't any relevant

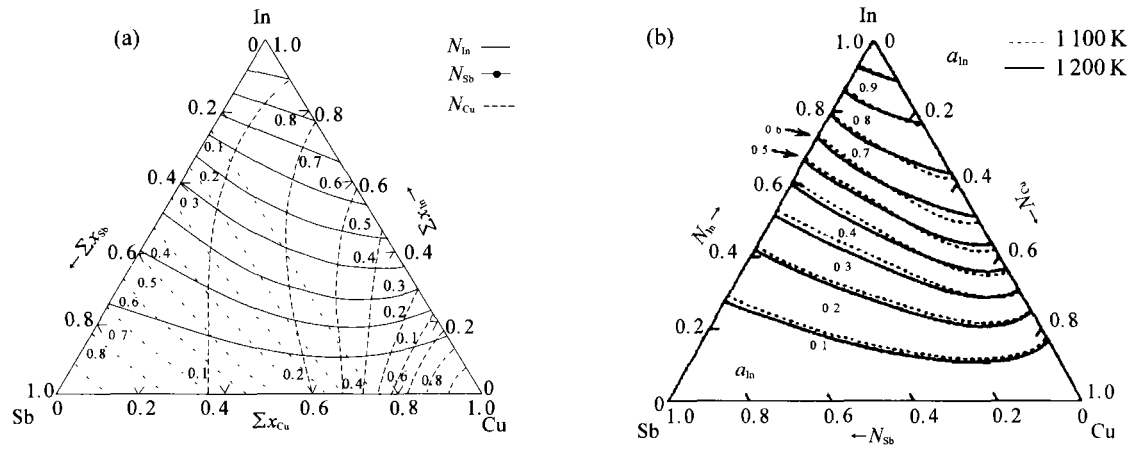

Figure 7 Comparison of calculated N_{In} and measured a_{In} for In-Sb-Cu melts at 1 000 K, (a) Calculated N_{In} ; (b) Measured a_{In}.

measured activities to be compared with, they serve as reference for scholars of same occupation.

From this example, it is clear that if all the binary melts constituting the ternary melts are homogeneous and their activities exhibit negative deviation with respect to the Raoult's law, then the ternary melts formed from them will certainly be homogeneous.

3 Conclusions

(1) Based on the phase diagrams, measured activities and the annexation principle, calculating model of mass action concentrations for In-Bi-Cu and In-Sb-Cu melts has been formulated. Calculated results not only agree well with practical values, but also obey the mass action law, showing that the model deduced can reflect the structural reality of given melts and that the annexation principle is applicable to these two ternary metallic melts.

(2) The determinative factor of whether the melts are homogeneous or heterogeous is the relation of the activity of their binary melts with respect to Raoult's law: so long as there is a binary system, in which the activities of one component exhibit positive deviation relative to Raoultian behavior, heterogeous calculating model should be used to calculate their mass action concentrations. On the contrary, if all the binary melts constituting the ternary melts are homogeneous and their activities exhibit negative deviation with respect to the Raoult's law, then the ternary melts formed from them will certainly be homogeneous.

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