Mater. Environ. Sci. 5 (S1) (2014) 2045-2051
ISSN : 2028-2508
CODEN: JMESCN
MPE14

Comparative study of thermodynamic predicting methods applied to the Au–In–Zn ternary system

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Received 7 Dec 2013, Revised 16 July 2014, Accepted 17 July 2014
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Abstract
The results of the calculation of integral enthalpies of mixing in liquid state for ternary Au-In-Zn alloys using the general solution model of Chou are presented in this paper. Five selected sections with x_{In}/x_{Zn} = 1/3, 1/2, 1/1, 2/1 and 3/1 were investigated at 973K. The other traditional geometric models such as Kohler, and Toop are also included in calculations for comparison and discussion. The Kohler-values are more exothermic than those obtained by Toop's model. The results obtained by Chou's model show that Au-In-Zn ternary system is asymmetric.

Keywords: Pb-free solders; Integral enthalpy of mixing; Geometric models; Au-In-Zn ternary system

1. Introduction
High-Pb solders as high-temperature solders have been widely used in advanced electronic packaging of the electronic and automotive industries. However, Pb is harmful to both the environment and human health. Therefore, the development of high-temperature Pb-free solders to replace the conventional high-Pb solders has become an important issue now. Unfortunately, there are only a limited number of reports on the research and development for high temperature lead-free alternative solders. Despite their high price, gold-based alloys as high temperature solders are known for good mechanical and thermal properties, as well as corrosion consistency and can be considered as potential candidates [1–4]. To reduce the costs of Au-based solders, alloying elements such as Ag, Al, Bi, Cu, In, Sb, Sn, Zn, etc., may be added to replace a part of the Au. Among these systems, the Au-In-Zn ternary alloys may be taken in consideration.
In order to predict the interface reactions between In-Zn-based solders and Au-substrate, knowledge of thermodynamic behavior of the ternary Au-In-Zn system should be known. One thermodynamic quantity that has to be known is the integral enthalpy of mixing. For the best knowledge of the authors, no direct measurement of the enthalpy of mixing of this ternary system is available in the literature. Probably the relatively high investigating temperatures and the evaporation of zinc could make experimental measuring difficult.
The main purpose of this study is the calculation of the enthalpies of mixing of the liquid phase in the ternary system Au-In-Zn at 973 K by using the ternary geometric models of Chou [5], Kohler [6], and Toop [7].

2. Literature survey
2.1. Binary Au-In, Au-Zn and In-Zn systems
Calorimetric investigations of Au–In alloys have been reported in the literature by direct reaction calorimetry [8-11]. The calorimetric results of Castanet et al. [11] are more exothermic than those of Itagaki and Yazawa [9]. The data of Béjà [8] and Castanet et al. [11] show that the enthalpies of mixing of Au–In alloys are

temperature dependent. The thermodynamic functions were assessed by Ansara and Nabot [12] and Liu et al. [13]. The calculated enthalpies of mixing of liquid Au-In alloys obtained by both the descriptions are similar and show the same dependence on temperature. The enthalpy of mixing of liquid Au-Zn alloys was measured extensively using high temperature calorimetry [14], and emf methods [15].
The enthalpy of mixing for liquid In-Zn alloys was determined calorimetrically [16-18]. Emf methods were applied to derive the corresponding values [19-21]. All experimental data show positive values for the enthalpy of mixing. Lee [22] presented a thermodynamic assessment based on the above-mentioned experimental data [16-21] for the enthalpy of mixing of liquid In-Zn alloys, and the calculated and experimental results were in good agreement.

2.2. Ternary Au-In-Zn system
To the best knowledge of the authors no data for the enthalpy of mixing of liquid alloys in the Au-In-Zn ternary system are available from literature.

3. Theoretical fundamentals

3.1 A general solution model of Chou [5]
There are several methods for calculating thermodynamic properties based on binary information [5-7, 23]. The method provided recently by Chou [5] has been proved to be the most reasonable one in all aspects among current geometrical models. This model can not only generalize various kinds of situations, break down the boundary between symmetrical and asymmetrical systems, but can also thoroughly rule out any human interference in the calculation process. The correctness of this model has already been proved theoretically and the accuracy of calculation has also been shown in some practical examples [24, 25]. Therefore, this model is applied for calculating the thermodynamic properties of the Au-In-Zn ternary system.
When the Chou's model is applied to the Au-In-Zn ternary system, first of all, it is necessary to calculate the similarity coefficients ξ_{ij} for three binaries which are defined by η_i called the deviation sum of squares:

$$\xi_{12} = \frac{\eta_{\mathrm{I}}}{\eta_{\mathrm{I}} + \eta_{\mathrm{II}}} \qquad \xi_{23} = \frac{\eta_{\mathrm{II}}}{\eta_{\mathrm{II}} + \eta_{\mathrm{III}}} \qquad \xi_{31} = \frac{\eta_{\mathrm{III}}}{\eta_{\mathrm{III}} + \eta_{\mathrm{I}}}$$

where

$$\eta_{\mathrm{I}} = \int_0^1 (\Delta_{mix}H_{12} - \Delta_{mix}H_{13})^2 \mathrm{d}X_1 \qquad \eta_{\mathrm{II}} = \int_0^1 (\Delta_{mix}H_{21} - \Delta_{mix}H_{23})^2 \mathrm{d}X_2$$

$$\eta_{\mathrm{III}} = \int_0^1 (\Delta_{mix}H_{31} - \Delta_{mix}H_{32})^2 \mathrm{d}X_3$$

and

$$X_{1(12)} = x_1 + x_3\xi_{12} \qquad X_{2(23)} = x_2 + x_1\xi_{23} \qquad X_{3(31)} = x_3 + x_2\xi_{31}$$

The basic equation of the general solution model, derived by Chou, is given as follows:

$$\Delta_{mix}H_{123} = x_1x_2\sum_{\nu} L_{12}^{\nu}(x_1 - x_2)^{\nu} + x_2x_3\sum_{\nu} L_{23}^{\nu}(x_2 - x_3)^{\nu} + x_3x_1\sum_{\nu} L_{31}^{\nu}(x_3 - x_1)^{\nu} + x_1x_2x_3f$$

$\Delta_{mix}H_{123}$ is an integral enthalpy of mixing for a ternary 1-2-3 system, x_1, x_2, x_3 are the mole fractions of a ternary alloy, L_{ij}^{ν} are parameters for binary "ij" independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\Delta_{mix}H_{ij} = X_iX_j\sum_{\nu} L_{ij}^{\nu}\left(X_i - X_j\right)^{\nu}$$

Where X_i and X_j indicate the mole fraction of component "i" and "j" in "ij" binary system. The function *f* is the ternary interaction coefficient expressed by:

$$\begin{aligned} f = (2\xi_{12} - 1)\left[L_{12}^2\left((2\xi_{12}-1)x_3 + 2(x_1 - x_2)\right) + L_{12}^1\right] \\ + (2\xi_{23} - 1)\left[L_{23}^2\left((2\xi_{23}-1)x_1 + 2(x_2 - x_3)\right) + L_{23}^1\right] \\ + (2\xi_{31} - 1)\left[L_{31}^2\left((2\xi_{31}-1)x_2 + 2(x_3 - x_1)\right) + L_{31}^1\right] \end{aligned}$$

3.2. A traditional Kohler [6], and Toop [7] models

There are several traditional models used to extrapolate the ternary thermodynamic properties based on the three constitutive binary systems, which are classified, according to Hillert [26], into two categories: symmetrical [6, 23] and asymmetrical [7, 26]. The use of a symmetrical model when an asymmetrical model is more appropriate can often give rise to errors.

The two different extrapolation models [6, 7] were used to calculate the enthalpy of mixing in the ternary Au-In-Zn system. A ternary system contains three binary systems, and the information of all these binary systems should be known before using the models.

The various predictive extensions from the binary to ternary systems are shown below.

Kholer model [6]:

$$\begin{aligned} \Delta_{\mathrm{mix}}H_{123} = (x_{1+}\,x_2)^2\Delta_{\mathrm{mix}}H_{12}\left(\frac{x_1}{x_1 + x_2};\frac{x_2}{x_1 + x_2}\right) + (x_{1+}\,x_3)^2\Delta_{\mathrm{mix}}H_{13}\left(\frac{x_1}{x_1 + x_3};\frac{x_3}{x_1 + x_3}\right) \\ + (x_{2+}\,x_3)^2\Delta_{\mathrm{mix}}H_{23}\left(\frac{x_2}{x_2 + x_3};\frac{x_3}{x_2 + x_3}\right) \end{aligned}$$

Toop model [7]:

$$\begin{aligned} \Delta_{\mathrm{mix}}H_{123} = (x_{2+}\,x_3)^2\Delta_{\mathrm{mix}}H_{23}\left(\frac{x_2}{x_2 + x_3};\frac{x_3}{x_2 + x_3}\right) + \frac{x_2}{(1 - x_1)}\Delta_{\mathrm{mix}}H_{12}(x_1\,;1 - x_1) \\ + \frac{x_3}{(1 - x_1)}\Delta_{\mathrm{mix}}H_{13}(x_1\,;1 - x_1) \end{aligned}$$

4. Results and discussion

The calculations in the investigated ternary system Au-In-Zn were carried out along the lines of a constant x_{In}/x_{Zn}. The five selected cross sections are given in Table 1.

Table 1: Five investigated sections

Section	A	B	C	D	E
x_{In}/x_{Zn}	3/1	2/1	1/1	1/2	1/3

For our calculations, we used the data of Hassam et al. [27] for the Au-In system, Hultgreen et al. [28] for In-Zn system, and Liu et al [13] for the Au-Zn system (Table 2).

Table 2: Binary interaction parameters of Au-In, In-Zn and Zn-Au sub-binary systems at 973 K.

Binary system	$L^{(0)}$	$L^{(1)}$	$L^{(2)}$	Reference
Au-In	-67586	-23091	2911	[27]
In-Zn	13095	-2682	0	[28]
Zn-Au	-93533	-5577	0	[13]

The significant influence of thermodynamic properties of constitutive binary systems on the thermodynamic characteristic of ternary Au-In-Zn alloys is noticeable from Figure 1. Enthalpies of mixing values of the three

constitutive binaries indicate that a strong chemical interaction between the components in this ternary system exists between gold and zinc (up to about -23000 J/mol) and between gold and indium (up to about -17000 J/mol), but the weakest between indium and zinc.

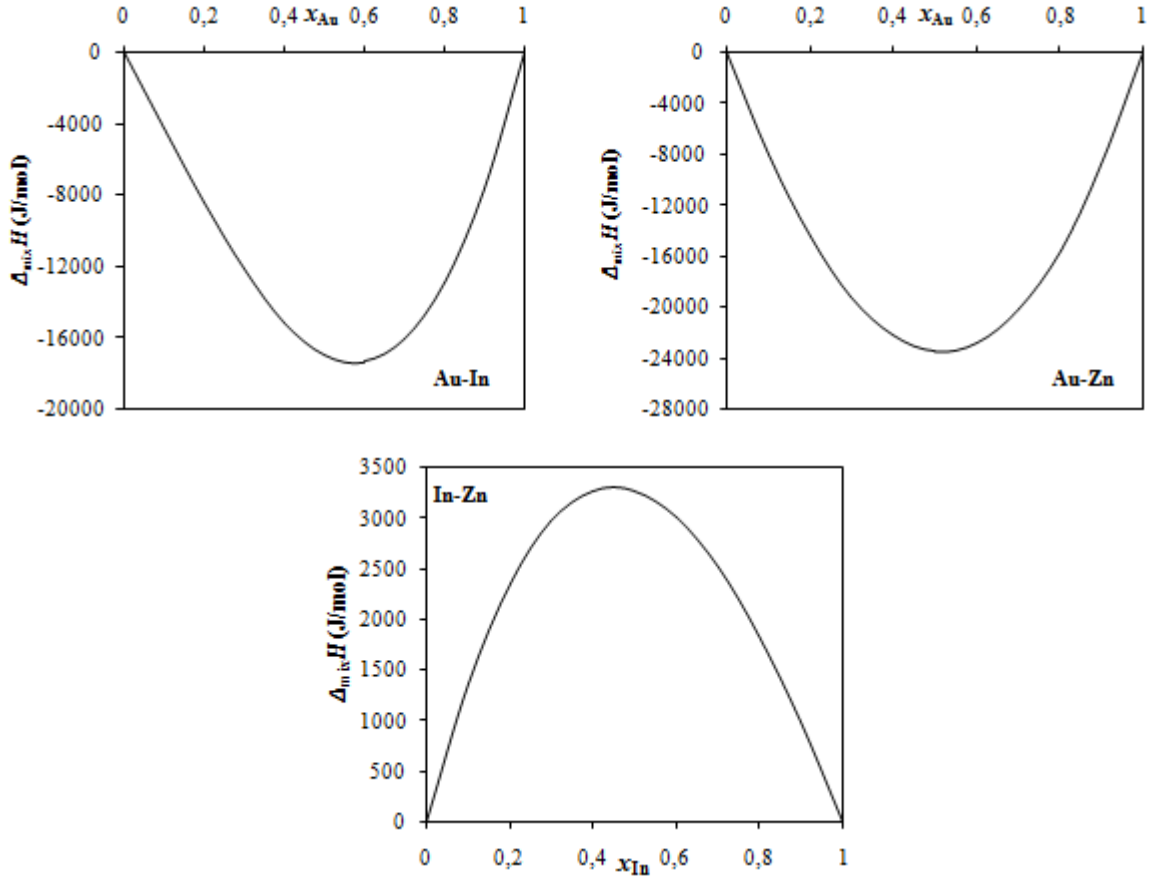

Figure 1: Integral enthalpies of mixing in the liquid Au-In, Au-Zn and In-Zn (at 973K) binary systems (standard states: pure liquid metals).

Using the Equations developed by Chou, the deviation sum of squares and the similarity coefficients for the three binaries Au-In, Au-Zn and In-Zn are listed in Table 3.

Table 3: Deviation sum squares and similarity coefficients for Chou's model [5] applied on Au-In-Zn.

Deviation sum of squares (J^2/mol^2)	η_I=27087952		η_{II}=216740921		η_{III}=379309161	
Interaction of	Au-In	Au-Zn	In-Au	In-Zn	Zn-Au	Zn-In
Similarity coefficients	ξ_{Au-In}=0.1111		ξ_{In-Zn}=0.3636		ξ_{Zn-Au}=0.9333	

From the values of similarity coefficients (Table 3), one can conclude that the integral enthalpies of mixing of Au-In and Au-Zn are more similar to each other than to In-Zn, respectively. These ξ-values indicate also that this system could be an asymmetrical system. The calculated results for the three models in all the ternary investigated sections (A-E) are listed in Table 4.

The curves $\Delta_{mix}H = f(x_{Au})$ at 973 K for all cross sections investigated according to the Chou, Kohler and Toop models are shown in Figure 2. Based on these results, it could be concluded that predicted values of integral enthalpies of mixing for the five selected sections obtained by the Chou's model are in better agreement with the results obtained by the Toop asymmetrical model than those from the Kohler symmetric model.

Table 4: Integral enthalpies of mixing of Au-In-Zn system at 973 K calculated by different predicting models

x_{Au}	x_{In}	x_{Zn}	Kohler's model	Toop's model	Chou's model
			$\Delta_{mix}H$ (J.mol^{-1})	$\Delta_{mix}H$ (J.mol^{-1})	$\Delta_{mix}H$ (J.mol^{-1})
Section A: (x_{In}/x_{Zn}=3/1)					
0	**0.75**	**0.25**	**2203**	**2203**	**2203**
0.1	**0.675**	**0.225**	**-3568**	**-3408**	**-3481**
0.2	**0.6**	**0.2**	**-8968**	**-8519**	**-8628**
0.3	**0.525**	**0.175**	**-13526**	**-12830**	**-12948**
0.4	**0.45**	**0.15**	**-16889**	**-16064**	**-16173**
0.5	**0.375**	**0.125**	**-18783**	**-17967**	**-18055**
0.6	**0.3**	**0.1**	**-18991**	**-18302**	**-18365**
0.7	**0.225**	**0.075**	**-17339**	**-16855**	**-16894**
0.8	**0.15**	**0.05**	**-13692**	**-13434**	**-13452**
0.9	**0.075**	**0.025**	**-7941**	**-7866**	**-7870**
1	**0**	**0**	**0**	**0**	**0**
Section B: (x_{In}/x_{Zn}=2/1)					
0	**0.666**	**0.334**	**2714**	**2714**	**2714**
0.1	**0.6**	**0.3**	**-3502**	**-3310**	**-3405**
0.2	**0.533**	**0.267**	**-9236**	**-8694**	**-8836**
0.3	**0.467**	**0.233**	**-14007**	**-13166**	**-13320**
0.4	**0.4**	**0.2**	**-17469**	**-16473**	**-16616**
0.5	**0.333**	**0.167**	**-19363**	**-18380**	**-18498**
0.6	**0.267**	**0.133**	**-19498**	**-18672**	**-18756**
0.7	**0.2**	**0.1**	**-17728**	**-17149**	**-17201**
0.8	**0.133**	**0.067**	**-13941**	**-13633**	**-13658**
0.9	**0.067**	**0.033**	**-8053**	**-7964**	**-7970**
1	**0**	**0**	**0**	**0**	**0**
Section C: (x_{In}/x_{Zn}=1/1)					
0	**0.5**	**0.5**	**3273**	**3273**	**3273**
0.1	**0.45**	**0.45**	**-3724**	**-3482**	**-3606**
0.2	**0.4**	**0.4**	**-10003**	**-9334**	**-9521**
0.3	**0.35**	**0.35**	**-15079**	**-14060**	**-14266**
0.4	**0.3**	**0.3**	**-18640**	**-17453**	**-17646**
0.5	**0.25**	**0.25**	**-20475**	**-19321**	**-19481**
0.6	**0.2**	**0.2**	**-20443**	**-19484**	**-19601**
0.7	**0.15**	**0.15**	**-18442**	**-17778**	**-17850**
0.8	**0.1**	**0.1**	**-14401**	**-14050**	**-14085**
0.9	**0.05**	**0.05**	**-8267**	**-8165**	**-8175**
1	**0**	**0**	**0**	**0**	**0**
Section D: (x_{In}/x_{Zn}=1/2)					
0	**0.334**	**0.666**	**3110**	**3110**	**3110**
0.1	**0.3**	**0.6**	**-4514**	**-4243**	**-4369**
0.2	**0.267**	**0.533**	**-11142**	**-10440**	**-10631**
0.3	**0.233**	**0.467**	**-16331**	**-15310**	**-15522**
0.4	**0.2**	**0.4**	**-19842**	**-18695**	**-18895**
0.5	**0.167**	**0.333**	**-21531**	**-20443**	**-20610**

0.6	**0.133**	**0.267**	**-21299**	**-20413**	**-20535**
0.7	**0.1**	**0.2**	**-19077**	**-18472**	**-18548**
0.8	**0.067**	**0.133**	**-14812**	**-14497**	**-14534**
0.9	**0.033**	**0.067**	**-8464**	**-8374**	**-8384**
1	**0**	**0**	**0**	**0**	**0**
Section E: (x_{In}/x_{Zn}=1/3)					
0	**0.25**	**0.75**	**2206**	**2706**	**2706**
0.1	**0.225**	**0.675**	**-5152**	**-4882**	**-4995**
0.2	**0.2**	**0.6**	**-11860**	**-11197**	**-11369**
0.3	**0.175**	**0.525**	**-17022**	**-16092**	**-16283**
0.4	**0.15**	**0.45**	**-20541**	**-19431**	**-19612**
0.5	**0.125**	**0.375**	**-22034**	**-21084**	**-21235**
0.6	**0.1**	**0.3**	**-21693**	**-20928**	**-21040**
0.7	**0.075**	**0.225**	**-19365**	**-18847**	**-18918**
0.8	**0.05**	**0.15**	**-15001**	**-14732**	**-14767**
0.9	**0.025**	**0.075**	**-8558**	**-8481**	**-8491**
1	**0**	**0**	**0**	**0**	**0**

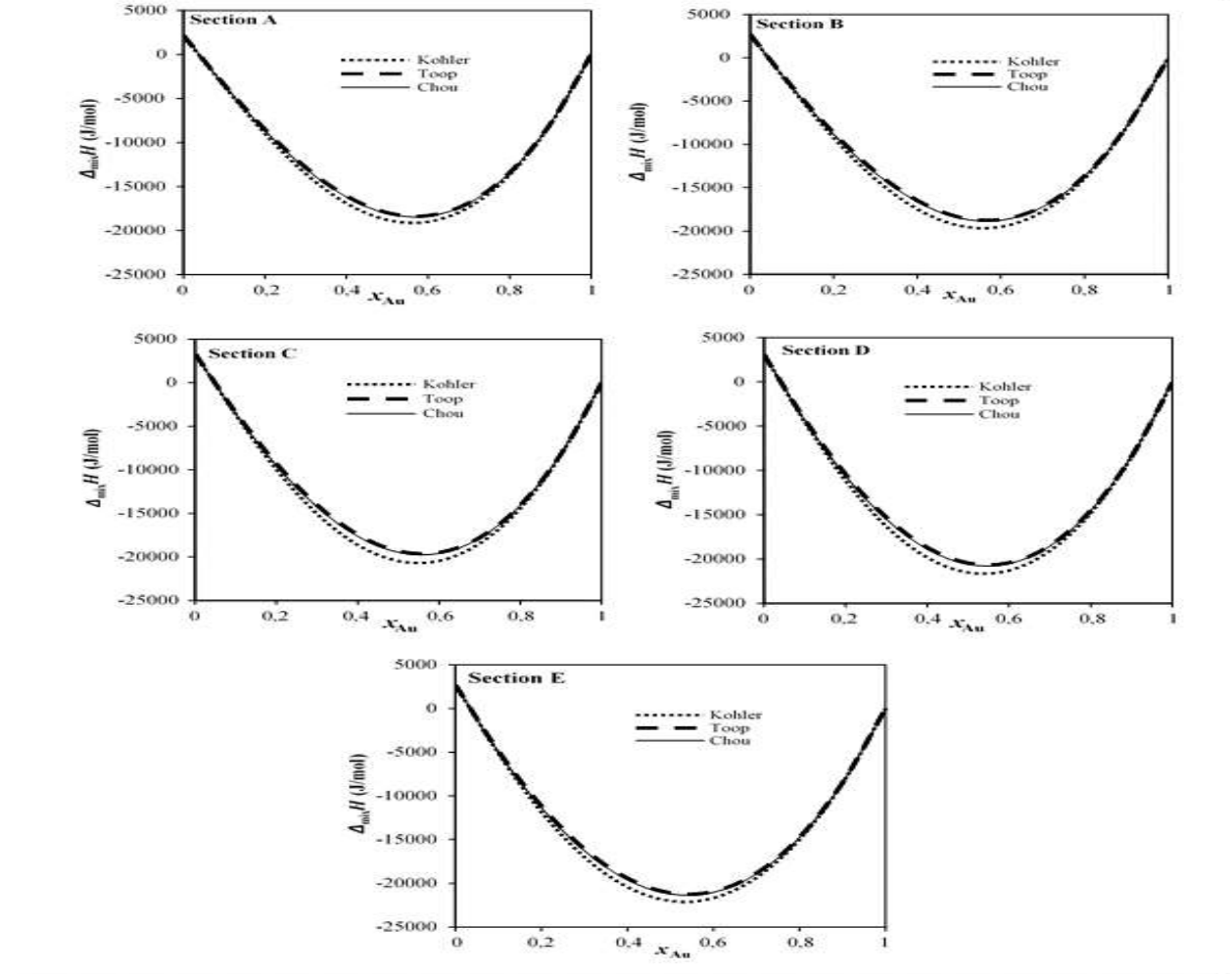

Figure 2: Integral enthalpies of mixing in the liquid Au-In -Zn alloys at 973 K using three different models (standard states: pure liquid metals).

Conclusion

The integral enthalpies of mixing of the ternary Au-In-Zn system were calculated by using the Chou, Kohler and Toop models. From the results obtained by Chou's model, one can conclude that Au-In-Zn ternary system is asymmetric. The Kohler-values are more exothermic than those obtained by Toop's model.

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