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Enthalpies of mixing estimation in the liquid X-In-Sn-Zn (X=Ag, Au) alloys

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Abstract
Results of thermodynamic predicting methods applied to the quaternary metallic X-In-Sn-Zn (X = Ag and Au) systems based on their sub-binary systems are presented in this work. The general solution model of Chou has been used to estimate the integral enthalpies of mixing of the investigated systems. The other traditional models such as Muggianu and Toop are also included in estimations for comparison. The estimations were carried out at 773 K along five starting ternary compositions $In_xSn_yZn_z$ with additions of Ag or Au. In the Ag-In-Sn-Zn system, the estimated enthalpies of mixing using Chou's model are close to those predicted by a symmetric Muggianu's model, while for the Au-In-Sn-Zn, the values obtained by Chou's model are in good agreement with those of an asymmetric Toop's model.

Keywords: Thermochemical properties, sub-binary system, geometric model, multicomponent systems, lead-free solder.

1.Introduction
Due to the high lead toxicity, the end of lead-containing solders industrial application is envisaged and the In-Sn-Zn system can be considered as a potential lead-free solder material. That is why the development of lead-free solders is a current task [1]. These materials are expected to be designed on the bases of systems including low-melting elements like tin alloy. On the other side, silver or gold metallization often appears as intrinsic part of the electronic devices.

Gold and silver-based alloys are known for good mechanical and thermal properties as well as corrosion consistency and can be considered as potential candidates. Among these systems, the Ag-In-Sn-Zn and Au-In-Sn-Zn quaternary systems may be taken in consideration. In, Sn and Zn can be used as component solder alloys and Au or Ag as a possible substrate element. For industrial applications, it is necessary to have access to reliable thermochemical properties (enthalpy of mixing, free enthalpy of mixing …) of various kinds of solution, especially for multicomponent systems. Therefore information on thermochemistry and phase relation of the Ag-In-Sn-Zn and Au-In-Sn-Zn quaternary systems forms the base for a systematic alloy design which is desired to avoid complex and time consuming trial and error developing methods. Unfortunately, there is a shortage of thermodynamic data for the multicomponent systems (especially for the systems with more than three components) probably due to the complexity of experiments. Therefore the calculations of thermodynamic properties and phase diagrams have been increasingly important. The traditional geometric models such as Kohler [2], Muggianu et al.[3], Hillert [4] and Toop [5] have been used extensively in ternary systems based on the binary information.

In this work, the integral enthalpies of mixing in the liquid X-In-Sn-Zn (X=Ag, Au) quaternary alloys have been estimated at 773 K along five starting ternary compositions: $In_{0.800}Sn_{0.100}Zn_{0.100}$, $In_{0.550}Sn_{0.225}Zn_{0.225}$, $In_{0.450}Sn_{0.450}Zn_{0.100}$, $In_{0.225}Sn_{0.550}Zn_{0.225}$, and $In_{0.100}Sn_{0.800}Zn_{0.100}$ with additions of silver or gold taking into consideration the experimental data (the dropped mole of Ag and Au). The estimations were made by means of the general solution model developed by Chou [6,7]. The predicted results have been compared to the experimental ones reported by our research group [8,9] at the same temperature (773 K). For comparison, the

traditional geometric Muggianu et al. [3] and Toop [5] models are also introduced in the estimations. It should be noted that our calculations of the mixing enthalpies are made based on the fact that the reference state is the pure liquid components.

2. Theoretical fundamentals

There are several geometrical models [2-5] for calculating thermodynamic properties based on binary information. According to Hillert [4], these traditional models can be classified into symmetrical models, such as Kohler [2] and Muggianu models [3], and asymmetrical models, such as Hillert [4] and Toop [5] models. The use of a symmetrical model when an asymmetrical model is more appropriate can often give rise to errors.

It is well known that in the current ternary geometric models the selected binary composition points are independent of ternary itself. This situation can cause inherent defects for both symmetrical [2,3] and asymmetrical [4,5] models. For example, the symmetrical models [2,3] cannot be reduced to a binary model even if two of three components are identical, which is abnormal. For the asymmetrical models [4,5], they require human intervention when arranging three components to three apexes of triangle. Different arrangements of these three components cause different thermodynamic properties values.

To overcome the inherent defects mentioned above, Chou [6,7] has proposed a generation geometric model. This model can not only generalize various kinds of situations, break down the boundary between symmetrical and asymmetrical models, but can also thoroughly rule out any human interference in the calculation process for ternary systems. In this new model, the selected binary composition points are related to the ternary itself by introducing a parameter called "similarity coefficient". The application of general solution model of Chou has already been proved in some practical examples for predicting ternary thermodynamic properties of some ternary alloys [10-15].

It is known that all the geometric models are firstly proposed to predict the thermodynamic properties in ternary systems. To the best knowledge of the authors, no thermodynamic calculations have been reported for the quaternary metallic systems using the general solution model of Chou. The only published work on quaternary systems has been done recently by Zhang et al. [16]. These authors have used the model to estimate the physicochemical properties (excess viscosity and molar volume) of a quaternary "Propan-2-ol + Methylacetate + *di*-Chloromethane + *n*-Pentane" system and the calculation results show that the new model works well in the high order system.

The aim of this work is to calculate the integral enthalpies of mixing in the liquid Ag-In-Sn-Zn and Au-In-Sn-Zn quaternary metallic systems at 773 K using the general solution model of Chou [6,7]. To compare our calculated results, we introduce the predicted values by using a symmetric Muggianu [3] and an asymmetric Toop [5] models. The calculated results are compared to the experimental ones measured, at 773K, by El Maniani and Sabbar [8], and Boulouiz and Sabbar [9] for Ag-In-Sn-Zn and Au-In-Sn-Zn quaternary systems, respectively.

2.1. Traditional geometric model equations

The various predictive extensions from the binary to quaternary system are well described in our previous papers [8, 9].

2.2. A general solution model of Chou

When the general solution model is applied to the quaternary system, first of all, it is necessary to calculate the similarity coefficients $\xi^k_{i(ij)}$ for six binaries which are defined by $\eta(ij,ik)$ called the deviation sum of squares:

$$\xi^k_{i(ij)} = \frac{\eta(ij,ik)}{\eta(ij,ik)+\eta(ji,jk)} \quad (1)$$

Where

$$\eta(ij,ik) = \int_0^1 (\Delta_{mix} H_{ij} - \Delta_{mix} H_{ik})^2 \mathrm{d}X_i \quad (2)$$

$$\eta(ij,ik) = \frac{1}{30}\left(L^0_{ij} - L^0_{ik}\right)^2 + \frac{1}{210}\left(L^1_{ij} - L^1_{ik}\right)^2 + \frac{1}{630}\left(L^2_{ij} - L^2_{ik}\right)^2 + \frac{1}{105}\left(L^0_{ij} - L^0_{ik}\right)\left(L^2_{ij} - L^2_{ik}\right) \quad (3)$$

and

$$X_{i(ij)} = x_i + \sum_{\substack{k=1 \\ k\neq ij}}^{4} \xi^k_{i(ij)}\, x_k \quad (4)$$

The basic equation of the general solution model is given as follows:

$$\Delta_{mix}\, H_{1234} = x_1x_2 \sum_{\nu=0}^{n} L_{12}^{\nu}\left(X_{1(12)} - X_{2(12)}\right)^{\nu} + x_1x_3 \sum_{\nu=0}^{n} L_{13}^{\nu}\left(X_{1(13)} - X_{3(13)}\right)^{\nu} + x_1x_4 \sum_{\nu=0}^{n} L_{14}^{\nu}\left(X_{1(14)} - X_{4(14)}\right)^{\nu} + x_2x_3 \sum_{\nu=0}^{n} L_{23}^{\nu}\left(X_{2(23)} - X_{3(23)}\right)^{\nu} + x_2x_4 \sum_{\nu=0}^{n} L_{24}^{\nu}\left(X_{2(24)} - X_{4(24)}\right)^{\nu} + x_3x_4 \sum_{\nu=0}^{n} L_{34}^{\nu}\left(X_{3(34)} - X_{4(34)}\right)^{\nu} \quad (5)$$

$\Delta_{mix}H_{1234}$ is an integral enthalpy of mixing for a quaternary system, x_1, x_2, x_3 and x_4 are the mole fractions of a quaternary alloy, L_{ij}^{ν} are the parameters for binary "ij" independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\Delta_{mix}\, H_{ij} = X_{i(ij)}X_{j(ij)} \sum_{\nu=0}^{n} L_{ij}^{\nu}\left(X_{i(ij)} - X_{j(ij)}\right)^{\nu} \quad (6)$$

$X_{i(ij)}$ indicates the mole fraction of component "i" in "ij" binary system.

3. Results and discussion

The investigated cross ternary $In_xSn_yZn_z$ used in this work are shown in figure 1.

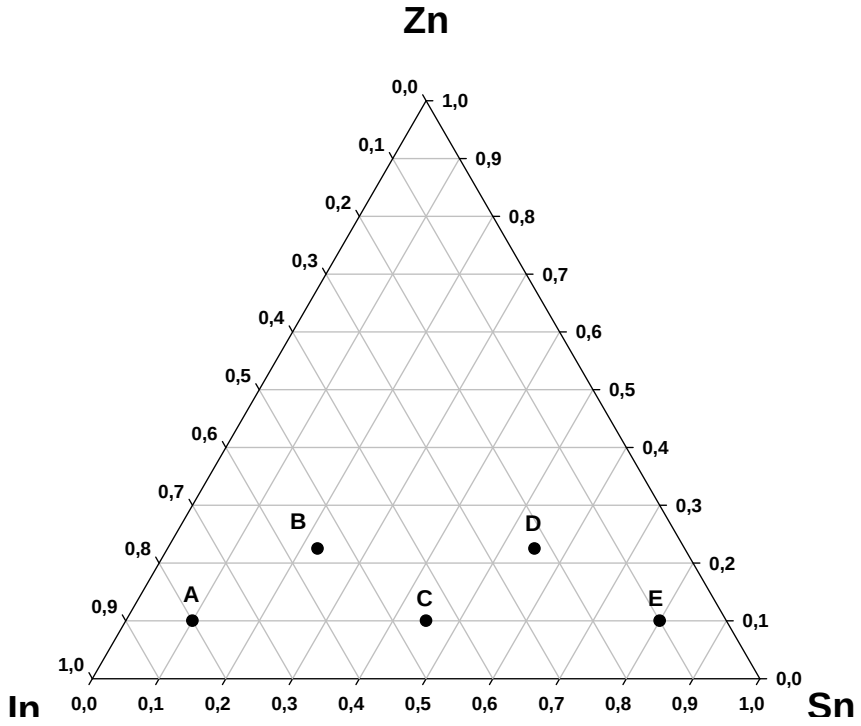

Figure 1: Ternary In-Sn-Zn starting compositions (mol fractions) for the calculations in the X-In-Sn-Zn (X = Ag and Au) systems at 773 K.

With Eq. (3) one can obtain $\eta(ij, ik)$ and the values are listed in table 1. Substituting values of $\eta(ij, ik)$ into Eq. (1), the similarity coefficients can be found, which are shown in table 2.

Table 1: Values of deviation sum of squares η(ij.ik) for the quaternary systems (X-In-Sn-Zn is set in 1-2-3-4 order)

X-In-Sn-Zn	$\boldsymbol{\eta(12,13)}$	$\boldsymbol{\eta(12,14)}$	$\boldsymbol{\eta(13,14)}$	$\boldsymbol{\eta(21,23)}$	$\boldsymbol{\eta(21,24)}$	$\boldsymbol{\eta(23,24)}$
X = Au	23126953	19464767	79295101	164484597	239628973	7101620
X = Ag	6108831	3012207	17688921	10638947	34435790	7101620
	$\boldsymbol{\eta(31,32)}$	$\boldsymbol{\eta(31,34)}$	$\boldsymbol{\eta(32,34)}$	$\boldsymbol{\eta(41,42)}$	$\boldsymbol{\eta(41,43)}$	$\boldsymbol{\eta(42,43)}$
X = Au	64615653	113616499	6914552	383358566	380700644	31736
X = Ag	3008517	14919337	6914552	54794568	53747415	31736

According to Eq. (4), the binary composition points can be calculated. Thus, the corresponding integral enthalpies of mixing are evaluated by Eq. (5). For our calculations we used the data of Hultgreen et al.[17] for the Ag-In, In-Zn and Sn-Zn systems, Flandorfer et al.[18] for the Ag-Sn system, Gomez-Acebo [19] for the Ag-Zn system, Rechchach et al. [20] for the In-Sn system, Liu et al. [21] for the Au-In system, Hayer et al. [22] for the Au-Sn system and Hayer [23] for the Au-Zn system. Based on this sub-binary information, calculations according to different predicting methods were done for all the investigated cross ternary sections. In general, due to a lack of good and comprehensive thermodynamic experimental data in multi-component systems, the accuracy of the models described above in the four component systems is extremely difficult to prove. In the case of our two quaternary systems investigated, the experimental data do not cover a wide range of compositions and relate only five ternary sections $In_xSn_yZn_z$.

Table 2: Values of similarity coefficient $\xi^k_{i(ij)}$ for the quaternary systems (X-In-Sn-Zn is set in 1-2-3-4 order)

X-In-Sn-Zn	$\xi^3_{1(12)}$	$\xi^4_{1(12)}$	$\xi^2_{1(13)}$	$\xi^4_{1(13)}$	$\xi^2_{1(14)}$	$\xi^3_{1(14)}$
X = Au	0.1233	0.0751	0.2636	0.4110	0.0483	0.1724
X = Ag	0.3648	0.0804	0.6700	0.5425	0.521	0.2476
	$\xi^1_{2(23)}$	$\xi^4_{2(23)}$	$\xi^1_{2(24)}$	$\xi^3_{2(24)}$	$\xi^1_{3(34)}$	$\xi^2_{3(34)}$
X = Au	0.7180	0.5067	0.3846	0.9956	0.2298	0.9954
X = Ag	0.7796	0.5067	0.3869	0.9956	0.2173	0.9954

Figures 2 and 3 illustrate the calculated results for the Ag-In-Sn-Zn and Au-In-Sn-Zn quaternary systems, respectively.
As it can be seen, for the two quaternary systems the values obtained by Toop's model are the less exothermic, in comparison with the two other geometric models, while the Muggianu's model gave the most exothermic values of the integral enthalpy of mixing.

For the Ag-In-Sn-Zn system, the calculated values (Fig. 2) show that the data offered by Chou's model are close to those predicted by Muggianu's model. Taking into account the experimental data, one can see that the results obtained by Toop's model are better than those of Muggianu's and Chou's models. It should be noticed that good agreement between experimental and Chou's values is obtained for the Sn-rich section ($In_{0.100}Sn_{0.800}Zn_{0.100}$).

For the Au-In-Sn-Zn quaternary system, the calculated enthalpies of mixing (Fig. 3) show that the results obtained by Chou's model are close to those of Toop's model over the composition range. In this system, the three geometric models give similar values to those reported experimentally. However, the values obtained from Muggianu's model are closer to the experimental one. On the other hand, all the calculated values, using the Chou's model, are exothermic with a minimum between -18.04 and -13.46 kJ/mol corresponding to the In-rich (section A) and Sn-rich (section E) sections, respectively. The coordinate of these minima vary according to the studied section (Table 3).

Table 3: Values of the coordinates of the minima for the various calculated sections (A–E) using the Chou's model

Section	x_{Au}	$\Delta_{mix}H$/ kJ.mol^{-1}
A: Au-$In_{0.800}Sn_{0.100}Zn_{0.100}$	0.57	-18.04
B: Au-$In_{0.550}Sn_{0.225}Zn_{0.225}$	0.56	-17.74
C: Au-$In_{0.450}Sn_{0.450}Zn_{0.100}$	0.55	-15.90
D: Au-$In_{0.225}Sn_{0.550}Zn_{0.225}$	0.55	-15.65
E: Au-$In_{0.100}Sn_{0.800}Zn_{0.100}$	0.54	-13.46

It is important to note that the main objective of this work is to compare the experimental enthalpies results of 773 K with those calculated using the general solution model of Chou for the two studied quaternary systems. However, considering the accuracy of the experimental technique and the thermodynamic data of the sub-binary systems, one can conclude that the prediction of enthalpies of mixing of Au-In-Sn-Zn liquid alloys is quite

reasonable, while in the case of Ag-based alloys the calculated and experimental results are slightly different. This difference could be explained by the presence of intermetallic compounds with strong metallic bonds in Ag-alloys (i.e ζAg_3In [24]) at the experimental temperature (773 K).

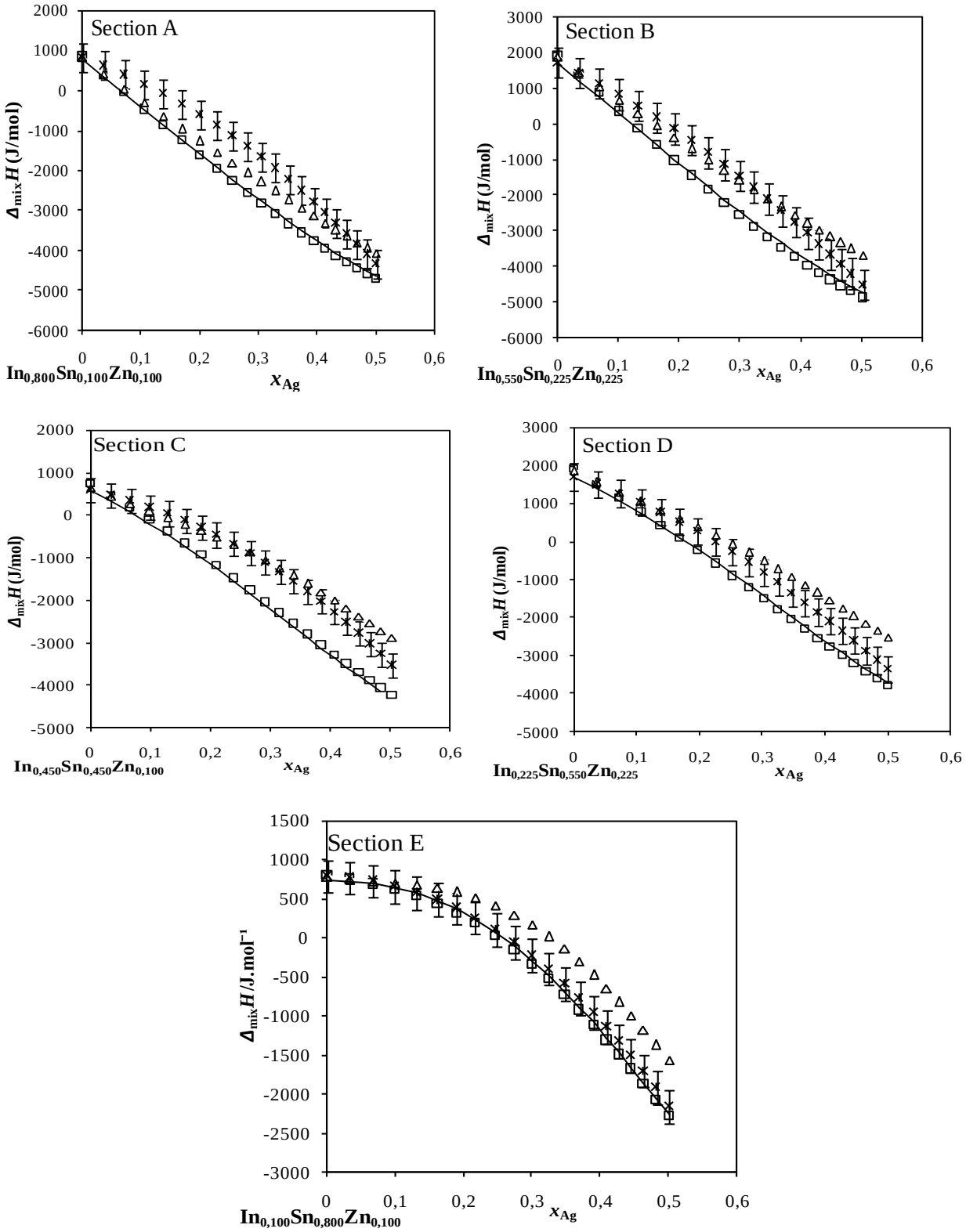

Figure 2: Calculated integral enthalpies of mixing in the liquid Ag-In-Sn-Zn alloys at 773 K using three different models (□ Muggianu [3], Δ Toop [6], — Chou [6, 7]), together with those reported *experimentally [8]

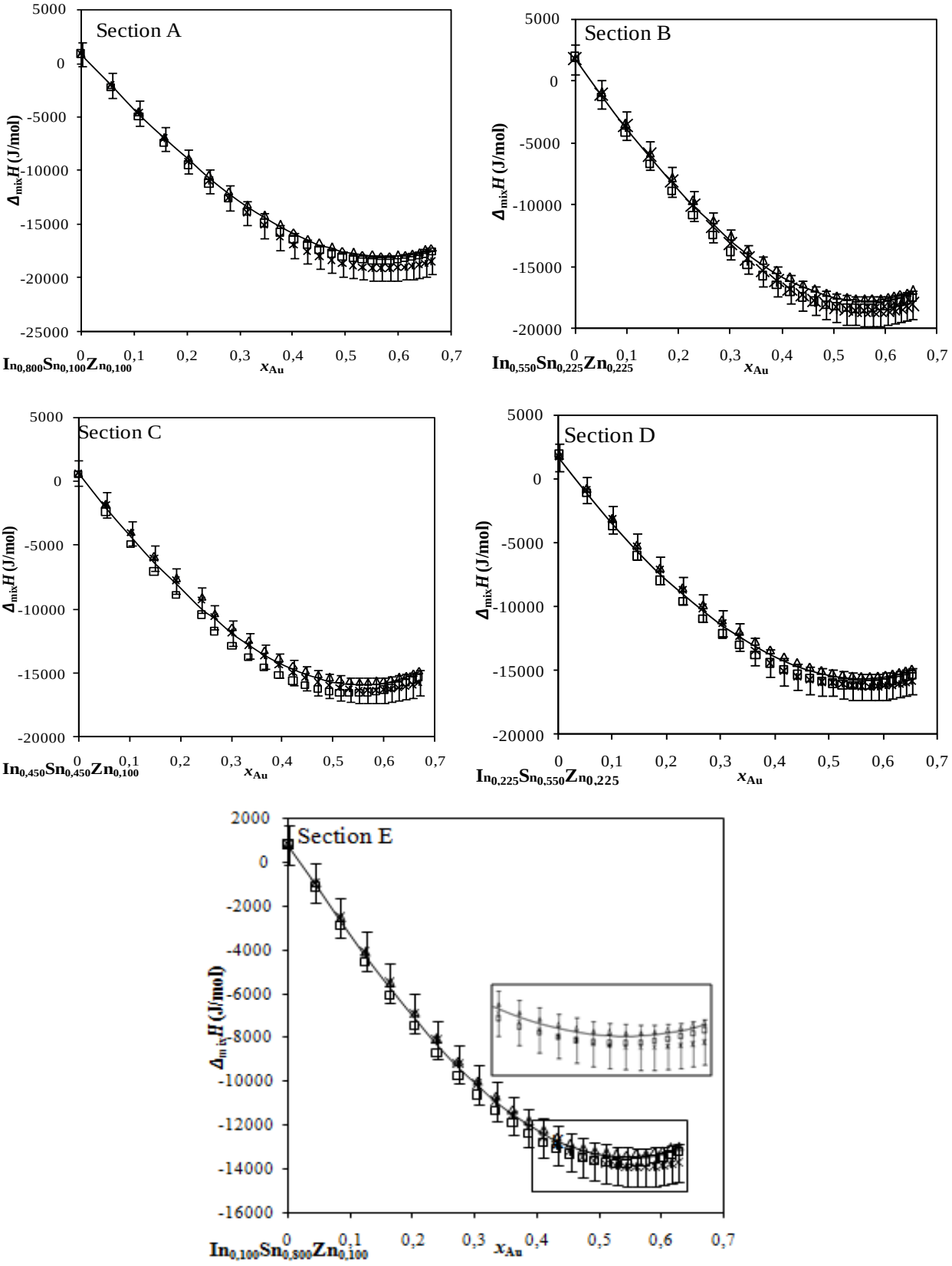

Figure 3: Calculated integral enthalpies of mixing in the liquid Au-In-Sn-Zn alloys at 773 K using three different models (□ Muggianu [3], Δ Toop [6], — Chou [6, 7]), together with those reported *experimentally

The comparison between the values obtained for the two quaternary systems by using Chou's model shows that the values reported by addition of gold are more exothermic than those reported by adding silver. In the case of Au-In-Sn-Zn system, for all the investigated sections, the integral enthalpies of mixing are almost negative. For the Ag-In-Sn-Zn quaternary system, the mixing enthalpies of the liquid phase show slightly positive values at low compositions of silver. The positive domain varies according to the studied section. The largest positive domain (up to 25 at. % Ag) is located in the Sn-rich side (section E), while the narrowest and positive range (up to 5 at. % Ag) is in the tin-rich side (section A). From our estimated results, we can conclude that the Ag-quaternary and Au-quaternary systems are asymmetric and symmetric, respectively.

The calculated results for the two quaternary systems according to the model of Chou were expressed in the following polynomial form (Eq. 7):

$$\Delta_{mix} H = a x_i^3 + b x_i^2 + c x_i + d \quad (i = Ag \text{ or } Au) \tag{7}$$

The parameters of the polynomial expressions (a-d) are summarized in Table 4.

Table 4: The parameters ($J.mol^{-1}$) of the polynomial expressions for integral enthalpies of mixing

Investigated section	a	b	c	d
	Ag- In-Sn-Zn			
A	6126	- 887	- 11953	774
B	12088	-4291	- 13748	1706
C	13002	- 12764	- 6591	565
D	12686	- 12977	- 7525	1670
E	482	- 13695	666	720
	Au- In-Sn-Zn			
A	41701	10031	- 52309	790
B	32865	24907	- 59019	1724
C	31245	19017	- 49958	614
D	21935	30123	- 54530	1631
E	30741	14856	- 43363	769

Conclusion

The general model of Chou has been used to estimate the integral enthalpies of mixing of the two quaternary Ag-In-Sn-Zn and Au-In-Sn-Zn systems at 773 K. Two traditional models (Muggianu and Toop) are also introduced in calculations for comparison. The calculations were carried out at 773 K along five starting ternary compositions : $In_{0.800}Sn_{0.100}Zn_{0.100}$, $In_{0.550}Sn_{0.225}Zn_{0.225}$, $In_{0.450}Sn_{0.450}Zn_{0.100}$, $In_{0.225}Sn_{0.550}Zn_{0.225}$, and $In_{0.100}Sn_{0.800}Zn_{0.100}$ for various additions of noble metals (Ag or Au).

In the Ag-In-Sn-Zn system, the calculated enthalpies of mixing using Chou's model are close to those predicted by Muggianu's model, while the experimental data are similar to those of Toop. For the Au-In-Sn-Zn system, the values obtained by Chou's model are in good agreement with those of Toop's model, whereas the Muggianu's model seems to be the best model to represent the experimental data in this quaternary system.

To verify the results predicted in this work, additional experimental studies are planned in order to cover a wide range of compositions and at different temperatures. In addition, a study by X-ray diffraction of some quaternary solid alloys appears to be necessary in order to show a different interaction between silver and gold with the In-Sn-Zn ternary system.

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