

## Energetics of compound formation in liquid Bi-Sb, Bi-Sn, and Sb-Sn binary alloys

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### Abstract

Energetics of mixing in thermodynamic properties in liquid Bi-Sb, Bi-Sn, and Sb-Sn alloys have been investigated using complex formation model. Assuming the interaction energy parameters  $w$ ,  $l_{12}$ ,  $l_{13}$ , and  $l_{23}$  are temperature dependent, the Gibbs free energies of mixing were modeled in terms of the interaction energy parameters. The parameters were then used to describe thermodynamic properties such as the concentration-concentration fluctuations in the long-wavelength limits, the Warren-Cowley short-range order parameter, the enthalpy and entropy of mixing. The detailed examinations of the systems suggest that both Bi-Sb and Sb-Sn liquid alloys exhibit very weak compound formation tendency over the whole concentration range while Bi-Sn alloy also shows a weak segregation tendency with positive deviations from ideal mixture behaviour as reported.

**Keywords:** Complex formation model; Binary liquid; chemical complex; BiSb; BiSn; Sb-Sn.

### 1. Introduction

Soldering is the most important for joining technology in the electronics industry. Compounds of Sn are very important as a substitute solder [1]. Because lead solder is poisonous and has dangerous health effect through surface contamination and lead dust [2]. Progress has been made in the area of lead-free solders that melt at a lower temperature while intensive efforts have been made by researchers worldwide to replace lead in high-temperature solder alloys applications [1, 3]. Among the solders that can operate in a high-temperature environment, for example, Au-based solders, zinc-based solder, and bismuth-based solder, as well as Sb-Sn alloys, are considered as potential candidates. To this end, the knowledge of bulk thermodynamic properties [4], surface and transport properties are very essential in developing alternative lead-free solders [5].

Based on the band structure of the alloy constituent elements and the formation of electron cavities, understanding the relevant thermodynamic quantities and microstructure of the alloy metal is very important in getting microscopic data about liquid alloys. In this light, to what extent do the properties of the alloy depart from an established course (ideal properties) with respect to this deviation, an alloy can either be classified as an hetero-coordinated (exhibiting preference of unlike atoms to pair as nearest neighbors) or homo-coordinated system (showing preference of like atoms pairing as nearest neighbors). The deviation is usually attributed to the atomic size factor, electronegativity or valence factor [6]. The accurate knowledge of the phase diagram and the behavior of the liquid mixture in solid state and their ability to form intermetallic compound at one or more stoichiometric composition provides theorists with the basic foundation to assume the presence of chemical complexes in binary liquid alloys.

It is thereby, inferred that the liquid mixture consists of chemical complexes of the form  $(P_{\mu}Q_{\nu})$  in the chemical equilibrium. The accessibility to all the required experimental data [7], phase diagram information and the behavior of both enthalpy of mixing  $H_M$  and entropy of mixing  $S_M$  at equiatomic composition arouse our curiosity in investigating the thermodynamic properties of Sb-Sn, Bi-Sb and Bi-Sn liquid alloys, where both the concentration-concentration fluctuations in the long wavelength limits,  $S_{cc}(0)$  and Warren-Cowley short-range order parameter  $\alpha_1$  show a tendency for an unlike atoms to pair as nearest neighbors in the liquid mixtures. The complex formation model (CFM) was first used by [8] and had been further used with lots of success by [8 – 11] is adopted in this work.

The present paper arrangement is as follows: The basic theory of the complex formation model is discussed in Sec. 2, results and discussion on Gibbs free energy with thermodynamic activities, concentration-concentration fluctuations in long wavelength limits, the short-range order parameter  $\alpha_1$ , enthalpy, and entropy of mixing are given in Sec. 3. And the concluding remarks in the last section

## 2. Theory

A statistical model based on the complex formation model (CFM) is employed [8]. Based on this model, a typical binary alloy forms a complex of the form  $P_\mu Q_\nu$  at one or more stoichiometric composition during the mixture of P and Q atoms leading to a chemical compound or privilege molecule, all in chemical equilibrium with each other. Therefore, if an alloy consists of a ternary mixture of  $N_P = N_c$  moles of P atoms and  $N_Q = N(1-c)$  g moles of Q atoms, and a type  $P_\mu Q_\nu$  of chemical complex with  $c$  the atomic fraction of P atoms,  $\mu$  and  $\nu$  are small integers, and  $N$  is the Avogadro's number. Following the complex formation model [8, 12], the mixture consists of  $x_1$  atoms of Sb,  $x_2$  atoms of Sn and  $x_3$  moles of the complex SbSn (thus  $\mu=1$  and  $\nu=1$ ). Using conservation of atoms, and setting  $N = 1$ , if there are in the solution  $x_1$  g moles of P atoms,  $x_2$  g of Q atoms and  $x_3$  g moles of  $P_\mu Q_\nu$ , an expression for the number of moles is written as:

$$x_1 = N_c - \mu x_3, \quad (1)$$

$$x_2 = (1 - c) - \nu x_3 \quad (2)$$

and

$$x = x_1 + x_2 + x_3 = N - (\mu + \nu - 1)x_3. \quad \text{where } c \text{ is the atomic fraction of Sb and Sn atoms.}$$

### EXPRESSION FOR GIBBS FREE ENERGY OF MIXING

With the frame of a complex formation model, the Gibbs free energy of mixing can be expressed as

$$G_M = -x_3 w + \Delta G \quad (3)$$

Because of the formation of complexes in the alloy, there is a decrease in the free energy of formation, which can be seen from the Eqn. (3) as  $-x_3 w$ , where  $w$  is the formation energy of the complex while  $\Delta G$  is the free energy of mixing of the ternary mixture of fixed  $x_1$ ,  $x_2$ , and  $x_3$ . Using  $\Delta G$  according to Flory's solution approximation [13]:

$$\Delta G = RT \left[ \sum_{i=1}^2 x_i \ln \frac{x_i}{N} + x_3 \ln \frac{(\mu + \nu)x_3}{N} + \sum_{i < j} \sum \left\{ \left( \frac{x_i x_j}{N} \right) \frac{l_{ij}}{RT} \right\} \right] \quad (4)$$

One obtains an expression for the free energy of mixing by combining Eqs. (3) and (4) as

$$G_M = -x_3 w + RT \left[ \sum_{i=1}^2 x_i \ln \frac{x_i}{N} + x_3 \ln \frac{(\mu + \nu)x_3}{N} + \sum_{i < j} \sum \left\{ \left( \frac{x_i x_j}{N} \right) \frac{l_{ij}}{RT} \right\} \right] \quad (5)$$

The interaction parameter ( $l_{ij}$ 's) does not depend on the composition of the constituent atom in the mixture, and  $R$  in the Eqn. (4) represents Universal gas constant. The equilibrium value of  $x_3$  at a fixed temperature and pressure can be obtained from the condition

$$\left( \frac{\partial G_M}{\partial x_3} \right)_{T,P,N,c} = 0 \quad (6)$$

Solving Eqs. (5) and (6) numerically gives the equilibrium values of  $x_3$  which can be used to determine the free energy of mixing using Eq. (5) through to Eq. (10):

$$x_1^\mu x_2^v = (x_3 N^{\mu+v-1}) K' \exp(Z) \quad (7)$$

where

$$K' = K (\mu + v) \exp - (\mu + v - 1), \quad (8)$$

and

$$K = \exp(-w/RT) \quad (9)$$

while

$$Z = \frac{-1}{xRT} [(x_1 - \mu x_3) l_{13} + (x_2 - v x_3) l_{23} - (\mu x_2 + v x_1) l_{12}] \quad (10)$$

The understanding of the interaction parameter  $l_{ij}'$ s and  $w$  play a vital role in the Gibbs free energy of mixing computation. At equilibrium, the derivative of free energy of mixing  $G_M$  with respect to a varying parameter such as  $T$  can be written as

$$\left(\frac{\partial G_M}{\partial T}\right)_{P,c,N} = \left(\frac{\partial G_M}{\partial x_3}\right)_{T,P,N,c} \left(\frac{\partial x_3}{\partial T}\right)_{P,c,N} + \left(\frac{\partial G_M}{\partial T}\right)_{P,c,x_3,N} \quad (11)$$

Which is likewise applicable to concentration  $c$  and Pressure  $P$  based on the condition in Eq. (6).

To determine the degree of ordering in the mixture, it is essential to know the effective concentration of the constituent elements in the alloy, in terms of thermodynamic activity. The expression for the thermodynamic activity can be obtained using the general relationship between Gibbs free energy of mixing and thermodynamic activity as given in Eq. (12) [10]:

$$RT \ln \alpha_p = \left(\frac{\partial G_M}{\partial N_p}\right)_{T,P,N_Q} = \frac{1}{N} \left[ G_M + (1 - c) \left(\frac{\partial G_M}{\partial c}\right)_{T,P,N} \right] \quad (12)$$

with  $G_M$  given by Eq. (5), we have

$$\ln \alpha_p = \ln \left(\frac{x_1}{x}\right) + \frac{1}{RT} \left[ \left(\frac{x_2}{x}\right) l_{12} + \left(\frac{x_3}{x}\right) l_{13} - \sum_{i < j} \left\{ \left(\frac{x_i}{x}\right) \left(\frac{x_j}{x}\right) l_{ij} \right\} \right] \quad (13)$$

In use complex formation model, the values of formation energy of the complex  $w$  and  $l_{ij}'$ s were adjusted several times by method of successive approximation until a good fit to the experimental values of Gibbs free energy of mixing  $G_M$  is obtained. The values of formation energy of the complex  $w$  and  $l_{ij}'$ s obtained for each liquid alloy studied are given in Table 1.

### 3. RESULTS AND DISCUSSION

#### 3.1 Free energy of mixing, $G_M/RT$

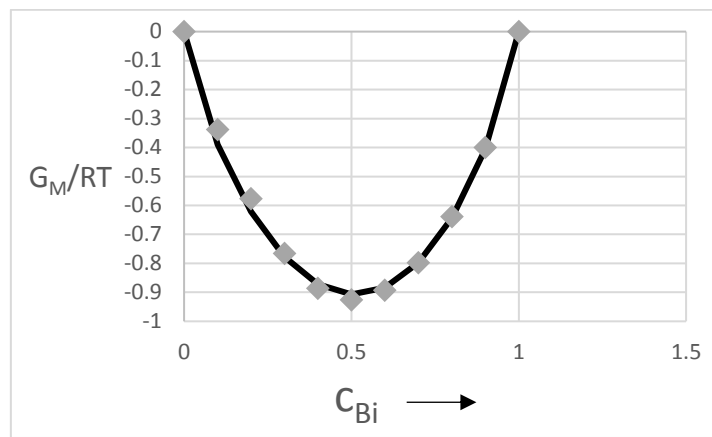
Based on the theory discussed above, various thermodynamic properties have calculated. The plot of the concentration-dependent  $G_M/RT$  for liquid Bi-Sb, Bi-S, and Sb-Sn liquid alloys are presented in Figs. 1-3. It is clear from the figures that both the calculated and experimental values of  $G_M/RT$  compare excellently well with each other and also indicates that calculated values for both the formation energy of the complex  $w$  and  $l_{ij}'$ s are quite reasonable for each of the binary liquid alloys at the investigation temperature.

A proper perusal of the figures further reveals that the Gibbs free energy of mixing is symmetrical around the equiatomic composition ( $C_{Bi/Sb} = 0.5$ ), with Bi-Sb [ $(G_M/RT)_{c_c} = -0.9265$ ] exhibiting a higher tendency for compound formation and is the most interacting of the three alloys; Sb-Sn [ $(G_M/RT)_{c_c} = -0.9193$ ] is also more interacting than Bi-Sn alloy with minimum [ $(G_M/RT)_{c_c} = -0.6406$ ]. It, however, noted that the symmetry behaviour observed in liquid Sb-Sn alloy at equiatomic composition at 905 K is quite at variance with the asymmetry behaviour reported by Anusionwu [5]. This behavior might perhaps be ascribed to the lower temperature considered in the current study, but the results compare quite well with the experimental results of some of the other previous works [14 – 15]. In addition, it noted that the values of  $w/RT$  (Table 1) which is the degree of the formation of complex in the alloy are quite very low for the three investigated binary liquid alloys when

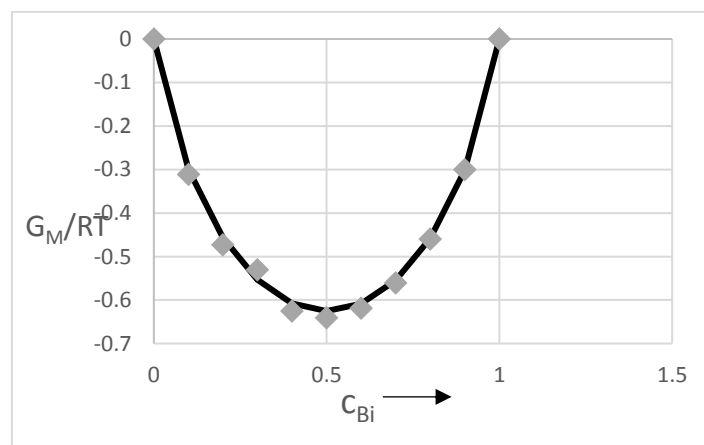
compared to the values of  $w/RT$  for some alloys with strong interaction such as 47.8 for K-Te, 2.80 for Al-Fe and 3.1 for Te-Tl, respectively [8]. For a strong interaction between the constituent elements, the Gibbs free energy of mixing,  $\frac{G_M}{RT} \leq -3$  [10]. Thus it is evidently clear that the three liquid alloys are weakly interacting systems.

**Table 1:** Calculated values of the interaction parameters for the binary liquid alloys

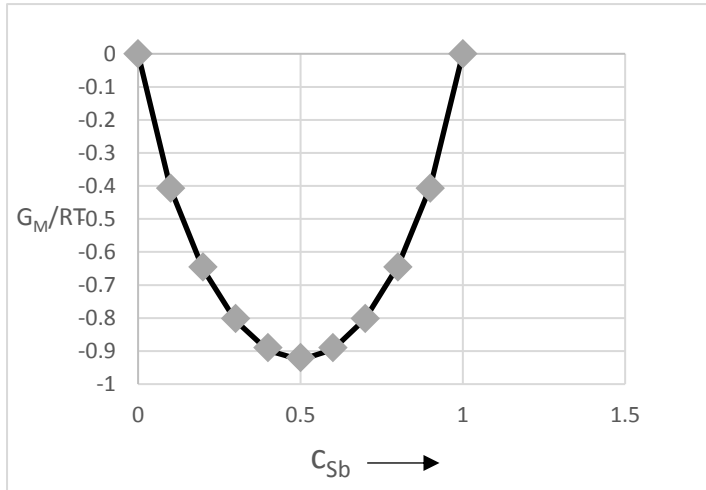
Alloy	$w/RT$	Temp/K	$l_{12}/RT$	$l_{13}/RT$	$l_{23}/RT$
Bi-Sb	0.10	1200	-0.13	0.16	0.59
Bi-Sn	-3.00	600	0.30	0.80	1.50
Sb-Sn	0.10	905	0.10	0.20	-0.10



**Fig. 1:** Concentration-dependence of  $G_M/RT$  for liquid Bi-Sb binary alloy at 1200 K. The solid lines denote calculated values while the squares denote experimental data. The experimental data are from Ref 7.



**Fig. 2:** Concentration-dependence of  $G_M/RT$  for liquid Bi-Sn binary alloy at 600 K. The solid lines denote calculated values while the squares denote experimental data. The experimental data are from Ref 7.



**Fig. 3:** Concentration-dependence of  $G_M/RT$  for liquid Sb-Sn binary alloy at 905 K. The solid lines denote calculated values while the squares denote experimental data. The experimental data are from Ref 7.

### 3.2 Concentration-concentration fluctuations in long-wavelength limits, $S_{cc}(0)$

The  $S_{cc}(0)$  is used to assess the response of any binary liquid alloy to either hetero-coordination or phase separation tendencies. It provides adequate understanding and explanation on the nature of chemical ordering and interaction between the constituent elements in the liquid alloy. The fundamental rule is that when calculated  $S_{cc}(0) < S_{cc}^{id}(0)$  (ideal value), it means a tendency for hetero-coordination in the alloy whereas when calculated  $S_{cc}(0) > S_{cc}^{id}(0)$  implies a tendency for homo-coordination. Using standard thermodynamic relationship in terms of the free energy of mixing or in terms of thermodynamic activity,  $\alpha_A$ , the concentration fluctuation (0) at  $q=0$  may be written as [8]:

$$S_{cc}(0) = RT \left( \frac{\partial^2 G_M}{\partial c^2} \right)_{T,P,N}^{-1} = (1-c)_{\alpha_P} \left( \frac{\partial \alpha_P}{\partial c} \right)_{T,P,N}^{-1} = c_{\alpha_Q} \left( \frac{\partial \alpha_Q}{\partial c} \right)_{T,P,N}^{-1} \quad (14)$$

where  $\alpha_P$  and  $\alpha_Q$  in Eq. (14) represent thermodynamic activities of element P and Q in the liquid binary alloy.

For an ideal solution

$$G_M^{id} = c \ln c + (1-c) \ln(1-c) \quad (15)$$

$G_M^{id}$  is the molar ideal Gibbs free energy of mixing and for ideal mixing,  $S_{cc}(0)$ , therefore becomes

$$S_{cc}^{id}(0) = c(1-c) \quad (16)$$

In determining the  $S_{cc}(0)$ , Bhatia and Ratti [12] provided a more reliable expression for  $S_{cc}(0)$  involving derivatives as well as the interaction parameter:

$$S_{cc}(0)^{-1} = \Lambda + Y \quad (17)$$

$$\Lambda = \left( \sum_{(i=1)}^3 \frac{(x_i)^2}{x_i} - \frac{1}{2} \frac{Z \partial^2 (x'_3)^2}{\Phi} \right) \quad (18)$$

and

$$Y = \frac{2}{\Phi RT} \sum_{i < j} l_{ij} \left( x'_i x'_j + \frac{\partial x'_3 (x'_i x_j + x_i x'_j)}{\Phi} \right) + \frac{\partial^2 (x'_3)^2 x_i x_j}{\Phi} \tag{19}$$

The prime denotes differentiation with respect to r while values of  $\partial = \frac{2(\mu+v-1)}{z}$ , z is taken as 12 and  $\Phi = 1 - \delta x_3$  in Eq. 18. Obtaining  $S_{cc}(0)$  data experimentally is a difficult task via diffraction experiments so, Eq. (15) is usually optimized to obtain the data theoretically and the data obtains in this way is referred to as experimental data in the literature.

Thus, for a given binary alloy, if concentration-concentration fluctuations at long-wavelength limits is greater than ideal concentration fluctuations, i.e.  $S_{cc}(0) > S_{cc}^{id}(0)$ , It signifies homo-coordination – tendency for like atoms pairing together as nearest neighbors, whereas if it is less than the ideal i.e.  $S_{cc}(0) < S_{cc}^{id}(0)$ , it shows level of interaction between constituent elements in the alloy and probable formation of chemical compounds in the mixture.

Fig. 4 to 6. shows the plot of  $S_{cc}(0)$  versus concentration for the three liquid alloys at the respective temperature. It is seen from the figure that calculated  $S_{cc}(0) < S_{cc}^{id}(0)$ , i.e., computed concentration fluctuations values is lower than the ideal concentration fluctuation at every composition ( $0 \leq c_i \leq 1.0$ ) (I =Bi, Sb) for both liquid Bi-Sb and Sb-Sn binary alloys. This indicates the tendency for hetero-coordination i.e. different atoms of Bi with Sb and Sb with Sn prefer to pair as nearest neighbours. The calculated  $S_{cc}(0)$  exhibits a maximum peak at about 0.172 and 0.171 for Bi-Sb and Sb-Sn alloys at equiatomic composition, respectively. While for Bi-Sn, calculated  $S_{cc}(0) > S_{cc}^{id}(0)$  i.e., computed concentration fluctuations values are greater than the ideal concentration fluctuations across the composition range, and thus indicating the tendency for homo-coordination i.e., like atoms of Bi-atoms with Bi-atoms and Sn-atoms with Sn-atoms prefer to pair as nearest neighbours. The calculated  $S_{cc}(0)$  also shows a maximum peak of about 0.289 at equiatomic composition. Hence, liquid Bi-Sn binary alloys is a segregating alloy and also the least interacting of the three liquid binary alloys as earlier submitted with respect to its free energy of mixing.

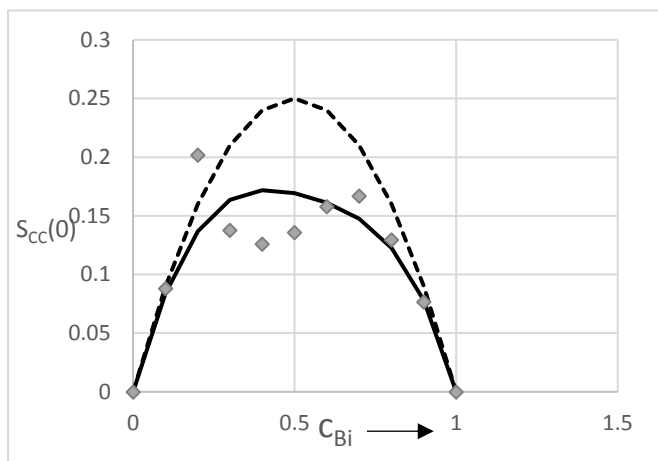


Fig. 4. Concentration-concentration fluctuations,  $S_{cc}(0)$  versus composition for Bi-Sb liquid alloys at 1200K. The solid line denotes calculated value while the dashed line represents ideal value, the diamond symbol represents experimental value respectively.  $c_{Bi}$  is the concentration of Bismuth in the alloy.

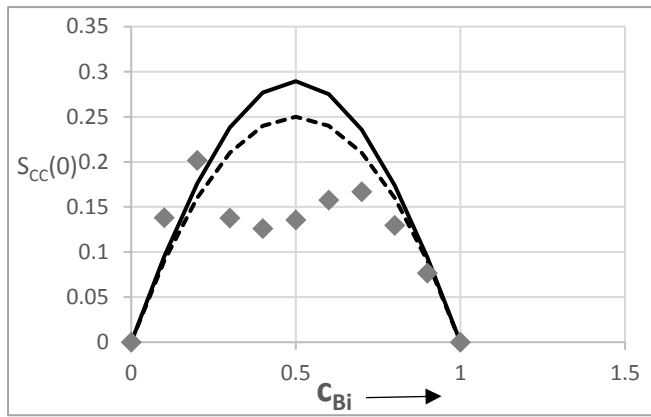


Fig. 5. Concentration-concentration fluctuations,  $S_{cc}(0)$  versus composition for Bi-Sn liquid alloys at 600K. The solid line denotes calculated value while the dashed line represents ideal value, the diamond symbol represents experimental value respectively.  $c_{Bi}$  is the concentration of Bismuth in the alloy.

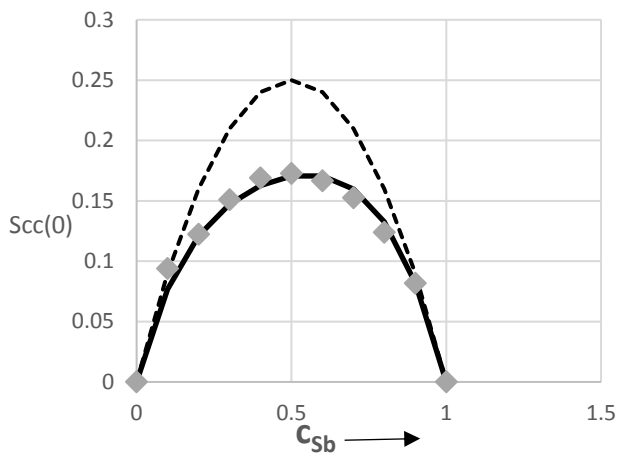


Fig. 6. Concentration-concentration fluctuations,  $S_{cc}(0)$  versus composition for Sb-Sn liquid alloys at 905 K. The solid line denotes calculated value while the dashed line represents ideal value, the diamond symbol represents experimental value respectively.  $c_{Sb}$  is the concentration of Antimony in the alloy.

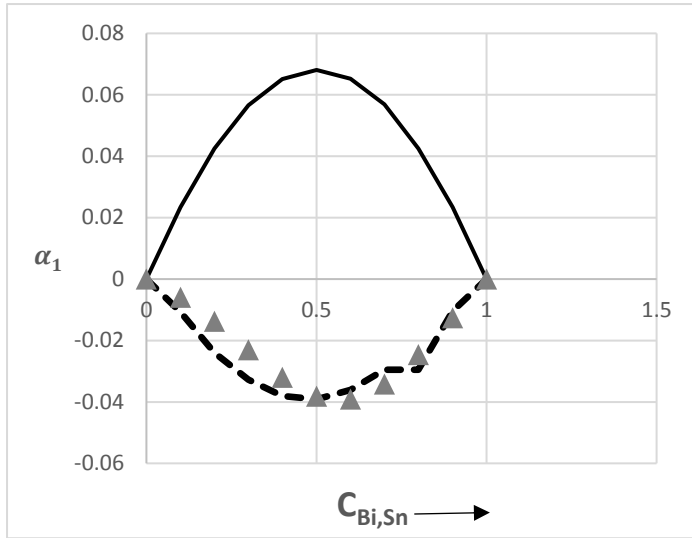
### 3.3 Short-Range Order Parameter $\alpha_1$

The arrangement and local ordering of atoms in the liquid binary alloy can be described with another thermodynamic parameter [16]. This quantity is known as Warren-Cowley short-range order parameter,  $\alpha_1$  which can be determined from the basic understanding of its relationship with  $S_{cc}(0)$ . The basic rule is that  $\alpha_1 = 0$  signifies a uniform distribution of atoms in the mixture, and when  $\alpha_1 < 0$ , it means different atoms in the mixture prefer unlike atoms pairing as nearest neighbors and signify chemical ordering in the system, on the other hand, if  $\alpha_1 > 0$ , like atoms paired together in the system [10, 17]. The relationship between  $\alpha_1$  and  $S_{cc}(0)$  is given by

$$\alpha_1 = \frac{S-1}{S(Z-1)+1}, \quad S = \frac{S_{cc}(0)}{c(1-c)} \tag{20}$$

It is noted from Fig. 8 that both Bi-Sb and Sb-Sn alloys have negative values of  $\alpha_1$  throughout the composition with minimum values of  $\alpha_1^{min} = -0.03819$  and  $= -0.03819$  at  $c = 0.5$ , respectively. An indication of chemical ordering the two liquid alloys while the interactions between constituent's elements of the alloys may be described as a very weak interaction in nature. On the contrary, positive values of  $\alpha_1$  at all concentration in liquid

Bi-Sn alloys with a maximum value of 0.06809 at  $c = 0.5$ , signifies tendency for segregation in the liquid alloy. The atoms in Bi-Sn alloys exhibit a higher tendency for likes atoms to pair together as nearest neighbours.



**Fig. 7.**  $\alpha_1$  versus concentration for liquid Bi-Sb, Bi-Sn, and Sb-Sn binary alloys at 1200 K, 600 K and 905 K, respectively. The dashed line denotes calculated  $\alpha_1$  values for Sb-Sn; the triangles represent calculated  $\alpha_1$  values for Bi-Sb and the solid line denote calculated  $\alpha_1$  values for Bi-Sn, respectively.

### 3.4 Enthalpy and entropy of mixing

The temperature dependences of the enthalpy of mixing and entropy of mixing are another important thermodynamic quantities which show the relationship between the interaction parameters and temperature [17]. Using the standard thermodynamic expressions the enthalpy of mixing is related to  $G_M$  as [8 – 13]:

$$H_M = G_M - T \left( \frac{\partial G_M}{\partial T} \right)_P \quad (21)$$

From the expression of  $G_M$  in Eqs (5), we have

$$H_M = -x_3 w + x_3 T \left( \frac{\partial w}{\partial T} \right)_P + \sum \sum_{i < j} \left( \frac{x_i x_j}{N} \right) \left[ l_{ij} - T \left( \frac{\partial l_{ij}}{\partial T} \right)_P \right] \quad (22)$$

and thus the entropy of mixing

$$S_M = -x \left( \frac{\partial g}{\partial T} \right)_P - R [x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln \{(\mu + v)x_3\}] - \sum \sum_{i < j} x_i x_j \left( \frac{\partial v_{ij}}{\partial T} \right)_P \quad (23)$$

From the expressions above, the disparity and the deviation noticed between the calculated values and experimental values of both  $H_M$  and  $S_M$  when the interaction parameters are being calculated can only be improved if the temperature dependence of the interaction parameters is incorporated in the computation [18]. The values of the fitted temperature dependences of the interaction parameters used in the calculation of the quantities are listed in Table 2 while Figs. 8 to 13 show that both the experimental and calculated values of  $H_M$  and  $S_M$  are in good reasonable agreement.



**Table 2:** Fitted values for temperature derivatives of interaction parameters for the liquid binary alloys

System	$\frac{\partial w}{\partial T}$	Temp/K	$\frac{\partial v_{12}}{\partial T}$	$\frac{\partial v_{13}}{\partial T}$	$\frac{\partial v_{23}}{\partial T}$
Bi-Sb	0.40	1200	-0.04	0.01	0.25
Bi-Sn	-6.00	600	0.02	0.01	0.02
Sb-Sn	1.20	905	-0.92	0.75	1.40

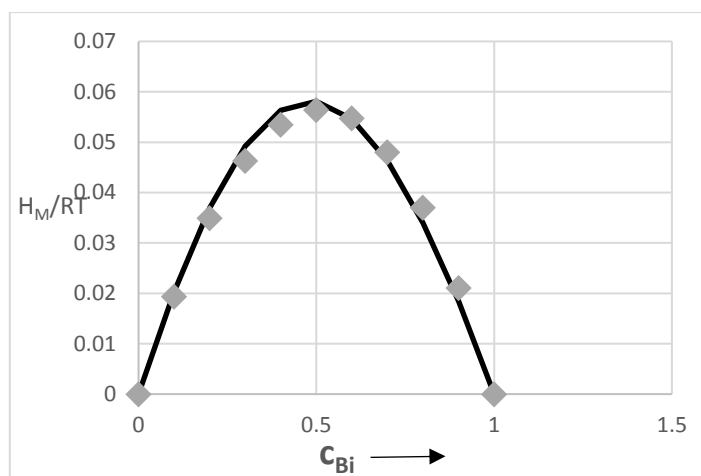


Fig. 8. Enthalpy of mixing  $\frac{H_M}{RT}$  versus concentration in Bi-Sb liquid alloys at 1200K. The solid lines denote calculated values while the diamond symbol denotes experimental values.

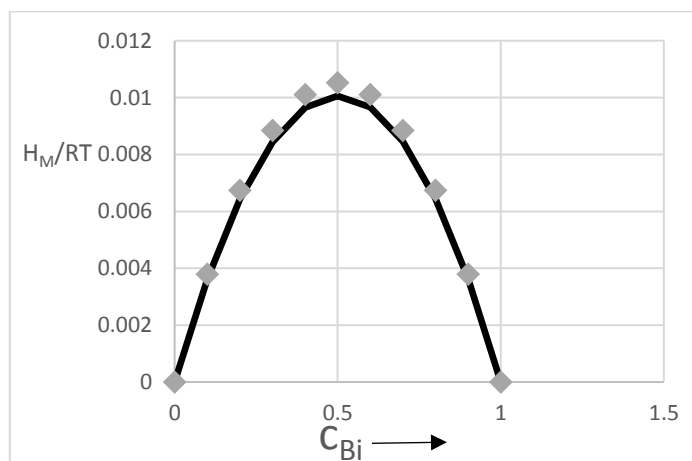


Fig. 9. Enthalpy of mixing:  $\frac{H_M}{RT}$  versus concentration in Bi-Sn liquid alloys at 600K. The solid lines denote calculated values while the diamond symbol denotes experimental values.

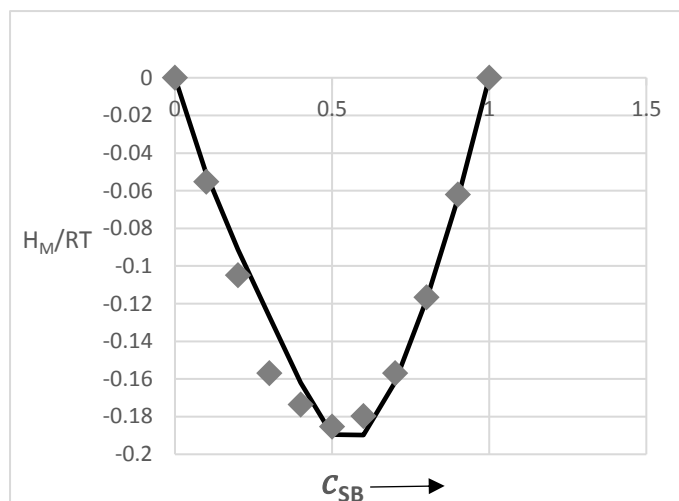


Fig. 10. Enthalpy of mixing:  $\frac{H_M}{RT}$  versus concentration in Sb-Sn liquid alloys at 905K. The solid lines denote calculated values while the diamond symbol denotes experimental values.

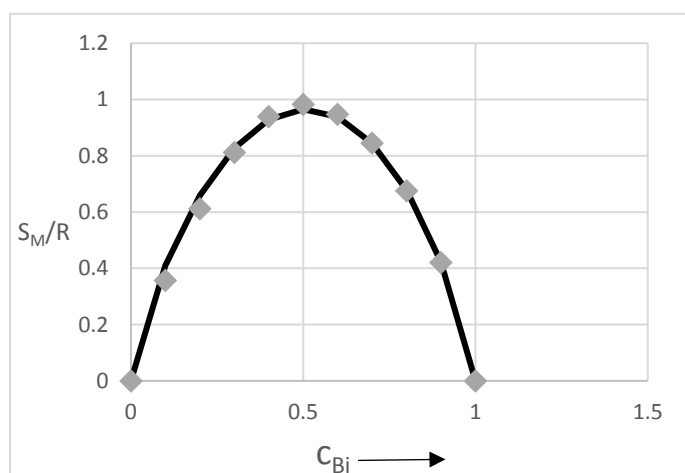


Fig. 11. The entropy of mixing:  $\frac{S_M}{R}$  versus concentration in Bi-Sb liquid alloys at 1200 K. The solid lines denote calculated values while the diamond symbol denotes experimental values.

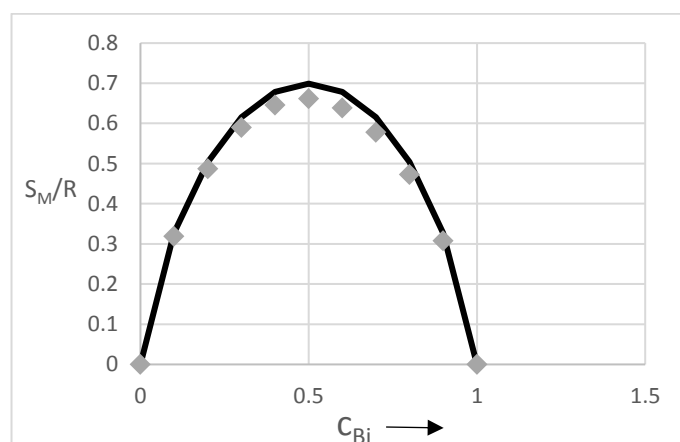


Fig. 12. The entropy of mixing:  $\frac{S_M}{R}$  as a function of concentration in Bi-Sn liquid alloys at 600 K. The solid lines denote calculated values while the diamond symbol denotes experimental values.

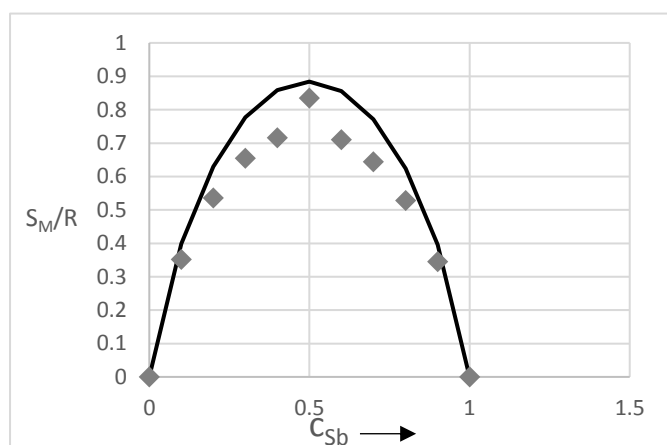


Fig. 13. The entropy of mixing:  $\frac{S_M}{R}$  as a function of concentration in Sb-Sn liquid alloys at 905K. The solid lines denote calculated value while the diamond symbol denotes experimental values.

## Conclusion

Using the complex formation model, energetics of alloying in bulk thermodynamic properties of liquid Bi-Sb, Bi-Sn, and Sb-Sn binary alloys have been reported at temperatures of 1200 K, 600 K, and 905 K respectively. The study indicates that both liquid Bi-Sb and Sb-Sn alloys are chemically-ordered alloys, while liquid Bi-Sn alloy exhibits a preference for segregation. The role of fitted interaction parameters has been explained with respect to the computed  $S_{cc}(0)$ ,  $\alpha_1$ ,  $H_M$  and  $S_M$ . It is evident that both Bi-Sb and Sb-Sn liquid alloys which showed negative deviations from ideal mixture behavior with respect to  $S_{cc}(0)$  and  $\alpha_1$  are very weakly compound forming alloys whereas Bi-Sn alloy with positive deviation from ideality is the least interacting liquid alloy of the three alloys investigated.

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