CONFORMAL SOLUTION MODEL FOR THE THERMODYNAMIC PROPERTIES OF ANTIMONY-INDIUM LIQUID ALLOYS

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Abstract: In the present work we have considered the antimony-indium liquid alloy which shows anomaly as regards its heat of mixing and the concentration fluctuations in the long-wavelength limit. On the other hand, the free energy of mixing and the entropy of mixing are found to be symmetric about the equi-atomic composition. Such alloying behaviour has been tried to explain on the basis of conformal solution model. This is a statistical mechanical model based on the formation of complex within the liquid alloy. In this model besides the interaction between unlike atoms, that between each constituent element and the complex too is taken into account. In course of theoretical treatment the activity of antimony is also computed for different concentrations. Our results indicate that Sb-In alloys are thermodynamically most stable around the equi-atomic composition.

Key words: Binary liquid alloy; Conformal solution model; Free energy of mixing; Activity; Heat of mixing; Entropy of mixing; Concentration fluctuations in the long-wavelength limit.

INTRODUCTION

When two metals are mixed together in their liquid phase, metallic bonds often come into play to form complex at one or more stoichiometric compositions. The thermodynamic properties of such complex forming binary molten alloys usually deviate from the ideal values to a great extent. The antimony-indium alloys in their solid phase exhibit only one stable intermetallic complex (*i.e.* SbIn) which melts congruently at 800 K. Warren and Clark emphasised that SbIn phase may also exist in the liquid state close to the melting temperature[1]. Recently a considerable effort has been made to understand the asymmetry in the thermodynamic properties of mixing by considering the existence of chemical complexes :

$\mu A + \nu B$ '! $A_\mu B_\nu$,

where A and B represent the constituent metals and μ and ν small integers[2–5]. The conformal solution model has been successfully used to explain the thermodynamic properties of a number of complex forming systems like Mg-Bi, Na-Pb, Li-Pb, Hg-Na, Hg-K etc.[6, 7]

Assuming the existence of SbIn phase in the liquid state Lele and Rao successfully studied the free energy of mixing, heat of mixing and entropy of mixing of Sb-In liquid alloys[8]. However, the alloying behaviour of binary liquid alloys could better be understood[9] if one considers the concentration fluctuations in the long-wavelength limit [$S_{cc}(0)$]. In this context we use the conformal solution model to study $S_{cc}(0)$ as a function of concentration of Sb in the Sb-In liquid alloys. This has also been used to compute the thermodynamic entities *e.g.* free energy of mixing, activity, heat of mixing and entropy of mixing.

FREE ENERGY OF MIXING AND ACTIVITY

Let a binary alloy contains N_A (=Nc) atoms of element A and N_B [=N(1–c)] atoms of element B so that according to the conformal solution model a binary mixture can be assumed as a ternary mixture consisting of n_1 gram moles of A, n_2 gram moles of B and n_3 gram moles of the complex $A_\mu B_\nu$. From the conservation of atoms we simply write

$$n_1 = c - \mu n_3 \quad \text{(i)}$$

$$n_2 = 1 - c - \nu n_3 \quad \text{(ii)}$$

$$n = n_1 + n_2 + n_3 \quad \text{(iii)}$$

The free energy of mixing of the binary alloy can be written as[10]

$$G_M = -n_3 g + RT \sum_{i=1}^{3} n_i (\ln n_i - \ln n) + \sum_{\substack{i=1 \\ i<j}}^{3} \sum_{j=1}^{3} \frac{n_i n_j}{n} \omega_{ij}, \quad \text{..... (iv)}$$

where 'g' is the formation energy of the complex and ω_{ij} the interaction energies.

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The equilibrium value of n_3 at a given temperature and pressure can be obtained by

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,c} = 0 \quad \text{..... (v)}$$

(iv) and (v) yield

$$\frac{n_1^{\mu} n_2^{\nu}}{n_3 n^{\mu+\nu-1}} = Ke^{Y},$$

where $K = e^{-g/RT}$

and $Y = \frac{\omega_{12}}{RT}\left[(\mu+\nu-1)\frac{n_1 n_2}{n^2} - \mu\frac{n_2}{n} - \nu\frac{n_1}{n}\right] +$

$$\frac{\omega_{13}}{RT}\left[(\mu+\nu-1)\frac{n_1 n_3}{n^2} - \mu\frac{n_3}{n} + \frac{n_1}{n}\right] + \frac{\omega_{23}}{RT}\left[(\mu+\nu-1)\frac{n_2 n_3}{n^2} - \nu\frac{n_3}{n} + \frac{n_2}{n}\right]$$

The activity (a_A) of the species A is given by

$$RT \ln a_A = \left(\frac{\partial G_M}{\partial N_A}\right)_{T,P,N_B} = G_M + (1-c)\left(\frac{\partial G_M}{\partial c}\right)_{T,P,N} \quad \text{..... (vi)}$$

From (iv) and (vi) we get

$$RT \ln a_A = RT \ln \frac{n_1}{n} + \frac{n_2}{n}\omega_{12} + \frac{n_3}{n}\omega_{13} - \frac{1}{n^2}\sum_{\substack{i=1\\i<j}}^{3}\sum_{j=1}^{3} n_i n_j \omega_{ij} \quad \text{.. (vii)}$$

Now the energy parameters i.e. 'g' and ω_{ij}'s are obtained using the limiting values of K, n_1 and n_2 *i.e.* K'!0, n_1'!0 for $c<c_c$ and n_2'!0 for $c>c_c$, where c_c is the stoichiometric composition [*i.e.* $c_c = \mu/(\mu+\nu) = 0.5$] :

$$\frac{g}{RT} = 1.124,\ \frac{\omega_{12}}{RT} = -0.55,\ \frac{\omega_{23}}{RT} = -0.7,\ \frac{\omega_{13}}{RT} = 0.01.$$

These energy parameters have been used to compute the free energy of mixing and activity at 900 K. using (iv) and (vii) respectively. The plots of G_M/RT versus c_{Sb} and ln a_{Sb} versus c_{Sb} at 900 K. are furnished in Figure 1 and Figure 2 respectively for both the computed and observed values. The computed and experimental values[11] are in good agreement with one another. These values indicate that a_{Sb} is quite substantial in the whole concentration of antimony. Though the rise in a_{Sb} is almost uniform with respect to concentration, the increment is larger for higher concentrations of Sb.

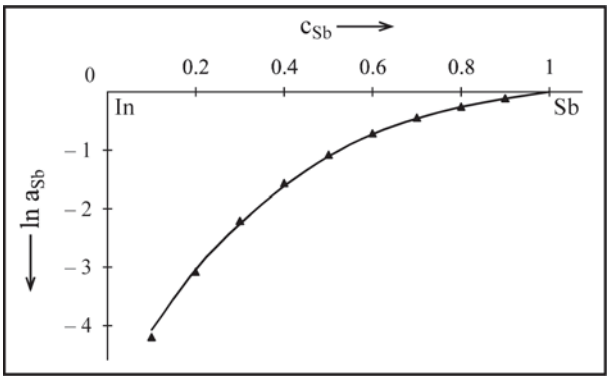


Figure 2: Activity of antimony (ln a_{Sb}) in Sb-In liquid alloys at 900 K. (–) and (Δ) refer to the theoretical and experimental values respectively.

HEAT OF MIXING AND ENTROPY OF MIXING

The heat of mixing of binary liquid alloys may be written as

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{P,N,c} \quad \text{..... (viii)}$$

Using (iv) in (viii) we get

$$H_M = -n_3(g - g'T) + \sum_{\substack{i=1\\i<j}}^{3}\sum_{j=1}^{3}\frac{n_i n_j}{n}(\omega_{ij} - \omega'_{ij}T), \quad \text{.....(ix)}$$

where the primed terms mean their temperature derivatives.

Hence, the entropy of mixing is given by

$$S_M = \frac{H_M - G_M}{T} \quad \text{(x)}$$

The temperature derivatives of the energy parameters used in the present work are

$$g' = 0.529R,\ \omega'_{12} = -0.253R,\ \omega'_{23} = -0.433R,\ \omega'_{13} = 0.$$

These are used in (ix) to compute the heat of mixing as a function of concentration and hence the entropy of mixing from (x). The plots of H_M/RT versus c_{Sb} and S_M/R versus c_{Sb} at

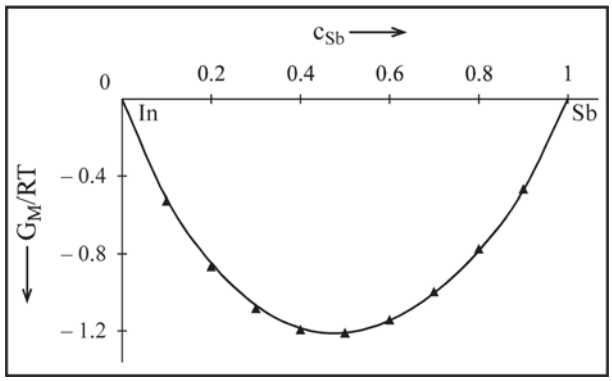


Figure 1: Free energy of mixing (G_M/RT) of Sb-In liquid alloys at 900 K. (–) and (Δ) refer to the theoretical and experimental values respectively.

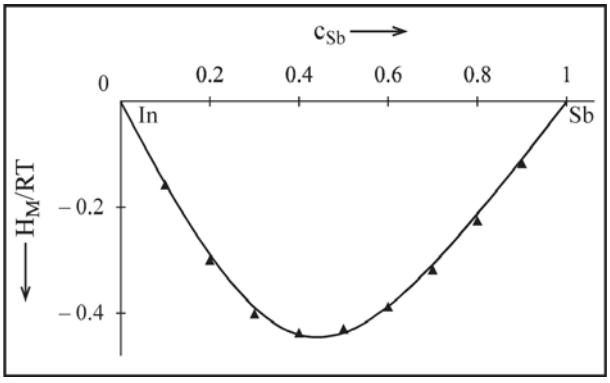


Figure 3: Heat of mixing (H_M/RT) of Sb-In liquid alloys at 900 K. (–) and (Δ) refer to the theoretical and experimental values respectively.

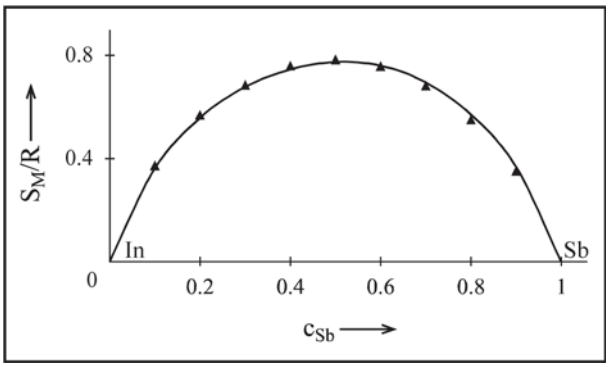


Figure 4: Entropy of mixing (S_M/R) of Sb-In liquid alloys at 900 K. (–) and (Δ) refer to the theoretical and experimental values respectively.

900 K. are shown in Figure 3 and Figure 4 respectively. The computed and experimental values[11] are in good agreement with one another.

CONCENTRATION FLUCTUATIONS IN THE LONG-WAVELENGTH LIMIT

The concentration fluctuations in the long-wavelength limit can be expressed as[9]

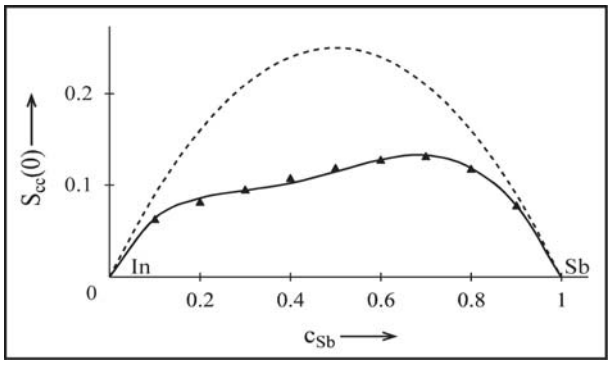
$$S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial c^2}\right)^{-1}_{T,P,N} = (1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} = c\,a_B\left[\frac{\partial a_B}{\partial (1-c)}\right]^{-1}_{T,P,N} \quad \text{..... (xi)}$$

(iv) and (xi) give

$$S_{cc}(0) = \left[\sum_{i=1}^{3}\frac{(n_i')^2}{n_i} - \frac{(n')^2}{n} + \frac{2n}{RT}\sum_{\substack{i=1\\ i<j}}^{3}\sum_{j=1}^{3}\left(\frac{n_i}{n}\right)'\left(\frac{n_j}{n}\right)'\omega_{ij}\right]^{-1}, \quad \text{..... (xii)}$$

the primes indicating here differentiations with respect to 'c'. The experimental values of $S_{cc}(0)$ can be obtained with the help of the last two equalities of (xi) on using the observed activity data.

(xii) is utilised to compute the concentration fluctuations in the long-wavelength limit at 900 K. as a function of concentration. The computed values of $S_{cc}(0)$ are plotted in Figure–5. These have also been obtained directly from the observed data of activity and plotted in the same figure. Though there is no deepening in $S_{cc}(0)$ at the complex forming concentration, $c_c = c_{Sb} = 0.5$, it deviates considerably from the ideal solution value [$S_{cc}(0) = c(1–c)$]. Our computed $S_{cc}(0)$ exhibits maximum value at $c_{Sb} = 0.7$. The observed asymmetry in $S_{cc}(0)$ obtained directly from the activity data has been successfully explained by our computed values. $S_{cc}(0)$ for larger contents of Sb are closer to the ideal values. Though Sb-In is a weak interacting system ($G_M/RT = –1.21$ only at the stoichiometric composition), $S_{cc}(0)$ is smaller than the ideal value at every concentration.



Figure–5: Concentration fluctuations in the long-wavelength limit [$S_{cc}(0)$] of Sb-In liquid alloys at 900 K. (–) refers to the theoretical values and (Δ) the experimental ones as computed directly from activity. (…) corresponds to ideal values.

SUMMARY AND CONCLUSION

The conformal solution model has been considered to study the concentration dependence of the free energy of mixing, activity, heat of mixing and entropy of mixing of Sb-In liquid alloys. The necessary energy parameters involved in the above investigation are used to compute the concentration fluctuations in the long-wavelength limit [$S_{cc}(0)$]. The latter is of great significance to understand the alloying behavior of the binary liquid alloys and has been used to assess the existence of chemical complexes in the liquid phase of a binary alloy.

The present investigation reveals that antimony-indium liquid alloys are most stable around the equi-atomic composition. $S_{cc}(0)$ deviates considerably from the ideal solution values and the maximum deviation occurs around $c_{Sb} = 0.5$.

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