HEAT OF MIXING OF SOME BINARY LIQUID ALLOYS

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ABSTRACT : There are a large number of binary liquid alloys the thermodynamic properties of mixing of which are not symmetrical about the equi-atomic composition—deviating maximally from those of the ideal alloys. Here we have considered three such alloys—indium-sodium, cadmium-sodium and copper-tin—and tried to calculate their heat of mixing at different concentrations of the ingredients. The liquidus lines of these alloys reveal that the constituent species form complexes. So, we have considered a quasi-lattice chemical model for computation of the thermodynamic entities. It is a statistical model in which grand partition function is used assuming that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not. For each alloy we have started with the expression for excess free energy of mixing according to this model and computed the free energy of mixing for different concentrations of the metals within it by deriving the value of interaction parameters through successive approximation method. Thereafter, the expression for excess entropy of mixing is taken into account and the entropy of mixing is computed for different concentrations after finding out the temperature derivative of interaction parameters by the method of successive approximation. Finally the heat of mixing is calculated from these free energy of mixing and entropy of mixing on using the standard thermodynamic relation. The results explain the observed asymmetry in the heat of mixing of the said binary liquid alloys around equi-atomic composition.

Key words : Binary liquid alloy; Quasi-lattice chemical model; Heat of mixing.

1. INTRODUCTION

A large number of binary liquid alloys exhibit interesting behaviour as a function of concentration as regards the thermodynamic properties. The anomalous behaviour of these liquid alloys is least understood and demands extensive theoretical investigation (Bhatia and Singh 1982, Lamparter *et al* 1984, Prasad *et al* 1996, Jha *et al* 2001, Chakrabarti *et al* 2007).

The alloying behaviour of liquid alloys can be studied by the help of two distinct theories *e.g.* electronic theory of mixing and statistical mechanical theory of mixing. According to the first theory a liquid alloy is assumed to consist of a system of ions and electrons. The problem, usually, in this approach is tackled through pseudo-potential theory (Harrison 1966, Heine 1970, Vora *et al* 2002, Thakur *et al* 2005) and hard sphere model (Theile 1963, Lebowitz 1964, Faber 1972, Shimoji 1977). The approach cannot be used to obtain information regarding the concentration fluctuations in the long wave-length limit $[S_{cc}(0)]$, an important thermodynamic function which determines the stability of alloys. The other theory can be successfully used to obtain the analytical expressions for various thermodynamic functions that are not possible otherwise. The conformal solution model (Longuet-Higgins 1951) has been used by many theoreticians to study $S_{cc}(0)$ of different binary alloys (Bhatia *et al* 1973, Alonso and March 1982). But this model cannot be used to study the short-range-order parameters. The quasi-chemical theory (Guggenheim 1952) is successful in studying the chemical short-range-order parameters of binary liquid alloys. But such theory cannot be used to explain the asymmetry in the properties of mixing as a function of concentration.

In the present work we have considered three complex forming alloys e.g. In-Na, Cd-Na and Cu-Sn, the thermodynamic properties of mixing of which are quite asymmetrical around the equi-atomic composition. The heat of mixing of these binary liquid alloys is taken into account and the quasi-lattice chemical model (Bhatia and Singh 1982) has been envisaged for computation of the same at different concentrations of the constituent species. It is a statistical model in which grand partition function is used assuming that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not.

In Section 2 the calculations under this quasi-lattice chemical model are summarised to general expressions. Section 3 deals with the results. A brief conclusion is provided in Section 4.

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2. FORMULATION

The quasi-lattice chemical model for the binary liquid alloys, in essence, assumes the existence of chemical complexes $A_\mu B_\nu$, where μ & ν are small integers and A & B the constituent species of the alloy :
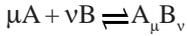
$$\mu A + \nu B \rightleftharpoons A_\mu B_\nu$$

According to this model the expression for excess free energy of mixing (Bhatia and Singh 1982) :

$$G_M^{xs} = N[c(1-c)\omega + \Phi_{AB}\Delta\omega_{AB} + \Phi_{AA}\Delta\omega_{AA} + \Phi_{BB}\Delta\omega_{BB}], \dots \text{(i)}$$

where N is the total number of atoms of A and B in the alloy, 'c' the concentration of A-atoms, ω's the ordering energies and Φ's some constants given by

$$K_B T\Phi_{\mu,\nu} = \Delta\omega_{AB}[2\beta(\mu+1,\nu) - 2\beta(\mu,\nu+1) + \beta(2\mu-1,2\nu) - \beta(2\mu,2\nu-1)] + \Delta\omega_{AA}[\beta(2\mu-2,2\nu+1) - 2\beta(\mu,\nu+1)] + \Delta\omega_{BB}[2\beta(\mu+1,\nu) - \beta(2\mu+1,2\nu-2)], \dots \text{(ii)}$$

K_B being the Boltzmann constant, T the absolute temperature and β's the usual beta functions.

Hence, the free energy of mixing of a complex forming binary liquid alloy,

$$G_M = G_M^{xs} + RT[c\ln c + (1-c)\ln(1-c)], \dots \text{(iii)}$$

where R is the universal gas constant.
The excess entropy of mixing is given by

$$S_M^{xs} = -\left(\frac{dG_M^{xs}}{dT}\right)_P$$

$$= -N[\Phi(c)\frac{d\omega}{dT} + \Phi_{AB}(c) \quad (\Delta\omega_{AB}) + \Phi_{AA}(c)\frac{d}{dT}(\Delta\omega_{AA}) +$$

$$\Phi_{BB}(c)\frac{d}{dT}(\Delta\omega_{BB}), \dots \text{(iv)}$$

where $\Phi(c) = c(1-c)$.

So, the entropy of mixing of such a binary liquid alloy,

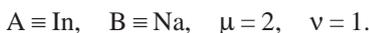$$S_M^{xs} = -R[c\ln c + (1-c)\ln(1-c)]. \dots \text{(v)}$$

Now, the heat of mixing can be found out by using equations (iii) and (v) :

$$H_M = G_M + TS_M. \dots \text{(vi)}$$

3. RESULTS AND DISCUSSION

3.1. Indium-Sodium Liquid Alloy

The phase diagram of In-Na alloy suggests that the complex In_2Na is most likely to be formed. So, for this alloy
$A \equiv In, \quad B \equiv Na, \quad \mu = 2, \quad \nu = 1.$
Finding the values of the β-functions in equation (ii), equation (i) becomes

$$G_M^{xs} = N\left[\omega c(1-c) + \Delta\omega_{AB}\left(\frac{1}{6}c + c^2 - \frac{5}{3}c^3 + \frac{1}{2}c^4\right) + \Delta\omega_{AA}\left(-\frac{1}{4}c + \frac{1}{2}c^2 - \frac{1}{4}c^4\right)\right]$$

$$[\because \text{coeff}(\Delta\omega_{BB}) = 0 \text{ as } \nu < 2]$$

The values of interaction parameters in equation (i) are determined from the experimental values of free energy of mixing of In-Na alloys at 713 K in the concentration range of indium from 0.1 to 0.9 (Hultgren *et al* 1973) by the method of successive approximation:

$$= 0.7, \qquad \frac{\Delta\omega_{AB}}{K_B T} = -2.2, \qquad \Delta\omega_{AA} \approx 0.$$

The observed values of entropy of mixing at 713 K in the concentration range of indium from 0.1 to 0.9 (Hultgren *et al* 1973) have been used to find out the temperature derivatives of interaction parameters in equation (iv) by the successive approximation method :

$$= 6.3, \frac{1}{K_B}\frac{d}{dT}(\Delta\omega_{AB}) = -3.6, \frac{d}{dT}(\Delta\omega_{AA}) \approx 0, \frac{d}{dT}(\Delta\omega_{BB}) \approx 0.$$

With these values, finally, the heat of mixing of the indium-sodium liquid alloys at 713 K has been computed as a function of concentration by using equation (vi). The computed values of the heat of mixing are furnished below in Table–1 along with its observed values in the concentration range of indium from 0.1 to 0.9 (Hultgren *et al* 1973).

Table 1: Heat of Mixing of In-Na liquid alloys at 713 K.

c_{In}	H_M/RT	
	Theoretical	**Experimental***
0.1	–0.3788	–0.3163
0.2	–0.7265	–0.6510
0.3	–1.0008	–0.9695
0.4	–1.2303	–1.2407
0.5	–1.3889	–1.4299
0.6	–1.4511	–1.4638
0.7	–1.3881	–1.2470
0.8	–1.1739	–0.8968
0.9	–0.7670	–0.4745

*Hultgren *et al*, 1973

The plot of H_M/RT versus c_{In} at 713 K is depicted in Figure–1 for both the theoretical and experimental values, which show good agreement. The theoretical value of H_M is minimum at $c_{In}=0.62$ while experimentally it is found to be minimum at $c_{In}=0.59$.
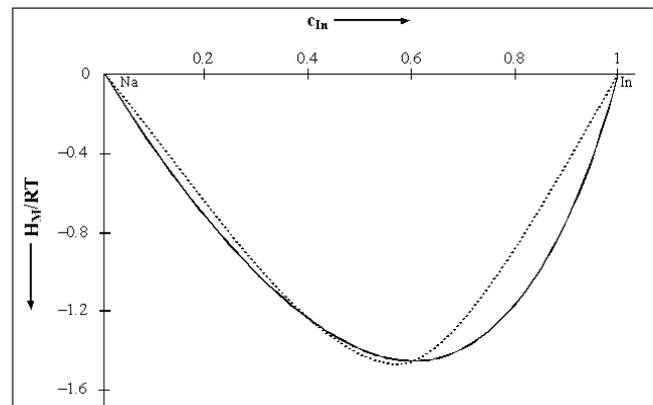

Figure 1 : Heat of mixing (H_M/RT) of In-Na liquid alloys at 713 K for different concentrations of indium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

3.2. Cadmium-Sodium Liquid Alloy

As revealed from the phase diagram Cd_2Na complex is formed within the cadmium-sodium alloy. So, for this liquid alloy

$$A \equiv Cd, \quad B \equiv Na, \quad \mu = 2, \quad \nu = 1.$$

Accordingly, from equations (i) and (ii) one has

$$G_M^{xs} = N\left[\omega c(1-c) + \Delta\omega_{AB}\left(\frac{1}{6}c + c^2 - \frac{5}{3}c^3 + \frac{1}{2}c^4\right) + \Delta\omega_{AA}\left(-\frac{1}{4}c + \frac{1}{2}c^2 - \frac{1}{4}c^4\right)\right]$$

$$[\because \text{coeff}(\Delta\omega_{BB}) = 0 \text{ as } \nu < 2]$$

Like before the values of interaction parameters have been found out from the experimental values of free energy of mixing at 673 K in the concentration range of cadmium from 0.1 to 0.9 (Hultgren *et al* 1973) by successive approximation method:

$$= 0.7, \qquad = -2.2, \qquad \Delta\omega_{AA} \quad 0.$$

The experimental values of entropy of mixing of Cd-Na alloys at 673 K in the concentration range of cadmium from 0.1 to 0.9 (Hultgren *et al* 1973) are used, like the case of In-Na alloys, to determine the temperature derivatives of interaction parameters by the method of successive approximation:

$$= 6.3, \qquad = -3.6, \quad \frac{d}{dT}(\Delta\omega_{AA}) \approx 0, \quad \frac{d}{dT}(\Delta\omega_{BB}) \approx 0.$$

The heat of mixing of Cd-Na liquid alloys at 673 K has been computed as a function of concentration from equation (vi) on taking the above values of interaction parameters and their temperature derivatives as used for the calculation of free energy of mixing and entropy of mixing. The computed values of the heat of mixing are tabulated in Table–2 together with its observed values in the concentration range of cadmium from 0.1 to 0.9 (Hultgren *et al* 1973).

Table 2: Heat of Mixing of Cd-Na liquid alloys at 673 K.

c_{Cd}	H_M/RT	
	Theoretical	**Experimental***
0.1	–0.1650	–0.0254
0.2	–0.2288	–0.1010
0.3	–0.3258	–0.2177
0.4	–0.4362	–0.3770
0.5	–0.5419	–0.5711
0.6	–0.6218	–0.7241
0.7	–0.6498	–0.8236
0.8	–0.6046	–0.7997
0.9	–0.4434	–0.5528

*Hultgren *et al*, 1973

The plot of H_M/RT versus c_{Cd} at 673 K is shown in Figure–2 for both the theoretical and experimental values. Slight deviations are found in the calculated and observed values of H_M. H_M shows a minimum at c_{Cd}=0.7 theoretically whereas experimentally the same is at c_{Cd}=0.76.
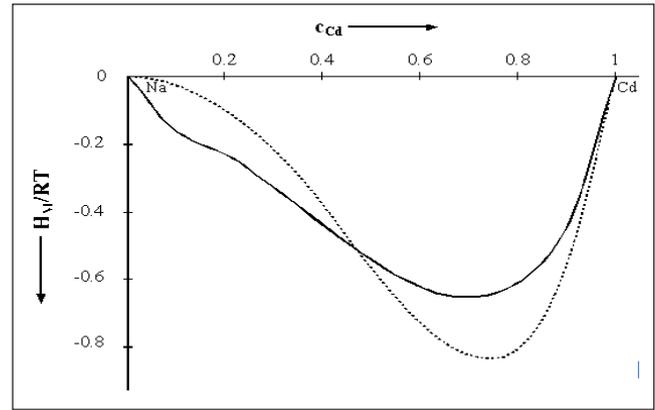

Figure 2 : Heat of mixing (H_M/RT) of Cd-Na liquid alloys at 673 K for different concentrations of cadmium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

3.3. Copper-Tin Liquid Alloy

Envisaging the formation of chemical complex Cu_4Sn one has for the copper-tin liquid alloy :

$$A \equiv Cu, \quad B \equiv Sn, \quad \mu = 4, \quad \nu = 1.$$

Finding the values of the β-functions in equation (ii), the expression for excess free energy of mixing for this alloy becomes

$$G_M^{xs} = N\left[\omega c(1-c) + \Delta\omega_{AB}\left(\frac{27}{140}c + \frac{1}{2}c^4 - \frac{4}{5}c^5 - \frac{1}{7}c^7 + \frac{1}{4}c^8\right) + \right.$$

$$\left. \Delta\omega_{AA}\left(-\frac{79}{840}c + \frac{1}{2}c^4 - \frac{2}{5}c^5 - \frac{1}{6}c^6 + \frac{2}{7}c^7 - \frac{1}{8}c^8\right)\right]$$

$$[\because \text{coeff}(\Delta\omega_{BB}) = 0 \text{ as } \nu < 2]$$

The interaction parameters in equation (i) are ascertained from the experimental values of free energy of mixing of Cu-Sn alloys at 1400 K in the concentration range of copper from 0.1 to 0.9 (Hultgren *et al* 1973) by the method of successive approximation :

$$= -0.1, \qquad = -4.2, \qquad \Delta\omega_{AA} \approx 0.$$

The observed values of entropy of mixing at 1400 K in the concentration range of copper from 0.1 to 0.9 (Hultgren *et al* 1973) are used to find out the temperature derivatives of interaction parameters in equation (iv) by the successive approximation method :

$$= -9.2, \qquad = -4.5, \quad \frac{d}{dT}(\Delta\omega_{AA}) \approx 0,$$

$$\frac{d}{dT}(\Delta\omega_{BB}) \approx 0.$$

The computed values of the heat of mixing of Cu-Sn liquid alloys at 1400 K are furnished in Table–3 along with its observed values in the concentration range of copper from 0.1 to 0.9 (Hultgren *et al* 1973).

Table 3: Heat of Mixing of Cu-Sn liquid alloys at 1400 K.

c_{Cu}	H_M/RT	
	Theoretical	**Experimental***
0.1	+0.0010	+0.0186
0.2	+0.1152	+0.0046
0.3	+0.1688	–0.0348
0.4	+0.1188	–0.0948
0.5	–0.0023	–0.1705
0.6	–0.1923	–0.2567
0.7	–0.3812	–0.3354
0.8	–0.4915	–0.3515
0.9	–0.4263	–0.2301

*Hultgren *et al*, 1973

The plot of H_M/RT versus c_{Cu} at 1400 K is depicted in Figure–3 for both the theoretical and experimental values. It is interesting to observe that H_M–c_{Cu} variation is clearly S-shaped. Theoretically, for $c_{Cu}<0.5$, H_M is positive and for $c_{Cu}>0.5$, H_M is negative—the maximum value of the heat of mixing occurring at $c_{Cu}=0.3$ and the minimum value at $c_{Cu}=0.8$.
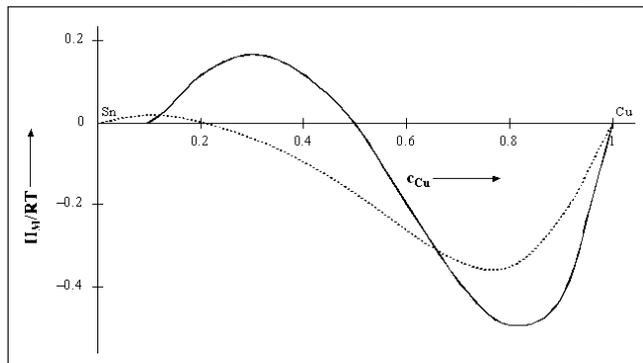

Figure 3 : Heat of mixing (H_M/RT) of Cu-Sn liquid alloys at 1400 K for different concentrations of copper. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

4. CONCLUSION

The anomaly in the heat of mixing of In-Na, Cd-Na and Cu-Sn liquid alloys is well explained by the present theoretical model. The nature of curves as found experimentally is corroborated to a great extent by our computed values of H_M for these complex forming binary liquid alloys for different concentrations of the ingredients.

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