QUASI-LATTICE CHEMICAL MODEL FOR THE THERMODYNAMIC PROPERTIES OF COPPER-TIN LIQUID ALLOY

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ABSTRACT

There are large number of binary liquid alloys which exhibit interesting behaviour as a function of concentration as regards the thermodynamic properties. The properties of mixing are not symmetrical about the equi-atomic composition and deviate maximally from that of the ideal alloys. It is found that the complex forming alloys exhibit such anomalous behaviour. Here we have taken into account the copper-tin liquid alloy in which it is envisaged that the constituent species form the chemical complex Cu_4Sn. So, we have applied a quasi-lattice chemical model in order to investigate its alloying behaviour. Special attention is given to the concentration dependence of the free energy of mixing, entropy of mixing and heat of mixing. The results explain the observed asymmetry in the properties of mixing of copper-tin liquid alloys around equi-atomic composition.

Key words : Binary liquid alloy, Quasi-lattice chemical model, Free energy of mixing, Entropy of mixing, Heat of mixing.

INTRODUCTION

There are a large number of binary liquid alloys whose thermodynamic properties deviate from the ideal values to a great extent (Lamparter *et al* 1984, Harada *et al* 1988, Kumar *et al* 2005, Chakrabarti *et al* 2007). The alloying behaviour of these liquid alloys can be studied by the help of either the electronic theory of mixing or the 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) 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, 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.

In the present work we tend to explain the concentration dependence of free energy of mixing,

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entropy of mixing and heat of mixing of copper-tin liquid alloy on the basis of quasi-lattice chemical model. It is a statistical model in which grand partition function is used (Bhatia and Singh 1984). The mixing properties of CuSn alloys are asymmetric around equi-atomic composition (c=0.5) although the value of free energy of mixing is small. This interesting aspect has led us to the theoretical investigation of copper-tin liquid alloys assuming the formation of chemical complex Cu_4Sn (Bhatia and Hargrove 1974).

In Section 2 the general calculations of quasi-lattice chemical model are summarised to simple expressions. Section 3 deals with the results of the free energy of mixing, entropy of mixing and heat of mixing of copper-tin liquid alloys at 1400 K. Section 4 provides a brief conclusion.

FORMULATION

The quasi-lattice chemical model envisages the existence of chemical complex $A_\mu B_\nu$ (Bhatia and Singh 1982), where μ & ν are small integers and A & B the constituent species of the alloy:

$$\rightleftharpoons \mu A + \nu B \quad A_\mu B_\nu.$$

The grand partition function is solved by assuming that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not. With this consideration the expression for excess free energy of mixing comes to be

$$G_M^{xs} = NK_B T \int_0^c \ln \gamma \, dc, \qquad \dots\dots\dots\dots(i)$$

where N is the total number of atoms in the alloy, 'c' the concentration of A-atoms, T the absolute temperature and K_B the Boltzmann constant. γ is the ratio of the activity co-efficients of atoms A to B and is given by

$$\ln \gamma = Z\ln \sigma + \frac{Z}{2K_B T}(P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB}) + \Phi, \quad ....(ii)$$

where Z is the co-ordination number, Φ a constant and P_{ij} the probability that an ij bond belongs to the complex and is given by

$$P_{AB} = c^{\mu-1}(1-c)^{\nu-1}[2 - c^{\mu-1}(1-c)^{\nu-1}] \text{ where } i, j = A, B, \quad ....(iii)$$
$$P_{AA} = c^{\mu-2}(1-c)^{\nu}[2 - c^{\mu-2}(1-c)^{\nu}] \text{ for } \mu \geq 2 \quad ....(iv)$$
$$P_{BB} = c^{\mu}(1-c)^{\nu-2}[2 - c^{\mu}(1-c)^{\nu-2}] \text{ for } \nu \geq 2 \quad ....(v)$$

P_{AA} and P_{BB} are zero for μ < 2 and ν < 2 respectively. ϵ_{ij} denotes the energy of ij bond if it is a free bond and $(\epsilon + \Delta\epsilon_{ij})$ its energy if it is one of the bonds in the complex $A_\mu B_\nu$. The term σ in the right-hand side of (ii) is given by

$$\ln \sigma = \qquad\qquad ,$$

where $\quad \theta = \qquad\qquad . ...(vi)$

In (vi), $\eta^2 =$

$$\exp\left[\frac{2\omega}{ZK_B T}\right] \exp\left[\frac{2P_{AB}\Delta\epsilon_{AB} - P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB}}{K_B T}\right]$$

where $\quad Z\left(\epsilon_{AB} - \frac{1}{2}\epsilon_{AA} - \frac{1}{2}\epsilon_{BB}\right) = \omega,$

the ordering energy. The constant Φ appearing in (ii) can now be determined by setting

$$\int_0^1 \ln \gamma dc = 0.$$

It, however, depends upon the values of μ & ν and on using (iii), (iv) and (v) we obtain

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

$\Delta\omega_{BB}[2\beta(\mu+1, \nu) - \beta(2\mu+1, 2\nu-2)], \quad ....(vii)$

where β's are the usual beta functions. Here for convenience we have introduced

$$\Delta\omega_{ij} = Z\Delta\epsilon_{ij}.$$

It is understood from (iv) and (v) that in (vii) the co-efficient of $\Delta\omega_{AA}$ is identically zero if μ=1 and that of $\Delta\omega_{BB}$ also zero if ν=1. In association with the above relations we get from (i) a closed form expression for the excess free energy of mixing :

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

Φ_{ij}'s can be expressed explicitly in terms of 'c' for given values of μ and ν. In case of copper-tin liquid alloy

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

Therefore, $\Phi_{AB}(c) = \dfrac{27}{140}c + \dfrac{1}{2}c^4 - \dfrac{4}{5}c^5 - \dfrac{1}{7}c^7 + \dfrac{1}{4}c^8$ ....(ix)

and $\Phi_{AA}(c) = -\dfrac{79}{840}c + \dfrac{1}{2}c^4 - \dfrac{2}{5}c^5 - \dfrac{1}{6}c^6 + \dfrac{2}{7}c^7 - \dfrac{1}{8}c^8$. ......(x)

Using (ix) and (x) in (viii),

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

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

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

$G_M = G_M^{xs} + RT[c\ln c + (1-c)\ln (1-c)]$, ...(xii)

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

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

$\left[\dfrac{d\omega}{dT}\Phi(c) + \dfrac{d}{dT}(\Delta\omega_{AB})\Phi_{AB}(c) + \dfrac{d}{dT}(\Delta\omega_{AA})\Phi_{AA}(c) + \dfrac{d}{dT}(\Delta\omega_{BB})\Phi_{BB}(c)\right]$

...............(xiii)

where $\Phi(c) = c(1-c)$.
So, the entropy of mixing of such a binary liquid alloy,

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

Now, with the help of (xii) and (xiv) the heat of mixing can be found out by using the standard thermodynamic relation :

$H_M = G_M + TS_M$. ....(xv)

3. RESULTS AND DISCUSSION
3.1 Free energy of mixing

The values of interaction parameters in (xi) are determined from the experimental values of G_M (Hultgren *et al* 1973) in the concentration range from 0.1 to 0.9. In this course we find that $\Delta\omega_{AA}$ has relatively minor influence. So, we have set $\Delta\omega_{AA}$=0. The remaining two parameters are found out to be

$$\frac{\omega}{K_B T} = -0.1 \quad \text{and} \quad = -4.2$$

at T=1400 K. Thus (xi) and (xii) are used to compute the free energy of mixing of CuSn liquid alloys. The theoretical and experimental values of G_M are furnished in the Table below.

Table
Thermodynamic Entities
for CuSn liquid alloy at 1400 K.

c_{Cu}	G_M/RT		S_M/R		H_M/RT	
	Theoretical	Experimental*	Theoretical	Experimental*	Theoretical	Experimental*
0.1	−0.4151	−0.4290	0.4161	0.4480	+0.0010	+0.0186
0.2	−0.6804	−0.6956	0.7956	0.6990	+0.1152	+0.0046
0.3	−0.8828	−0.8916	1.0516	0.8570	+0.1688	−0.0348
0.4	−1.0490	−1.0370	1.1678	0.9420	+0.1188	−0.0948
0.5	−1.1480	−1.1370	1.1457	0.9660	−0.0023	−0.1705
0.6	−1.1940	−1.1850	1.0017	0.9280	−0.1923	−0.2567
0.7	−1.1480	−1.1470	0.7668	0.8110	−0.3812	−0.3354
0.8	−0.9730	−1.0170	0.4815	0.6660	−0.4915	−0.3515
0.9	−0.6210	−0.6900	0.1947	0.4500	−0.4263	−0.2301

*Hultgren *et al*, 1973

The computed values of free energy of mixing are in well agreement with the observed values vide G_M/RT–c_{Cu} curve in Fig–1. Both the experimental and theoretical values of G_M show minimum at c_{Cu}=0.6.
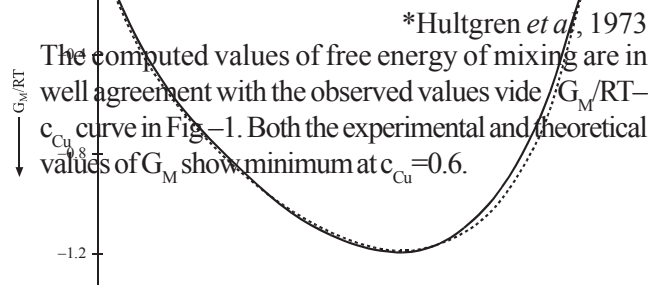
Fig.–1. Free energy of mixing (G_M/RT) of CuSn liquid alloy at 1400 K. for different concentrations of copper; (———) theoretical and (..........) experimental (Hultgren *et al* 1973).

3.2 Entropy of mixing

To determine the entropy of mixing we need the temperature derivative of interaction parameters in (xiii). The observed values of S_M (Hultgren *et al* 1973) are used to obtain the temperature derivative of interaction parameters. It is noticed that the temperature derivatives of $\Delta\omega_{AA}$ and $\Delta\omega_{BB}$ are negligibly small. We, therefore, set

$$\frac{d}{dT}(\Delta\omega_{AA}) = 0 \quad \text{and} \quad \frac{d}{dT}(\Delta\omega_{BB}) = 0.$$

The remaining two parameters are found out to be

$$\frac{1}{K_B}\frac{d\omega}{dT} = -9.2 \quad \text{and} \quad = -4.5.$$

Now the entropy of mixing of the copper-tin liquid alloys is calculated by using (xiii) and (xiv). The concentration dependence of S_M/R at 1400 K. is shown in the Table above and plotted in Fig.–2. The theoretical and experimental values of the entropy of mixing are in reasonable agreement. It is noticed that S_M is positive at all the concentrations. The experimental values of S_M exhibit maximum at c_{Cu}=0.5 but our theoretical values show maximum at c_{Cu}=0.45
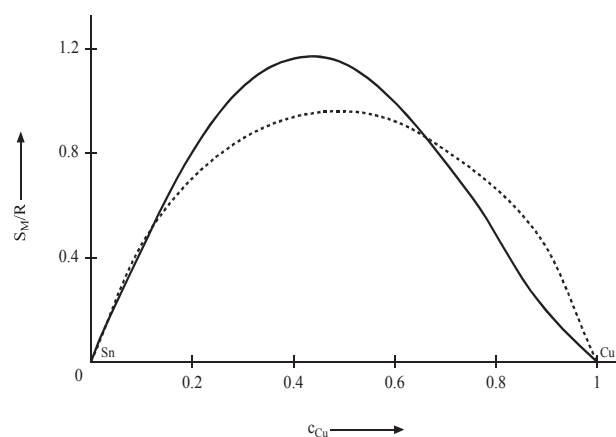

Fig.–2. Entropy of mixing (S_M/R) of CuSn liquid alloy at 1400 K. for different concentrations of copper; (———) theoretical and (..........) experimental (Hultgren *et al* 1973).

3.3 Heat of mixing

The heat of mixing of the copper-tin liquid alloys has been computed as a function of concentration from equation (xv) on taking the same values of $d\omega/dT$ and $d(\Delta\omega_{AB})/dT$. It is tabulated in the Table above. The plot of H_M/RT versus c_{Cu} at 1400 K. is depicted in Fig.–3 for both the theoretical and experimental values (Hultgren

et al 1973). 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.
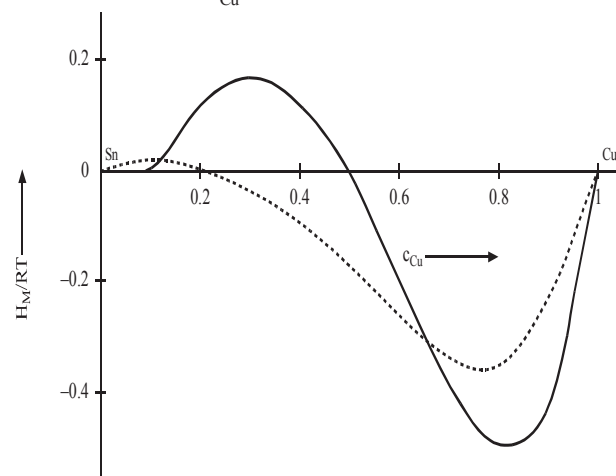

Fig.–3. Heat of mixing (H_M/RT) of CuSn liquid alloy at 1400 K. for different concentrations of copper; (———) theoretical and (..........) experimental (Hultgren *et al* 1973).

1.   SUMMARY AND CONCLUSION

The alloying behaviour of copper-tin liquid alloy is well explained by the above theoretical model. The observed free energy of mixing and heat of mixing are quite asymmetrical around the equi-atomic composition. Both the theoretical and experimental values of G_M and H_M show minimum at c_{Cu}=0.6 and c_{Cu}=0.8 respectively. In case of entropy of mixing only a slight deviation has taken place. The observed value of the entropy of mixing is maximum at c_{Cu}=0.5 but our theoretical values show S_M to be maximum at c_{Cu}=0.45.

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