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A Theoretical study of thermodynamic properties of Cd-Bi liquid alloy

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Abstract

Flory's model has been used for the study of thermodynamic properties of Cd-Bi liquid alloys. Free energy of mixing, heat of mixing, entropy of mixing and activity of Cd have been determined. All of these computed quantities have been found to be in a good agreement with observed values.

Keywords: Flory's model; thermodynamic properties; Cd-Bi liquid alloy; weakly interacting system; interaction energy parameter

1. Introduction

The liquid state of matter such as, liquid metal alloys is characterized as disorder system and hence it is much more difficult to understand the properties of liquid alloys than that of crystal. In order to solve the complexity of obtaining thermodynamic properties of binary liquid alloys several models [1-9] have been employed by the theoreticians. Moreover Cadmium is highly reactive element and it is difficult to conduct diffraction experiment on it. Therefore a theoretical investigation giving structural information on a system of Cd is highly desirable.

Experience shows that the thermodynamic properties of binary liquid alloys can be explained by Flory's model [2] if there is larger size mismatch between the constitute metals. In case of Bi-Cd binary alloy the size factor ($\Omega_{Bi}/\Omega_{Cd} = 1.63$, Ω being the atomic volume of the constituent of the alloy) is greater than 1.5. Thus, in present investigation, we have used Flory's model to understand the thermodynamic properties of Bi-Cd liquid alloy at 773 K.

Theoretical formalism is given in section 2, section 3 deals with the numerical results and discussion. Conclusion is provided in section.

2. Theory

We consider N_c mole of Cd atoms and $N(1-c)$ mole of Bi atoms are mixed in molten state at 773 K. Then Flory's expression for free energy of mixing of a binary mixture Cd-Bi is given by [2]

$$G_M = RT[c \ln c + (1-c) \ln(1-c) + c \ln(1-\beta) - \ln(1-\beta c)] + \omega c \frac{1-c}{1-\beta c} \quad (1)$$

where $\beta = 1 - \frac{(\Omega_{Cd})}{(\Omega_{Bi})} = 0.385$

The standard thermodynamic relation for activity of Cd in binary liquid is given by

$$RT \ln a_{Cd} = G_M + (1-c) \frac{\partial G_M}{\partial c} \quad (2)$$

Differentiating equation (1) with respect to 'c' and substituting the value of $\frac{\partial G_M}{\partial c}$, one gets

$$\ln a_{Cd} = \ln c + \ln(1-\beta) - \ln(1-\beta c) + \frac{\beta(1-c)}{1-\beta c} + \frac{\omega}{RT} \frac{(1-c)^2}{(1-\beta c)^2} \quad (3)$$

Once the expressions for G_M is obtained, other thermodynamic functions follow readily. Heat of mixing and entropy of mixing are related to G_M through standard thermodynamic relations

$$H_M = G_M - T \left(\frac{\partial G_M}{\partial T} \right)_P \quad (4)$$

$$S_M = \frac{H_M - G_M}{T} \quad (5)$$

Differentiating equation (1) with respect to T and substituting in equation (4), we get

$$H_M = \omega \frac{c(1-c)}{1-\beta c} - T \frac{c(1-c)}{1-\beta c} \frac{\partial \omega}{\partial T} + RT^2 \frac{c(1-c)}{1-\beta c} \left[\frac{\beta}{1-\beta} - \frac{c}{1-\beta c} \frac{\omega}{RT} \right] \frac{\partial \beta}{\partial T} \quad (6)$$

where $\frac{\partial \beta}{\partial T} = (\alpha_{Bi} - \alpha_{Cd}) \frac{\Omega_{Cd}}{\Omega_{Bi}}$, α_{Cd} and α_{Bi} are expansivities of Cd and Bi respectively.

3. Results and Discussion

The value of interchange energy (ω) was determined from the observed data [10] of G_M in the concentration range from 0.1 to 0.9. The best fit value of ω used in the present work was found to be -51.4 J mol⁻¹. The negative value of ω indicates that there is a tendency of compound formation (preferred with unlike atoms pairing) in Cd-Bi alloy in molten state. The computed values of G_M obtained from equation (1) are plotted against c_{Cd} (concentration of Cd) in figure 1 along with its observed values at 773K. The computed and observed values of G_M are in a good agreement in all concentration range. Both the theoretical and observed values are minimum at equiatomic composition, $c_{Cd} = 0.5$. Theoretical calculation of free energy of mixing for Cd-Bi liquid alloy shows that it is weakly interacting system. This indicates that the tendency of compound formation is weak.

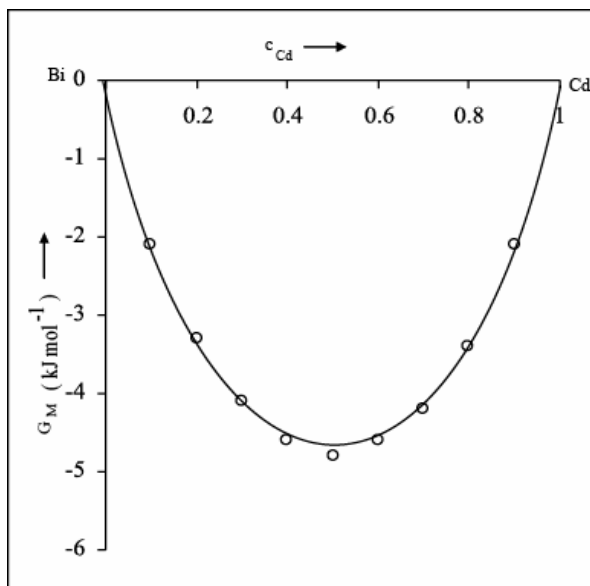


Fig.1 : Free energy of mixing (G_M) versus c_{Cd} (concentration of Cd) in the liquid Cd-Bi solution (773K); (—) theory, (ooo) experiment [10].

Activity is a very important thermodynamic function because it is one of the fortune functions which is obtained directly from experiment and it can be used to obtain other thermodynamic functions. . The graph between the experimental and theoretical values of $\ln a_{Cd}$ with respect to c_{Cd} is shown in figure 2. It is clear from the graph that theoretical values of $\ln a_{Cd}$ are in a good agreement with experimental values.

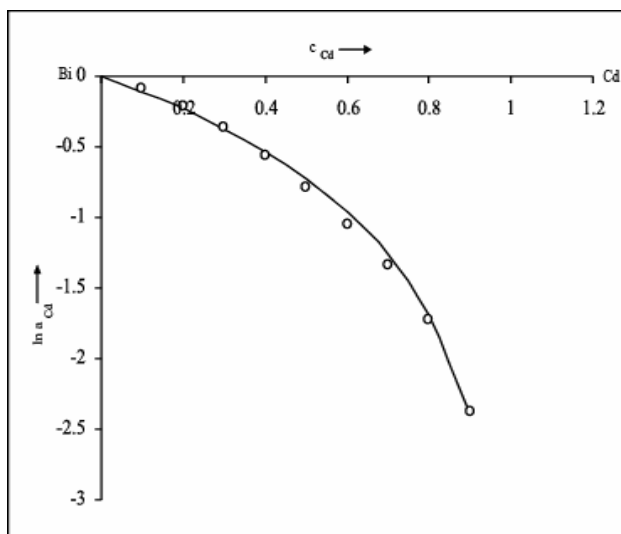


Fig. 2: Activity ($\ln a_{Cd}$) versus c_{Cd} (concentration of Cd) in the liquid Cd-Bi solution (773K); (—) theory, (ooo) experiment [10].

To determine heat of mixing and entropy of mixing we need the variation of interchange energy with temperature [11,12]. For this, observed values of heat of mixing (H_M) are used. In present work the value of $\partial\omega/\partial T = -4.8 \text{ Jmol}^{-1}\text{K}^{-1}$ is considered as a best fit value. The heat of mixing at 773K is calculated using equation (6). The minimum value of the heat of mixing show that the intermolecular forces between Bi and Cd is also small.

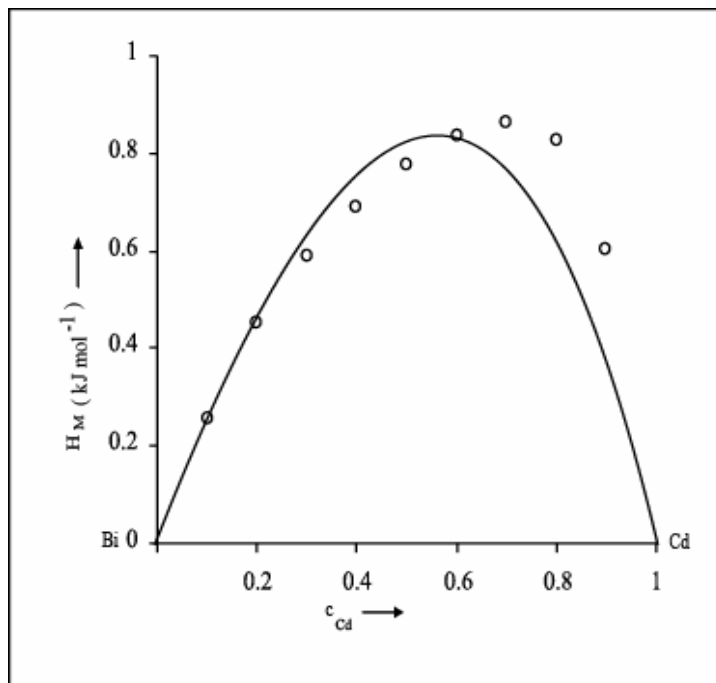


Fig. 3 : Heat of mixing (H_M) versus c_{Cd} in the liquid Cd-Bi solution (773K); (—) theory, (ooo) experiment [10].

Equation (5) is used to calculate S_M for the concentration $c_{Cd} = 0.1$ to 0.9 . The computed values of S_M are plotted in figure 4 along with their observed values. The computed and observed values of S_M are in a good agreement. The calculated and observed both values of entropy of mixing show that Cd-Bi alloy is not ordered system at 773 K.

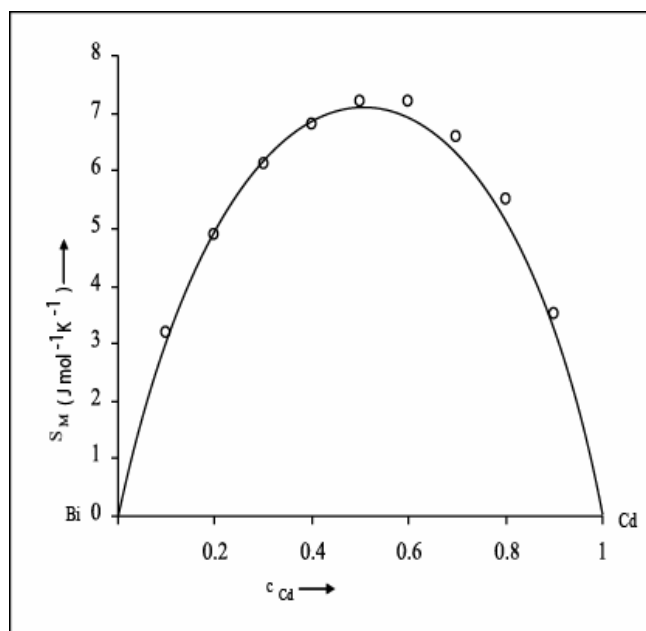


Fig. 4 : Entropy of mixing (S_M) versus c_{Cd} in the liquid Cd-Bi solution (773K); (—) theory, (ooo) experiment [10].

4. Conclusion

The Cd-Bi melts at 773 K is weakly interacting system. The interaction energy parameter is temperature dependent. The intermolecular force between like or unlike atoms in Cd-Bi alloy in liquid state is very weak.

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