Theoretical Investigation of Energetic and its Effect on Cd-Hg Amalgam

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Abstract

The observed anomaly in properties of mixing of Cd-Hg alloys in the molten state is successfully explained on the basis of the quasi-lattice model. The thermodynamic functions such as free energy of mixing, heat of mixing, entropy of mixing and chemical activity of the constituent atom of the alloys and microscopic functions like concentration-concentration fluctuation in long wavelength limit and Warren-Cowley short range order parameter of the alloys have been computed within the frame work of presented model. Most of the computed values are in good agreement with the experimental data. The pair-wise interaction energies between the species of the melt are found to depend considerably on temperature. Theoretical analysis suggests that hetero-coordination leading to the formation of complex Cd_2Hg is likely to exist but is of weakly interacting in nature.

Keywords: *Hetero-coordination; chemical activity; entropy; pair-wise interaction energy.*

1. Introduction

Liquid alloys display a remarkable variety of local chemical order. The knowledge of mixing properties of liquid alloys is necessary for the design and development of industrial materials for high temperature application [*Koirala et al., 2014*]. Cadmium alloys have been widely used in fabricating solid state electronic components. Cadmium-mercury amalgam is used in Weston cell to produce a highly stable voltage. It is very difficult to conduct diffraction experiment on cadmium metal because of its highly reactive nature. Therefore theoretical investigation giving mixing properties of cadmium alloys are highly desirable. There has been considerable interest of theoreticians to explain the concentration

dependent asymmetry in the properties of mixing of binary liquid alloys and hence to extract additional structural or microscopic information. Present day, various theoretical models [*Prasad et al.,*1991,1998; *Singh et al.*, 1990,1992; *Anusionwu et al.*,1998; *Novakovic et al.,*2010; *Akinlade et al.,* 2002; *Jha et al.*, 2014; *Guggenheim*, 1952]. have been focused to study of the alloying behavior of alloys in the molten state. In the present investigation, the Quasi-lattice model [*Bhatia & Singh,*1992; *Bhatia & Hargoov,* 1974] has been used to estimate the thermodynamic and microscopic properties of the alloys at 600K assuming Cd_2Hg complex in the melt. Thermodynamic properties provide information on the interaction, stability and

bonding strength among the constituent atoms in the alloys. The free energy of mixing, heat of mixing, entropy of mixing and activity of the species of the alloys are nearly symmetrical but concentration- concentration fluctuation at long wavelength limit and chemical short range order parameter are asymmetrical around equi-atomic composition [*Hultgren et al.,* 1973]. The microscopic properties are useful in obtaining the microscopic information on structure of molten alloys. The size factor (V_{Hg}/V_{Cd} = 1.14, where V is atomic volume) and electro-negativity ($E_{Hg} - E_{Cd} = 0.31$) are not so large to account for the anomalous behavior observed in the properties of mixing of Cd-Hg liquid alloys [*Singh & Sommer,* 1992]. Therefore, it is expected that concentration dependent anomaly arises due to energy effects.

2. Methodology

The present work is purely theoretical in nature and the following method are used for our investigations:

In present work, we use a quasi-lattice model to understand the mixing properties of simple binary liquid alloys with respect to concentration. In this model a grand partition function is constructed to deduce the relations for thermodynamic and microscopic functions. The quasi-lattice model is applicable for binary liquid alloys, which in solid or liquid state form a chemical compound at one or more well defined chemical composition and the complexes or the privileged group of atoms exist in the molten state. In this model, it is assumed that the energy of a given nearest neighbor bond is different if it belongs to the complex than if it does not. The model envisages the existence of

chemical complexes $A_m B_n$, where A and B are the constituent species of the alloys and m and n are the small integers:

$$mA+nB = A_m B_n$$
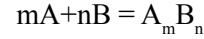
With this consideration, grand partition function is solved and expression for excess free energy of mixing [Guggenheim, 1952] comes out to be

$$G_M^{XS} = Nk_BT \int_0^c \ln\gamma \, dc$$
$$= N[\Phi\omega + \Phi_{AB}\Delta\omega_{AB} + \Phi_{AA}\Delta\omega_{AA} + \Phi_{BB}\Delta\omega_{BB}] \quad (1)$$

Where N is the total number of the atoms in the alloys; k_B, the Boltzmann constant; T, absolute temperature; γ, ratio of the activity coefficient of atom A to B; c, the concentration of atom A; ω's are the ordering energies; $\Phi = c(1-c)$ and Φ_{ij} (i,j = A,B) are the simple polynomials in c depending on the values of m and n, which is given by

$$k_BT\Phi_{m,n} = \Delta\omega_{AB}[2\beta(m+1,n) - 2\beta(m,n+1) + \beta(2m-1,2n) + \beta(2m,2n-1)] +$$
$$\Delta\omega_{AA}[\beta(2m-2,2n+1) - 2\beta(m,n+1)] + \Delta\omega_{BB}[2\beta(m+1,n) - \beta(2m+1,2n-2)] \quad (2)$$

Where β's are the usual beta functions. The free energy of mixing of a complex forming binary liquid alloys is

$$G_M = G_M^{XS} + Nk_BT[c\ln c + (1-c)\ln(1-c)]$$
$$= RT[\Phi\frac{\omega}{k_BT} + \Phi_{AB}\frac{\Delta\omega_{AB}}{k_BT} + \Phi_{AA}\frac{\Delta\omega_{AA}}{k_BT} + \Phi_{BB}\frac{\Delta\omega_{BB}}{k_BT} + c\ln c + (1-c)\ln(1-c)] \quad (3)$$

Where R is the universal molar constant. The heat of mixing is easily found out by using the standard thermodynamic relation:

$$\frac{H_M}{RT} = \frac{G_M}{RT} - \frac{1}{R}\left(\frac{dG_M}{dT}\right)_{c,N,P}$$
$$= \Phi\left(\frac{\omega}{k_BT} - \frac{1}{k_B}\frac{d\omega}{dT}\right) + \Phi_{AB}\left(\frac{\Delta\omega_{AB}}{k_BT} - \frac{1}{k_B}\frac{d(\Delta\omega_{AB})}{dT}\right) + \Phi_{AA}\left(\frac{\Delta\omega_{AA}}{k_BT} - \frac{1}{k_B}\frac{d(\Delta\omega_{AA})}{dT}\right) + \Phi_{AB}\left(\frac{\Delta\omega_{BB}}{k_BT} - \frac{1}{k_B}\frac{d(\Delta\omega_{BB})}{dT}\right) \quad (4)$$

The standard thermodynamic relation for entropy of mixing is

$$\frac{S_M}{R} = \frac{H_M}{RT} - \frac{G_M}{RT} \qquad (5)$$

The chemical activity of the component atom in the alloys is deduced from standard relation

$$RT \ln a_i \, (i = A, B) = G_M + (1 - c_i)(\partial G_M / \partial c_i)_{T,P,N} \quad (6)$$

$$\ln a_A = \frac{G_M}{RT} + \frac{1-c}{k_B T} [(1-2c)\omega + \Phi'_{AB} \Delta\omega_{AB} +$$
$$\Phi'_{AA} \Delta\omega_{AA} + \Phi'_{BB} \Delta\omega_{BB} + \ln(c/1-c)] \quad (7)$$

Which are given by

$$\ln a_B = \frac{G_M}{RT} - \frac{c}{k_B T} [(1-2c)\omega + \Phi'_{AB} \Delta\omega_{AB} +$$
$$\Phi'_{AA} \Delta\omega_{AA} + \Phi'_{BB} \Delta\omega_{BB} + \ln(c/1-c)] \quad (8)$$

Where Φ', Φ'_{AB}, Φ'_{AA} and Φ'_{BB} are the derivatives of Φ, Φ_{AB}, Φ_{AA} and Φ_{BB} respectively.

The concentration-concentration fluctuation in long wavelength limit [*Bhatia and Thornton, 1970*] for the alloy system is easily derived from standard relation

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

$$= \frac{c(1-c)}{1 + c(1-c) \left[-2\frac{\omega}{k_B T} + \Phi''_{AB} \frac{\Delta\omega_{AB}}{k_B T} + \Phi''_{AA} \frac{\Delta\omega_{AA}}{k_B T} + \Phi''_{BB} \frac{\Delta\omega_{BB}}{k_B T} \right]} \quad (9)$$

Where $\Phi''_{ij} = \dfrac{\partial^2 \Phi_{ij}}{\partial c^2}$ (i, j = A, B)

For ideal mixing, concentration-concentration fluctuations are usually computed from:

$$S_{cc}^{id}(0) = c(1-c) \qquad (10)$$

The Warren-Cowley short range order parameter [*Warren,* 1969; *Cowley,* 1950] is related with the concentration-concentration fluctuation in long wavelength limit. Theoretical expression for the short range order parameter for the first neighbor shell is given by

$$\alpha_1 = \frac{S-1}{S(Z-1)+1}, \quad S = \frac{S_{cc}(0)}{S_{cc}^{id}(0)} \qquad (11)$$

where z is the coordination number, which is taken as 10 for our purposes.

For Cd_2Hg system,

A = Cd, B = Hg, m = 2, n = 1

$$\Phi_{AB} = \frac{c}{6} + c^2 - \frac{5c^3}{3} + \frac{c^4}{2}$$

$$\Phi_{AA} = -\frac{c}{4} + \frac{c^2}{2} - \frac{c^4}{4}$$

$$\Phi_{BB} = 0, \text{ for } n < 2$$

3. Result and Discussion
3.1. Free energy of mixing

The method of successive approximation is suitable for the determination of energy parameters used for the calculation of the free energy of mixing for Cd-Hg liquid alloys. The parameters have been determined by using the experimental value of G_M [*Hultgren et al.,* 1973] in the concentration range from 0.1 to 0.9. The best fit values of the parameter are

$$\frac{\omega}{k_B T} = -2.75, \quad \frac{\Delta\omega_{AB}}{k_B T} = +1.12, \quad \frac{\Delta\omega_{AA}}{k_B T} = -3.55, \quad \frac{\Delta\omega_{BB}}{k_B T} = 0 \quad (12)$$

The free energy of mixing (G_M) for Cd-Hg liquid alloys at 600K is computed through Eq.(3). The plot of free energy of mixing verses concentration of cadmium is deposited in fig.1. The computed and experimental values of G_M are in reasonable agreement throughout the concentration range from 0.1 to 0.9 of Cd. Theoretical calculation of free energy of mixing for Cd-Hg liquid alloys shows that

the minimum value of free energy of mixing for Cd-Hg is -1.15018RT at c_{Cd} = 0.5. This is excellent agreement with the experimental value [*Hultgren et al.,* 1973]. Further, the negative values of all interaction energies suggest that Cd and Hg atoms are attracted to each other and consequently tendency of the system is found to be ordering (complex formation). The minimum value of free energy of mixing indicates that Cd-Hg alloy in liquid state is moderately interacting system and hence, the tendency of compound formation is not strong in this alloy.

3.2. Heat of mixing

To determine the heat of mixing for liquid Cd-Hg alloys, we need temperature derivatives of interaction energy parameters. The observed values of H_M [*Hultgren et al.,* 1973] are used to obtain the temperature derivatives by successive approximation method. The best fit values of these parameters are found to be

$$\frac{1}{k_B}\frac{\partial \omega}{\partial T}=1.42, \ \frac{1}{k_B}\frac{\partial (\Delta \omega_{AB})}{\partial T}=-1.82, \ \frac{1}{k_B}\frac{\partial (\Delta \omega_{AA})}{\partial T}=0.23 \quad (13)$$
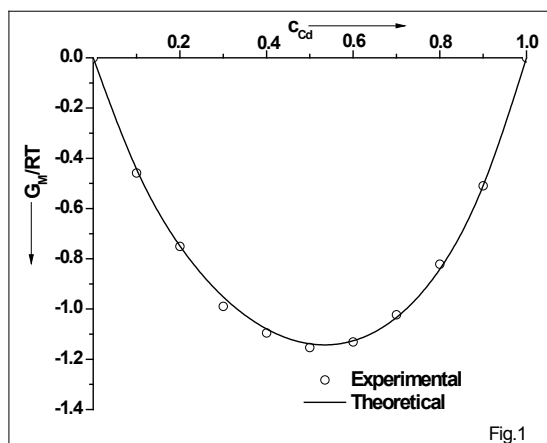
Heat of mixing (H_M) for liquid Cd-Hg alloys at 600K is computed by using eq.(4). The graph is plotted for heat of mixing with both theoretical and experimental values against concentration of cadmium, which is shown in fig.(2).The figure shows that theoretical values of H_M are in good agreement along with the experimental values [*Hultgren et al.,*1973] in the whole range of concentration of Cd. The heat of mixing for Cd-Hg alloy in liquid state is negative in whole composition with minimum of -0.52406RT at c_{Cd} = 0.5, which is very close to experimental value (-0.52587RT) at the same concentration of Cd. The contribution from the formation of complex on the heat of mixing is maximum at c_{Cd} =0.66, while the contribution from mixing terms is the greatest around c_{Cd} = 0.5.

3.3. Entropy of mixing

Using equation (5) along with eq.(3) and (4), entropy of mixing (S_M) for liquid Cd-Hg alloys is computed. For the theoretical calculation of S_M, same energy parameters (Eq.
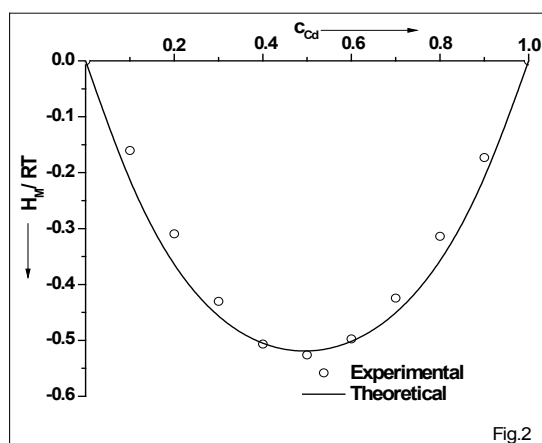

Figure 1. Free energy of mixing (G_M)Vs concentration of Cd (c_{Cd}) in liquid Cd-Hg alloy at 600K.

Figure 2. Heat of mixing (H_M) Vs concentration of Cd (c_{Cd}) in liquid Cd-Hg alloy at 600K.

(12) and (13)) are used. The plot of entropy of mixing (S_M) verses concentration of Cd is depicted in fig.(3),for both the computed and observed values. It is also observed that concentration dependence of asymmetry in S_M can be explained only when one considers the temperature dependence of the pair-wise interaction energies. The computed values of S_M are in very good agreement with experiment values. The theoretical and experimental both values of S_M are positive in whole range of concentration of cadmium. The computed result indicates that Cd-Hg alloy in liquid state is more ordered in higher concentration of Cd.

3.4. Chemical activity

The deviations from ideal behavior of the alloys can be incorporated into activities. The pair of equations (7) and (8) is used for theoretical calculation of chemical activity of the constituent atom in Cd-Hg alloys. Figure (4) shows the comparison between computed and observed values of chemical activity of the species of Cd-Hg alloys. There is good

agreement between the computed and observed values of activity of Cd and Hg in Cd-Hg system at 600K at all concentration of Cd. The agreement between theory and experiment for the both components is comparatively better in lower concentration of Cd.

3.5. The concentration-concentration fluctuation in long wavelength limit and Warren-Cowley short range order parameter:

The Concentration fluctuations in the long-wavelength limit ($S_{cc}(0)$) is an essential structural function which has been widely used to study the nature of atomic order in binary liquid alloys [Bhatia & Thronton, 1970]. There are difficulties in diffraction experiment, therefore theoretical determination of $S_{cc}(0)$ is of great importance when nature of interactions in the melt has to be analyzed. The mixing behavior of liquid alloys can be deduced from the deviation of $S_{cc}(0)$ from $S_{cc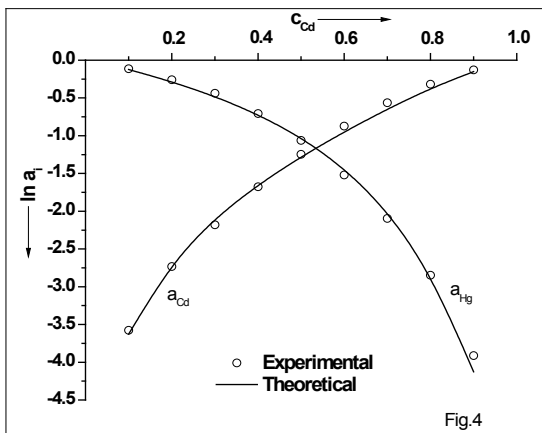}^{id}(0)$. At a given composition if $S_c(0) < S_c^{id}(0)$, ordering in liquid alloy is expected while $S_c(0) > S_c^{id}(0)$

Figure 3. Entropy of mixing (S_M) Vs concentration of Cd (c_{Cd}) in liquid Cd-Hg alloy at 600K.
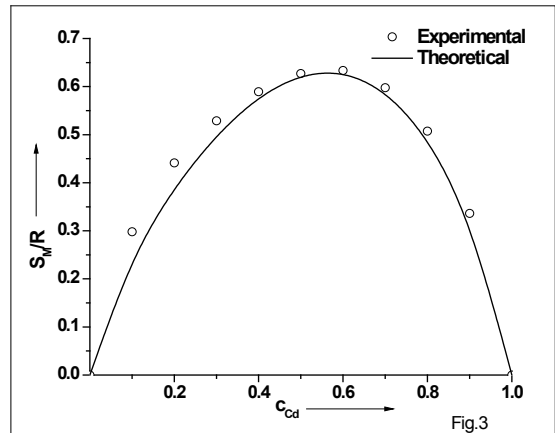

Figure 4. Chemical activity (a_i) Vs concentration of Cd(c_{Cd}) in liquid Cd-Hg alloy at 600K.

gives the indication of tendency of segregation. $S_{cc}(0)$ can also be obtained directly from the measured activity[*Bhatia & Hargoov,*1974] data as

$$S_{cc}(0)=(1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N}=ca_B\left(\frac{\partial a_B}{\partial(1-c)}\right)^{-1}_{T,P,N} \quad (14)$$

where a_A and a_B are the observed chemical activities of the component atom respectively. The $S_{cc}(0)$, obtained from Eq.(14) are taken as experimental values.

The Warren-Cowley [Warren, 1969; Cowley,1950] short-range order parameter (α_1) is useful parameter to quantify the degree of chemical order in th alloy melt. It provides insight into the local arrangement of the atoms in the molten alloys. For the equi-atomic composition, the chemical short range order parameter is found to be $-1 \le \alpha_1 \le 1$. Negative values of α_1 indicate ordering in the melt, which is complete if $\alpha_1 = -1$. On the other hand, positive values of α_1 indicate segregation, leading to complete only if $\alpha_1 = 1$. But $\alpha_1 = 0$, corresponds to random distribution of the atoms in the mixture.

The $S_{cc}(0)$ and α_1 have been computed as a function of concentration of Cd using Eqs.(9) and (11) respectively. The plot of theoretical, experimental and ideal values of $S_{cc}(0)$ and theoretical value of α_1 are displayed in fig.5. The computed values for $S_{cc}(0)$ shows good agreement with the experimental values. Our theoretical analysis shows that computed values of $S_{cc}(0)$ are lesser than the ideal values at all concentration range of Cd. We have found that the deviation of $S_{cc}(0)$ from ideal value is maximum (0.113) at $c_{Cd}= 0.61$,which
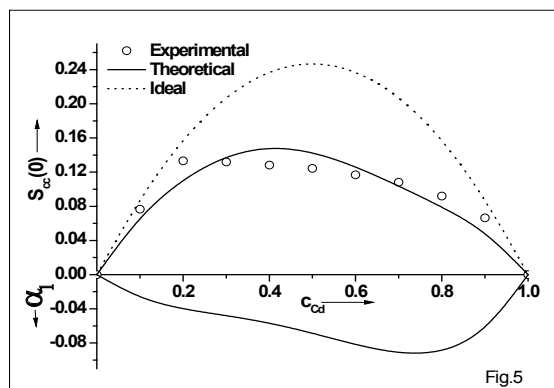

Figure 5. Concentration fluctuation at long wavelength limit ($S_{cc}(0)$) and short range order parameter (α_1) Vs concentration of cadmium (C_{Cd}) in liquid Cd-Hg alloy at 600K.

is close to stoichiometric composition, c_{Cd} = 0.67. Fig.5 also shows that α_1 are negative throughout all concentration, showing Cd-Hg is ordering system of unlike atoms pairing at all compositions. There is maximum depth near the compound forming composition. The asymmetry in α_1 is distinctly observed.

4. Conclusions

The presented theoretical model successfully explains the observed concentration dependent asymmetries reproduced by considering the existence of chemical complexes Cd_2Hg in molten phase. The analysis suggests that the tendency of hetero-coordination of atom depends very much on concentration and the Cd-Hg system is moderately interacting. The analysis also reveals that most of the energy parameters depend considerably on temperature.

Acknowledgments

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