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Optimization of Concentration Fluctuations in Zn-X (X ≡ In and Cd)Binary Liquid Alloys at different Temperatures

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Abstract- A theoretical formalism, obtained by considering the coupled effect of size ratio and energetic contribution, has been used to explain the thermodynamic properties of binary liquid alloys Zn-In at temperature 700K, and of binary liquid alloys Zn-Cd at temperature 800K. For this purpose, the best fit value of order energy parameter (W) has been estimated over the entire range of concentration in Zn-In as well as Zn-Cd liquid alloys at the mentioned temperatures. These values of W at different temperatures have been used for the optimization procedure in order to determine the corresponding values of excess free energy of mixing, partial excess free energy of mixing and activity of all the components involved in binary liquid alloys Zn-In and Zn-Cd at different temperatures which are then used to predict the concentration fluctuations in long wavelength limit ($S_{cc}(0)$) at different temperatures in both alloys.

Keyword- Activity, Concentration Fluctuations, Entropy of mixing, Excess free energy of mixing, Partial excess free energy of mixing, Order energy parameter, Optimization procedure.

1 INTRODUCTION

Alloys have wide applications in modern technologies based in electronic industry, photonic industry, fiber optic communication, etc. The rapid advances in these technologies have been made possible due to the availability of a variety of crystalline materials. However, they are grown from the liquid state near the melting temperature of constituent elements. Thus, the study of the thermodynamic, surface, transport and structural properties of alloys in liquid state is very important to explain the mixing behaviors of the constituents and subsequently the corresponding properties of crystalline materials.

Indium is a chemical element which is soft, highly ductile with bright shining. It has low melting point so that it is used in fusible alloys, solders, semiconductor related appliances, etc. Zinc is bluish-white and diamagnetic element which can be used in lead replacement because of high density, inexpensive, easily worked material and non-toxic nature. Zinc is also widely used in galvanization and in many alloys, especially in brass. Further, zinc and indium are used inmaking an alloy which exhibits good mechanical, electrical and thermal conductivity properties. The Zn-In alloy does not form intermetallic compounds over the entire range of composition and temperature so that it does not show brittle nature. It can be used in a protective molding to avoid reaction with moisture. The Zn-In alloy may be used as a reliable high temperature lead free solder and alkaline battery anodes [1].

In the other hand, cadmium is a highly reactive element which is widely used in standard electromotive cells, photovoltaic cells, fire protection system, electroplating of automotive aircraft, nuclear reactor to control the atomic fission, etc. Also, the cadmium can be used as a protective layer by depositing on other metals because of its resistance to corrosion [2]. The zinc and cadmium are also used in making alloys which have potential applications in step and radiation soldering. The presence of a small quantity of cadmium in the alloys can improve the hardness, mechanical and tensile strength, fatigue strength, wear resistance, etc.

Several theoretical models [2], [3], [4], [5], [6], [7], [8], [9], [10], [11] have long been used by metal physicists to understand the mixing properties of alloys in molten state. In this paper we have used quasi-lattice theory by considering the coupled effect of size ratio and energetic contribution to predict the values of thermodynamic and structural properties of Zn-In and Zn-Cd liquid alloys at different temperatures [6], [10], [12]. We have used the optimization procedure [10] to determine the excess free energy of mixing and optimized coefficients of Zn-In and Zn- Cd liquid alloys which are then used to determine the partial excess free energy of mixing as well as activity of the components and hence concentration fluctuations in long wavelength limit (Scc(0)) of Zn-In and Zn-Cd liquid alloys at different temperatures over the entire range of concentration.

2 FORMALISM

2.1 Free Energy of Mixing (G_M) and Concentration Fluctuation in Long Wave-length Limit (Scc(0))

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We consider one mole binary liquid mixture of c_A=c atoms of constituent A (≡Zn) and c_B= (1-c) of constituent B (≡In, Cd). If G_M be the free energy of mixing, then the concentration fluctuation in long wavelength limit (Scc(0)) at a temperature (T) as defined by Bhatia and Thornton [4], [13] is given by

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

where R is the molar gas constant.

Let the constituent atoms A and B of the binary mixture differ from one another in shape and size. If we consider the entropic effect as well as energetic effect of the binary mixture (i.e. $H_M \neq 0$), Quasi- Lattice Theory (QLT) of liquid mixture as explained by Guggenheim [6] in the limit Z(the coordination number)→ ∞ provides an expression for G_M as

$$G_M = RT[(1-c)\ln\psi + c\ln(1-\psi) + c\,\psi\,W] \quad \text{-------(2)}$$

with $\psi = \frac{\varphi C_B}{C_A + \varphi C_B} = \frac{\varphi(1-C)}{C+\varphi(1-C)}$ ------- (3)

and $W = \beta_A\left(\frac{\omega}{K_B T}\right)$ ------- (4)

which represents order energy parameter, where β_A is the number of a group of lattice sites, occupying by N atoms of the constituent A and ω is the interchange energy, given by

$$\omega = \left(\epsilon_{AB} - \frac{\epsilon_{AA}+\epsilon_{BB}}{2}\right) \quad \text{------- (5)}$$

Here, ϵ_{ij} are i-j bond strength, K_B is the Boltzmann constant and φ ($=\frac{\varphi_B}{\varphi_A}; \varphi_A < \varphi_B$) is the size ratio.

In "(2)," the first two terms on right hand side appear due to entropic contribution and last term is due to enthalpic contribution. With "(1)," and "(2)," we obtain

$$S_{cc}(0) = \frac{C_A C_B}{1 - C_A C_B\, g(\varphi, W)} = \frac{C(1-C)}{1 - C(1-C)\, g(\varphi, w)} \quad \text{------- (6)}$$

with $g(\varphi, w) = \frac{2\varphi^2 W - (\varphi-1)^2\{C + \varphi(1-C)\}}{\{C+\varphi(1-C)\}^3}$ -------(7)

By using the concept of activity, the concentration fluctuations is also determined from the relation

$$S_{cc}(0) = c_i a_j \left(\frac{\partial a_j}{\partial c_j}\right)^{-1}_{T,P} \quad \text{------- (8)}$$

where c_i and a_j are the concentration and activity of component i, and j (i, j ≡ A, B) respectively.

Also, the ideal value of concentration-concentration fluctuations, when the interchange energy ω is zero, is normally calculated from the relation

$$s^{id}_{cc}(0) = c(1-c) \quad \text{------- (9)}$$

The concentration fluctuations (Scc(0)) is the structural property of binary liquid alloys which is very useful to know the nature of liquid alloys. Though it is very difficult to measure the value of Scc(0) directly from experiment, it can be calculated from the experimental value of activity by using "(8)," which represents its experimental value. The mixing behavior, i.e. the nature of interaction of components in binary liquid alloys can be analyzed with the help of deviation of Scc(0) from $s^{id}_{cc}(0)$. For the given composition, the binary liquid alloy of ordering nature is expected if Scc(0) < $s^{id}_{cc}(0)$, and the tendency of segregation is expected if Scc(0) > $s^{id}_{cc}(0)$.

2.2 Activity (a)

From the standard thermodynamic relation, the activity of a constituent i of the binary alloys is given by

$$\ln a_i = G_M + c_j\left(\frac{\partial G_M}{\partial c_i}\right) \quad \text{------(10)}$$

where a_i and c_j are the activity and concentration of component i and j (i, j ≡A, B) respectively.
On solving, " (2)," and "(10)," provide

$$\ln a_A = \ln(1-\psi) + \psi\left\{\frac{(\varphi-1)}{\varphi}\right\} + \psi^2 W \quad \text{------(11)}$$

and

$$\ln a_B = \ln\psi - (1-\psi)(\varphi-1) + W\varphi(1-\psi)^2 \quad \text{------(12)}$$

Where a_A and a_B are the activity of the constituent A and B respectively.

3 RESULTS AND DISCUSSION

For the calculation of concentration fluctuations, Scc(0), in liquid alloys at a temperature, we require two parameters i.e. φ, and W. The parameter φ for a binary liquid alloy has been determined by knowing the atomic volumes of the constituents A and B at the required temperature T from the relation

$$\varphi_i(T) = \varphi_i(T_m)\,[1 + \alpha_{p\,i}\,(T - T_m)] \quad \text{------(13)}$$

where i = A; B, $\varphi_i(T_m)$ is the atomic volume at the melting temperature (T_m) and $\alpha_{p\,i}$ is the coefficient of thermal expansion of the constituent i.

For Zn-In binary liquid alloy at 700K, the values of $\alpha_{p\,i}$ and $\varphi_i(T_m)$ are taken from Shimoji [14] and the value of size ratio, φ is found to be 1.68763. The value of order energy parameter, W has been estimated to reproduce simultaneously an overall fit for the experimental values of free energy of mixing, G_M , and activity a_i (i= A, B) of Zn-In liquid alloys at 700K from Hultgren et al. [15]. The best fit value of W at 700K is found to be 1.42. The theoretical

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values of G_M/RT as computed by using "(2)," and experimental values of G_M /RT of Zn-In liquid alloys at 700 K in the entire concentration range from 0.1 to 0.9 are shown in "Fig-1(a)," which are in excellent agreement. The experimental value of G_M/RT at 700K is minimum at the concentration, c = 0.4, which is found to be -0.294181 and the theoretical value of G_M/RT at 700K is minimum at the concentration, c= 0.3 which is found to be -0.297758.

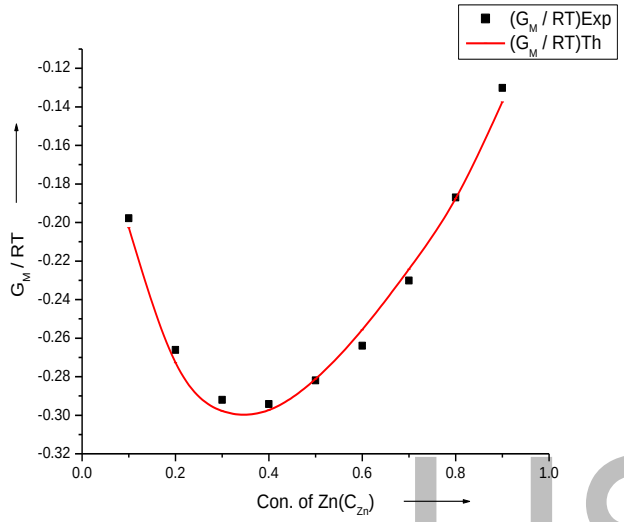

Fig-1(a):Graph for $(G_M/RT)_{Exp}$ and $(G_M/RT)_{Th}$ versus C_{Zn} of Zn-In at 700 K

For Zn-Cd binary liquid alloys at 800 K, the value of size ratio, φ is found to be 1.4276 according to values of α_{pi} and φ_i (Tm) from Shimoji [14]. But the theoretical values of G_M/RT as computed by using "(2)," on taking this value of φ in the entire concentration range from 0.1 to 0.9 are not found in good agreement with the corresponding experimental values of G_M/RT. However, the value of φ is adjusted to match the theoretical and experimental values of G_M/RT over the entire concentration range and the best fit value of φ at 800K is found to be 1.1276. The value of order energy parameter, W has been estimated to reproduce simultaneously an overall fit for the experimental values of free energy of mixing, G_M , and activity a_i (i= A, B) of Zn-Cd liquid alloys at 800K from Hultgren et al. [15]. The best fit value of W at 800K is found to be 1.15. The theoretical values of G_M/RT as computed by using "(2)," and experimental values of G_M/RT of Zn-Cd liquid alloys at 800K in the entire concentration range from 0.1 to 0.9 are shown in "Fig-1(b)" which are in excellent agreement. The experimental value of G_M/RT at 800K is minimum at the concentration, c = 0.5, which is found to be -0.392721 and the theoretical value of G_M/RT at 800K is minimum at the same concentration, c= 0.5 which is found to be - 0.390206 .

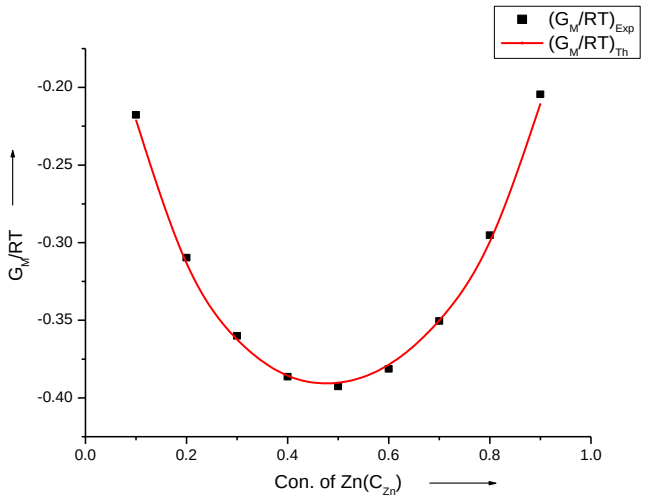

Fig-1(b): Graph for $(G_M/RT)_{Exp}$ and $(G_M/RT)_{Th}$ versus C_{Zn} of Zn-Cd at 800 K

The theoretical values of $\ln a_i$ (i = A, B) as computed by using "(11)," and "(12)," (on taking φ = 1.68763 and W = 1.42), and experimental values of $\ln a_i$ (i = A, B) of Zn-In liquid alloys at 700K over the entire concentration range are shown in "Fig-2(a)," which are in good agreement. Again, the theoretical values of $\ln a_i$ (i = A, B) as computed by using "(11)," and "(12)," (on taking φ = 1.1276 and W = 1.15), and experimental values of lnai (i = A, B) of Zn-Cd liquid alloys at 800K over the entire concentration range are shown in "Fig-2(b)," which are also in good agreement.

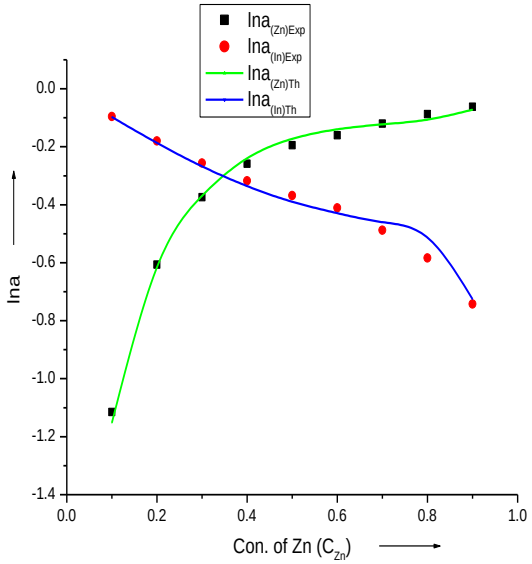

Fig-2(a):Graph for $\ln a_{(Zn)Exp}$ and $\ln a_{(Zn)Th}$; $\ln a_{(In)Exp}$ and $\ln a_{(In)Th}$ versus C_{Zn} of Zn-In at 700 K

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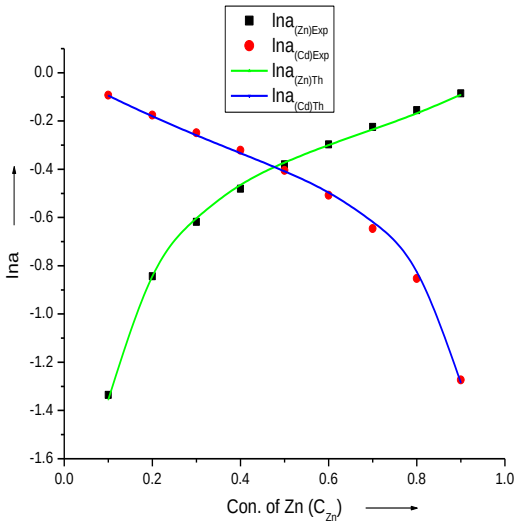

Fig-2(b): Graph for $lna_{(Zn)Exp}$ and $lna_{(Zn)Th}$; $lna_{(Cd)Exp}$ and $lna_{(Cd)Th}$ versus C_{Zn} of Zn-Cd at 800 K

For Zn- In liquid alloys at 700K, the theoretical values of Scc(0) over the entire concentration range have also been calculated by taking the above mentioned value of φ (i.e. 1.68763) and W (i.e. 1.42) in "(6)" while the experimental values of Scc(0) have been calculated by taking the experimental values of activity in "(8)". The theoretical and experimental values Scc(0) at 700K of Zn-In liquid alloys in the entire concentration are shown in "Fig-3(a)" which are in reasonable agreement with some deviations in the concentration, c = 0.6 to 0.7. The experimental value of Scc(0) is maximum at concentration, c = 0.5 which is found to be 1.137 while the theoretical value of Scc(0) is maximum at concentration, c = 0.7 which is found to be 2.089. It is obvious that the concentration fluctuations, Scc(0), at 700K of Zn-In liquid alloy is greater than the value of $S_{cc}^{id}(0)$ (≡ c (1-c)) at each concentration which indicates the segregating nature of Zn-In liquid alloys.

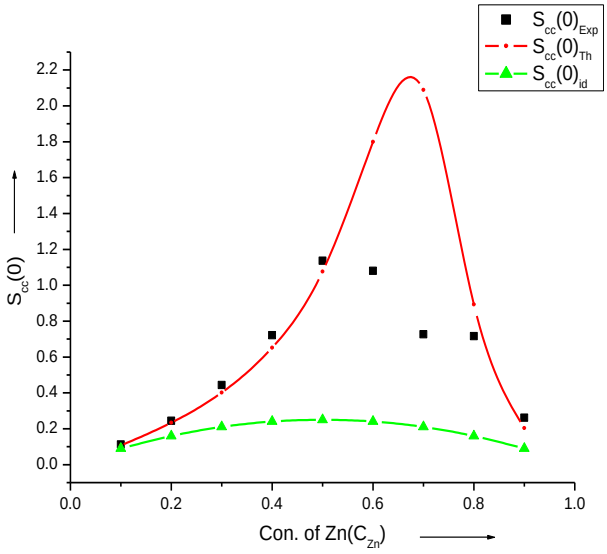

Fig-3(a):Graph for $S_{cc}(0)_{Exp}$; $S_{cc}(0)_{Th}$ and $S_{cc}(0)_{id}$ versus C_{Zn} of Zn-In at 700 K

For Zn-Cd liquid alloy at 800K, the theoretical values of Scc(0) over the entire concentration range have also been calculated by taking the above mentioned values of φ (i.e. 1.1276) and W (i.e. 1.15) in "(6)" while experimental values of Scc(0) have been calculated by taking the experimental values of activity in "(8)". The theoretical and experimental values of Scc(0) at 800K of Zn-Cd liquid alloys in the entire concentration range are shown in "Fig-3(b)" which are in good agreement with some deviations in the concentration region, c = 0.5 to 0.6. The experimental value of Scc(0) is maximum at concentration, c = 0.5 which is found to be 0.552 and the theoretical value of Scc(0) is also maximum at concentration, c = 0.5 which is found to be 0.631. It is obvious that the concentration fluctuations, Scc(0), at 800 K of Zn-Cd liquid alloy is greater than the value of $S_{cc}^{id}(0)$ (≡ c (1-c)) at each concentration which indicates the segregating nature of Zn-Cd liquid alloy.

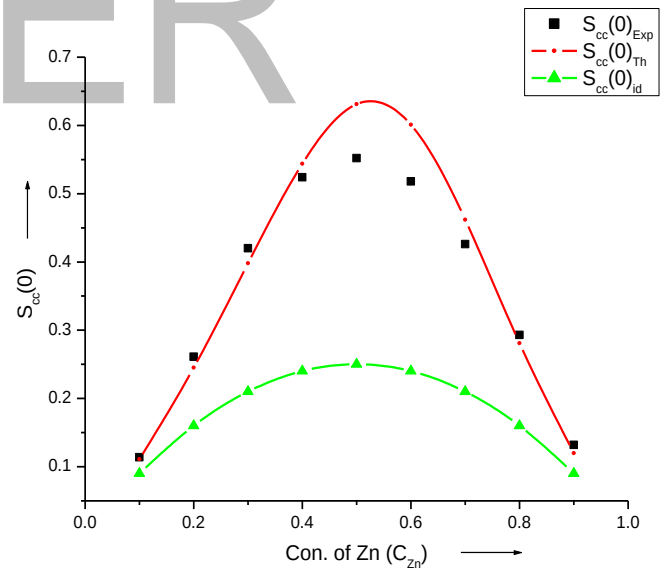

Fig-3(b): Graph for $S_{cc}(0)_{Exp}$; $S_{cc}(0)_{Th}$ and $S_{cc}(0)_{id}$versus C_{Zn} of Zn-Cd at 800 K

4 OPTIMIZATION OF FREE ENERGY OF MIXING; ACTIVITY; CONCENTRATION FLUCTUATIONS

Optimization procedure[10] is the thermodynamic description, obtained by using statistical thermodynamics or polynomial expressions. The adjustable coefficients, used in this process, are estimated by least-square method. This procedure has good strength to obtain a consistent set of model parameters in an analytical approach which gives

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idea to extrapolate into temperature and concentration region in which the direct experimental determination is unavailable.

The various thermodynamic properties, described by a power-series law whose coefficients are A, B, C, D, E, …….(say), are determined by least-square method. The heat capacity can be expressed as

$$Cp = - C - 2DT - 2ET^{-2} - \ldots\ldots\ldots\ldots \quad \text{----- (14)}$$

From the thermodynamic relation, the enthalpy is given by

$$H = H(T_0) + \int_0^T C_p dT$$

$$= A - CT - DT^2 + 2ET^{-1} - \ldots\ldots\ldots\ldots \quad \text{------(15)}$$

Also, the entropy is given by

$$S = S(T_0) + \int_0^T \frac{C_p}{T} dT$$

$$= - B - C(1 + \ln T) - 2DT + ET^{-2} - \ldots\ldots\ldots \quad \text{------ (16)}$$

By using "(15)," and "(16)" in the Thermodynamic relation, G = H – TS, we get the temperature(T) dependent free energy as

$$G = A + BT + CT \ln T + DT^2 + ET^{-1} + \ldots\ldots \quad \text{------ (17)}$$

The composition dependence of excess free energy of mixing is given by Redlich-Kister polynomial equation as

$$G_M^{XS}(c,T) = c(1-c)\sum_{l=0}^{m} K_l(T)[c-(1-c)]^l \quad \text{----- (18)}$$

with $K_l(T) = A_l + B_l T + C_l T \ln T + D_l T^2 + \ldots\ldots$ ------ (19)

The coefficients K_l depend upon the temperature same as that of G in "(17)". The least-square method can be used to obtain the parameters involved in "(18)". For this purpose, we require the excess free energy of mixing (G_M^{XS}) of the binary liquid alloys at different temperatures. The values of G_M^{XS} can be determined by the relation

$$G_M^{XS} = G_M - G_M^{Id}$$

$$= G_M - RT[c \ln c + (1-c)\ln(1-c)] \quad \text{----- (20)}$$

Thus, we require the values for the free energy of mixing (G_M) of binary liquid alloys at different temperatures which can be calculated from "(2)," for different temperatures by knowing the values of order energy parameter (W) at different temperatures from the relation

$$W(T_k) = W(T) + \frac{dW}{dT}(T_k - T) \quad \text{------(21)}$$

where W(T) is the order energy parameter at the given temperature T, $W(T_k)$ is order energy parameter at required temperature T_k and $\frac{dW}{dT}$ represents temperature derivative of order energy parameter for the given liquid alloy.The temperature derivative of order energy parameter $(\frac{dW}{dT})$ has been estimated by using the experimental data of entropy of mixing (S_M) of the given liquid alloy at temperature T with the help of the relation

$$S_M = -\left(\frac{\partial G_M}{\partial T}\right)$$

$$= -R[(1-c)\ln\psi + c\ln(1-\psi) + c\,\psi(W + T\frac{dW}{dT})] \quad \text{------(22)}$$

The best fit value of $\frac{dW}{dT}$ for Zn-In liquid alloy is found to be –0.00255 K^{-1}. The calculated and experimental values of $\frac{S_M}{R}$ over entire concentration range are in good agreement as shown in "Fig-4(a)".

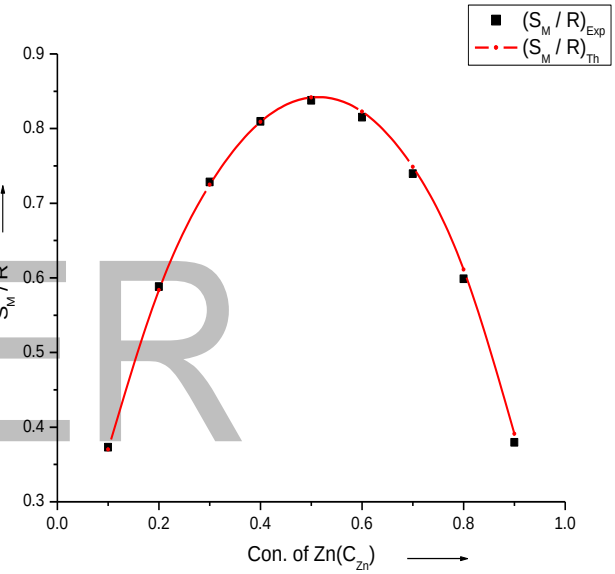

Fig-4(a):Graph for $(S_M/R)_{Exp}$ and $(S_M/R)_{Th}$ versus C_{Zn} of Zn-In at 700 K

By using the best fit value of $\frac{dW}{dT}$ and W(T) at the temperature T= 700K (as obtained in section-3 for Zn-In liquid alloy) in "(21)," the values of $W(T_k)$ at temperature T_k = 750K, 800K, 900K are estimated and listed in Table-1.

Table-1: Estimated values of order energy parameter (W) at different temperatures in Zn-In liquid alloy.

Temperature (T_k) in K	Order Energy Parameter, $W(T_k)$
750	1.2925
800	1.1650
900	0.9100

The best fit value of $\frac{dW}{dT}$ for Zn-Cd liquid alloy is found to be –0.0015 K^{-1}. The calculated and experimental values of $\frac{S_M}{R}$ over entire concentration range are in good agreement as shown in "Fig-4(b)".

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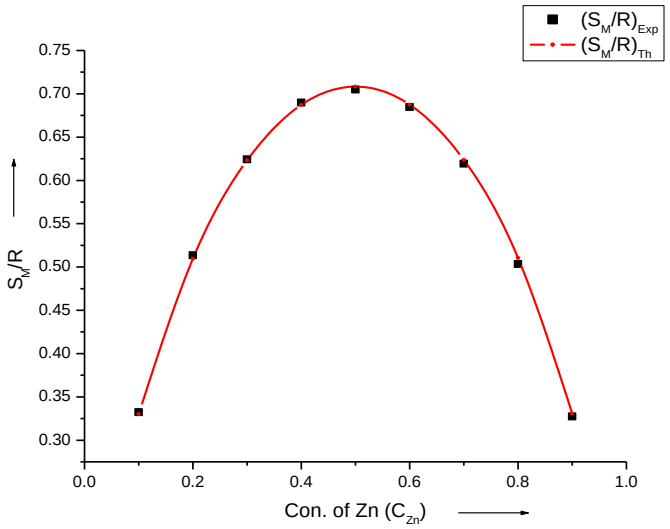

Fig-4(b): Graph for $(S_M/R)_{Exp}$ and $(S_M/R)_{Th}$ versus C_{Zn} of Zn-Cd at 800 K

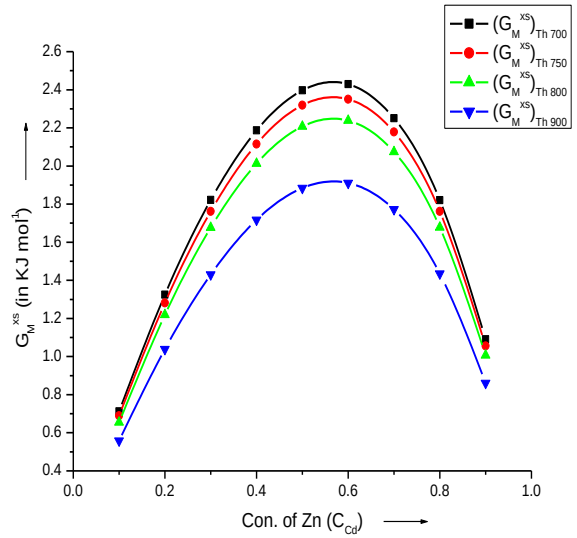

Fig-5(a): Graph for $(G_M^{XS})_{Th\ 700}$, $(G_M^{XS})_{Th\ 750}$, $(G_M^{XS})_{Th\ 800}$ and $(G_M^{XS})_{Th\ 900}$ versus C_{Zn} of Zn-In

By using the best fit value of $\frac{dW}{dT}$ and W(T) at the temperature T= 800 K (as obtained in section-3 for Zn-Cd liquid alloy) in "(21)," the values of $W(T_k)$ at temperature T_k = 850K, 900K, 1000K are estimated and listed in Table-2.

Table-2: Estimated values of order energy parameter (W) at different temperatures in Zn-Cd liquid alloy.

Temperature (T_k) in K	Order Energy Parameter, $W(T_k)$
850	1.075
900	1.000
1000	0.850

It is also to be mentioned that the values of various thermodynamic properties due to change in size ratio because of change in temperature in both alloys change only in negligible amount. Thus, for entire calculation, the value of size ratio is taken constant (i.e. φ = 1.68763 for Zn-In and φ = 1.1276 for Zn-Cd alloys). The values of free energy of mixing (G_M) of Zn-In liquid alloys at different temperatures (i.e. at 700K, 750K, 800K and 900K) have been computed by using the corresponding values of W in "(2)" over the entire range of concentration ranging from 0.1 to 0.9 and then they are used to calculate the corresponding excess free energy of mixing (G_M^{XS}) of Zn-In liquid alloys at different temperatures (i.e. 700K, 750K, 800 K and 900 K) by using "(20)" which are shown in "Fig.-5(a)".

The least-square method has been used to calculate the parameters involved in "(18)" which are again used to determine the optimized coefficients involved in "(19)" for Zn-In liquid alloy and they are listed in the Table-3.

Table-3: Calculated values of optimized coefficients A_l, B_l, C_l, D_l (l = 0 to 3) for Zn-In liquid alloy

Values of l	A_l (J mol^{-1})	B_l (J mol^{-1} K^{-1})	C_l (J mol^{-1}K^{-1})	D_l (Jmol^{-1}K^{-2})
0	0.000000002	32.336030819	0.000000000	-0.026623211
1	0.000000017	8.367880093	0.000000000	-0.006811547
2	-0.000000032	2.211345724	0.000000000	-0.001789592
3	0.000000008	0.567678668	0.000000000	-0.000457867

Similarly, the values of free energy of mixing (G_M) of Zn-Cd liquid alloys at different temperatures (i.e. at 800K, 850K, 900K and 1000K) have been computed by using the corresponding values of W in "(2)" over the entire range of concentration ranging from 0.1 to 0.9 and then they are used to calculate the corresponding excess free energy of mixing (G_M^{XS}) of Zn-Cd liquid alloys at different temperatures (i.e. 800K, 850K, 900K and 1000K) by using "(20)" which are shown in "Fig.-5(b)".

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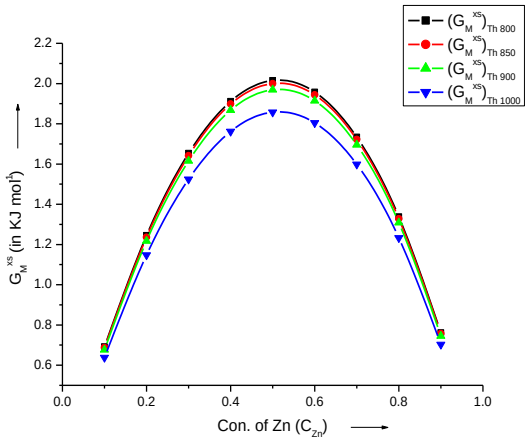

Fig-5(b): Graph for $(G_M^{XS})_{Th\ 800}$, $(G_M^{XS})_{Th\ 850}$, $(G_M^{XS})_{Th\ 900}$ and $(G_M^{XS})_{Th\ 1000}$ versus C_{Zn} of Zn-Cd

The least-square method has been used to calculate the parameters involved in "(18)" which are again used to determine the optimized coefficients involved in "(19)" for Zn-Cd liquid alloy and they are listed in the Table-4.

Table-4: Calculated values of optimized coefficients A_l, B_l, C_l, D_l ($l = 0$ to 3) for Zn-Cd liquid alloy.

Values of l	A_l (J mol^{-1})	B_l (J mol^{-1} K^{-1})	C_l (J mol^{-1} K^{-1})	D_l (J mol^{-1} K^{-2})
0	-0.000000028	20.649739776	0.000000000	-0.013218929
1	0.000000006	1.239637804	0.000000000	-0.000792788
2	0.000000038	0.074488766	0.000000000	-0.000047615
3	-0.000000004	0.004468659	0.000000000	-0.000002856

Again, the partial quantities, i.e. the partial excess free energy of mixing of the components A(≡ Zn) and B(≡In) in Zn-In liquid alloys, and A(≡ Zn) and B(≡Cd) in Zn-Cd liquid alloys are given by

$$\tilde{G}_{M,\ A}^{X\ S}(c,T) = (1-c)^2 \sum_{l=0}^{m} K_l(T)[\,(1+2l)c-(1-c)]\,(2c-1)^{l-1} \qquad \text{------(23)}$$

And $$\tilde{G}_{M,\ B}^{X\ S}(c,T) = c^2 \sum_{l=0}^{m} K_l(T)\,[\,c-(1+2l)(1-c)]\,(2c-1)^{l-1} \qquad \text{------(24)}$$

The "(23)," and "(24)" have been used to compute the partial excess free energy of mixing for Zn and In component separately in Zn-In liquid alloys at different temperatures (i.e. 700K, 750K, 800K and 900K) with the help of optimized coefficients. Further, the activity coefficients (γ_i), (i ≡ Zn or In), at different temperatures over the entire range of concentration for Zn or In component separately have been computed from the relation

$$\tilde{G}_{M,\ i}^{X\ S} = RT\ \ln\gamma_i \qquad \text{------(25)}$$

with $$\gamma_i = \frac{a_i}{c_i} \qquad \text{------(26)}$$

where a_i and c_i be the activity and concentration of the component i (i ≡Zn or In) respectively of Zn-In liquid alloy at corresponding temperature. Finally, the optimized values of the activity of both the components have been used to calculate the concentration fluctuations in long wave-length limit (Scc(0)) of Zn-In liquid alloys at different temperatures by using "(8)," which are shown in "Fig.-6(a)".

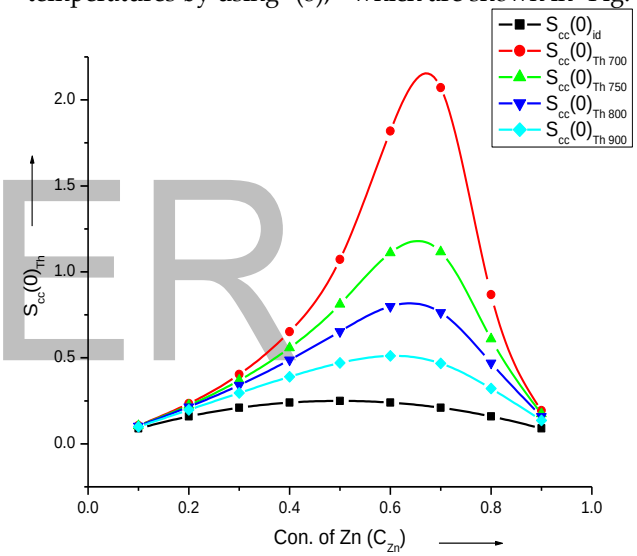

Fig-6(a): Graph for $S_{cc}(0)_{Th}$ at different Temperatures versus C_{Zn} of Zn-In liquid alloy

Again, the "(23)," and "(24)" have also been used to compute the partial excess free energy of mixing for Zn and Cd component separately in Zn-Cd liquid alloys at different temperatures (i.e. 800K, 850K, 900K and 1000K) with the help of optimized coefficients. Further, the activity coefficients (γ_i), (i ≡ Zn or Cd), and hence activity of Zn or Cd component at different temperatures over the entire range of concentration have been computed from the "(25)," and "(26)". Finally, the optimized values of the activity of both the components have been used to calculate the concentration fluctuations in long wavelength limit (Scc(0)) of Zn-Cd liquid alloys at different temperatures by using "(8)," which are shown in "Fig-6(b)".

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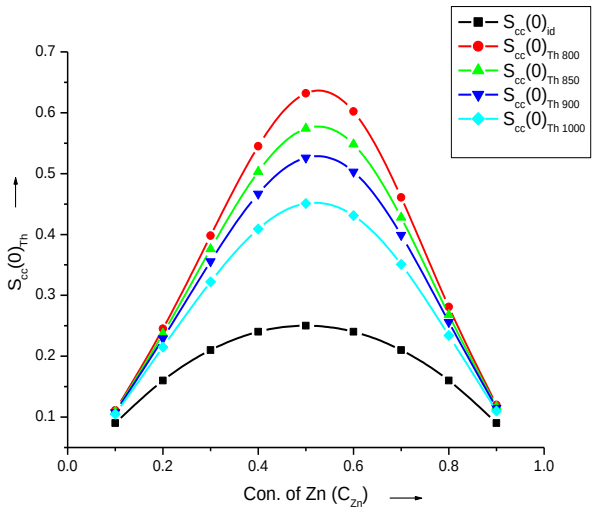

Fig-6(b): Graph for $S_{cc}(0)_{Th}$ at different Temperatures versus C_{Zn} of Zn-Cd liquid alloy

It is obvious that the concentration fluctuations in long wavelength limit of Zn-In liquid alloy at the temperature above 700K decreases and moves sharply towards the ideal value of concentration fluctuations $(S_{cc}^{id}(0))$ on increasing the temperature but remains greater than the ideal value of concentration fluctuations which indicates that the segregating nature of Zn-In liquid alloy decreases on increasing the temperature. In case of Zn-Cd liquid alloy, the concentration fluctuations in long wavelength limit at the temperature above 800K decreases and moves slowly towards the ideal value of concentration fluctuations $(S_{cc}^{id}(0))$ on increasing the temperature but remains greater than the ideal value of concentration fluctuations which indicates that the segregating nature of Zn-Cd liquid alloy also decreases on increasing the temperature.

On comparing the two alloys, it can be concluded that the Zn-In binary liquid alloy is more interactive than the Zn-Cd binary liquid alloy, and the segregating tendency in Zn-In binary liquid alloy decreases sharply than that of Zn-Cd binary liquid alloy as the temperature increases.

5 CONCLUSION

From this theoretical investigations in Zn-In and Zn-Cd liquid alloys, following conclusions may be drawn:

- The size ratio (φ) and order energy parameter (W) play important role in the mixing properties of both the alloys.
- In both alloys, the free energy of mixing (G_M), entropy of mixing (S_M) and concentration fluctuations (Scc(0)) are symmetrical or very close to it at the equiatomic composition (i.e. c = 0.5) so that they are symmetric alloys.
- The values of concentration fluctuations over the temperature range 700K to 900K in Zn-In and 800K to 1000K in Zn-Cd alloys are always greater than the ideal value of concentration fluctuations which indicate the segregating nature of both the alloys in this range of temperature.
- In both alloys, the order energy parameter (W) is temperature dependent. The values of W at the temperature above 700K in Zn-In as well as above 800K in Zn-Cd liquid alloys are +ve and their values decrease with the increase in temperature which show that the segregating nature of both the alloys decrease as the temperature increase.
- In both alloys, the change in various thermodynamic properties due to change in size ratio because of change in temperature is only negligible so that the size ratio is assumed as constant during the whole calculation, though the temperature changes.
- The value of concentration fluctuations nearby equiatomic composition in case of Zn-In liquid alloy decreases sharply in comparison to Zn-Cd liquid alloy as the temperature increases over the temperature range 700K to 1000 K which indicates that the Zn-In liquid alloy is more interactive than the Zn-Cd liquid alloy.

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