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# Entropy of Mixing of Cadmium-based Liquid Alloys

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## *Abstract*

*Cadmium is a highly reactive metal. At the time of formation of binary alloys in liquid phase it often forms complexes. In the present work we have considered two such complex forming binary liquid alloys of cadmium e.g. Cd-Na and Cd-Mg. The former alloy shows anomaly in its thermodynamic properties of mixing. On the other hand, the alloying behavior of the latter one is symmetric around the equi-atomic composition. We have computed their entropy of mixing ($S_M$) for different concentrations of the ingredients by using the quasi-lattice chemical model. The results explain the observed anomaly as well as symmetry in $S_M$ of the present alloys.*

***Keywords:*** *Binary liquid alloys of cadmium, Quasi-lattice chemical model, Entropy of mixing*

## Introduction

A large number of binary liquid alloys, especially the complex forming ones, exhibit interesting behavior as a function of concentration as regards the thermodynamic and electrical properties. The properties of mixing are not generally symmetrical about the equi-atomic composition—deviating maximally from those of the ideal alloys. Some of these alloys also depict metal-nonmetal transition across a narrow band of concentrations. The liquidus lines are usually S-shaped and the heat of mixing and excess free energy of mixing are large negative quantities at one or other concentrations[1–3]. The anomalous behavior of these liquid alloys is least understood and demands extensive theoretical investigation[4–7].

The alloying behavior 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 [8,9] and hard sphere model[10–13]. But they 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 conformal solution model[14] has been used by many theoreticians to study $S_{cc}(0)$ of different binary alloys[15,16]. But this model cannot be used to study the short-range order parameters. However, in the

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eighty's decade of the last century soft sphere model[17] and one-component plasma theory[18] came into being for the binary liquid alloys to supplement the electronic theory of mixing. But the approach as a whole is found to be suitable for explaining mainly the electrical properties of alloys. On the other hand, the statistical mechanical theory of mixing can be successfully used to obtain the analytical expressions for various thermodynamic functions.

In the present work two binary liquid alloys of cadmium have been considered *e.g.* Cd-Na and Cd-Mg. The liquidus lines of these alloys reveal that the constituent species form complexes. So, we have considered the quasi-lattice chemical model[19] for computation of their entropy of mixing. It is a statistical mechanical model in which grand partition function is used with the assumption that the energy of a given nearest neighbor bond is different if it belongs to the complex than if it does not.

In Section 2 the general theory of quasi-lattice chemical model is briefly narrated and working expressions are furnished. Section 3 deals with the results of computation of the entropy of mixing of these complex forming binary liquid alloys of cadmium. Section 4 provides a brief conclusion.

## Experimental Methods

*Basic formalism*

The quasi-lattice chemical model for the binary liquid alloys, in essence, assumes the existence of chemical complexes $A_\mu B_\nu$, where $\mu$ & $\nu$ 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[20]:

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

where N is the total number of 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

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

$K_B$ being the Boltzmann constant and T the absolute temperature.

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

$$G_M = G_M^{xs} + RT[c\ln c + (1-c)\ln(1-c)], \quad (3)$$

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

$$H_M = N\left[\Phi\left(\omega - T\frac{d\omega}{dT}\right) + \Phi_{AB}\left\{\Delta\omega_{AB} - T\frac{d}{dT}(\Delta\omega_{AB})\right\} +\right.$$

$$\Phi_{AA}\left\{\Delta\omega_{AA} - T\frac{d}{dT}\left(\Delta\omega_{AA}\right)\right\} + \Phi_{BB}\left\{\Delta\omega_{BB} - T\frac{d}{dT}\left(\Delta\omega_{BB}\right)\right\}\Bigg], \quad (4)$$

where $\Phi(c) = c(1 - c)$. Now, the entropy of mixing can be found out by using (3) and (4) :

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

## Results and discussion

*Cadmium-sodium liquid alloy*

In this case the phase diagram reveals that the complex $Cd_2Na$ is most likely to be formed within the liquid alloy[21]. So, for this alloy

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

Finding the values of the $\beta$-functions in (ii), (i) becomes

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

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

The value of the interaction parameters in (i) has been determined from the experimental values of free energy of mixing at 673 K. in the concentration range of cadmium from 0.1 to 0.9[21] by the method of successive approximation:

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

The observed values of heat of mixing at 673 K. in the concentration range of cadmium from 0.1 to 09[21] are used to find out the temperature derivative of interaction parameters in (iv) by successive approximation method:

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

Finally, the entropy of mixing of Cd-Na liquid alloys has been computed at 673 K. as a function of concentration from (v) on taking the corresponding values of free energy of mixing and heat of mixing. The computed values of the entropy of mixing of cadmium-sodium liquid alloys are furnished in Table 1 along with its observed values at 673 K. in the concentration range of cadmium from 0.1 to 0.9[21].

The plots of $S_M/R$ versus $c_{Cd}$ are depicted in Figure 1 for both the theoretical and experimental values, which show good agreement. The theoretical value of $S_M$ is maximum at $c_{Cd}$=0.35 while experimentally it is found to be maximum at $c_{Cd}$=0.3.

***Table 1**: Entropy of mixing of Cd-Na liquid alloys at 673 K.*

| $c_{Cd}$ | $S_M/R$ | |
|---|---|---|
| | Theoretical | Experimental* |
| 0.1 | 0.1520 | 0.2447 |
| 0.2 | 0.2916 | 0.3368 |
| 0.3 | 0.3558 | 0.3599 |
| 0.4 | 0.3609 | 0.3217 |
| 0.5 | 0.3198 | 0.2391 |
| 0.6 | 0.2457 | 0.1435 |
| 0.7 | 0.1542 | 0.0529 |
| 0.8 | 0.0583 | –0.0126 |
| 0.9 | –0.0208 | –0.0232 |

*Hultgren *et al*, 1973

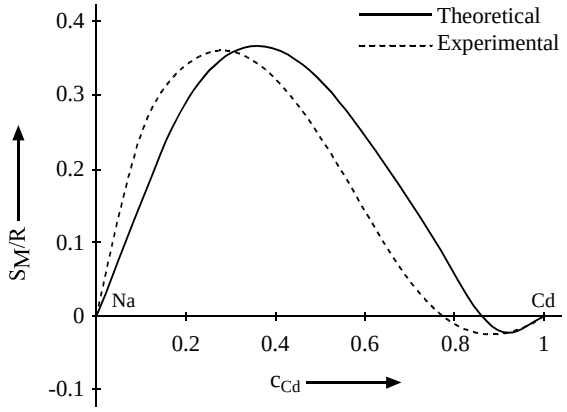


***Figure 1.** Entropy of mixing ($S_M/R$) of Cd-Na liquid alloys at 673 K. for different concentrations of cadmium.*

*Cadmium-magnesium liquid alloy*

The phase diagram of Cd-Mg alloy suggests that the complex $Cd_3Mg$ is formed within the alloy[21]. So, for the cadmium-magnesium liquid alloy

$$A \equiv Cd, \quad B \equiv Mg, \quad \mu = 3, \quad \nu = 1.$$

Finding the values of the β-functions in (ii), we have from (i)

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

$$\left. \Delta\omega_{AA}\left(-\frac{3}{20}c + \frac{2}{3}c^3 - \frac{3}{4}c^4 + \frac{2}{5}c^5 - \frac{1}{6}c^6\right)\right] \quad [\because \text{ coeff } (\Delta\omega_{BB}) = 0 \text{ for } \nu<2]$$

Like before the value of interaction parameters is determined from the observed values of free energy of mixing at 923 K[21] in the concentration range of cadmium from 0.1 to 0.9 by successive approximation method:

$$\frac{\omega}{K_B T} = -2.21, \qquad \frac{\Delta\omega_{AB}}{K_B T} = -0.35, \qquad \Delta\omega_{AA} \approx 0.$$

The experimental values of heat of mixing at 923 K[21] in the concentration range of cadmium from 0.1 to 0.9 have been used, as in the case of Cd-Na alloys, to find out the temperature derivative of interaction parameters in (4) by the method of successive approximation:

$$\frac{1}{K_B}\frac{d\omega}{dT} = -4.2, \qquad \frac{1}{K_B}\frac{d}{dT}(\Delta\omega_{AB}) = -2.3, \qquad \frac{d}{dT}(\Delta\omega_{AA}) \approx 0, \qquad \frac{d}{dT}(\Delta\omega_{BB}) \approx 0.$$

The computed values of the entropy of mixing, by using (5), of Cd-Mg liquid alloys at 923 K. are furnished in Table 2 along with its observed values in the concentration range of cadmium from 0.1 to 0.9[21].

***Table 2**: Entropy of mixing of Cd-Mg liquid alloys at 923 K.*

| $c_{Cd}$ | $S_M/R$ | |
|---|---|---|
| | Theoretical | Experimental* |
| 0.1 | 0.1001 | 0.2559 |
| 0.2 | 0.2718 | 0.4000 |
| 0.3 | 0.4312 | 0.4972 |
| 0.4 | 0.5564 | 0.5510 |
| 0.5 | 0.6323 | 0.5666 |
| 0.6 | 0.6441 | 0.5515 |
| 0.7 | 0.5796 | 0.5048 |
| 0.8 | 0.4326 | 0.4193 |
| 0.9 | 0.2114 | 0.2795 |

*Hultgren *et al*, 1973

The plots of $S_M/R$ versus $c_{Cd}$ at 923 K. are shown in Fig. 2 for both the computed and observed values. They are in fine agreement. $S_M$ is maximum at $c_{Cd}$=0.58 theoretically whereas experimentally the same is at $c_{Cd}$=0.5.

## Conclusions

The anomaly in the entropy of mixing of cadmium-sodium liquid alloys is well explained by the present theoretical model. The symmetry in $S_M$ around equi-atomic composition in case of cadmium-magnesium liquid alloys is also explained nicely by this model. The nature of curves as found experimentally is corroborated to a great extent by the computed values of entropy of mixing of these complex forming binary liquid alloys of cadmium for different concentrations of the ingredients.

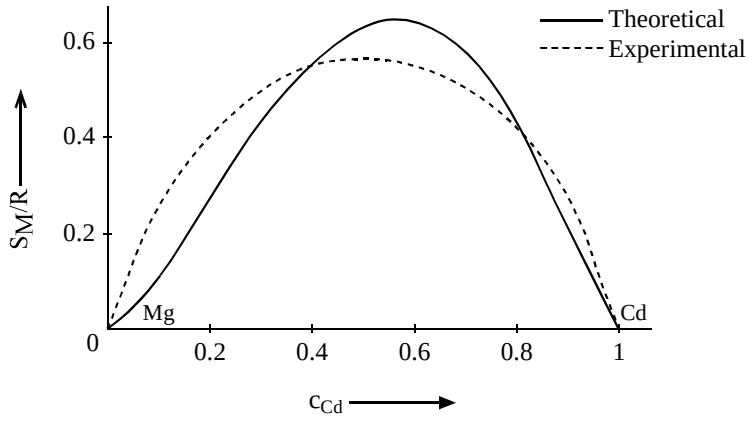


***Figure 2.*** *Entropy of mixing ($S_M/R$) of Cd-Mg liquid alloys at 923 K. for different concentrations of cadmium.*

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