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MATHEMATICAL STUDY OF THE THERMODYNAMICS OF Cd-Na LIQUID ALLOY

R. R. Thapa
Department of Mathematics
Tribhuvan University, Post-Graduate Campus, Biratnagar, Nepal

ABSTRACT
The concentration dependent thermodynamic properties of cadmium-sodium liquid alloy are interesting in many ways. The free energy of mixing, entropy of mixing and heat of mixing are quite asymmetric about the equi-atomic composition. The phase diagram of Cd-Na alloy shows a wavy liquidus line with a small hump around the stoichiometric composition. The quasi-lattice chemical model is used for computation of its thermodynamic entities. The results explain the observed asymmetry in the properties of mixing of Cd-Na liquid alloy around equi-atomic composition.

Key words: Binary alloy, Equi-atomic composition, Quasi-lattice model, Ordering energy, Free energy of mixing, Entropy of mixing, Heat of mixing.

INTRODUCTION

There are large number of binary alloys the properties of mixing of which are not symmetrical about the equi-atomic composition and deviate maximally from that of the ideal alloys. The anomalous behaviour of these liquid alloys is least understood and demands extensive investigations. Since long metal physicists—experimentalists [4, 5, 8] as well as theoreticians [1, 3, 6, 7]—are trying to interpret the physical properties of liquid alloys so that their alloying behaviour could adequately be comprehended. The thermodynamics of cadmium-sodium liquid alloy is due to the formation of complex Cd_2Na as revealed from its phase diagram [5].

MATERIALS AND METHOD

FORMULATION

The quasi-lattice model, as developed by Bhatia and Singh for the binary liquid alloys, is a statistical model in which grand partition function is used. The model, in essence, assumes the existence of chemical complexes $A_\mu B_\nu$, where μ & ν are small integers and A & B the constituent species of the alloy. 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. Considering the cadmium-sodium alloy for which A ≡ Cd, B ≡ Na, $\mu=2$ and $\nu=1$, the expression for excess free energy of mixing comes to be [2]

$$G_M^{xs} = N[\omega c(1-c)+\Delta\omega_{AB}\{(1/6)c+c^2-(5/3)c^3+(1/2)c^4\}+\Delta\omega_{AA}\{-(1/4)c+(1/2)c^2-(1/4)c^4\}], \quad \text{(i)}$$

where N is the total number of atoms of A and B in the alloy, 'c' the concentration of A-atoms and ω's the ordering energies. Hence, the free energy of mixing of a complex forming binary liquid alloy,

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

where R is the universal gas constant and T the absolute temperature.

The excess entropy of mixing is given by

$$S_M^{xs} = -(d\, G_M^{xs}/dT)_P \quad \text{(iii)}$$

So, the entropy of mixing of such a binary liquid alloy

$$S_M = S_M^{xs} + R[c\ln c + (1-c)\ln (1-c)] \quad \text{(iv)}$$

Now, the heat of mixing can be found out by using equations (i) and (iii):

$$H_M = G_M^{xs} + TS_M^{xs} \quad \text{(v)}$$

RESULT AND DISCUSSION

The values of interaction parameters are determined from the experimental values [5] of G_M in the concentration range from 0.1 to 0.9. We have envisaged

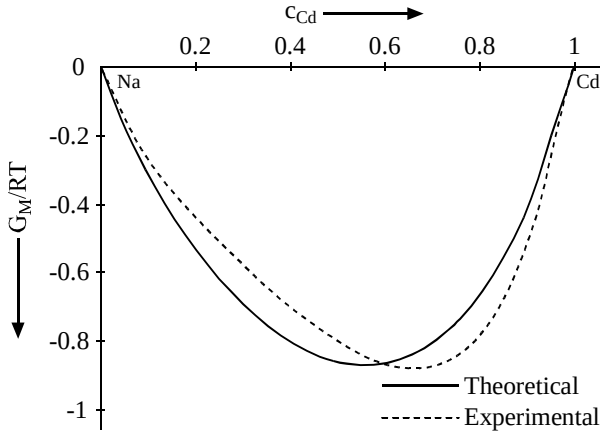
$$\omega/K_BT = 0.7,\ \Delta\omega_{AA} \approx 0 \text{ and } \Delta\omega_{AB}/K_BT = -2.2,$$

where K_B is the Boltzmann constant and T=673 K. The theoretical and experimental values of the free energy of mixing are in well agreement vide following table and the G_M/RT-c_{Cd} curve in Figure–1.

Table-1.THERMODYNAMIC ENTITIESCd-Na liquid alloys at 673 K.

c_{Cd}	G_M/RT		S_M/R		H_M/RT	
	Theoretical	**Experimental***	**Theoretical**	**Experimental***	**Theoretical**	**Experimental***
0.1	–0.3170	–0.2701	0.1520	0.2447	–0.1650	–0.0254
0.2	–0.5204	–0.4376	0.2916	0.3368	–0.2288	–0.1010
0.3	–0.6816	–0.5775	0.3558	0.3599	–0.3258	–0.2177
0.4	–0.7971	–0.6987	0.3609	0.3217	–0.4362	–0.3770
0.5	–0.8617	–0.8005	0.3198	0.2391	–0.5419	–0.5711
0.6	–0.8675	–0.8678	0.2457	0.1435	–0.6218	–0.7241
0.7	–0.8048	–0.8768	0.1542	0.0529	–0.6498	–0.8236
0.8	–0.6629	–0.7870	0.0583	–0.0126	–0.6046	–0.7997
0.9	–0.4226	–0.5296	–0.0208	–0.0232	–0.4434	–0.5528

*Hultgren et al, 1973

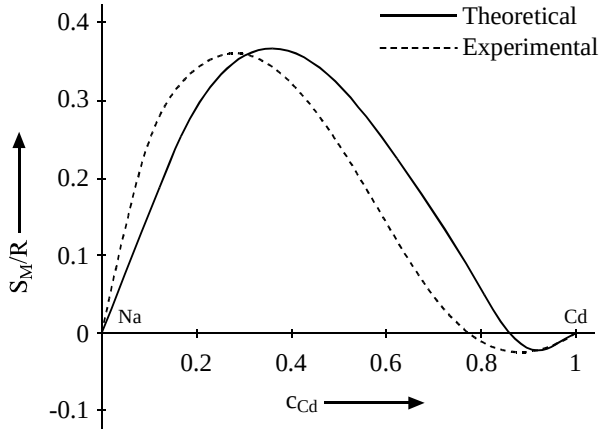


Figure–1: G_M/RT-c_{Cd} curve for Cd-Na liquid alloy at 673 K.

The observed values [5] of S_M are used to obtain the temperature derivatives of interaction parameters. We have found out:

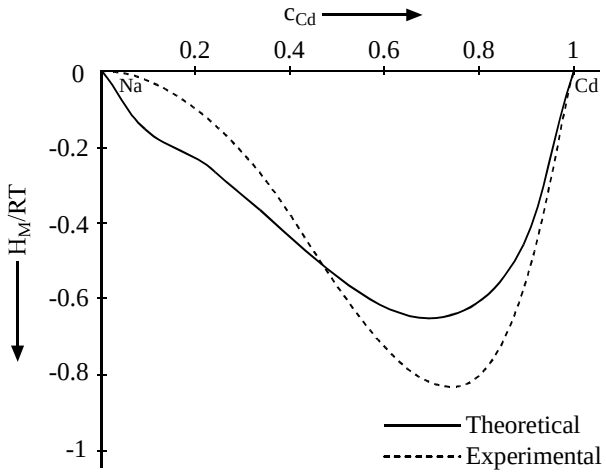
$$K_B^{-1}\, d\omega/dT = 6.3 \text{ and } K_B^{-1}\, d(\Delta\omega_{AB})/dT = -3.6.$$

The theoretical values of the entropy of mixing (S_M/R) of Cd-Na alloy are furnished in the above table as a function of c_{Cd} along with the experimental values. The concentration dependence of S_M/R at 673 K. is plotted in Figure–2. The theoretical and experimental values are in well agreement. The experimental value of S_M is maximum at c_{Cd}=0.3 but our theoretical values show a maximum at c_{Cd}=0.35.



Figure–2: S_M/R-c_{Cd} curve for Cd-Na liquid alloy at 673 K.

The heat of mixing of the cadmium-sodium alloys has been computed as a function of concentration from equation (v) on taking the same values of $d\omega/dT$ and $d(\Delta\omega_{AB})/dT$ as used for the calculation of entropy of mixing. The theoretical and experimental values are tabulated above. The plot of H_M/RT versus c_{Cd} at 673 K. is depicted in Figure–3 for both the theoretical and experimental values [5]. Slight deviations are found in the theoretical and observed values of H_M. H_M shows a minimum at c_{Cd}=0.7 theoretically whereas experimentally the same is at c_{Cd}=0.76.



Figure–3: H_M/RT-c_{Cd} curve for Cd-Na liquid alloy at 673 K.

CONCLUSION

The alloying behaviour of Cd-Na liquid alloy is well explained by the above theoretical model. The nature of curves as found experimentally is corroborated to a great extent by our theoretical values for different thermodynamic entities.

REFERENCES

[1]. AB Bhatia; RN Singh. Phys. Chem. Liq., **1982**, 11, 285.
[2]. AB Bhatia; RN Singh. Phys. Chem. Liq., **1982**, 11, 343.
[3]. SK Chakrabarti; IS Jha; BP Singh. J. Nepal Phys. Soc., **2007**, 23, 40.
[4]. S Harada; S Takahashi; S Takeda; S Tamaki; P Grey; NE Cusack. J. Phys., **1988**, F 18, 559.
[5]. R Hultgren; PD Desai; DT Hawkins; M Gleiser; KK Kelley. Selected Values of the Thermodynamic Properties of Binary Alloys, American Society for Metals, Ohio, **1973**.
[6]. V Heine. Solid State Physics, Academic Press, New York, **1970**.
[7]. F Sommer. Bunsen-Ges. Phys. Chem., **1983**, 87, 749.
[8]. CNJ Wagner. J. Rap. Quen. Met., **1985**, B V, 405.

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