Free Energy of Mixing of the Binary Liquid Alloys of Sodium

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Abstract
Sodium is a highly reactive alkali metal. Within a binary liquid alloy it generally forms complexes. Due to formation of such complexes the thermodynamic properties of the binary alloys of sodium often show anomaly—deviating maximally from that of the ideal alloys. In the present work we have confined our investigation into the free energy of mixing (G_M) of two binary alloys of sodium in liquid phase—Na-Pb and Na-Hg—near the melting point. For this purpose we have used Flory's model and started with the activity of sodium in the sodium-lead liquid alloy and that of mercury in the sodium amalgam at molten stage. By the method of successive approximations we have ascertained the value of interchange energy for each alloy in the light of the experimental values of activity and finally computed G_M for different concentrations of the constituent species. Our computation explains the observed symmetry and anomaly in the free energy of mixing of the Na-Pb and Na-Hg liquid alloys respectively.

Keywords: *Binary liquid alloys, Flory's model, Activity, Free energy of mixing.*

Introduction
The concentration dependent thermodynamic properties of binary liquid alloys, especially the complex forming ones, are interesting in many ways. The properties of mixing are not, generally, symmetrical about the equi-atomic composition (Faber 1972, Bhatia and Singh 1982, Chakrabarti 2010). Some of these alloys also depict metal non-metal transition across a narrow band of concentration. The anomalous behaviour of these liquid alloys is least understood and demands extensive theoretical investigation. From a metallurgical standpoint it is instructive to have a good understanding of the properties of liquid alloys because most of the binary solid alloys are formed by cooling from the liquid state.

In this article we tend to explain the symmetry and anomaly in the free energy of mixing of the sodium-lead liquid alloy and the molten sodium amalgam respectively on the basis of Flory's model (Flory 1942). It is a statistical mechanical model for the binary liquid alloys in which the size factor of the constituent species is taken into account. For each alloy, after knowing the ratio of the atomic volumes of the constituent species within it, the prime task becomes the determination of the interchange energy between them. For this purpose the experimental values of activity (a) for different concentrations of the ingredients are collected. From these known values interchange energy (ω) has been computed by using the expression for 'a' according to Flory's model. A suitable value of ω is chosen within the range of values so obtained. Putting this value of ω the activity is calculated for several concentrations and then compared with its observed values. Accordingly, a modified value of ω has been considered and the calculations are repeated. The process is continued. In this way by the method of successive approximations we have ascertained the value of the interchange energy. Thereafter free energy of mixing (G_M) has been computed from the mathematical expression of it according to the said model.

In Section 2 the working formula according to Flory's model is furnished. Section 3 deals with the results of computation for the free energy of mixing of these liquid alloys. Section 4 provides a brief conclusion.

Formulation
Activity is one of the fortunate thermodynamic

functions which are obtained directly by experiment. Activity of an element in a binary liquid alloy is given by $KT \ln a = -zFE$,
where 'z' is the valency of carrier ions of the element, F the Faraday's constant, K the Boltzmann constant, T the absolute temperature and E the electromotive force which is observed directly from the experiment.

According to Flory's model the activity (a) of a metal within a binary liquid alloy is given by

$$\ln a = \ln \frac{c(1-\upsilon)}{1-\upsilon c} + \frac{\upsilon(1-c)}{1-\upsilon c} + \frac{\omega}{RT}\frac{(1-c)^2}{(1-\upsilon c)^2}, \quad (1)$$

$$\text{where} \upsilon = 1 - \frac{V_A}{V_B}, \quad (2)$$

V_A and V_B being the atomic volumes of species A and B respectively.

Now, let us recall the standard thermodynamic relation

$$RT \ln a = G_M + (1-c)\frac{\partial G_M}{\partial c}, \quad (3)$$

where R is the universal gas constant and 'c' the concentration of the element within the mixture.

Putting in (3) the expression for ln a from (1) and solving for G_M we get the expression for the free energy of mixing of a binary liquid alloy :

$$G_M = RT[c\ln c + (1-c)\ln(1-c) + c\ln(1-\upsilon) - \ln(1-\upsilon c)] + \omega c\frac{1-c}{1-\upsilon c}. \quad (4)$$

Results and Discussion

1.1 Sodium-Lead Liquid Alloy

In case of sodium-lead liquid alloy it is considered that

A ≡ Na and B ≡ Pb.

The ratio of the atomic volumes of sodium to lead at 700 K. (Jha 1989) is given by $\frac{V_A}{V_B} = 1.3918$.

So, we have from (2) $\upsilon = -0.3918$.

The value of the interchange energy (ω) has been ascertained by using (1) from the experimental values of the activity of sodium in the liquid alloys at 700 K. for different concentrations (Hultgren *et al* 1973) by the method of successive approximations :

$$\frac{\omega}{RT} = -10.$$

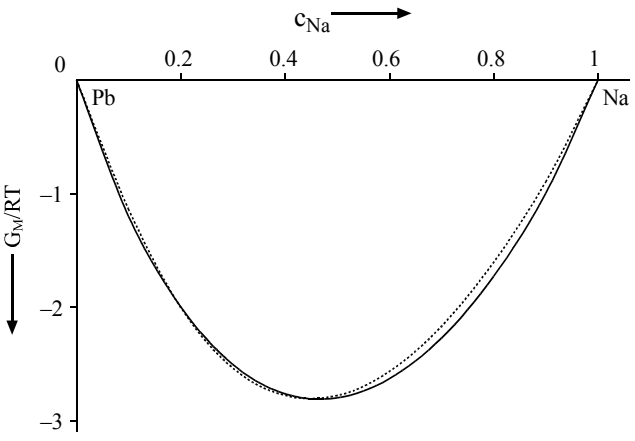
The computed values of the free energy of mixing (G_M/RT), on using (4), of Na-Pb liquid alloys at 700 K. are furnished in Table–1 along with its observed values (Hultgren *et al* 1973) in the concentration range of sodium from 0.1 to 0.9.

Table 1: Free Energy of Mixing of Na-Pb liquid alloys at 700 K.

c_{Na}	G_M/RT	
	Theoretical	**Experimental***
0.1	–1.1965	–1.1311
0.2	–1.9935	–1.9969
0.3	–2.5019	–2.5323
0.4	–2.7612	–2.7730
0.5	–2.7972	–2.7745
0.6	–2.6290	–2.5618
0.7	–2.2698	–2.1637
0.8	–1.7268	–1.6003
0.9	–0.9950	–0.8939

*Hultgren *et al*, 1973

The plot of G_M/RT versus c_{Na} is depicted in Figure–1 for both the theoretical and experimental values. The graph with the observed values reveals that the free energy of mixing of sodium-lead liquid alloy exhibits symmetry around equi-qtomic composition. Our computed values of G_M show a minimum at c_{Na}=0.48. The entire set of computed values is in good agreement with the corresponding experimental values. Thus the symmetry in the free energy of mixing of this liquid alloy is fairly explained.



Figure–1 : Free energy of mixing (G_M/RT) of sodium-lead liquid alloys at 700 K. for different concentrations of sodium. The full curve represents the computed values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

3.2 Sodium amalgam at molten stage

For the sodium amalgam we have considered

A ≡ Hg and B ≡ Na.

The ratio of the atomic volumes of mercury to sodium at 673 K. (Simoji 1977),

$$\frac{V_A}{V_B} = 0.5889,$$

leads to $\upsilon = 0.4111$.

The value of the interchange energy (ω) has been found out like before from the experimental values of the activity of mercury within the liquid amalgams at 673 K. for different concentrations (Hultgren *et al* 1973) by the method of successive approximations :

$$\frac{\omega}{RT} = -7.46.$$

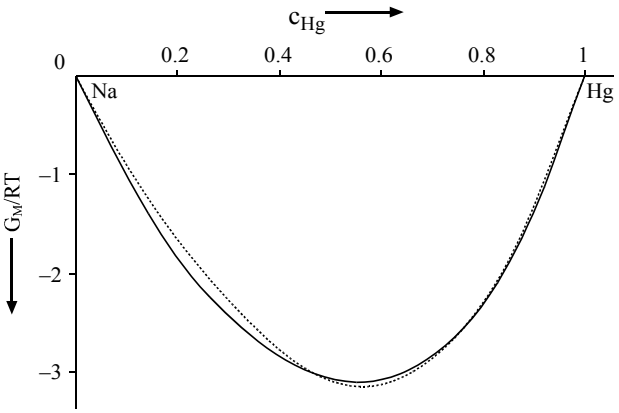
The computed values of the free energy of mixing (G_M/RT) of Hg-Na liquid alloys at 673 K. are tabulated in Table–2 along with its experimental values (Hultgren *et al* 1973) in the concentration range of mercury from 0.1 to 0.9.

Table 2: Free Energy of Mixing of Na-Hg liquid alloys at 673 K.

c_{Hg}	G_M/RT	
	Theoretical	**Experimental***
0.1	–1.0362	–0.9141
0.2	–1.8210	–1.6495
0.3	–2.4251	–2.2744
0.4	–2.8479	–2.7744
0.5	–3.0753	–3.0831
0.6	–3.0841	–3.1249
0.7	–2.8417	–2.8708
0.8	–2.3037	–2.2908
0.9	–1.4053	–1.3536

*Hultgren *et al*, 1973

The graphs of G_M/RT against c_{Hg} are furnished in Figure–2 for both the computed and experimental values. The graphs show that G_M of sodium amalgam exhibits asymmetry around equi-atomic composition. For all the concentrations the observed and our computed values are nicely in agreement. Thus the anomaly in the free energy of mixing of this molten amalgam is well explained.



Figure–2 : Free energy of mixing (G_M/RT) of molten sodium amalgams at 673 K. for different concentrations of mercury. The full curve represents the computed values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

Conslusion

Flory's model has been applied to study the free energy of mixing (G_M) of the binary liquid alloys of sodium. In the present work sodium-lead alloy and sodium amalgam have been taken into account. Though both the alloys form complexes G_M is found to be symmetric around equi-atomic composition in case of the former alloy. Such symmetry in the free energy of mixing of sodium-lead liquid alloys is nicely explained by the said theoretical model. The anomaly in G_M in case of molten sodium amalgams is also well explained by this model. The nature of curves as found experimentally is corroborated fairly by the computed values of free energy of mixing of these complex forming binary liquid alloys of sodium for different concentrations of the ingredients.

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