Free Energy of Mixing of Two Magnesium Based Binary Liquid Alloys

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Abstract

There are a large number of binary liquid alloys which exhibit interesting behavior as a function of concentration as regards the thermodynamic properties. The anomalous behavior of these liquid alloys is least understood and demands extensive theoretical investigations. In the present work we have considered two binary molten alloys of magnesium-magnesium-bismuth and magnesium-tin-and tried to calculate their free energy of mixing (G_M) at different concentrations of the ingredients. Flory's model has been applied to study the asymmetric behavior of G_M of them. It is a statistical mechanical model for the binary liquid alloys based on the size factor of the constituent metals. For each alloy we have started with the expression for activity of magnesium within it according to this model. Activity (a) is one of the fortunate thermodynamic functions which are obtained directly from experiment. After knowing the ratio of the atomic volumes of the constituent species of the alloy we have determined the interchange energy (ω) between them from the experimental values of 'a' by the method of successive approximations. Thereafter G_M has been computed from the mathematical expression of it by using this value of ω. The results explain the observed anomaly in the free energy of mixing of the present liquid alloys.

Key words: Binary liquid alloys of magnesium, Flory's model, free energy of mixing

Introduction

It is well known that most of the metals dissolve in one another readily when they are in liquid phase but the same is not true for the solid alloys. The solubility of a homogeneous solid phase is governed predominantly by the size factor, electrochemical effect and electron concentration. Experiences say that these factors cannot be used effectively to explain the alloying behavior of liquid alloys in details. So, liquid alloys generate manifold interest for both the experimentalists and the theoreticians[1–8]. A good understanding of the properties of liquid alloys is really a matter of interest because most of the binary solid alloys are formed by cooling from the liquid state.

In this article we have considered two strongly interacting systems—Mg-Bi and Mg-Sn alloys. Magnesium is an alkaline earth metal and quite reactive. We have confined our work in studying the free energy of mixing of these magnesium based binary liquid alloys by the application of Flory's model[9].

In Section 2 the working expression according to this model is furnished. Section 3 deals with the results of computation for the free energy of mixing of the present molten alloys. Section 4 provides a brief conclusion.

Basic formalism: Activity is an important thermodynamic function obtained directly from the experiment. Activity (a) of an element in a binary liquid alloy is given by

$$K_B T \ln a = -zFE,$$

where 'z' is the valency of carrier ions of the element, F the Faraday's constant, K_B the Boltzmann

constant, T the absolute temperature and E the electromotive force which can be measured directly from experiment.

According to Flory's model the activity of a metal within a binary liquid alloy:

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

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

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

Magnesium-Bismuth Liquid Alloy: For this alloy let A ≡ Mg, B ≡ Bi, knowing the ratio of the atomic volume of magnesium to that of bismuth[10] *i.e.*

$$\frac{V_A}{V_B} = 0.6517,$$

we have from (2)

$$\upsilon = 0.3483.$$

The value of the interchange energy (ω) has been ascertained on using (1) from the experimental values of the activity of magnesium within the liquid alloy at 975 K. by the method of successive approximations[1] :

$$\frac{\omega}{RT} = -7.5.$$

The computed values of the free energy of mixing (G_M/RT) of Mg-Bi liquid alloys at 975 K. are furnished in Table–1 along with its observed values in the concentration range from 0.1 to 0.9 of magnesium[1].

Table–1: Free energy of mixing of Mg-Bi liquid alloys at 975 K

c_{Mg}	G_M/RT	
	Theoretical	**Experimental***
0.1	–1.032	–0.836
0.2	–1.804	–1.521
0.3	–2.388	–2.136
0.4	–2.786	–2.691
0.5	–2.986	–3.174
0.6	–2.971	——
0.7	–2.714	–2.921
0.8	–2.180	–2.179
0.9	–1.318	–1.214

*Hultgren *et al,* 1973

The plots of G_M/RT versus c_{Mg} are shown in Figure–1 for both the theoretical and experimental values. The graphs reveal that G_M of Mg-Bi liquid alloy exhibits asymmetry around equi-atomic composition. However, the observed and our computed values are in good agreement. Thus the asymmetry in the free energy of mixing of this molten alloy is well explained.

Magnesium-Tin Liquid Alloy: In case of magnesium-tin alloy we have considered A ≡ Mg, B ≡ Sn. The ratio of the atomic volume of magnesium at 1073 K to that of tin[10] *i.e.*

$$\frac{V_A}{V_B} = 0.8993$$

gives rise to

$$\upsilon = 0.1007.$$

The value of the interchange energy (ω) has been found out from the experimental values of the activity of magnesium within this liquid alloy at 1073 K. on using (1) by the method of successive approximations[1] :

$$\frac{\omega}{RT} = -6.4.$$

The computed values of the free energy of mixing (G_M/RT) of Mg-Sn liquid alloys at 1073 K. are tabulated in Table–2 along with its experimental

values in the concentration range from 0.1 to 0.9 of magnesium[1].

Table–2: Free energy of mixing of Mg-Sn liquid alloys at 1073 K

c_{Mg}	G_M/RT	
	Theoretical	**Experimental** *
0.1	–0.907	–0.725
0.2	–1.546	–1.285
0.3	–1.998	–1.741
0.4	–2.275	–2.080
0.5	–2.379	–2.281
0.6	–2.309	–2.316
0.7	–2.058	–2.154
0.8	–1.615	–1.758
0.9	–0.959	–1.079

*Hultgren *et al,* 1973

G_M/RT is plotted against c_{Mg} and furnished in Figure–2 for both the computed and observed values. The theoretical and experimental values of the free energy of mixing are in well agreement. The experimental value of G_M is minimum at c_{Mg}=0.58 but our theoretical values show a minimum at c_{Mg}=0.52.

Conclusion

The anomaly in the free energy of mixing (G_M) of magnesium-bismuth liquid alloy is nicely explained by the present theoretical model. The asymmetry in G_M around equi-atomic composition in case of magnesium-tin liquid alloy is also explained to a great extent by this model. The nature of curves as found experimentally is corroborated well by the computed values of free energy of mixing of these molten alloys for different concentrations of magnesium. However, our computation reveals that the size effect does not play an important role for shaping the free energy of mixing of the latter alloy.

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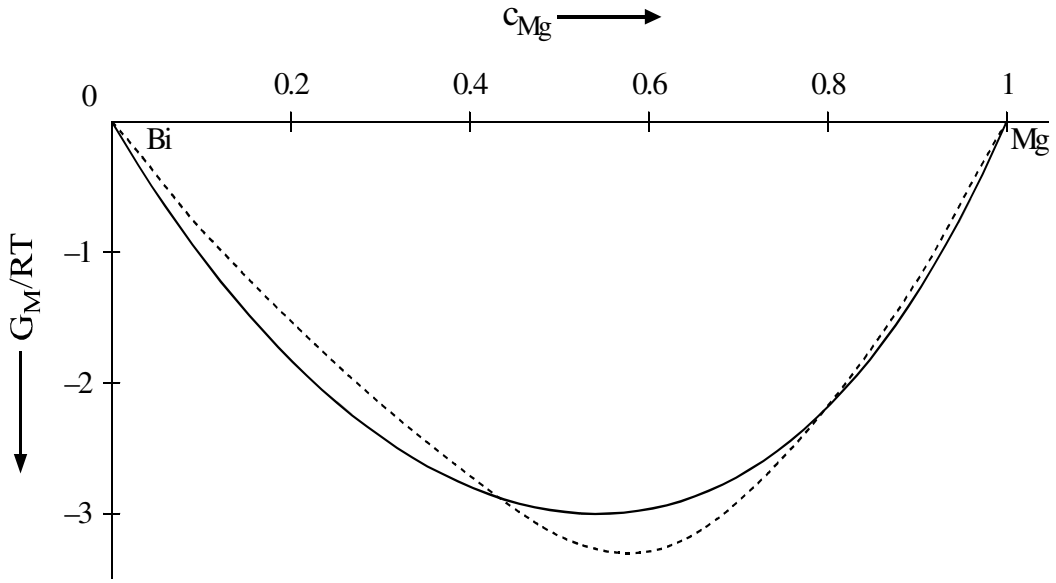
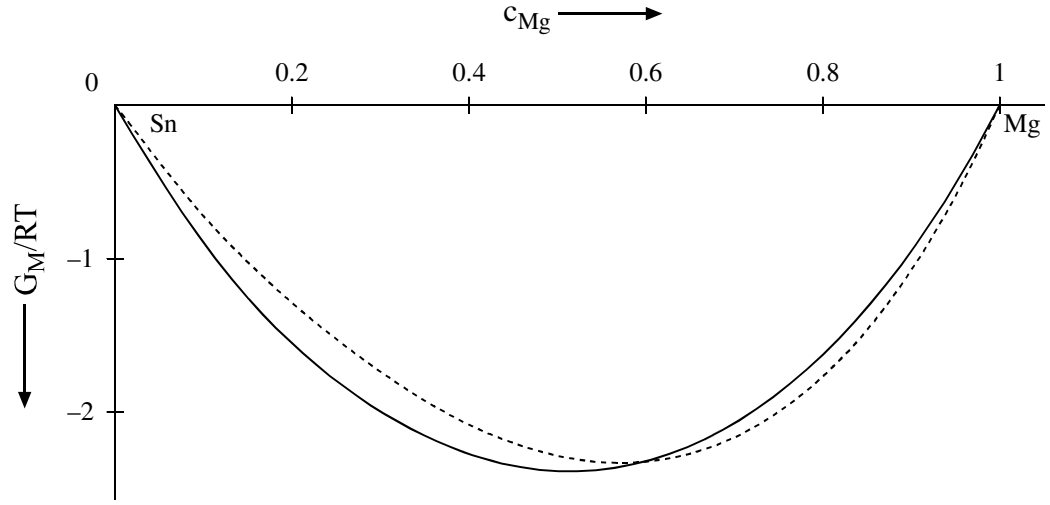


Figure–1: Free energy of mixing (G_M/RT) of magnesium-bismuth liquid alloy at 975 K. for different concentrations of magnesium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973)



Figure–2: Free energy of mixing (G_M/RT) of magnesium-tin liquid alloy at 1073 K. for different concentrations of magnesium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973)