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FREE ENERGY OF MIXING OF THE BINARY LIQUID ALLOYS OF POTASSIUM

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ABSTRACT

There are a large number of binary liquid alloys which exhibit interesting behaviour as a function of concentration as regards the thermodynamic and electrical properties. The thermodynamic properties of mixing, especially in case of complex forming alloys, are not symmetrical about the equi-atomic composition—deviating considerably from that of an ideal alloy. Here we have considered two such molten alloys of potassium—potassium-lead and potassium amalgam—and tried to calculate their free energy of mixing at different concentrations of the ingredients by using Flory's model. It is a statistical mechanical model based on the size factor of the constituent species of binary alloys. Our results explain the observed asymmetry in the free energy of mixing of the said binary liquid alloys around equi-atomic composition.

Key words: Binary liquid alloy, Free energy of mixing, Interchange energy, Activity, Flory's model.

INTRODUCTION

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. On the basis of the variation of properties with concentration the alloys can be grouped into three major heads: ideal alloys, regular alloys and complex-forming alloys. In the last case the properties of mixing are often found to be anomalous deviating considerably from that of the ideal alloys. Some of these alloys also show metal non-metal transition across a narrow band of concentration. The liquidus lines are usually S-shaped and the heat of mixing and free energy of mixing are large negative quantities at one or other concentrations. The anomalous behaviour of these liquid alloys is least understood and demands extensive theoretical investigation. Since long metal physicists—experimentalists [1–3] as well as theoreticians [4–7]—are trying to interpret the physical properties of liquid alloys so that their alloying behaviour could adequately be comprehended.

The alloying behaviour 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, 11]. 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 [12] has been used by many theoreticians to study $S_{cc}(0)$ of different binary alloys. But this model cannot be used to study the short-range order parameters. However, in the eighty's decade soft sphere model [13] and one-component plasma theory [14] 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 this article we have considered two strongly interacting systems—K-Pb and Hg-K alloys—both in liquid state near their melting point. Potassium is a group I metal according to the periodic table. It is an alkali metal and highly reactive, often forming complexes within the binary alloys of it. The liquidus lines of the present alloys also reveal that the ingredients form complexes. The thermodynamic properties of them show anomaly around equi-atomic composition. We have confined our work in studying such anomaly in the free energy of mixing of these binary liquid alloys of potassium. For this purpose we have considered Flory's model [15]. It is a statistical mechanical model for the binary molten 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 of 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 (□) has been computed by using the expression for 'a' according to Flory's model. A suitable value of □ is chosen from within the range of values so obtained. Putting this value of □ the activity is calculated for several concentrations and then compared with its observed values. Accordingly, a modified value of □ has been considered and the calculations are repeated. The process is repeated again and again. In this way by the method of successive numerical approximations we have ascertained the value of the interchange energy. Thereafter free energy of mixing has been computed from the mathematical expression of it according to the said model.

In Section 2 the working formula 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.

MATERIALS AND METHOD

FORMULATION

Activity is one of the fortunate thermodynamic functions which are obtained directly from experiment. Activity 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 is observed directly from the experiment.

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

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

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

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

Now, let us recall the standard thermodynamic relation

$$RT \ln a = G_M + (1- c)\frac{\partial G_M}{\partial c}, \qquad \text{(iii)}$$

where R is the universal gas constant and 'c' the concentration of the element within the mixture Putting in (iii) the expression for ln a from (i) and solving for G_M we get the expression for the free energy of mixing of a binary liquid alloy:

$$G_M = RT [c \ln c + (1- c) \ln (l - c) + c \ln (1- \upsilon) - \ln (1- \upsilon c)] + \omega c \frac{1-c}{1-\upsilon c}. \qquad \text{(iv)}$$

RESULTS AND DISCUSSION

Potassium-Lead Liquid Alloy

For this alloy we have considered

A ≡ K, B ≡ Pb.

Knowing the ratio of the atomic volume of potassium to that of lead [16] i.e.

$\frac{V_A}{V_B} = 2.4833,$

we have from (ii)

$\upsilon = -1.4833.$

The value of the interchange energy (□□ has been ascertained by using (i) from the experimental values of the activity of potassium within the liquid alloy at 848 K. [1] by the method of successive numerical approximations:

$$\frac{\omega}{RT} = -11.5.$$

The computed values of the free energy of mixing (G_M/RT), on using (iv), of K-Pb liquid alloys at 848 K. are furnished in Table –1 along with its observed values [1] in the concentration range of potassium from 0.1 to 0.9. The experimental and our theoretical values are in good agreement.

Table–1

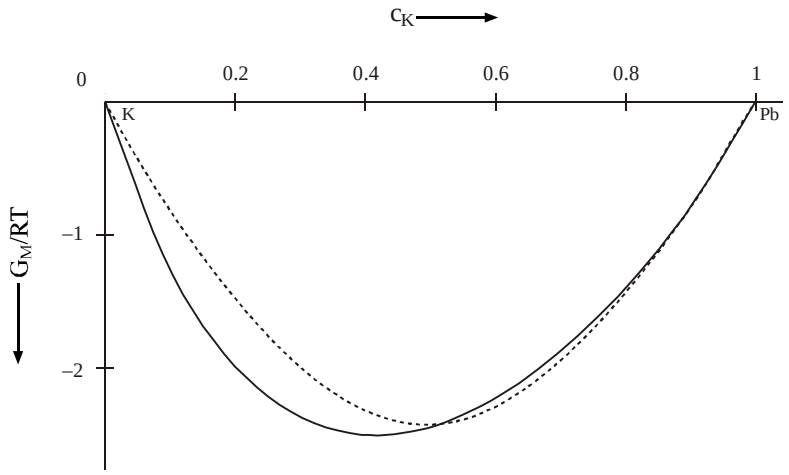
FREE ENERGY OF MIXING
K-Pb liquid alloys at 848 K.

c_K	G_M/RT	
	Theoretical	**Experimental***
0.1	–1.2737	–0.8310
0.2	–1.9973	–1.4811
0.3	–2.3774	–1.9871
0.4	–2.5072	–2.3187
0.5	–2.4439	–2.4261
0.6	–2.2242	–2.2885
0.7	–1.8711	–1.9426
0.8	–1.3966	–1.4337
0.9	–0.7977	–0.7972

*Hultgren *et al*, 1973

The computed values of the free energy of mixing (G_M/RT) of K-Pb liquid alloys at 848 K. are furnished graphically in Figure–1 along with its observed values for different concentrations of potassium from 0.1 to 0.9. The graphs reveal that G_M of the alloy exhibits asymmetry around equi-

atomic composition. The observed and our computed values are in reasonable agreement. Thus the asymmetry in the free energy of mixing of this molten alloy is explained to a great extent.



Figure–1: Free energy of mixing (G_M/RT) of potassium-lead liquid alloy at 848 K. for different concentrations of potassium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

Potassium Amalgam in Liquid Phase

In case of potassium amalgam
A≡Hg, B≡K.
Knowing the ratio of the atomic volumes of mercury to potassium at 600 K. [17] i.e.

$$\frac{V_A}{V_B} = 0.303,$$

we get from (ii)
$\upsilon = 0.697$.

The value of the interchange energy has been found out from the experimental values of the activity of Hg within this liquid amalgam at 600 K. [1] on using (i) by successive numerical approximations method:

$$\frac{\omega}{RT} = -5.5.$$

The computed values of the free energy of mixing (G_M/RT) of Hg-K liquid alloys at 600 K. are tabulated in Table–2 along with its experimental values [1] in the concentration range of mercury from 0.1 to 0.9.

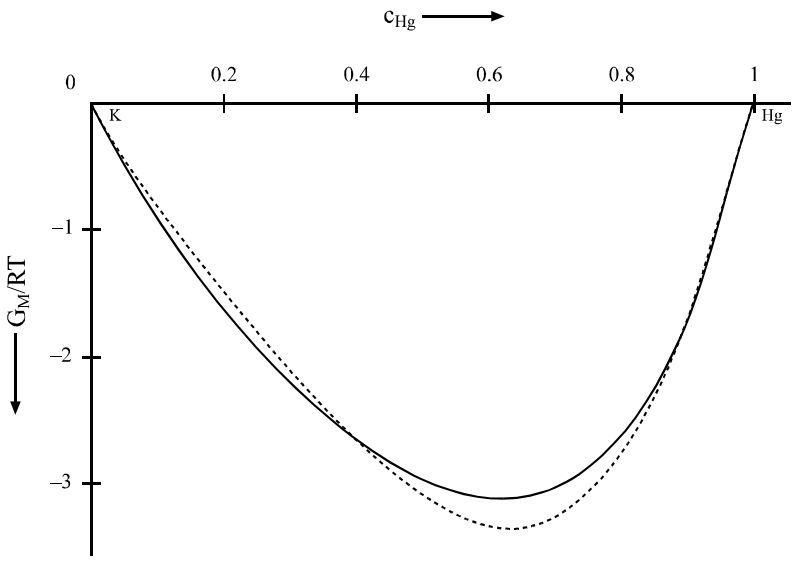
Table–2

FREE ENERGY OF MIXING
Hg-K liquid alloys at 600 K.

c_{Hg}	G_M/RT	
	Theoretical	**Experimental***
0.1	–0.9043	–0.8174
0.2	–1.6116	–1.4822
0.3	–2.1948	–2.0908
0.4	–2.6541	–2.6467
0.5	–2.9722	–3.0935
0.6	–3.1166	–3.3433
0.7	–3.0329	–3.2779
0.8	–2.6292	–2.7774
0.9	–1.7409	–1.7203

*Hultgren *et al*, 1973

G_M/RT is plotted against c_{Hg} 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. From the graphs the asymmetry in G_M around equi-atomic composition is readily revealed. Both the curves show the free energy of mixing to be minimum at $c_{Hg} = 0.63$.



Figure–2: Free energy of mixing (G_M/RT) of molten potassium amalgam at 600 K. for different concentrations of mercury. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

CONCLUSION

The anomaly in the free energy of mixing (G_M) of potassium-lead liquid alloy is explained to a great extent by the present theoretical model. The asymmetry in G_M around equi-atomic composition in case of molten potassium amalgam is also nicely explained by this model. The nature of $G_M/RT–c$ curves as found experimentally is corroborated well by our computed values of free energy of mixing of the present molten alloys of potassium.

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