

## Heat of Mixing of the Lead-based Binary Liquid Alloys of Alkali Metals

S. K. CHAKRABARTI<sup>1\*</sup>, I. S. JHA<sup>1</sup>, R. N. YADAV<sup>2</sup> and B. P. SINGH<sup>3</sup>

<sup>1</sup>Department of Physics, M. M. A. M. Campus, Tribhuvan University, Biratnagar, Nepal

<sup>2</sup>Department of Mathematics, M. M. A. M. Campus, Tribhuvan University, Biratnagar, Nepal

<sup>3</sup>Department of Physics, T. M. Bhagalpur University, Bhagalpur, Bihar, India

\*E-mail: skc\_2007@yahoo.com

*Received : 9.6.2015 ; Accepted : 11.6.2015*

**Abstract :** Binary alloys, especially the complex-forming ones, are often found to exhibit anomalous behaviour as regards their thermodynamic properties. In this theoretical work we have considered three lead-based binary alloys—lithium-lead, sodium-lead and potassium-lead—all in molten state near their respective melting points. We have tried to calculate their heat of mixing for different concentrations of the alkali metals. All these alloys forming strongly interacting systems, we have used Flory's model. It is a statistical mechanical model based on the size factor of the constituent species of a binary liquid alloy. Our results explain the observed asymmetry in the heat of mixing of the present binary liquid alloys around equi-atomic composition.

**Keywords:** Binary liquid alloy, Free energy of mixing, Interchange energy, Entropy of mixing, Heat of mixing.

### 1. 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<sup>1-3</sup> as well as theoreticians<sup>4-7</sup> - are trying to interpret the physical properties of liquid alloys so that their alloying behaviour could adequately be comprehended.

The alloying behaviour of the liquid alloys can be studied by the help of either the electronic theory of mixing or the 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 pseudopotential theory<sup>8, 9</sup> and hard sphere model<sup>10, 11</sup>. These theory and model cannot be used to obtain information regarding the concentration fluctuations in the long wave-length limit, an important thermodynamic function which determines the stability 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 we tend to explain the deviation from the ideal values of the heat of mixing of the lead-based binary alloys of alkali metals e.g. Li-Pb, Na-Pb and K-Pb alloys—all in liquid phase near their melting point. For this purpose Flory's model has been used<sup>12</sup>. For the binary liquid alloys it is a statistical mechanical model in which the size factor of the constituent species is taken into account.

For each alloy we have started with the expression for the free energy of mixing ( $G_M$ ) according to this model and found out the value of the interchange energy at the concerned temperature by the method of successive numerical approximations in the light of the observed values of  $G_M$  for different concentrations of the alkali metal within it. Thereafter the expression for the entropy of mixing ( $S_M$ ) is taken into account and the value of the temperature derivative of interchange energy has been ascertained from the experimental values of  $S_M$  for different concentrations by successive numerical approximations. Finally, the heat of mixing has been calculated from the computed values of free energy of mixing and entropy of mixing on using the standard thermodynamic relation.

Working expressions are summarised in the next section. The following section deals with the results. A brief conclusion is provided in the last section.

## **2. Formulation**

Flory's expression for the free energy of mixing of a binary mixture consisting of  $Nc$  mole of species A and  $N(1-c)$  mole of species B is given by

$$G_M = RT [c \ln c + (1-c) \ln (1-c) + c \ln (1-\nu) - \ln (1-\nu c)] + \omega c \frac{1-c}{1-\nu c}, \quad (i)$$

*Heat of Mixing of the Lead-based Binary....*

where 
$$v = 1 - \frac{V_A}{V_B}, \tag{ii}$$

$V_A$  and  $V_B$  being the atomic volumes of species A and B respectively and  $\omega$  the interchange energy.

The entropy of mixing is related to the free energy of mixing through the standard thermodynamic relation:

$$S_M = -\frac{\partial G_M}{\partial T}. \tag{iii}$$

Differentiating equation (i) partially with respect to temperature T, we have from equation (iii)

$$S_M = -R [c \ln c + (1-c) \ln (1-c) + c \ln (1-v) - \ln (1-vc)] - \frac{c(1-c)}{1-vc} \frac{\partial \omega}{\partial T} + \frac{RTc(1-c)}{1-vc} \left[ \frac{v}{1-v} - \frac{\omega}{RT} \frac{c}{1-vc} \right] \frac{\partial v}{\partial T}, \tag{iv}$$

where 
$$\frac{\partial v}{\partial T} = (\gamma_B - \gamma_A) \frac{V_A}{V_B},$$

$\gamma_A$  and  $\gamma_B$  being the volume expansivities of pure species A and B respectively.

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

$$H_M = G_M + TS_M. \tag{v}$$

### 3. Results and Discussion

#### *Lithium-Lead Liquid Alloy*

For the purpose of equation (ii) considering

$$A \equiv \text{Li and } B \equiv \text{Pb},$$

we have<sup>13</sup>

$$\frac{V_A}{V_B} = 0.741$$

at 932 K. After finding

$$v = 0.259,$$

the value of interchange energy at 932 K. has been determined on using equation (i) from the observed data<sup>2</sup> of  $G_M$  in the concentration range of lithium from 0.1 to 0.9 by the method of successive numerical approximations. In the present work we have used

S.K. Chakrabarti *et al.*

$$\frac{\omega}{RT} = -8.7.$$

The observed values of entropy of mixing<sup>2</sup> at 932 K. in the concentration range of lithium from 0.1 to 0.9 have been used to find out the temperature derivative of interchange energy in equation (iv) by the successive numerical approximations method:

$$\frac{1}{R} \frac{\partial \omega}{\partial T} = 2.9.$$

With the set of values of  $G_M$  and  $S_M$  so obtained, finally, the heat of mixing of the lithium-lead liquid alloys at 932 K. has been computed as a function of concentration of lithium by using equation (v). The computed values of the heat of mixing are furnished below in Table–1 along with its observed values<sup>2</sup> in the concentration range of lithium from 0.1 to 0.9.

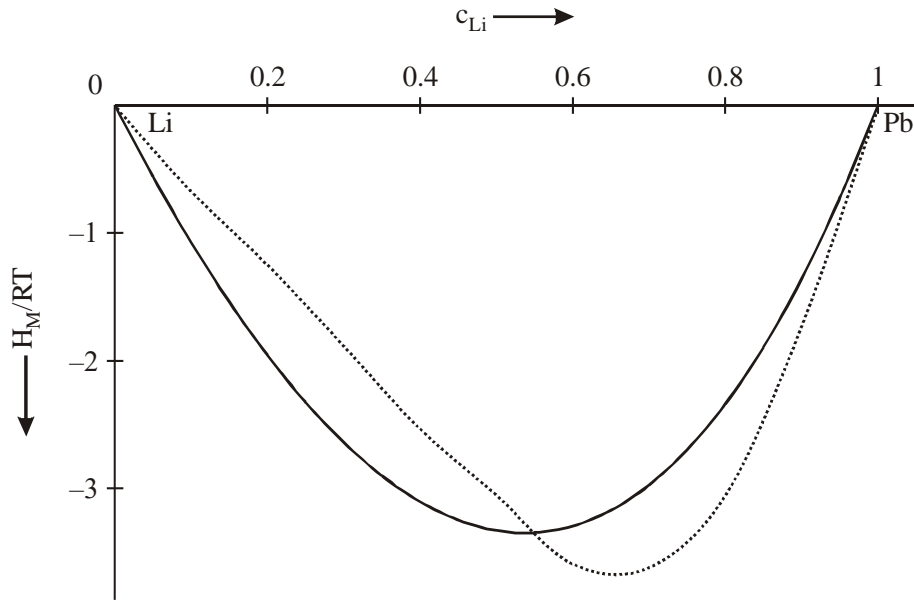
**Table–1:** Heat of mixing (Li-Pb liquid alloys at 932 K).

$c_{Li}$	$H_M/RT$	
	Theoretical	Experimental*
0.1	-1.0717	-0.6710
0.2	-1.9574	-1.2450
0.3	-2.6412	-1.8800
0.4	-3.1058	-2.5300
0.5	-3.3314	-3.0500
0.6	-3.2962	-3.5900
0.7	-2.9754	-3.6200
0.8	-2.3410	-3.0500
0.9	-1.3614	-1.7200

\*Saboungi *et al.*, 1978

The plot of  $H_M/RT$  versus  $c_{Li}$  is depicted in Figure–1 for both the theoretical and experimental values. The computed and observed values of the heat of mixing are in reasonable agreement. The graphs show that the heat of mixing of the Li-Pb liquid alloys is quite asymmetric about the equi-atomic composition. The observed values of  $H_M$  are slightly smaller than the computed values for  $c_{Li} < 0.55$  and in the concentration range  $c_{Li} > 0.55$  the theoretical values are slightly

greater than the experimental ones. The experimental value of the heat of mixing is minimum at  $c_{Li}=0.66$  while the computed value of it is minimum at  $c_{Li}=0.55$ . Thus the asymmetry in the values of  $G_M$  for Li-Pb liquid alloys is well explained. Slight deviation between the computed and experimental values of  $H_M$  may be due to the formation of several complexes<sup>1</sup> as well as temperature dependence of the interchange energy.



**Fig.1:** Heat of mixing ( $H_M/RT$ ) of Li-Pb liquid alloy at 932 K. for different concentrations of lithium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Sabounji et al (1978).

*Sodium-Lead Liquid Alloy*

Considering

$$A \equiv Na \text{ and } B \equiv Pb,$$

we get<sup>3</sup>

$$\frac{V_A}{V_B} = 1.3918$$

at 700 K. and so

$$v = -0.3918.$$

On using equation (i) the value of interchange energy is determined from the observed data of free energy of mixing<sup>1</sup> at 700 K. in the concentration range of

sodium from 0.1 to 0.9 by successive numerical approximations method. For this alloy we have used

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

The experimental values<sup>1</sup> of  $S_M$  of molten Na-Pb alloys at 700 K. in the concentration range of sodium from 0.1 to 0.9 are used to determine the temperature derivative of interchange energy by

the method of successive numerical approximations:

$$\frac{1}{R} \frac{\partial \omega}{\partial T} = 3.5.$$

The heat of mixing of Na-Pb liquid alloys at 700 K. has been computed as a function of concentration of sodium from equation (v) after such calculation of the free energy of mixing and entropy of mixing. Our computed values of  $H_M/RT$  are depicted in Table–2 along with its observed values<sup>1</sup> in the concentration range of sodium from 0.1 to 0.9.

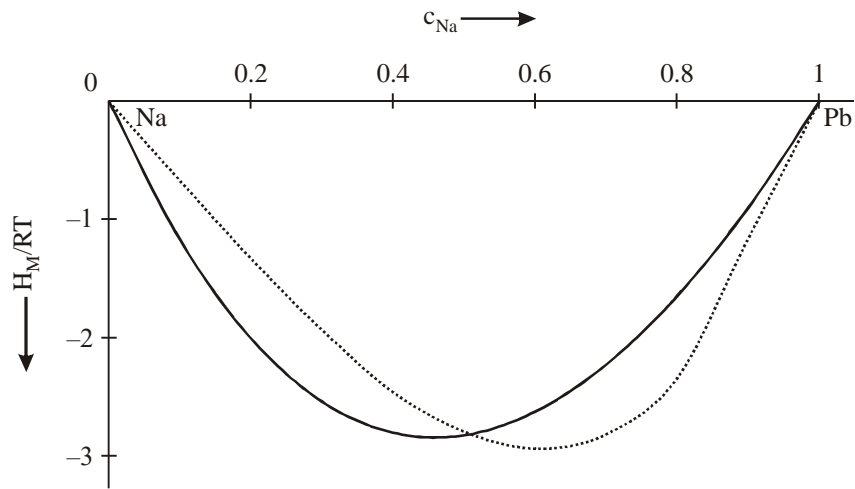
**Table 2 :** HEAT OF MIXING (Na-Pb liquid alloys at 700 K.)

$c_{Na}$	$H_M/RT$	
	Theoretical	Experimental*
0.1	-1.1692	-0.6690
0.2	-2.0031	-1.3279
0.3	-2.5368	-1.9316
0.4	-2.8010	-2.4583
0.5	-2.8221	-2.7903
0.6	-2.6233	-2.9354
0.7	-2.2248	-2.8140
0.8	-1.6446	-2.3397
0.9	-0.8983	-1.1598

\*Hultgren et al, 1973

The plot of  $H_M/RT$  versus  $c_{Na}$  at 700 K. is shown in Figure–2 for both the theoretical and experimental values. The calculated and observed values of  $H_M$  are fairly in agreement. The graphs show that the heat of mixing for the Na-Pb

alloys is not at all symmetric about the equi-atomic composition.  $H_M$  shows a minimum at  $c_{Na}=0.46$  theoretically whereas experimentally the same is at  $c_{Na}=0.61$ . At  $c_{Na}=0.51$  our computed value and the experimental one have become identical. The large negative values of  $H_M/RT$  about the minima suggest that there is a strong interaction between sodium and lead within the alloy. Slight difference between the theoretical and experimental values of the heat of mixing may be due to the formation of different complexes<sup>1</sup> as well as the temperature dependence of interchange energy.



**Fig. 2:** Heat of mixing ( $H_M/RT$ ) of Na-Pb liquid alloy at 700 K. for different concentrations of sodium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren et al (1973).

*Potassium-Lead Liquid Alloy*

In this case considering

$$A \equiv K \text{ and } B \equiv Pb$$

we obtain<sup>14</sup>

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

giving rise to

$$v = -1.4833.$$

By successive numerical approximations the value of interchange energy has been determined from the observed data of the free energy of mixing<sup>1</sup> at 848 K. in the concentration range of potassium from 0.1 to 0.9. We have used here

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

The experimental values of entropy of mixing<sup>1</sup> at 848 K. in the concentration range of potassium from 0.1 to 0.9 are used to find out the temperature derivative of interchange energy, in equation (iv), by successive numerical approximations method:

$$\frac{1}{R} \frac{\partial \omega}{\partial T} = 8.$$

The computed values of the heat of mixing of K-Pb liquid alloys at 848 K. from the set of theoretical values of  $G_M$  and  $S_M$  are furnished in Table-3 along with its observed values<sup>1</sup>. The computed and observed values are in considerable agreement.

**Table 3.** Heat of mixing (K-Pb liquid alloys at 848 K.)

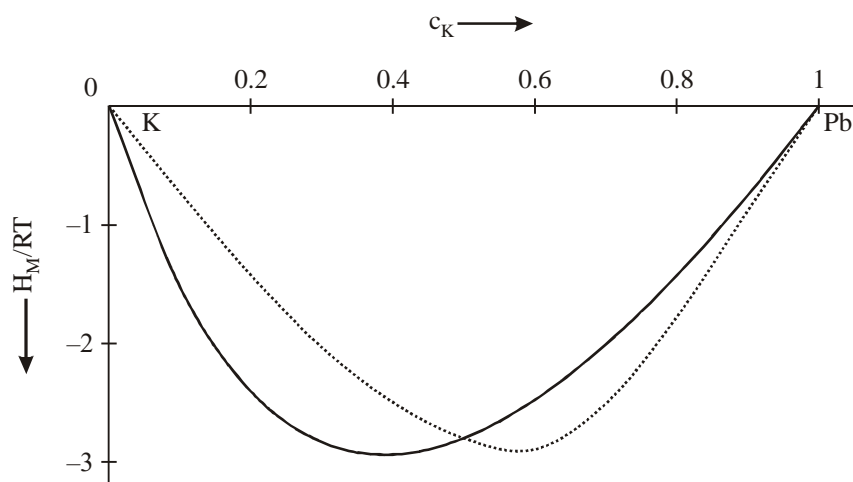
$c_K$	$H_M/RT$	
	Theoretical	Experimental*
0.1	-1.5283	-0.7308
0.2	-2.4062	-1.4278
0.3	-2.8339	-2.0358
0.4	-2.9372	-2.4972
0.5	-2.7991	-2.8010
0.6	-2.4763	-2.8947
0.7	-2.0090	-2.5085
0.8	-1.4269	-1.7777
0.9	-0.7516	-0.8820

\*Hultgren et al, 1973

$H_M/RT$ - $c_K$  graphs for the theoretical and experimental values are shown in Figure-3. From the graphs it is clear that  $H_M$  is asymmetric about the equi-atomic composition. Below this equi-atomic composition our computed values have



come slightly smaller than the observed ones. Above  $c_K=0.5$  the case is just reversed. The theoretical values of  $H_M$  show a minimum at  $c_K=0.39$ . Experimentally the same is at  $c_K=0.58$ . Slight difference in between these two curves may be due to the formation of several complexes within the alloy<sup>1</sup> and high temperature sensitiveness of the interchange energy.



**Fig. 3:** Heat of mixing ( $H_M/RT$ ) of K-Pb 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).

#### 4. Conclusion

The nature of  $H_M/RT-c$  curves as found experimentally is corroborated well by our computed values of the heat of mixing of the above-mentioned lead-based binary liquid alloys for different concentrations of the alkali metals. The anomaly in the heat of mixing of lithium-lead liquid alloy is explained to a great extent by the present theoretical model. The asymmetry in  $H_M$  around equi-atomic composition in case of sodium-lead liquid alloy is also explained well by this Flory's model. For the molten potassium-lead alloy too the deviation of the heat of mixing from that of an ideal alloy is explained reasonably by the said model with the application of the method of successive numerical approximations as mentioned above.

## References

- [1] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley, *Selected values of the thermodynamic properties of binary alloys*. American Society for Metals, Ohio, 1973
- [2] M. L. Saboungi, J. Marr and M. Blander, *J. Chem. Phys.*, **68**, 1375 (1978).
- [3] S. Harada, S. Takahashi, S. Takeda, S. Tamaki, P. Grey and N. E. Cusack, *J. Phys.*, **F18**, 559 (1988).
- [4] E. A. Guggenheim, *Mixtures*. (Oxford University Press, Oxford, 1952).
- [5] A. B. Bhatia and D. E. Thornton, *Phys. Rev.*, **B2**, 3004 (1970).
- [6] R. N. Singh and F. Sommer, *Rep. Prog. Phys.*, **60**, 57 (1997)
- [7] S. K. Chakrabarti, I. S. Jha, B. K. Jha and B. P. Singh, *Sci. World*, **9**, 13 (2011).
- [8] W. A. Harrison, *Pseudopotential in the theory of metals*. Benjamin, (New York, 1966).
- [9] V. Heine, *Solid state physics*. (Academic Publishers, New York, 1970).
- [10] E. Thiele, *J. Chem. Phys.*, **39**, 474 (1963).
- [11] T. E. Faber, *Introduction to the theory of liquid metals*. (Cambridge University Press, Cambridge, 1972).
- [12] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
- [13] H. Ruppertsberg and W. Speicher, *Z. Naturforsch.*, **31A**, 47 (1976).
- [14] P. C. Rakshit and A. Das, *Organic chemistry*. (Scientific Book Agency, Kolkata, 1973).