A Statistical Mechanical Study of the Thermodynamics of Lithium-Lead Liquid Alloy

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Abstract. Most metals dissolve in one another readily once they are in liquid phase. The solubility of a homogeneous solid phase is governed predominantly by the size factor, electrochemical effect and electron concentration. But these factors cannot be used effectively to explain the alloying behaviours of liquid alloys to a great deal—thus generating manifold interests for the theoreticians. There are large numbers of binary liquid alloys whose thermodynamic properties deviate from the ideal values to a great extent. The large asymmetry observed in the properties of mixing of lithium-lead liquid alloys is discussed here by using Flory's model. On the basis of size factor the concentration dependence of free energy of mixing, activity, heat of mixing and entropy of mixing of Li-Pb alloys is tried to explain. The temperature dependence of interchange energy has been introduced to compute the heat of mixing and entropy of mixing. The results considerably exhibit the anomalous behaviour of Li-Pb liquid alloys.

Keywords. Interchange energy, Free energy of mixing, Activity, Entropy of mixing, Heat of mixing.

1.   Introduction

The growing interest in the thermodynamics of lithium-lead liquid alloys is due to large deviation of the electrical and thermodynamic properties from the ideal values [1-3, 7, 10-12]. The observed free energy of mixing and heat of mixing are asymmetric around equiatomic composition [12]. The volume of mixing is minimum [11] at the concentration $c_{Li}=0.8$. The concentration fluctuations $[S_{cc}(0)]$ and partial structure factor indicate anomalies [3-5] at $c_{Li}=0.8$. In Li-Pb alloys the associative tendency between unlike atoms is strong and the first principle statistical mechanical or pseudopotential type calculation of the physical properties is difficult [13, 15].

In the present work Flory's expression for the free energy of mixing (G_M) has been used to explain the alloying behaviour of Li-Pb liquid alloys. To obtain the expressions for heat of mixing and entropy of mixing we have considered the interchange energy (ω) to be temperature dependent.

Working expressions and the results for free energy of mixing and activity are given in Section 2. The heat of mixing and entropy of mixture are dealt in Section 3, which is followed by brief summary and conclusion in Section 4.

2. General formalism: free energy of mixing and activity

Flory's expression for the free energy of mixing of a binary mixture consisting of Nc mole of species A ($\equiv$Li) and $N(1-c)$ mole of species B ($\equiv$Pb) is given by [6]

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

where $\quad \phi(c) = c\ln (1-\beta) - \ln (1-\beta c)$

and $\quad \beta = 1 - \dfrac{V_A}{V_B},$

V_A and V_B being the atomic volumes of species A and B respectively. For the present alloy [11] we have $V_A/V_B = 0.741$ at 932 K.

Activity is a very important thermodynamic function because it is one of the fortunate functions which are obtained directly from experiment. The activity (a_A) of the element A in a binary liquid alloy is given by

$$K_B T\ln a_A = -zFE, \tag{ii}$$

where z is the valency of carrier ion A, F the Faraday's constant, K_B the Boltzmann constant and E the electromotive force, which is observed directly from the experiment.

In order to obtain the expression for a_A let us recall the standard thermodynamic relation:

$$RT\ln a_A = G_M + (1-c)\frac{\partial G_M}{\partial c}. \tag{iii}$$

Differentiating equation (i) with respect to c,

$$\frac{\partial G_M}{\partial c} = RT\left[\ln c - \ln (1-c) + \ln (1-\beta) + \frac{\beta}{1-\beta c}\right] + \omega\left[\frac{1-2c}{1-\beta c} + \frac{\beta(1-c)c}{(1-\beta c)^2}\right]. \tag{iv}$$

Using equations (i) and (iv) in equation (iii) we get

$$\ln a_A = \ln \frac{c(1-\beta)}{1-\beta c} + \frac{\beta(1-c)}{1-\beta c} + \frac{\omega}{RT}\frac{(1-c)^2}{(1-\beta c)^2}. \qquad \text{(v)}$$

The value of interchange energy (ω) was determined from the observed data [12] of G_M in the concentration range from 0.1 to 0.9. The value of ω/RT used in the present work is –8.8. The computed values of G_M/RT from equation (i) are plotted against c_{Li} in Figure 1 along with its observed values at 932 K. The computed and observed values of G_M are in reasonable agreement. The observed values of G_M are more than the computed values for $c_{Li}<0.6$ and in the concentration range $c_{Li}>0.6$ the computed values of G_M are more than the experiment values. The experimental value of G_M/RT is minimum at $c_{Li}=0.6$ while the computed value of G_M/RT is minimum at $c_{Li}=0.56$. Thus the asymmetry in the values of G_M for Li-Pb alloys is well explained.
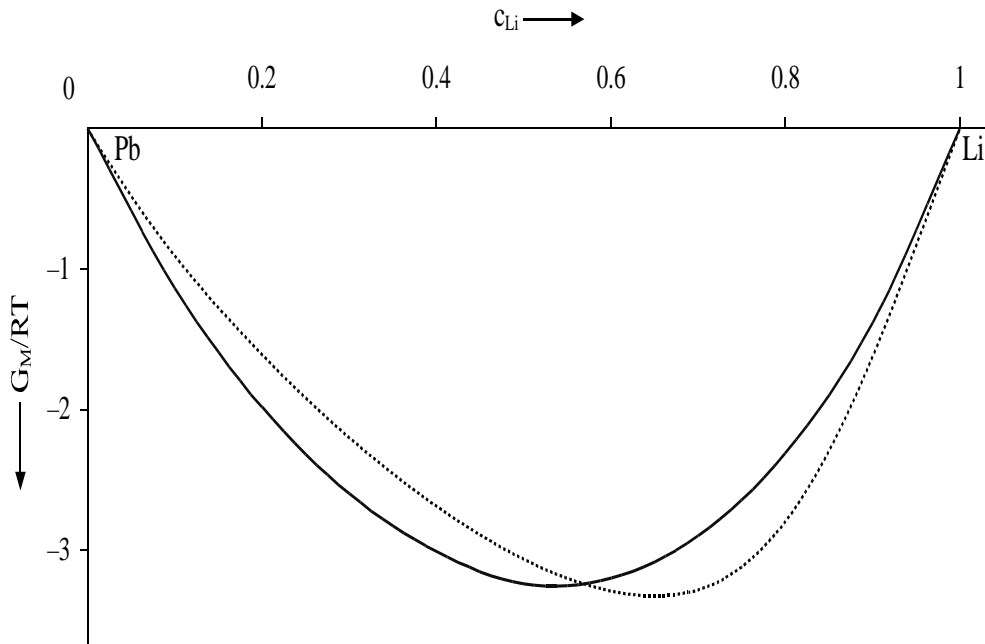

Fig. 1: G_M/RT-c_{Li} curve for Li-Pb liquid alloys at 932 K. Full curve represents theoretical values; dotted curve experimental values.

Equation (v) has been used to compute ln a_{Li} which is plotted against c_{Li} in Figure 2 along with its experimental values [12] at 932K. The computed and observed values are in reasonable agreement though some discrepancies may also be noted. In the concentration range c_{Li}<0.31 the computed values of ln a_{Li} are smaller than observed values but in the concentration range c_{Li}>0.31 the computed values are greater than observed ones.
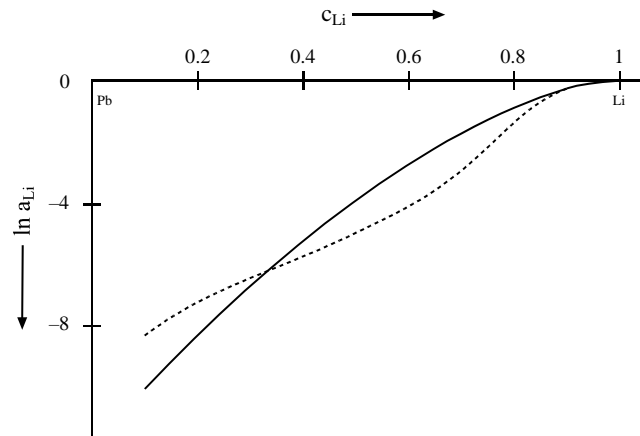

Fig. 2: ln a_{Li}-c_{Li} curve for Li-Pb liquid alloys at 932 K. Full curve represents theoretical values; dotted curve experimental values.

3. Heat of mixing and entropy of mixing

The theoretical understanding of the heat of mixing as a function of temperature is very useful because it leads directly to the nature of interaction among the constituent species of an alloy [8, 9].

The relation among the free energy of mixing (G_M), entropy of mixing (S_M) and heat of mixing (H_M) is given by

$$S_M = \frac{H_M - G_M}{T}.$$ (vi)

Here we use the standard thermodynamic relation

$$S_M = -\frac{\partial G_M}{\partial T}.$$ (vii)

From equation (vi) we have

$$\frac{H_M}{RT} = \frac{G_M}{RT} + \frac{S_M}{R}. \tag{viii}$$

Differentiating equation (i) with respect to T,

$$\frac{\partial G_M}{\partial T} = R\left[c\ln c + (1-c)\ln (1-c) + c\ln (1-\beta) - \frac{cT}{1-\beta}\frac{\partial \beta}{\partial T} - \ln (1-\beta c) + \frac{cT}{1-\beta c}\frac{\partial \beta}{\partial T} \right] +$$

$$c(1-c)\left[\frac{1}{1-\beta c}\frac{\partial \omega}{\partial T} + \frac{\omega c}{(1-\beta c)^2}\frac{\partial \beta}{\partial T} \right]. \tag{ix}$$

Using equations (vii) and (ix) we obtain

$$S_M = -R[c\ln c + (1-c)\ln (1-c)] - R\phi(c) - \frac{c(1-c)}{1-\beta c}\frac{\partial \omega}{\partial T} +$$

$$RT\frac{c(1-c)}{1-\beta c}\left[\frac{\beta}{1-\beta} - \frac{c}{1-\beta c}\frac{\omega}{RT} \right]\frac{\partial \beta}{\partial T}, \tag{x}$$

where $\quad \dfrac{\partial \beta}{\partial T} = (\alpha_B - \alpha_A)\dfrac{V_A}{V_B},$

α_A and α_B being the coefficients of thermal expansion of pure species A and B respectively.

Now, using equations (i) and (x) in equation (viii) we get

$$\frac{H_M}{RT} = c\ln c + (1-c)\ln (1-c) + \phi(c) + \frac{\omega}{RT}\frac{c(1-c)}{1-\beta c} - [c\ln c + (1-c)\ln (1-c)] -$$

$$\phi(c) - \frac{1}{R}\frac{c(1-c)}{1-\beta c}\frac{\partial \omega}{\partial T} + Tc\frac{1-c}{1-\beta c}\left[\frac{\beta}{1-\beta} - \frac{c}{1-\beta c}\frac{\omega}{RT} \right]\frac{\partial \beta}{\partial T}$$

$$\Rightarrow \frac{H_M}{RT} = \frac{\omega}{RT}\frac{c(1-c)}{1-\beta c} - \frac{1}{R}\frac{c(1-c)}{1-\beta c}\frac{\partial \omega}{\partial T} + Tc\frac{1-c}{1-\beta c}\left[\frac{\beta}{1-\beta} - \frac{c}{1-\beta c}\frac{\omega}{RT} \right]\frac{\partial \beta}{\partial T} \tag{xi}$$

To determine the heat of mixing and entropy of mixing we need the variation of interchange energy with temperature. With this in mind we have used equation (xi) to ascertain the variation of interchange energy with temperature in the light of observed heat of mixing [12]. In the present work the value of $(1/R)\partial\omega/\partial T$ is 2.4. The concentration dependence of H_M/RT for Li-Pb liquid

alloys at 932 K. is plotted in Figure 3. The computed and observed values are in reasonable agreement. It may be noted that H_M for Li-Pb alloys is quite asymmetric around the equiatomic composition. The position of minimum in H_M is at $c_{Li}=0.56$ whereas the observed values of H_M exhibit minimum at $c_{Li}=0.7$. The large negative value of H_M/RT ($= -3.62$) seems to suggest that there is a strong interaction between the constituent species of the alloy.
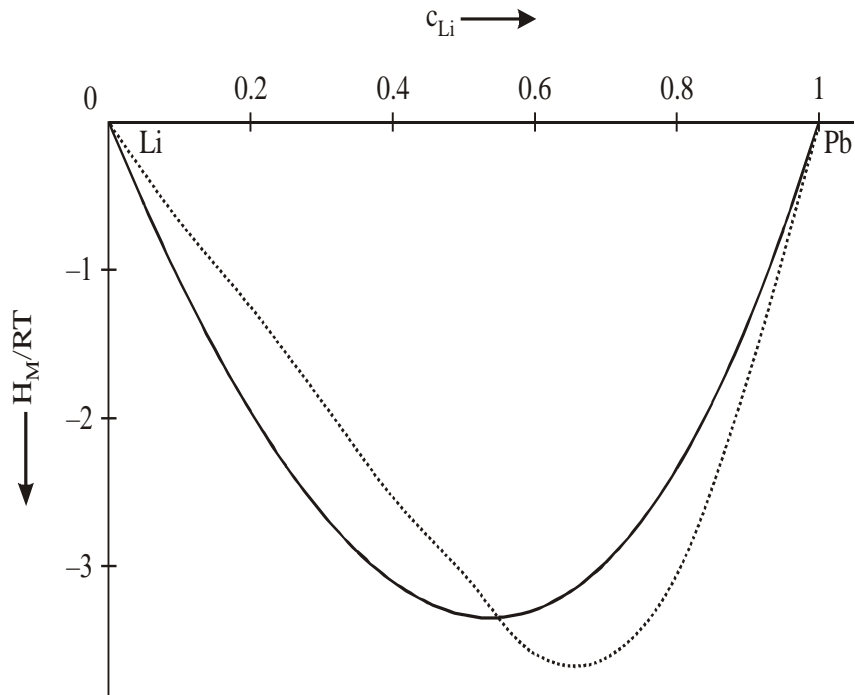

Fig. 3: H_M/RT-c_{Li} curve for Li-Pb liquid alloys at 932 K. Full curve represents theoretical values; dotted curve experimental values.

The entropy of mixing has been computed as a function of concentration from equation (x) by putting the same values of ω/RT and $\partial\omega/\partial T$ as used in equation (xi). Plot of S_M/R versus c_{Li} at 932 K. is shown in Figure 4. It is interesting to observe that S_M-c_{Li} variation is clearly S-shaped. According to computation, for $c_{Li} \leq 0.31$, S_M is positive and for $c_{Li} > 0.31$, S_M is negative. The maximum in S_M occurs at $c_{Li}=0.1$ and minimum at $c_{Li}=0.65$. The study of entropy of mixing indicates that Li-Pb liquid alloys are structurally disordered for lower concentration range of c_{Li} and become ordered in the higher concentration region of c_{Li}.
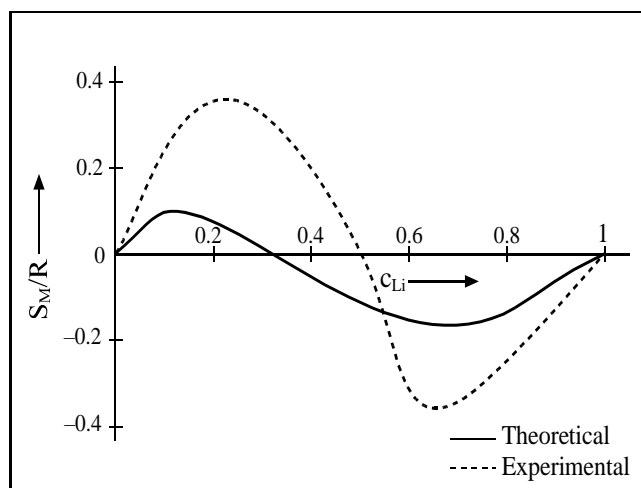
Fig. 4: S_M/RT-c_{Li} curve for Li-Pb liquid alloys at 932 K. Full curve represents theoretical values; dotted curve experimental values.

4. Summary and conclusion

The Flory´s model has been considered to study the concentration dependence of free energy mixing, activity, heat of mixing and entropy of mixing of lithium-lead liquid alloys. Present work explains the observed asymmetry of the properties of mixing of Li-Pb liquid alloys. The free energy of mixing and heat of mixing have been successfully explained and the nature of ln a_{Li}-c_{Li} curve is also explained to a great extent. There is a discrepancy between the theoretical and observed values of S_M, which may be due to formation of complexes.

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