# Concentration Dependence of Thermodynamic Properties of NaPb Liquid Alloy

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## ABSTRACT

*We have determined integral excess free energy of mixing, heat of mixing and entropy of mixing of NaPb alloys in molten state at 700 K. The observed asymmetry in the properties of mixing of NaPb alloy in molten state is successfully explained on the basis of regular associated solution model. The theoretical analysis reveals that the pairwise interaction energies between the species depend considerably on temperature.*

## 1. Introduction

Most of the binary alloys are grown from their corresponding liquid phase. In order to improve the quality of growth and to understand the energetic of the formation of alloys, it is important to have as good an understanding as possible of the properties of the liquid alloys. The thermodynamic properties of liquid Na-Pb alloy in molten state exhibits anomalous behaviour as a function of concentration [1]. In present paper, we have used regular associated solution model to understand the thermodynamic properties of Na-Pb alloys in the liquid state at 700 K. Regular associated solution model has been proved to study the thermodynamic and structural properties of weakly, moderately and highly interacting liquid alloys [2-6] by assuming the formation of complex. Such assumptions have been used in different models [7-13]. We have assumed Na and Pb atoms are energetically favoured to form NaPb complex in the molten state.

Theoretical formalism is given in Section 2; Section 3 deals with the numerical result and discussion. Conclusions are provided in Section 4.

## 2. Theory

Let one mole of binary solution of NaPb alloy comprising of $x_1$ mole of A (=Na) atoms and $x_2$ moles of B (=Pb) atoms. The presence of AB (=NaPb) type complex in the solution results in a depletion of concentration of free atoms of the components of A and B. The liquid solution is thus composed of three species namely free atoms A and B and the complex AB. As a result of associations, the thermodynamic behaviour of the components A and B is governed by the true mole fractions $x_A$ and $x_B$ rather than the gross mole fraction $x_1$ and $x_2$. Thus it is convenient to operate with two frames of references, one referring to gross mole fractions $x_1$ and $x_2$ and other referring to actual mole fractions of each species ($x_A$, $x_B$ and $x_{AB}$). Further, it is assumed that there are $n_1$ moles of species A, $n_2$ moles of species B and $n_3$ moles of species AB per mole of the binary solution. From the conservation of mass, the two frames of reference can be interrelated as follows:

$$n_1 = x_1 - n_3, \quad n_2 = x_2 - n_3$$

and
$$n = n_1 + n_2 + n_3 = 1 - n_3 \tag{1}$$

$$x_A = \frac{n_1}{n_1 + n_2 + n_3} = \frac{n_1}{1 - n_3}, \quad x_B = \frac{n_2}{n_1 + n_2 + n_3} = \frac{n_2}{1 - n_3}$$

and

$$x_{AB} = \frac{n_3}{n_1 + n_2 + n_3} = \frac{n_3}{1 - n_3} \tag{2}$$

Here,

$$\frac{1}{n} = \frac{1}{1 - n_3} = 1 + \frac{n_3}{1 - n_3} = 1 + x_{AB} \tag{3}$$

Now using Equation (3) in Equation (2), we have,

$$n_1 = \frac{x_A}{1 + x_{AB}}, \quad n_2 = \frac{x_B}{1 + x_{AB}}$$

$$n_3 = \frac{x_{AB}}{1 + x_{AB}} \tag{4}$$

For the sake of convenience one or more of these frames of reference may be used.

Now $x_A$, $x_B$ and $x_{AB}$ can be inter-related with each other as follows

$$x_1 x_2 = x_2 x_1$$

Using $n_1 = x_1 - n_3$ and $n_2 = x_2 - n_3$, we get

$$(n_1 + n_3) x_2 = (n_2 + n_3) x_1$$

After performing some algebraic operations and rearranging the terms, we obtain

$$n_1 (x_1 + x_2) + x_2 n_3 = x_1 (n_1 + n_2 + n_3)$$

and

$$x_A = x_1 - x_2 x_{AB} \tag{5a}$$

Similarly we can obtain

$$x_B = x_2 - (1 - x_2) x_{AB} \tag{5b}$$

In regular associated solution, the gross chemical po-tentials of components 1 and 2 are equal to the chemical potentials of the monomeric species A and B [2-7]. The activity coefficients $\gamma_A$, $\gamma_B$ and $\gamma_{AB}$ of monomers and complex can be expressed in terms of pairwise interaction energies through [3-5]

$$RT \ln \gamma_A = x_B^2 \omega_{12} + x_{AB}^2 \omega_{13} + x_B x_{AB} (\omega_{12} - \omega_{23} + \omega_{13}) \tag{6a}$$

$$RT \ln \gamma_B = x_{AB}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{AB} (\omega_{23} - \omega_{13} + \omega_{12}) \tag{6b}$$

$$RT \ln \gamma_{AB} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_B x_A (\omega_{13} - \omega_{12} + \omega_{23}) \tag{6c}$$

where $\omega_{12}$, $\omega_{13}$ and $\omega_{23}$ are interaction energies for the species A, B; A, AB and B, AB respectively, $T$ the temperature and $R$ stands for the universal gas constant. The equilibrium constant in a regular associated can be obtained [3,4] as

$$\ln k = \ln \left( \frac{x_A x_B}{x_{AB}} \right) + \frac{\omega_{12}}{RT} \left[ x_B (1 - x_A) + x_A \right] + \frac{\omega_{13}}{RT} \left[ x_{AB} (1 - x_A) - x_A \right] + \frac{\omega_{23}}{RT} \left[ x_{AB} (1 - x_B) - x_B \right] \tag{7}$$

Now using the equations listed above the free energy G is given by

$$G = \frac{1}{(1 + x_{ApB})} (x_A x_B \omega_{12} + x_A x_{AB} \omega_{13} + x_B x_{AB} \omega_{23}) + \frac{RT}{(1 + x_{AB})} \times (x_A \ln x_A + x_B \ln x_B + x_{AB} \ln x_{AB}) + \frac{x_{AB}}{(1 + x_{AB})} RT \ln k \tag{8}$$

Once the expressions for $G$ are obtained, other thermodynamic and microscopic functions follow readily. Enthalpy of mixing ($H$), entropy of mixing ($S_M$) are related to G through standard thermodynamic relations

$$H = G - T \left( \frac{\partial G}{\partial T} \right)_P \tag{9}$$

$$S_M = \frac{H - G}{T} \tag{10}$$

In a regular associated solution $x_1 \gamma_1 = x_A \gamma_A$ and $x_2 \gamma_2 = x_B \gamma_B$, where $\gamma_1$ and $\gamma_2$ are respective gross activity coefficients of components 1 and 2. Thus

$$\ln \gamma_1 = \ln \gamma_A + \ln \frac{x_A}{x_1} \tag{11a}$$

and

$$\ln \gamma_2 = \ln \gamma_B + \ln \frac{x_B}{x_2} \tag{11b}$$

The pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution can be written as [5]

$$\ln \gamma_1^0 = \frac{\omega_{12}}{RT} + \left[ 1 - \left( 1 + k \exp \frac{\omega_{23} - \omega_{12}}{RT} \right)^{-1} \right] \tag{12a}$$

$$\ln \gamma_2^0 = \frac{\omega_{12}}{RT} + \left[ 1 - \left( 1 + k \exp \frac{\omega_{13} - \omega_{12}}{RT} \right)^{-1} \right] \tag{12b}$$

where $\gamma_1^o$ and $\gamma_2^o$ are the respective activity coefficients of component A and that of B at zero concentrations. Solving Equations (6a) and (6b) we obtain

$$\frac{\omega_{13}}{RT} = \frac{x_B \ln \left( \frac{a_2}{x_B} \right) + (1 - x_B) \ln \left( \frac{a_1}{x_A} \right) - x_B (1 - x_B) \frac{\omega_{12}}{RT}}{x_{AB}^2} \tag{13a}$$

$$\frac{\omega_{23}}{RT} = \frac{x_A \ln \left( \frac{a_1}{x_A} \right) + (1 - x_A) \ln \left( \frac{a_2}{x_B} \right) - x_A (1 - x_A) \frac{\omega_{12}}{RT}}{x_{AB}^2} \tag{13b}$$

where $a_1$ and $a_2$ are activities of the components Na and Pb

Using Equations (7), (12) and (13) we can derive

$$\ln k + \frac{\omega_{13}}{RT} = \left( \frac{1 + x_A}{x_{AB}} \right) \ln \left( \frac{a_1}{x_A} \right) + \frac{x_B}{x_{AB}} \left[ \ln \left( \frac{a_2}{x_B} \right) - \frac{\omega_{12}}{RT} \right] + \ln \left( \frac{a_1 a_2}{x_{AB}} \right) \tag{14a}$$

$$= \ln \gamma_1^0 - \ln \left[ 1 - \gamma_2^0 \exp(-\omega_{12} / RT) \right] \tag{14b}$$

At equiatomic composition, where $x_1 = x_2$; $x_A = x_B$, we have

$$x_{AB} = \frac{\ln\left(\gamma_2/\gamma_1\right)_{x_1=x_2=0.5}}{\ln\left[\dfrac{\gamma_1^0}{\gamma_2^0}\cdot\dfrac{1-\gamma_2^0\exp\left(-\omega_{12}/RT\right)}{1-\gamma_1^0\exp\left(-\omega_{12}/RT\right)}\right]} \qquad (15)$$

## 3. Results and Discussion

We have calculated the concentration of complex, equilibrium constant and pairwise interaction energies following the method employed by Lele and Ramchancrarao [2] and D. Adhikari *et al* [3,5,6] using Equations (11)-(15) by iterative procedure. The equilibrium constant and interaction energies for the alloy Na-Pb in liquid state at 700 K are found to be $K = 0.0118$, $\omega_{12} = -27.747$ kJ·mol$^{-1}$, $\omega_{13} = -21.930$ kJ·mol$^{-1}$ and $\omega_{23} = -7.562$ kJ·mol$^{-1}$. The calculated and observed value of integral excess free energy of mixing ($G^{xs}$) is in good agreement (**Figure 1**). The calculated integral excess free energy of mixing is minimum ($-12.22$ kJ·mol$^{-1}$) at $x_{Na} = 0.6$ which almost matches with the observed value [1]. The observed asymmetry in integral excess free energy of mixing is well explained by our theoretical model.

We have observed that if the interaction energies are supposed to be independent of temperature, *i.e.* $\dfrac{\partial\omega_{12}}{\partial T} = 0$, then H and $S_M$ so obtained are in very poor agreement with experimental data. This simply suggests importance of the dependence of interaction energies on temperature. On using Equation (10) and observed values of $H$ [11] we have chosen the following values for the given parameters as the best fit values for the heat of formation of NaPb complex

$$\frac{\partial\omega_{12}}{\partial T} = +2.5 \;\; \text{Jmol}^{-1}\cdot\text{K}^{-1}, \qquad \frac{\partial\omega_{13}}{\partial T} = +1.5 \;\; \text{Jmol}^{-1}\cdot\text{K}^{-1},$$

$$\frac{\partial\omega_{23}}{\partial T} = -15.5 \;\; \text{Jmol}^{-1}\cdot\text{K}^{-1}$$

and $RT^2\dfrac{\partial\ln k}{\partial T} = 43530 \pm 1200$ J·mol$^{-1}$. The dependence of energy parameters on temperature can be observed from the study of $H$ and $S_M$. It is found that the pairwise interaction energies to be considerably dependent on temperature. It is found from the analysis that the heat of mixing is negative at all concentration. Our theoretical calculation shows that the minimum value of the heat of mixing is $-18.02$ kJ·mol$^{-1}$ at $x_{Na} = 0.6$. The observed minimum value is also at $x_{Na} = 0.6$ [1]. The calculated values are in reasonable agreement with the observed values (**Figure 2**). The concentration dependence of asymmetry in $H$ is well explained.

We have calculated entropy of mixing of NaPb alloy in liquid state using Equation (10). The calculated values always match in sign with observed values. The calcu-

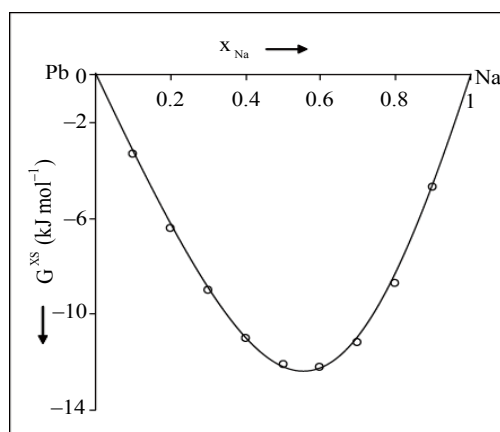lated values and experimental values are in reasonable agreement at all concentration range (**Figure 3**).



**Figure 1.** Integral excess free energy of mixing ($G^{xs}$) versus $x_{Na}$ (concentration of Na) in the liquid NaPb solution (700 K); (——) theory, (ooo) experiment [1].
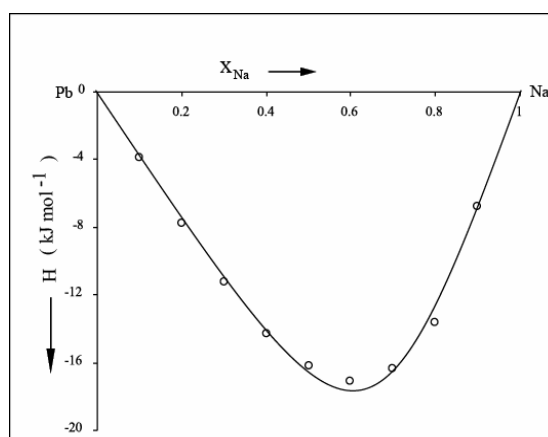


**Figure 2.** Heat of mixing ($H$) versus $x_{Na}$ of liquid NaPb solution (700 K); (——) theory, (ooo) experiment [1]
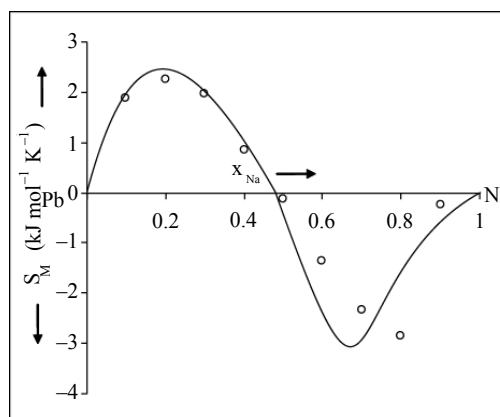


**Figure 3.** Entropy of mixing ($S_M$) versus $x_{Na}$ of liquid NaPb (700 K) (——) theory, (ooo) experiment [1]

## 4. Conclusions

The asymmetry in thermodynamic properties like, integral excess free energy of mixing, heat of mixing and entropy of mixing of NaPb liquid alloys at 700 K is well explained by the present theoretical model. Present theoretical analysis shows that there exist complexes NaPb in NaPb alloy in molten state and the pairwise interaction energies are temperature dependent.

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