# Hetero-Coordination in Liquid Pb-K Alloys

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**Abstract:** *The observed asymmetry in properties of mixing of Pb-K alloys in the molten state is successfully explained on the basis of the quasi-lattice model. The thermodynamic functions such as free energy of mixing, enthalpy of mixing, entropy of mixing and chemical activity of the constituent atom of the alloys have been computed within the frame work of presented model. Most of the computed values are in good agreement with the experimental data. The pair-wise interaction energies between the species of the melt are found to depend considerably on temperature. Theoretical analysis suggests that hetero-coordination leading to the formation of complex Pb2K is likely to exist but is of weakly interacting in nature.*

**Keywords:** Hetero-coordination; Chemical activity; Entropy; Pair-wise interaction energy.

## 1. INTRODUCTION:

Liquid alloys display a remarkable variety of local chemical order. The knowledge of mixing properties of binary liquid alloys is necessary for the design and development of reliable materials for high temperature application. Experimental determination of mixing properties of liquid alloys is a long and expensive task that becomes more complicated for some system which may be chemically active or radioactive or even may contain scarce components. Theoretical method, on the other hand reduces the time and efforts required, and are of great importance in predicting the properties. There has been considerable interest of theoreticians to explain the concentration dependent asymmetry in the properties of mixing of binary liquid alloys and hence to extract additional structural or microscopic information. Present day, various theoretical models [1-10] have been focused to study of the alloying behavior of alloys in the molten state. In the present investigation, the Quasi-lattice model [11, 12] has been used to estimate the thermodynamic properties of the alloys at 848K assuming $Pb_2K$ complex in the melt. Thermodynamic properties provide information on the interaction, stability and bonding strength among the constituent atoms in the alloys. The free energy of mixing, heat of mixing and activity of the species of the alloys are quite asymmetrical around equi-atomic composition but entropy of mixing of the Pb-K system is S – shaped [13]. The size factor ($V_K/V_{Pb}$ = 2.5, where V is atomic volume) and electro-negativity ($E_K - E_{Pb}$ = -1.5) are not so large to account for the anomalous behavior observed in the properties of mixing of PbK liquid alloys [9].Therefore, it is expected that concentration dependent anomaly arises due to energy effects.

## 2. METHODOLOGY:

The present work is purely theoretical in nature and the following methods shall be used for our investigations:

In present work, we will use a quasi-lattice model to understand the mixing properties of simple binary liquid alloys with respect to concentration. In this model a grand partition function is constructed to deduce the relations for thermodynamic and microscopic functions. The quasi-lattice model is applicable for binary liquid alloys, which in solid or liquid state form a chemical compound at one or more well defined chemical composition and the complexes or the privileged group of atoms exist in the molten state. In this model, it is assumed that the energy of a given nearest neighbor bond is different if it belongs to the complex than if it does

not. The model envisages the existence of chemical complexes $A_\mu B_\nu$, where A and B are the constituent species of the alloys and $\mu$ and $\nu$ are the small integers:
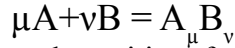
$$\mu A + \nu B = A_\mu B_\nu$$

With this consideration, grand partition function is solved and expression for excess free energy of mixing [10] comes out to be

$$G_M^{XS} = Nk_BT \int_0^x \ln\gamma \, dx$$

$$= N[x(1-x)\omega + \phi_{AB}\Delta\omega_{AB} + \phi_{AA}\Delta\omega_{AA} + \phi_{BB}\Delta\omega_{BB}] \quad (1)$$

Where N is the total number of the atoms in the alloys; $k_B$, the Boltzmann constant; T, absolute temperature; $\gamma$, ratio of the activity coefficient of atom A to B ; x, the concentration of atom A; $\omega$'s are the ordering energies and $\phi_{ij}$ ( i,j = A,B) are the simple polynomials in x depending on the values of $\mu$ and $\nu$, which is given by

$$k_BT\phi_{\mu,\nu} = \Delta\omega_{AB}[2\beta(\mu+1,\nu) - 2\beta(\mu,\nu+1) + \beta(2\mu-1,2\nu) + \beta(2\mu,2\nu-1)] +$$

$$\Delta\omega_{AA}[\beta(2\mu-2,2\nu+1) - 2\beta(\mu,\nu+1)] + \Delta\omega_{BB}[2\beta(\mu+1,\nu) - \beta(2\mu+1,2\nu-2)] \quad (2)$$

Where $\beta$'s are the usual beta functions.

The free energy of mixing of a complex forming binary liquid alloys is

$$G_M = G_M^{XS} + Nk_BT[x \ln x + (1-x)\ln(1-x)]$$

$$= RT[x(1-x)\frac{\omega}{k_BT} + \phi_{AB}\frac{\Delta\omega_{AB}}{k_BT} + \phi_{AA}\frac{\Delta\omega_{AA}}{k_BT} +$$

$$\phi_{BB}\frac{\Delta\omega_{BB}}{k_BT} + x \ln x + (1-x)\ln(1-x)] \quad (3)$$

Where R is the universal molar constant.

The heat of mixing is easily found out by using the standard thermodynamic relation:

$$\frac{H_M}{RT} = \frac{G_M}{RT} - \frac{1}{R}\left(\frac{dG_M}{dT}\right)_{x,N,P}$$

$$= x(1-x)\left\{\frac{\omega}{k_BT} - \frac{1}{k_B}\frac{d\omega}{dT}\right\} + \phi_{AB}\left\{\frac{\Delta\omega_{AB}}{k_BT} - \frac{1}{k_B}\frac{d(\Delta\omega_{AB})}{dT}\right\} +$$

$$\phi_{AA}\left\{\frac{\Delta\omega_{AA}}{k_BT} - \frac{1}{k_B}\frac{d(\Delta\omega_{AA})}{dT}\right\} + \phi_{AB}\left\{\frac{\Delta\omega_{BB}}{k_BT} - \frac{1}{k_B}\frac{d(\Delta\omega_{BB})}{dT}\right\} \quad (4)$$

dynamic relation for entropy of mixing is

$$\frac{S_M}{R} = \frac{H_M}{RT} - \frac{G_M}{RT} \quad (5)$$

The chemical activity of the component atom in the alloys is deduced from standard relation

$$RT\ln a_i(i=A,B) = G_M + (1-x_i)(\partial G_M / \partial x_i)_{T,P,N} \quad (6)$$

Which are given by

$$\ln a_A = \frac{G_M}{RT} + \frac{1-x}{k_BT}[(1-2x)\omega + \phi'_{AB}\Delta\omega_{AB} +$$

$$\phi'_{AA}\Delta\omega_{AA} + \phi'_{BB}\Delta\omega_{BB} + \ln(x/1-x)] \quad (7)$$

$$\ln a_B = \frac{G_M}{RT} - \frac{x}{k_BT}[(1-2x)\omega + \phi'_{AB}\Delta\omega_{AB} +$$

$$\phi'_{AA}\Delta\omega_{AA} + \phi'_{BB}\Delta\omega_{BB} + \ln(x/1-x)] \quad (8)$$

Where $\phi'$, $\phi'_{AB}$, $\phi'_{AA}$ and $\phi'_{BB}$ are the derivatives of $\phi, \phi_{AB}, \phi_{AA}$ and $\phi_{BB}$ respectively.

For $Pb_2K$ system,
A = Pb, B = K, $\mu = 2$, $\nu = 1$

$$\phi_{AB} = \frac{x}{6} + x^2 - \frac{5x^3}{3} + \frac{x^4}{2}$$

$$\phi_{AA} = -\frac{x}{4} + \frac{x^2}{2} - \frac{x^4}{4}$$

$$\phi_{BB} = 0, \text{ for } \nu < 2$$

## 3. RESULT AND DISCUSSION:
### 3.1. Free energy of mixing:
The method of successive approximation is suitable for the determination of energy parameters used for the calculation of the free energy of mixing for Pb-K liquid alloys. The parameters have been determined by using the experimental value of $G_M$[13] in the concentration range from 0.1 to 0.9. The best fit values of the parameter are

$$\frac{\omega}{k_BT} = 4.92, \frac{\Delta\omega_{AB}}{k_BT} = -16.85, \frac{\Delta\omega_{AA}}{k_BT} = 21.21, \frac{\Delta\omega_{BB}}{k_BT} = 0 \quad (9)$$

The free energy of mixing ($G_M$) for Pb-K liquid alloys at 848K is computed through Eq.(3). The plot of free energy of mixing verses concentration of lead is deposited in fig.1. The computed and experimental values of $G_M$ are in reasonable agreement throughout the concentration range from

88

0.1 to 0.9 of Pb. Theoretical calculation of free energy of mixing for Pb-K liquid alloys shows that the minimum value of free energy of mixing for Pb-K is -2.42737RT at $x_{Pb}$ = 0.5. This is good agreement with the experimental value [13]. Further, the negative values of all interaction energies suggest that Pb and K atoms are attracted to each other and consequently tendency of the system is found to be ordering (complex formation). The minimum value of free energy of mixing indicates that Pb-K alloy in liquid state is moderately interacting system and hence, the tendency of compound formation is not strong in this alloy.
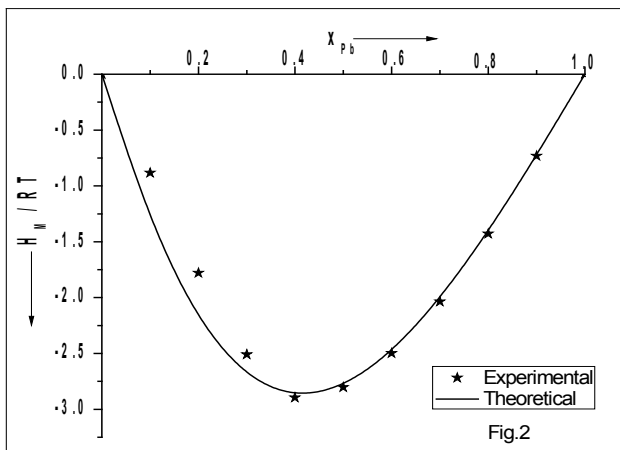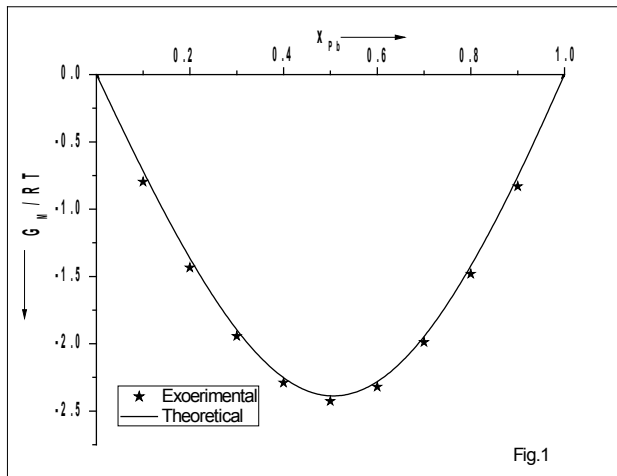


Fig.2



Fig.1

**Figure1**-Free energy of mixing ($G_M$)Vs concentration of Pb ($x_{Pb}$) in liquid Pb-K alloy at 848K.
**Figure 2**- Heat of mixing ($H_M$) Vs concentration of Pb ($x_{APb}$) in liquid Pb-K alloy at 848K.

## 3.2. Heat of mixing:
To determine the heat of mixing for liquid Pb-K alloys, we need temperature derivatives of interaction

energy parameters. The observed values of $H_M$ [13] are used to obtain the temperature derivatives by successive approximation method. The best fit values of these parameters are found to be

$$\frac{1}{k_B}\frac{\partial \omega}{\partial T}=+19.83, \quad \frac{1}{k_B}\frac{\partial(\Delta\omega_{AB})}{\partial T}=-23.55, \quad \frac{1}{k_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}=+13.29 \quad (10)$$

Heat of mixing ($H_M$) for liquid Pb-K alloys at 848K is computed by using eq.(4). The graph is plotted for heat of mixing with both theoretical and experimental values against concentration of lead, which is shown in fig.(2).The figure shows that theoretical values of $H_M$ are in good agreement along with the experimental values[13].

## 3.3. Entropy of mixing:
Using equation (5) along with eq.(3) and (4), entropy of mixing ($S_M$) for liquid Pb-K alloys is computed. For the theoretical calculation of $S_M$, same energy parameters (Eq.(9) and (10) ) are used. The plot of entropy of mixing ($S_M$) verses concentration of Pb is depicted in fig.(3),for both the computed and observed values. It is interesting to observe that the variation of $S_M$ with $x_{Pb}$ is clearly in S – shaped. Theoretically, $S_M$ is negative for $x_{Pb} \leq 0.7$ but for $x_{Pb} > 0.7$, $H_M$ is positive.  Minimum value of entropy of mixing is found at $x_{Pb}$ = 0.3 and maximum value is occurred at $x_{Pb}$ = 0.9. It is also observed that concentration dependence of asymmetry in $S_M$ can be explained only when one considers the temperature dependence of the pair-wise interaction energies.
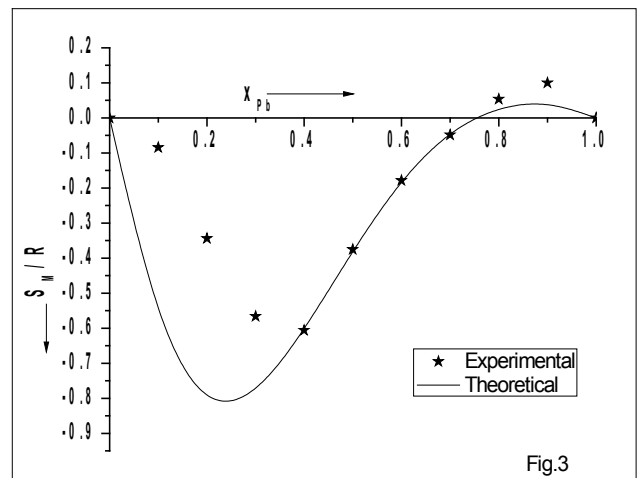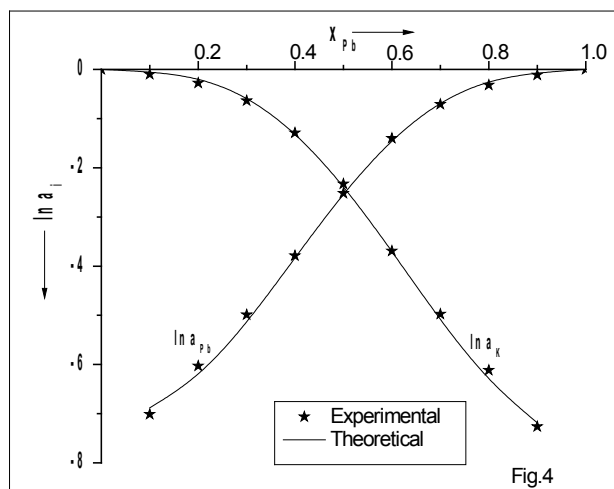


Fig.3

existence of chemical complexes $Pb_2K$ in molten phase. The analysis suggests that the tendency of hetero-coordination of atom depends very much on concentration and the Pb-K system is moderately interacting. The analysis also reveals that most of the energy parameters depend considerably on temperature.

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**Figure 3**- Entropy of mixing ($S_M$ ) Vs concentration of Pb ($x_{Pb}$ ) in liquid Pb-K alloy at 848K.
**Figure 4**-Chemical activity ($a_i$ ) Vs concentration of Pb ($x_{Pb}$ ) in liquid Pb-K alloy at 848K.

## 3.4. Chemical activity:

The deviations from ideal behavior of the alloys can be incorporated into activities. The pair of equations (7) and (8) is used for theoretical calculation of chemical activity of the constituent atom in Pb-K alloys. Figure (4) shows the comparison between computed and observed values of chemical activity of the species of Pb-K alloys. There is good agreement between the computed and observed values at all concentration of Pb.

## 4. CONCLUSIONS:

The presented theoretical model successfully explains the observed concentration dependent asymmetries reproduced by considering the