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Study of Thermodynamic Properties of Bi-Pb Liquid Alloy

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Abstract. We have used quasi-lattice theory to describe the mixing behavior of Bi-Pb liquid alloys at a temperature of 700K by computing thermodynamic functions and structural functions. The thermodynamic functions includes free energy of mixing(G_M), activity (a), heat of mixing (H_M), entropy of mixing (S_M). The structural functions includes concentration fluctuation in the long-wavelength limit ($S_{cc}(0)$) and chemical short range order parameter (α_1). Most of the computed values are in good agreement with the experimental data. The pair-wise interaction energies between the species of the liquid alloys play important role and are found to temperature dependent. Theoretical analysis suggests that Pb_3Bi complex exists in the liquid state at 700K. And, it has hetero-coordination (i.e. ordering) nature but is of weakly interacting in nature.

Keywords: Liquid alloys, Ordering, Interaction energy, Quasi-lattice theory

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1. INTRODUCTION

The primary objective for metallurgical science researchers and engineers is to design and/or optimize alloy microstructure in order to obtain the necessary properties and therefore desired efficiency. While alloys have profound solid-state applications, their properties arise in the liquid state. The properties of alloys in the liquid state are therefore important to understand. An appreciation of the phase stability and thermodynamics of binary subsystems is mandatory in order to understand the mixing behaviour of complex alloys. This knowledge can not be derived solely from experiments because they are costly, time-consuming, slow, and frequently pose challenges related to high melt reactivity at high temperatures. In this respect, thermodynamic modeling is a useful tool for understanding the nature and predicting the alloying behavior of liquid alloys. In addition, for decades, asymmetries and variations in the mixing properties of liquid alloys have received significant attention from researchers in the field of materials science.

Alloys are a kind of metallic substance composed of two or more pure components. The properties of alloys such as melting point, boiling point, density, specific gravity, high malleability, ductility, thermal and electrical conductivity are different from those of their components that can be altered as required. Consequently, alloys have a large range of uses. Alloy are of different types. Based on atom mixing characteristics: If two atoms are combined to form an alloy, it is considered a binary alloy. If there are three kinds of atoms combined, it is called a ternary alloy, and so on.

One of the topics of great interest to physicists, chemists and metallurgists is the study of physical properties such as thermodynamic, electrical, surface and structural properties of binary liquid alloy, and one of the intense fields of research of metallurgical science. Models and experimental techniques have been developed by both theoreticians and experimentalists to get through the anomalies in alloy thermodynamic, microscopic structural and surface properties for decades.

Bismuth is a pinkish-tinted white, crystalline, brittle metal. The chemical symbol 'Bi' represents it and its atomic number is 83. An alloy of Bismuth is used in soldering, magnetic memory devices,thermocouple etc. Bi-Pb alloy has a melting temperature of 398 K and boiling temperature of 1943 K [1] used for the coolant of new generation fast reactors. Due to a uses of Bi-Pb alloy in the nuclear reactor, the study of various properties of Bi-Pb alloy become great interest for researcher.

Many theoretician [2]- [5] and experimentalists [6]- [9] have been trying to interpret the behavior of binary alloys in liquid state using various models/methods. In 2010, the thermodynamic properties and microscopic structure of Cd-Na liquid alloys at 670 K was researched by using regular associated solution model and found that Cd-Na system is a weakly interacting [10]. In 2012, Awe and Olawole studied the correlation between bulk properties and surface properties in Cd-X (X=Hg, Mg) liquid alloys [11]. In 2013, thermodynamic, transport and surface properties of liquid In–Pb alloys have been investigated using the simple statistical model and found that liquid In–Pb alloy is weakly interacting and phase separating system [12]. In 2017, the concentration fluctuations in long wavelength limit and thermodynamic properties of Zn-Sn binary liquid alloys at various temperatures were investigated [13]. In 2020, thermodynamic and structural properties of liquid Ag-Sb alloys at 1250K was investigated by using quasi-lattice model and found that the alloy interacts moderately in the nature and does not have a heavy tendency to formation of compound [14].

In the present work, we have used a Quasi Lattice model [17] to study the thermodynamical properties such as free energy of mixing (G_M), activity (a), the heat of mixing (H_M) and entropy of mixing (S_M), and hence to study the structural properties such as concentration fluctuation in the long-wavelength limit ($S_{CC}(0)$) and Warren-Cowley short-range order parameter (α_1) of Bi-Pb liquid alloys at molten state at 700 K.

2. THEORETICAL FORMALISM

2.1 Thermodynamic properties

The grand partition function for simple binary liquid alloys consisting of N_A (=Nx) and N_B (=N(1-x)) can be generalized as follows [17]

$$\Xi = \sum q_A^{N_A}(T) q_B^{N_B}(T) \exp\left[(\mu_A N_A + \mu_B N_B - E)/K_B T\right], \tag{1}$$

Where $q_i(T)(i = A, B)$ denote the partition functions associated with the inner and translational degrees of freedom of atoms i and the μ_i are the chemical potentials. N_A and N_B are the numbers of A and B atoms in the alloy with the configurational energy (E) and T is absolute temperature.

The standard thermodynamic relation for free energy of mixing is [16]

$$G_M^{exc} = G_M - G_M^{id} \tag{2}$$

Where G_M^{id} is the free energy of mixing for ideal solution given by

$$G_M^{id} = RT \sum_i C_i ln C_i \tag{3}$$

Solution of equation (1) can be written in the form of analytical expression for the ratio of activity coefficients of pure element as

$$\ln \gamma = z[\ln \sigma + (2K_B T)^{-1}(P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB})] + \vartheta \tag{4}$$

Where z is the coordination number, ϑ is temperature and pressure dependent parameter and other symbols mean as follows

$$\ln \sigma = \frac{1}{2} \ln \frac{(1-c)}{c} \frac{\beta + 2c - 1}{\beta - 2c + 1} \tag{5}$$

Where

$$\beta = \sqrt{1 + 4c(1-c)(\eta^2 - 1)} \tag{6}$$

with

$$\eta^2 = exp[\frac{2\omega}{zK_B T}] exp[\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{K_B T}] \tag{7}$$

$\Delta\varepsilon_{ij}$ (i,j=A,B) represents the difference in the energy of ij bond when it belongs to the complex $A_\mu B_\nu$, and ω is the usual interchange energy and is defined by the equation

$$\omega = Z[\varepsilon_{AB} - (\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2})] \tag{8}$$

Where ε_{AB}, ε_{AA} and ε_{BB} are the energies for AB, AA and BB pairs of atoms. P_{ij} denote the probability that an ij bond belongs to the complex and in the approximation, they are described as follows

$$P_{AB} = C^{\mu-1}(1-c)^{\nu-1}[2 - C^{\mu-1}(1-c)^{\nu-1}] \tag{9}$$

$$P_{AA} = C^{\mu-2}(1-c)^{\nu}[2 - C^{\mu-2}(1-c)^{\nu}], \mu \geq 2 \tag{10}$$

$$P_{BB} = C^{\mu}(1-c)^{\nu-2}[2 - C^{\mu}(1-c)^{\nu-2}], \mu \geq 0 \tag{11}$$

Where P_{AA} and P_{BB} are respectively zero for $\mu < 2$ and $\nu < 2$. Using equations (5), (6), (7), equation (4) can be written as

$$\ln \gamma = (K_B T)^{-1}[(1-2c)(\omega + \Delta\omega_{AB} P_{AB}) + c\Delta\omega_{AA} P_{AA} - (1-c) P_{BB}\Delta\omega_{BB}] + \vartheta \tag{12}$$

We observe from equation (12) that if all $\Delta\omega[ij] \equiv 0$, then

$$\ln \gamma = (K_B T)^{-1}[(1-2c)\omega, \tag{13}$$

Which is just the well-known expression of $\ln\gamma$ for a conformal solution or for a regular solution in the zeroth approximation.
With $\ln\sigma$ given by the approximation equation (4), the integrand involved in equation (13) for determining G_M^{exc} are simple polynomials in c and the integral is readily evaluated in closed form for special values of μ and ν.
First, if no complexes are formed ($\Delta\omega_{ij}\equiv 0$), one has

$$G_M^{exc} = Nc(1-c)\omega \tag{14}$$

Which is just again usual conformal solution expression. Also as in equation (13), for $\mu=\nu=1$, ω is just replaced by $\omega+\Delta\omega$. Explicit expressions for G_M^{exc} for (μ,ν) with $\mu=3$, $\nu=1$ is given as

$$G_M^{exc} = N[\omega c(1-c)+\Delta\omega_{AB}(\frac{1}{5}c+\frac{2}{3}c^3-c^4-\frac{1}{5}c^5+\frac{1}{3}c^6) + \Delta\omega_{AA}(-\frac{3}{20}c+\frac{2}{3}c^3-\frac{3}{4}c^4+\frac{2}{5}c^5-\frac{1}{6}c^6)] \tag{15}$$

Now, the free energy of mixing of binary liquid alloys for $\mu=3$ and $\nu=1$ is given by
$\frac{G_M}{RT} = \frac{G_M^{exc}}{RT} + c\ln c + (1-c)\ln(1-c)$
Substituting the value of $\frac{G_M^{exc}}{RT}$ from (15), we get

$$\frac{G_M}{RT} = [\frac{\omega}{K_BT}c(1-c)+\frac{\Delta\omega_{AB}}{K_BT}(\frac{1}{5}c+\frac{2}{3}c^3-c^4- \frac{1}{5}c^5+\frac{1}{3}c^6)+\frac{\Delta\omega_{AA}}{K_BT}(-\frac{3}{20}c+\frac{2}{3}c^3-\frac{3}{4}c^4+\frac{2}{5}c^5-\frac{1}{6}c^6)]+ c\ln c+(1-c)ln(1-c) \tag{16}$$

Which is the required expression for free energy of mixing of binary liquid alloys when $\mu=3$ and $\nu=1$. The activity a_A and a_B of in binary liquid alloy for a element A and B respectively is given as

$$\ln a_A = \frac{G_M}{RT}+\frac{c_B}{RT}(\frac{\partial G_M}{\partial c_A})_{T,P,N} \tag{17}$$

$$\ln a_B = \frac{G_M}{RT}+\frac{c_A}{RT}(\frac{\partial G_M}{\partial c_B})_{T,P,N} \tag{18}$$

where $c_A = c$ and $c_B = 1-c$.
Using equation (16) in equation (17) and (18) , we get

$$\ln a_A = \frac{G_M}{RT}+(1-c)[\frac{\omega}{K_BT}(1-2c)+\frac{\Delta\omega_{AB}}{K_BT}(\frac{1}{5}+2c^2- 4c^3-c^4+2c^5)+\frac{\Delta\omega_{AA}}{K_BT}(-\frac{3}{20}+2c^2-3c^3+2c^4- c^5)+\ln(\frac{c}{1-c})] \tag{19}$$

Which is the required expression of activity of component A in binary alloy.

$$\ln a_B = \frac{G_M}{RT}+c[\frac{\omega}{K_BT}(2c-1)+\frac{\Delta\omega_{AB}}{K_BT}(-\frac{1}{5}-2c^2+4c^3+ c^4-2c^5)+\frac{\Delta\omega_{AA}}{K_BT}(\frac{3}{20}-2c^2+3c^3-2c^4+c^5)+\ln(\frac{c}{1-c})] \tag{20}$$

Which is our required expression for activity of component B in binary liquid alloys when $\mu=3$ and $\nu=1$.
The entropy of mixing is defined as

$$S_M = -[\frac{\partial G_M}{\partial T}]_P \tag{21}$$

$$\frac{S_M}{R} = -[\frac{1}{K_B}\frac{\partial\omega}{\partial T}c(1-c)+\frac{1}{K_B}\frac{\partial(\Delta\omega_{AB})}{\partial T}(\frac{1}{5}c+\frac{2}{3}c^3-c^4- \frac{1}{5}c^5+\frac{1}{3}c^6)+\frac{1}{K_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}(-\frac{3}{20}c+\frac{2}{3}c^3-\frac{3}{4}c^4+\frac{2}{5}c^5- \frac{1}{6}c^6)]-[c\ln c+(1-c)\ln(1-c)] \tag{22}$$

Which is required expression for entropy of mixing of binary liquid alloys for $\mu=3$ and $\nu=1$.
The standard thermodynamic relation for heat of mixing is

$$H_M = G_M + TS_M \tag{23}$$

or,

$$\frac{H_M}{RT} = \frac{G_M}{RT}+\frac{S_M}{R} \tag{24}$$

After subtitution and solving we get

$$\frac{H_M}{RT} = \{\frac{\omega}{K_BT}-\frac{1}{K_B}\frac{\partial\omega}{\partial T}\}c(1-c)+\{\frac{\Delta\omega_{AB}}{K_BT}-\frac{1}{K_B}\frac{\partial(\Delta\omega_{AB})}{\partial T}\} (\frac{1}{5}c+\frac{2}{3}c^3-c^4-\frac{1}{5}c^5+\frac{1}{3}c^6)+\{\frac{\Delta\omega_{AA}}{K_BT}-\frac{1}{K_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}\} (-\frac{3}{20}c+\frac{2}{3}c^3-\frac{3}{4}c^4+\frac{2}{5}c^5-\frac{1}{6}c^6) \tag{25}$$

Which is the required expression for heat of mixing $\frac{H_M}{RT}$ of binary liquid alloys for $\mu=3$ and $\nu=1$.

2.2 Structural properties

The expression for concentration fluctuation in long wavelength limit ($S_{cc}(0)$) was introduced and derived by Bhatia and Thornton [3]. It is a very important thermodynamic function to visualize the nature of microscopic

structure as regards to the local arrangements of atoms in molten binary alloys [15]. It provides an idea about ordering and segregating nature of a solution. This structure factor readily leads to the knowledge of chemical short range order parameter (α_1) which indicates the degree of atomic ordering in the liquid alloy. The knowledge of ($S_{cc}(0)$) is very helpful to examine the stability of a solution.

Singh & Mishra have clearly demonstrated that any deviation of $S_{CC}(0)$ from ideal values $S^{id}_{cc}(0)$ is of great importance to visualize the degree of ordering in the alloys. They have demonstrated that $S_{CC}(0) > S^{id}_{cc}(0)$ corresponds to segregation and $S_{CC}(0) < S^{id}_{cc}(0)$refers to ordered alloys [17]. $S_{CC}(0)$ is thermodynamically related to free energy of mixing (G_M) as [16]

$$S_{CC}(0) = [NK_BT(\frac{\partial^2 G_M}{\partial c^2})^{-1}]_{T,P,N} \tag{26}$$

Here, $G_1^{(0)}$ and $G_2^{(0)}$ do not contribute for the evaluation of $\frac{\partial^2 G_M}{\partial c^2}$. By making the use of standard thermodynamic relations, we can also express equation (26) as

$$S_{CC}(0) = [NK_BT(\frac{\partial^2 G_M}{\partial c^2})^{-1}]_{T,P,N} = (1-c)a_A[\frac{\partial a_A}{\partial c}]^{-1}_{T,P,N}$$
$$= ca_B[\frac{\partial a_B}{\partial c}]^{-1}_{N,T,P} \tag{27}$$

Where a_A and a_B are the thermodynamic activities of components A and B in the binary mixture.

Using ($\frac{\partial^2 G_M}{\partial c^2}$) and solving, we get

$$S_{CC}(0) = \frac{c(1-c)}{[1+c(1-c)\{-\frac{2\omega}{K_BT} + \frac{\Delta\omega_{AB}}{K_BT}(4c-12c^2-4c^3 + 10c^4) + \frac{\Delta\omega_{AA}}{K_BT}(4c-9c^2+8c^3-5c^4)\}]} \tag{28}$$

Which is required expression for concentration fluctuation $S_{CC}(0)$ of binary liquid alloys.

Warren–Cowley short-range parameter (α_1) is useful to quantify the degree of chemical order, and it provides insight into the local arrangement of the atoms in the liquid alloys. α_1 can be estimated from the knowledge of $S_{CC}(0)$ as [4]

$$\alpha_1 = \frac{s-1}{s(z-1)+1} \tag{29}$$

where, z is coordination number and is defined as the number of nearest neighbours to an atom in a given structure and

$$S = \frac{S_{cc}(0)}{S^{id}_{cc}(0)} \tag{30}$$

3. RESULT AND DISCUSSION

3.1 Thermodynamic properties

Free energy of mixing ($\frac{G_M}{RT}$) of Bi-Pb liquid alloy at 700K

For the calculation of $\frac{G_M}{RT}$, energy parameters ω, $\Delta\omega_{AB}$, $\Delta\omega_{AA}$ are required.These parameters have been determined by the method of successive approximation on using the experimental value of $\frac{G_M}{RT}$ [18]. We have found that all three parameters play important role to compute $\frac{G_M}{RT}$ of Bi-Pb liquid alloys. These parameters have been found to be

$\frac{\omega}{K_BT} = -0.52077$, $\frac{\Delta\omega_{AB}}{K_BT} = -0.41299$, $\frac{\Delta\omega_{AA}}{K_BT} = 1.07659$

Using this energy parameters, free energy of mixing($\frac{G_M}{RT}$) of Bi-Pb liquid alloys have been computed from equation (16).The theoretical and experimental values of free energy of mixing are in good agreement [18]. Both theoretical and experimental values are negative at all concentrations and the minimum values are G_M^{min} = -0.9037RT and -0.9036RT at the equiatomic composition respectively. Hence the concentration dependent symmetry in free energy of mixing (G_M) observed from the experiment is well explained by quasi-lattice model. The values of $\frac{G_M}{RT}$ lies between 0 and -1, which results that Bi-Pb alloy systems is weakly interacting system.

The plot of $\frac{G_M}{RT}$ as a function concentration for Bi-Pb alloy is shown in Figure(1). The negative value of $\frac{G_M}{RT}$ is minimum at $C_{Pb} = 0.1$ and maximum at $C_{Pb} = 0.5$ for both the theoretical and experimental conditions. Hence the plot of $\frac{G_M}{RT}$ versus concentration shows the symmetry in free energy of mixing of Bi-Pb liquid alloy about the concentration $c = 0.5$. Further, the negative values of interaction energies suggest that Bi and Pb atoms are attracted to each other and consequently tendency of the system is found to be ordering (complex formation).

Activity of Bi-Pb liquid alloy at 700K

We have computed the activity of Bi and Pb of Bi-Pb liquid alloys in molten state at 700K by using equation (18) and (20). The activities of species in the binary Bi-Pb liquid alloy has been obtained in the framework of quasi-lattice model using the same ordering and interaction energies ω, $\Delta\omega_{AB}$, and $\Delta\omega_{AA}$ as the basic inputs for the computation, in order to maintain consistency with the calculation of the free energy of mixing. The comparison of computed and observed chemical activity values of Bi-Pb alloy species is shown in figure (2). At 700K, there is good agreement between computed and observed values

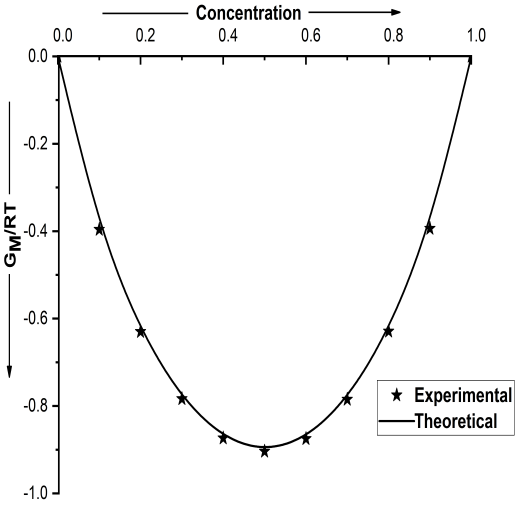

FIGURE 1. Free energy of mixing $\frac{G_M}{RT}$ versus C_{Pb} of liquid alloy Bi-Pb at 700K (—) theoretical and ($\star$) experimental.

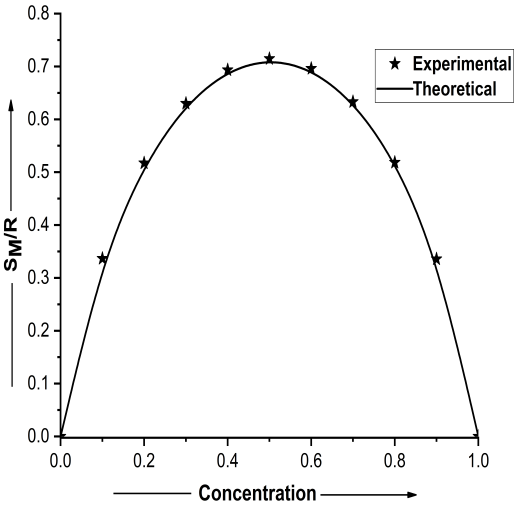

FIGURE 3. Entropy of mixing $\frac{S_M}{R}$ versus concentration of Bi-Pb liquid alloy at 700K (—) theoretical and ($\star$) experimental.

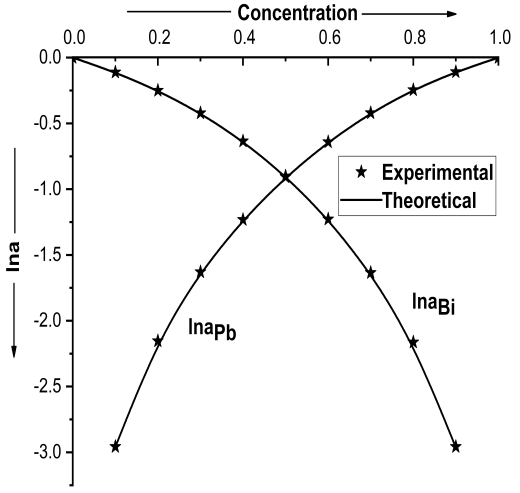

FIGURE 2. Activity $\ln a_{Bi}$ and $\ln a_{Pb}$ of Bi-Pb alloy at 700K.(—) theoretical and ($\star$) experimental.

of Bi and Pb activity in the Bi-Pb system at all concentration. It is possible to incorporate deviations from ideal behavior into activity. The interactions among the system's constituent species are considered to determine their magnitudes, which in turn determine the bond energies. Thus, it is reasonable to expect that measuring activities within a class of similar systems will provide at least a foundation for behavior correlation, which can then be used to extrapolate the behavior of more complex systems.

Entropy of mixing ($\frac{S_M}{R}$) for Bi-Pb liquid ally at 700K

The computation for the entropy of mixing ($\frac{S_M}{R}$) from equation (22) requires temperature derivatives of interaction energy parameters. These temperature derivatives have been determined by the method of successive approximation. The results are then compared with the experimental value of $\frac{S_M}{R}$ for Bi-Pb liquid alloy at 700K. The best fit derivatives value are found to be $\frac{1}{K_B}\frac{\partial\omega}{\partial T}$ =0.3202, $\frac{1}{K_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}$ =-0.2595 and $\frac{1}{K_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}$ =0.9617

The theoretical and experimental value of $\frac{S_M}{R}$ against C_{Pb} are plotted in figure (3). It is also observed that concentration dependence of asymmetry in $\frac{S_M}{R}$ can be explained only when one considers the temperature dependence of the pair-wise interaction energies. The computed values of $\frac{S_M}{R}$ are in very good agreement with experimental values. The reliability depends on the estimation of the temperature derivatives of energy parameters. The theoretical and experimental values of $\frac{S_M}{R}$ are positive in the whole range of concentration. Both theoretical and experimental values show maximum in S_M, (S_M^{max}) = 0.7146R at c_{Pb} = 0.5.

Heat of mixing (H_M) for Bi-Pb liquid alloy at 700K

Equation (25) has been used to compute the heat of mixing of Bi-Pb liquid alloys at 700K. There is a good agreement between theoretical and experimental values [13].

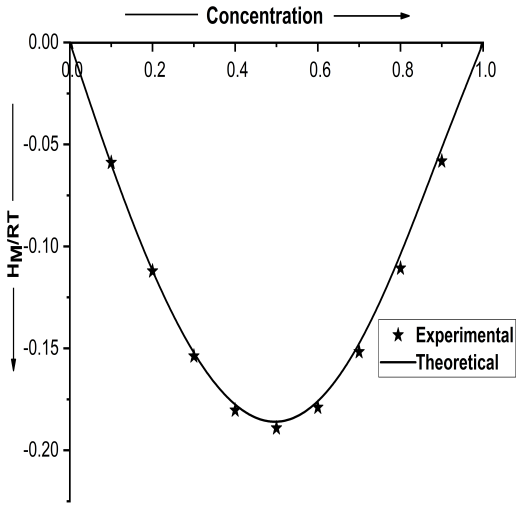

FIGURE 4. Heat of mixing $\frac{H_M}{R}$ versus concentration of Bi-Pb liquid alloy at 700K (—) theoretical and ($\star$) experimental.

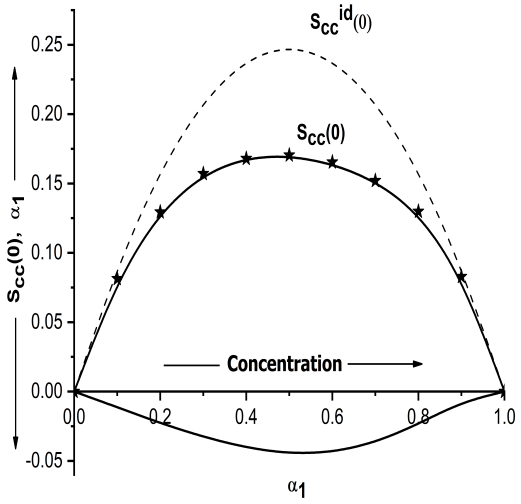

FIGURE 5. Upper part: concentration fluctuation in long wave length limit $S_{cc}(0)$ versus concentration of Bi-Pb liquid alloy at 700K; Lower part: short range order parameter, α_1 versus concentration of Bi-Pb liquid alloy at 700K.; (—) theoretical and ($\star$) experimental,(.....)ideal values.

The theoretical and experimental both values remain negative for full range of concentration. The theoretical analysis shows minimum value of $H_M(H_M^{min} = -0.1891RT$ at c=0.5.
From the plot of $\frac{H_M}{RT}$ versus concentration in figure (4), it is observed that the heat of mixing is symmetric around equiatomic composition. It is interesting to note that the concentration dependent symmetry in H_M as observed from experiment is well explained by the quasi-lattice model. For Bi-Pb liquid alloys, the heat of mixing is found to be negative for full range of concentration and have U-shaped nature in accordance with the observed values.

3.2 Structural properties

The theoretical values of $S_{cc}(0)$ of Bi-Pb liquid alloys is computed from Eq. (28) by taking the same interaction energy parameters as used for the computation of $\frac{G_M}{RT}$ i.e. $\frac{\Delta\omega}{K_BT} = -0.52077$, $\frac{\Delta\omega_{AB}}{K_BT} = -0.41299$ and $\frac{\Delta\omega_{AA}}{K_BT} = 1.07659$. The computed values are in good agreement with values of $S_{cc}(0)$ computed from activity data using equation (27). We have plotted computed, experimental and ideal values of $S_{cc}(0)$ together with computed values of α_1 in Figure (5). The computed values of $S_{cc}(0)$ are less than the ideal values of $S_{cc}(0)$ in the entire concentration range indicating that Bi-Pb system is an ordered system of unlike atom pairing at all concentration (hetero-coordinating nature).

In addition, Warren-Cowley parameter α_1 provides an immediate insight into the nature of the local arrangement of atoms in the mixture. The minimum possible value of α_1 is -1 and it indicates complete ordering of unlike atom pairing at nearest atoms. On the other hand the maximum value of α_1 is +1, which implies complete segregation leading to phase separation and α_1=0 corresponds to a random distribution of atoms. Figure (5) shows that for Bi-Pb system, α_1 is found negative throughout concentration. The negative values of α_1 throughout whole concentration range is the signatures of chemical ordering in the Bi-Pb liquid alloys at 700K.

4. CONCLUSION

Following conclusions are drawn from the theoretical investigation on Bi-Pb liquid alloys at 700K:

- Bi-Pb alloy is chemically ordered and ordering energies are temperature dependent.
- According to theoretical study, the tendency of atoms to hetero-coordinate in Bi-Pb liquid alloy is highly dependent on concentration.
- Pb_3Bi complex exists in the liquid state of Bi-Pb alloy at 700K.
- Bi-Pb liquid alloy is weakly interacting in nature.
- The quasi lattice model successfully explains the thermodynamics of Bi-Pb liquid alloy.

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