Calculation of Thermodynamic Properties of Sn-Zn Liquid Alloy at 750 K using Self Association Model

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ABSTRACT

This paper uses self-association model to compute the concentration dependence of free energy of mixing (G_M), activity (a), and the microscopic properties such as concentration fluctuation in the long wavelength limit (S_{cc}), and Warren-Cowley short range order parameter (α_1) for Sn-Zn *binary liquid alloy.*

The calculation reveals the homo-coordination or phase separation at all concentrations with moderate interaction for Sn-Zn *liquid alloy at* 750 K.

Keywords: Metallic materials, Alloys, Hypothetical modeling, Asymmetric.

INTRODUCTION

Background to research

Alloys are metallic materials consisting of two or more elements combined in such a way that they cannot be readily separated by physical means. An alloy could be a mixture of two or more metals or a metal and a non-metal. For example, Tin (Sn) and Zinc (Zn) when mixed, form a good plating system. Iron (Fe) and carbon (C) mix to give carbon steel [1]. However, a good understanding of the properties of molten alloys is necessary because many binary solid alloys are formed by cooling from their liquid state. The size factor, electrochemical effect, and electron concentration features that predominantly govern the solubility of a homogeneous solid phase cannot effectively explain the alloying behavior of molten alloy. Hence, great interest aroused in both experimentalists and the theoreticians [2]. For this reason, in the present work, the effort is made towards the calculation of the thermodynamic properties of the binary liquid alloy at a particular temperature.

Validation for the research

In choosing the alloy for this investigation, industrial relevance and availability of adequate experimental data necessary have been considered. Hence, Sn-Zn alloy is been investigated. Tin (Sn) is a block P, group 14, period 5 element while Zinc (Zn) is a block D, group 12, period 4 elements of the periodic table accordingly. The compounds and alloys of these groups have usefulness in electrical and electronics applications.

In the present investigation, the self-association models have been used to compute the thermodynamic properties (free energy of mixing and activity) and the microscopic properties (concentration fluctuation in long wavelength limit and Warren-Cowley chemical short-range order parameter).

The layout of the dissertation

The layout of this dissertation is as follows: a critical review of existing knowledge for the thermodynamics of liquid alloys and a brief description of one of the existing theoretical models is given in section two; Section three deals with the methods employed in the present work for the study of Sn-Zn liquid alloy; Section four presents the computational result, discussion, and deductions and; section five is the conclusion.

LITERATURE REVIEW

Theoretical background

From the perspective of hypothetical modeling, the binary liquid alloys may be broadly grouped into two categories: symmetric and asymmetric alloys. This is obvious from the following properties akin to the free energy of mixing, the heat of mixing- Enthalpy, concentration fluctuations, the entropy of mixing, etc, of symmetric alloys (for example, CuZn, CdAl, NaK, etc.) which are symmetrical, or within an ace of it about concentration c=0.5. These alloys are usually referred to as regular alloys.

Conversely, the mixing properties of the asymmetric alloys are not symmetrical about c=0.5. So, much attention has been given in the past decades to either on the side effect (as in Bi-Zn, Cu-Pb, K-Pb, and K-Ti) or on the existence of chemical complexes in the molten state (as in MgBi, CuZn, AgAl, etc.) [3]. The complex-forming alloys have been extensively studied theoretically and can be found in papers with different names like complex-forming solutions, compound-forming solutions, or regularly associated solutions.

A binary alloy is usually formed when elements A and B mix together. They form a binary A-B solution. Let the binary solution contains in all $=Nc$ and $NB=N(1-c)$ gm moles of A and B atoms respectively, where c being the atomic fraction of the A atoms. One type of complex $A\mu B\nu$ (μ and ν are small integers and they denote the number of the A atoms and B atoms respectively in the complex) is assumed to be formed. If, in the solution n_1 g mole the A atoms and n_2 g mole of B atoms and n_3 g mole of $A\mu B\nu$ are formed, then from the law of conservation of atoms,

$$n_1 = Nc - \mu n_3$$

$$n_2 = N(1-c) - V n_3 \tag{1}$$

$$n = n_1 + n_2 + n_3 = N - (\mu + v - 1) n_3$$

Where n is the total number of atoms in the case of compound formation, c is concentration.

Thermodynamic methodology

The macroscopic study of the properties of an alloy without any recourse to the atomistic behavior of the alloy can be called Thermodynamic Approach or Methodology. This is done by taking the experimental values of some parameters which are then fitted into some suitable models of choice. Here the Self Association Model is applied. Some of the studied thermodynamic and microscopic properties are:

Enthalpy (H): The Enthalpy of a thermodynamic system is the heat content of the system or the energy it contains. It is simply represented thus:

$$H = U + PV \tag{2}$$

The absolute enthalpy of a system cannot be measured directly. But, it is possible to measure changes in enthalpy (ΔH) by measuring temperature changes (dT) that represent heat lost or gained. The enthalpy change can be measured from the specific heat capacity obtained using a calorimeter, then applying the relation below:

$$\Delta H = \int_{T_1}^{T_2} C_p dT \tag{3}$$

Entropy (S): Entropy is the quantitative measure of disorder in a system. It is a very important concept in thermodynamics which deals with the transfer of heat energy within a system. Hence, the change in entropy (dS) that takes place in a specific thermodynamic process is of interest to us (Physicists) than some form of absolute entropy.

$$RT \ln a_K = \left(\frac{\partial G_M}{\partial N_k} \right)_{T,p,N} \tag{4}$$

Gibbs function (G): The Gibbs free energy is the energy associated with a chemical reaction that can be used to do work and it combines enthalpy (H) and entropy (S) into a single value.

$$G = H - TS \tag{5}$$

In a simple compressible system, change in Gibbs free energy (dG) is:

$(dG)=Vdp-SdT$ (6)

In alloy systems, we talk about entropy of mixing (S_M) enthalpy of mixing (H_M) and their relationship with Gibbs free energy of mixing (G_M) as in:

$G_M=H_M+TS_M$ (7)

Activity ($\alpha 1$): Activity of a constituent atom can be derived with respect to activity coefficient (γ) and concentration (c), hence

$aA=c\gamma A$ (8)

$aB=(1-c)\gamma B$ (9)

The activity, aK ($k=A,B$), can be obtained using the general expression

$$RT \ln a_K = \left(\frac{\partial G_M}{\partial N_k} \right)_{T,p,N}$$ (10)

Activity is one of those thermodynamic functions which can be measured directly from an experiment such as electromotive force technique, Knudsen effusion method. Therefore, it can be used to check the validity of the theory derived expressions [2].

Concentration fluctuation in the long wavelength limit $[S_{cc}(0)]$: Concentration-Concentration Structure Factor $S_{cc}(q)$ at q=0 is in the long wavelength limit which in a binary mixture may be expressed as

$S_{cc}(0)=N\langle(\Delta c)^2\rangle$ (11)

Where $\langle(\Delta c)^2\rangle$ represents the mean square fluctuation in the concentration and are readily derived from statistical mechanics in terms of the Gibbs free energy G, that is,

$$\left\langle (\Delta c)^2 \right\rangle = \frac{k_B T}{\left(\dfrac{\partial^2 G}{\partial c^2} \right)_{T,p,N}}$$ (12)

In principle $S_{cc}(0)$ can be determined directly from small-angle diffraction experiments, but it poses a much more difficult experimental problem that has never been successfully solved.

For an ideal solution, where Gibbs free energy of mixing (G_M),

$G_M=cInc+(1-c)In(1-c)$ (13)

$S_{cc}(0)$, Therefore, becomes an ideal value $S_{cc}^{id}(0)$. This is of great interest to visualize the degree of interaction in a mixture of the alloy.

$$S_{cc}^{id}(0) = c(1-c)$$ (14)

Short-range order parameter (α): The Warren-Cowley short-range order parameter α_1 for the first-neighbour shell usually defines the orderliness of atoms and molecules in solids and liquids. This orderliness is over a small distance comparable to inter-atomic distances. The α_1 also describes any situation where there is a particular deviation on a local length scale. These deviations define three cases $\alpha_1=0$ for a random distribution of atoms, $\alpha_1<0$ for unlike atoms pairing while $\alpha_1>0$ implies a tendency to cluster or like atoms pairing. By taking a probabilistic approach, the limiting values of α_1 will be shown to lie in the range

$$-\frac{c}{(1-c)} \le \alpha_1 \le 1, \, c \le 0.5$$ (15)

$$-\frac{(1-c)}{c} \le \alpha_1 \le 1, \, c \ge 0.5$$ (16)

The relation becomes $-1 \leq \alpha_1 \leq 1$ at $c=0.5$ for equi-atomic compositions. The possible value, $\alpha_1^{min} = -1$ which means the cothe mplete ordering of A-B pairs in the melt, on the other hand, the maximum value, $\alpha_1^{max} = 1$ implies total segregation in the melt leading to like atoms as nearest neighbours [4].

Theoretical models

The problem of obtaining values for some measurable mixing properties at a high temperature increases the drive to investigate quantities such as G_M and α_1 as well as the need to give answers to the behaviour of alloys necessitate the modelling of theories over the years. Examples of few of the models are Quasi-chemical mode-to be discussed in the next sub-section Quasi-chemical model, Percus-Yevick (PY) hard sphere model, Self-Association Models-to be employed and described in section 3.1, etc.

Quasi-chemical model: The fact that alloys form compounds in the solid state at one or more theoretical compositions led to the assumption of the existence of chemical complexes $A_\mu B_\nu$ in the liquid state. The basic form of the quasi-chemical expression for a binary mixture has the number of unlike atom pairs *NAB* where A and B signify constituent atoms, like atom pairs N_{AA} and N_{BB} and the interchange energy (ω) in its relation:

$$\frac{4N_{AA}N_{BB}}{N_{AB}^2} = \eta^2 \tag{17}$$

Where $\eta = (\omega/zkBT)$ and z is the coordination number for the first shell [5]. The non-zero value for ω leads to an expression for the free energy of mixing [6], as

$$G_M = G_M^{id} + G_M^{xs} \tag{18}$$

Where G_M^{xs} and G_M^{xs} is ideal and excess Gibbs free energy of mixing respectively

$$G_M^{id} = RT\left\{c \ln c + (1-c) \ln(1-c)\right\} \tag{19}$$

And,

$$G_M^{xs} = RT\left\{c \ln \gamma_A + (1-c) \ln \gamma_B\right\} \tag{20}$$

The concentration of *A* and *B* atoms in the alloy are *c* and $(1-c)$ respectively while the activity coefficient γ_A and γ_B are

$$\gamma_A = \left\{\frac{\beta - 1 + 2c}{c(1-\beta)}\right\}^{\frac{1}{2}Z} = \left(\frac{\phi_1}{c\phi_2}\right)^{\frac{1}{2}Z} \tag{21}$$

$$\gamma_B = \left\{\frac{\beta + 1 - 2c}{(1-c)(1-\beta)}\right\}^{\frac{1}{2}Z} = \left(\frac{\phi_3}{(1-c)\phi_2}\right)^{\frac{1}{2}Z} \tag{22}$$

$$\beta = \left\{1 + 4c(1-c)\left(\eta^2 - 1\right)\right\}^{\frac{1}{2}} \tag{23}$$

The expression for the entropy of mixing (S_M) can easily be obtained from equation (18) and by using c, *R, T*, ω, γ_A, , etc.

$$S_M = -\left(\frac{\partial G_M}{\partial T}\right)_P \tag{24}$$

Then obtain,

$$S_M = S_{id} + S_0 + S_1, \tag{25}$$

$$S_{id} = -R\{c \ln c + (1-c)\ln(1-c)\}, \tag{26}$$

$$S_0 = -\frac{1}{2}Rz\{c \ln \gamma_A + (1-c)\ln \gamma_B\}, \tag{27}$$

$$S_1 = -\frac{8Rc^2(1-c)^2\eta^2}{\phi_1\phi_2\phi_3}\left\{\frac{1}{K_B}\frac{d\omega}{dT} - \frac{\omega}{\frac{1}{K_BT}}\right\} \tag{28}$$

Now by applying equation (18) and (25), we will have the heat of mixing ($H_M = G_M + TS_M$)

$$\frac{H_M}{RT} = -\frac{8c^2(1-c)^2\eta^2}{\phi_1\phi_2\phi_3}\left\{\frac{1}{K_B}\frac{d\omega}{dT} - \frac{\omega}{K_BT}\right\} \tag{29}$$

However, for equi-atomic composition (c=0.5), equation (29) becomes

$$\frac{H_M}{RT} = -0.5\left\{1 + \exp\left(\frac{\omega}{zK_BT}\right)\right\}^{-1} \times \left\{\frac{1}{K_B}\frac{d\omega}{dT} - \frac{\omega}{K_BT}\right\} \tag{30}$$

Also derivable from equation (18) is the concentration fluctuation (0) at q=0 (long wavelength limit)

$$S_{cc}(0) = \frac{RT}{\left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}} = \frac{c(1-c)}{1 + \frac{1}{2}z(1-\beta)/\beta} \tag{31}$$

At length, the expression of Warren-Cowley for short-range order parameter (α_1) for the first coordination shell can be derived from equation (17) above as,

$$\alpha_1 = \frac{\beta - 1}{\beta + 2} \tag{32}$$

Noteworthy, for ω<0, β<1 and α_1<0 there is a predilection for unlike atoms pairing then again, ω>0, β>1 ensures α_1>0 there is a preference for like atoms association as the nearest neighbors corresponding to segregation in the alloy [4].

METHODS AND COMPUTATION

The self-association model (SAM)

The Self Association Model was formulated by Singh and Sommer in 1992 to investigate the thermodynamic properties of liquid alloys with miscibility gaps [7-9].

The expression for the Gibbs free energy of mixing: There exist some contributors to the free energy of mixing of the alloy. They are:

1. The concentration of the atoms: c for atoms A and $(1-c)$ for atoms B

2. The ordered energy, $W = \mu\omega$ where ω is the interchange energy

3. The number of self-associates, $n = \mu/\nu$

The free energy of mixing *GM* is expressed as

$$G_M = RT[cInc + (1-c)In(1-c) + cIn(1-\beta) + In\gamma] + c(1-c)\gamma W \tag{33}$$

Where $\beta = 1 - 1/n$, $\gamma = 1/(1-c\beta)$

The activity of the components: Activity is a very important quantity which can be obtained directly from the

experiment. The magnitudes of activities are assumed to be determined by the interactions among the constituent species of the system, which in turn determine the bond energies. Thus measurement of activities within a class of similar system can be expected to provide, at least, a basis for correlation of the behavior, which can then be used for extrapolation of the behavior of more complex system. The activity of a component in a solution also provides a measure of tendency to leave the solution [10].

This can be determine using the general expression in equation (8)

$$RT \ln a_K = \left(\frac{\partial G_M}{\partial N_k} \right)_{T,p,N}$$

Substituting (33) into (8) above, we will have the activities as

$$\ln a_A = \ln \left(c\gamma(1-\beta) \right) + (1-c)\gamma\beta + (1-c)^2 \gamma^2 \frac{W}{RT} \tag{34}$$

And,

$$\ln a_B = \ln(c\gamma) + c(1-\beta)\gamma(1-n) + nc^2(1-\beta)\gamma^2 \frac{W}{RT} \tag{35}$$

The enthalpy of mixing: The enthalpy of mixing relation is derived from the thermodynamics relationship

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T} \right)_p \tag{36}$$

for this reason, the enthalpy of mixing *HM* will be

$$H_M = c(1-c)\gamma W - c(1-c)\gamma T \frac{\partial W}{\partial T} + RT^2 c(1-c)\gamma \left[\frac{\beta}{1-\beta} - c\gamma \frac{W}{RT} \right] \frac{\partial \beta}{\partial T} \tag{37}$$

The entropy of mixing: This is given as

$$S_M = R\left[c\ln c + (1-c)\ln(1-c) \right] + R(c\ln n - \ln\gamma) - c(1-c)\gamma \frac{\partial W}{\partial T} + RTc(1-c)\gamma \left[\frac{\beta}{1-\beta} - c\gamma \frac{W}{RT} \right] \frac{\partial \beta}{\partial T} \tag{38}$$

The concentration-concentration fluctuation in the long wavelength limit: Using the following equations (33) and (34) or (35) in this way

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial c^2} \right)_{T,P,N}^{-1} = (1-c)a_A \left(\frac{\partial a_A}{\partial c} \right)_{T,P,N}^{-1} = ca_A \left[\frac{\partial a_A}{\partial (1-c)} \right]_{T,P,N}^{-1} \tag{39}$$

We will then have

$$S_{cc}(0) = \frac{c(1-c)}{1 - c(1-c)g(n,W)} \tag{40}$$

Where,

$$g(n,W) = \frac{zn^2 \left(\frac{W}{RT} \right) - (n-1)^2 \left[c + n(1-c) \right]}{\left[c + n(1-c) \right]^3} \tag{41}$$

The short-range order parameter: The Warren-Cowley short-range order parameter $\alpha 1$ is expressed as:

$$\alpha_1 = \frac{s-1}{s(Z-1)+1} \tag{42}$$

Where,

$$S = \frac{S_{cc}(0)}{c(1-c)} \tag{43}$$

Z is the coordination number.

RESULTS AND ANALYSIS

The thermodynamic properties and microscopic functions of Sn-Zn binary liquid alloy are computed by using C++ programming language. This is to ease the rigors of manual computation. The C++ allow object-oriented (OO) programming theory in general; for generic (i.e. type-independent) programming even in a strongly typed language, just to mention few merits of the language.

The result obtained and plotted against the full range of concentration (0.0-1.0) show remarkable agreement with the experimental values.

The experimental data for the interactive parameters and their temperature derivatives are collected from the American Society of Metals (ASM).

Deductions from the value of ordering energy parameter, W/RT for Sn-Zn liquid Alloy at RT 750 K

This parameter remains a constant throughout the calculations. The positive value of W checks that the attraction between unlike atoms (Sn-Zn) is not more than that of like atoms (Sn- Sn or Zn-Zn), indicating that there is a tendency of segregation in the Sn-Zn alloys in a molten state.

Deductions from the Gibbs free energy of mixing, GM/RT for Sn-Zn alloy at 750 K

Theoretical computation and the Graph of Gibbs Free energy of mixing, *GM/RT* versus concentration, C_{Zn} illustrate that there is just about the agreement between the experimental and calculated free energies (Figure 1). Small divergence from this may originate from the term rising from the entropy of mixing.
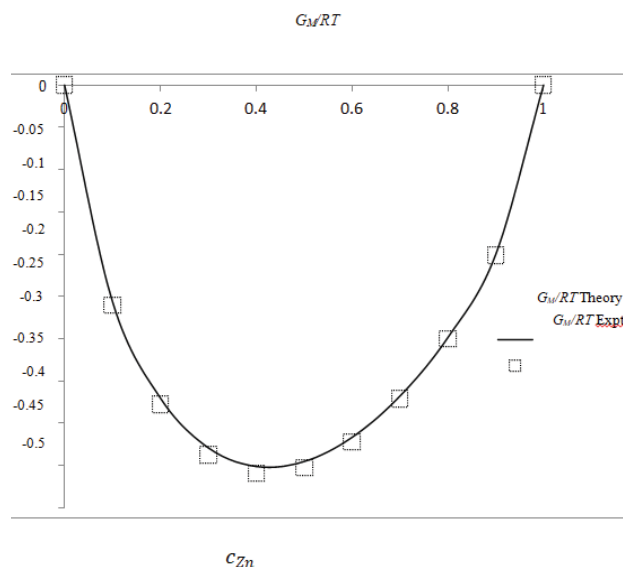

Figure 1: The graph of gibbs free energy of mixing, G_M/RT versus concentration, c_{Zn} in Sn-Zn alloy at 750 K; The Solid line represents calculated values and square boxes for experimental values.

Deductions from the activity (a) for Sn-Zn alloy at 750 K

The activity for the Sn-Zn liquid has been calculated using Equation 33. There is a correlation in the plot of the

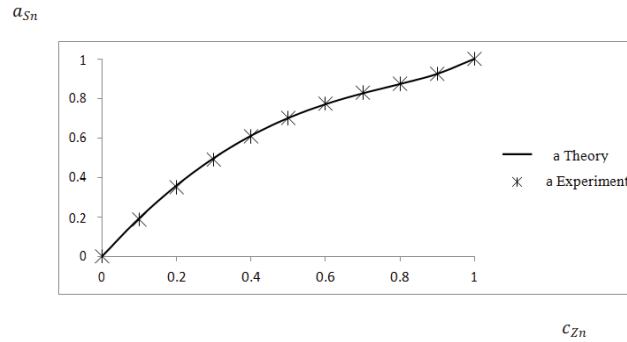activity between the computed and observed values (Figure 2).

Figure 2: The Graph of thermodynamic activity, a_{Sn} versus concentration, C^{Zn} for Sn-Zn alloy at 750 K; The solid line for calculated values, hook for experimental values.

Deductions from the microscopic functions-concentration fluctuation, $S_{cc}(0)$ and short-range order parameter, α_1 for **Sn-Zn** *alloy at* **750 K**

The nature and degree of segregation in binary liquid alloys is observable from the values of $S_{cc}(0)$ and α_1. The value of $S_{cc}(0) > S_{cc}^{id}(0)$ indicates segregating tendency of the Sn-Zn alloy, presented. The knowledge of α_1 makes available an instantaneous insight into the nature of the local arrangements of the atoms (Sn and Zn) in the mixture (See Short-range Order Parameter). The strength of the local order of atoms is supply by the normalized values of this parameter (α_1). In addition the calculated, experimental and ideal values of $S_{cc}(0)$ are depicted in Figure 3. Over the all range of concentration both the computed and experimental values of $S_{cc}(0)$ are found to be greater than the ideal values. The values of α_1 have been found all positive for all compositions (Figure 4). The implication of the calculated values of both $S_{cc}(0)$ and α_1 is that the Sn-Zn alloy in liquida state at 750 K is a segregating system.
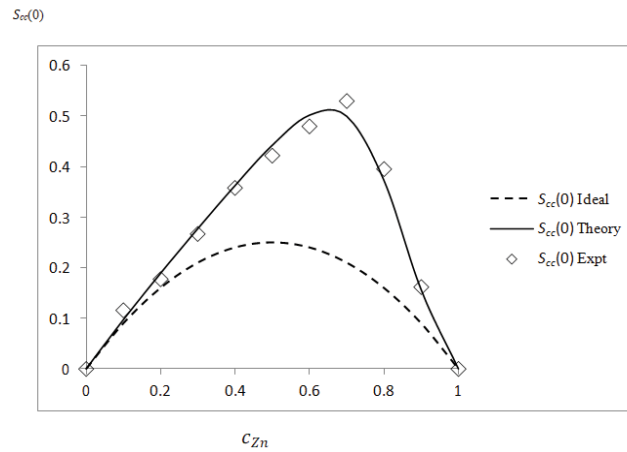

Figure 3: The graph of concentration fluctuation, $S_{cc}(0)$ versus concentration, C_{Zn} in Sn- Zn alloy at 750 K; The Solid line for calculated values, round dot line for ideal values and diamonds for experimental values.
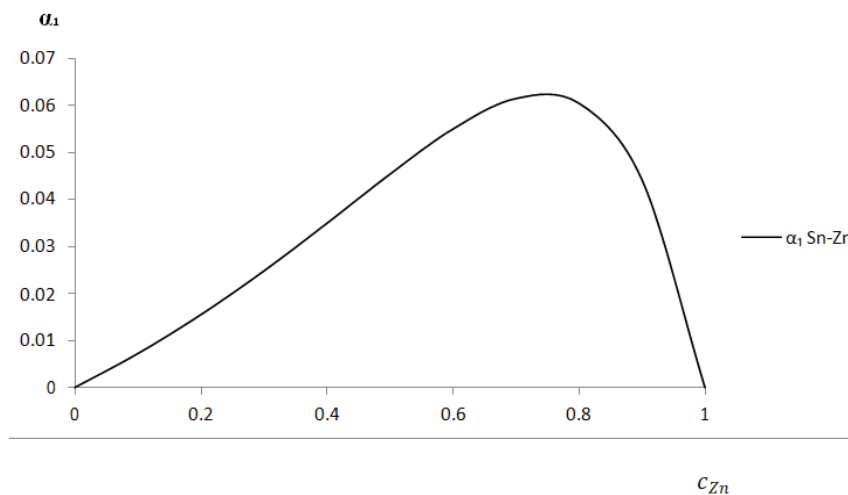
Figure 4: Calculated Warren-Cowley short-range order parameter, a_1 versus concentration, c_{Zn} for Sn-Zn alloy at 750 K.

CONCLUSION

The theoretical analysis of free energy of mixing, activity, concentration fluctuations in long wavelength limit and Warren-Cowley chemical short-range order parameter of Sn-Zn alloy in the liquid state have been performed using the self-association model. The calculation suggests that the alloy is a moderate interacting system showing a significant tendency of formation of homo-pairs or phase separation (preference of like atoms pairing: Sn-Sn and Zn-Zn) at all compositions [11].

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