

Calculation of Thermodynamic Properties of Sn-Zn Liquid Alloy

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Abstract—This study employs a self-association model to analyze the concentration dependence of the free energy of mixing (G_M), activity (a), and various microscopic properties, including concentration fluctuations in the long wavelength limit (Sc) and the Warren-Cowley short-range order parameter (α_1) for the Sn-Zn binary liquid alloy. The calculations indicate the presence of homo-coordination or phase separation across all concentrations, characterized by moderate interactions for the Sn-Zn liquid alloy at a temperature of 750 K. The theoretical findings regarding the thermodynamic properties closely align with the corresponding experimental data and the results derived from the R-K equation at 750 K. Furthermore, it is observed that the ordering behavior, viscosity, and surface tension of the alloy diminish as the temperature increases.

Index Terms—Metallic materials, Alloys, Hypothetical modeling, Asymmetric, Energy parameters

I. INTRODUCTION

Alloys are metallic substances composed of two or more elements that are combined in such a manner that they cannot be easily separated through physical methods. An alloy may consist of a combination of multiple metals or a metal alongside a non-metal. For instance, when Tin (Sn) and Zinc (Zn) are combined, they create an effective plating system. Additionally, the combination of Iron (Fe) and carbon (C) results in carbon steel[1]. A comprehensive understanding of the characteristics of molten alloys is essential, as many binary solid alloys are produced by cooling from their liquid form. The factors of size, electrochemical effects, and electron concentration that primarily influence the solubility of a uniform solid phase do not adequately account for the alloying behavior of molten alloys. Consequently, there has been significant interest from both experimentalists and theorists.[2] Therefore, this study aims to calculate the thermodynamic properties of binary liquid alloys at a specified temperature.

In selecting the alloy for this study, considerations of industrial significance and the availability of

sufficient experimental data have been prioritized. Consequently, the Sn-Zn alloy has been chosen for investigation. Tin (Sn) is classified as a block P element in group 14, period 5, while Zinc (Zn) is categorized as a block D element in group 12, period 4 of the periodic table. The compounds and alloys from these groups are known for their applications in electrical and electronic fields. In this study, self-association models have been employed to calculate the thermodynamic properties, including the free energy of mixing and activity, as well as the microscopic properties, such as concentration fluctuations in the long wavelength limit and the Warren-Cowley short-range order parameter.

The structure of this paper is organized as follows: Section two provides a critical review of the current understanding of the thermodynamics of liquid alloys, along with a concise overview of one of the theoretical models available. Section three outlines the methodologies utilized in this study of the Sn-Zn liquid alloy. Section four presents the computational results, followed by a discussion and analysis of these findings. Finally, section five concludes the paper.

II. LITERATURE REVIEW

A. Theoretical background

From the standpoint of hypothetical modeling, binary liquid alloys can be classified into two main categories: symmetric and asymmetric alloys. This classification is evident from various properties related to the free energy of mixing, such as the heat of mixing (enthalpy), concentration fluctuations, and the entropy of mixing. Symmetric alloys, such as CuZn, CdAl, and NaK, exhibit properties that are symmetrical or nearly symmetrical around a concentration of $c=0.5$. These types of alloys are commonly designated as regular alloys.

The mixing characteristics of asymmetric alloys exhibit asymmetry around $c=0.5$. Consequently,

significant research efforts over the past several decades have focused on either the side effects observed in systems such as Bi-Zn, Cu-Pb, K-Pb, and K-Ti, or on the presence of chemical complexes in the molten phase, as seen in alloys like MgBi, CuZn, and AgAl [3]. Theoretical investigations into complex-forming alloys have been thorough, and these alloys are often referred to in the literature by various terms, including complex-forming solutions, compound-forming solutions, or regularly associated solutions.

A binary alloy typically arises when elements A and B are combined, resulting in a binary A-B solution. This solution is characterized by a total of Nc gm moles of A and $N(1-c)$ gm moles of B atoms, where c represents the atomic fraction of A atoms. It is assumed that a complex denoted as $A_\mu B_\nu$ is formed, with μ and ν being small integers that indicate the quantities of A and B atoms in the complex, respectively. If the solution contains n_1 gm moles of A atoms, n_2 gm moles of B atoms, and n_3 gm moles of $A_\mu B_\nu$, then according to the law of conservation of atoms, the following relationships must hold.

$$\begin{aligned} n_1 &= Nc - \mu n_3 \\ n_2 &= N(1-c) - \nu n_3 \end{aligned} \quad \dots\dots(1)$$

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

In the context of compound formation, n represents the total number of atoms, while c denotes the concentration.

B. Thermodynamic methodology

The examination of an alloy's macroscopic properties, independent of its atomistic behavior, is referred to as the Thermodynamic Approach or Methodology. This process involves utilizing experimental data for specific parameters, which are subsequently integrated into appropriate models. In this context, the Self Association Model is employed. Among the thermodynamic and microscopic properties analyzed are:

Enthalpy (H): The enthalpy of a thermodynamic system refers to the thermal energy contained within the system. It is commonly denoted as follows:

$$H = U + PV \quad \dots\dots(2)$$

The absolute enthalpy of a system cannot be directly measured. However, changes in enthalpy (ΔH) can be determined by observing temperature variations (dT) that indicate heat transfer, either lost or gained.

The enthalpy change can be calculated using the specific heat capacity obtained through a calorimeter, followed by the application of the relevant equation.

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad \dots\dots(3)$$

Enthalpy (S): Entropy (S) is a quantitative assessment of disorder within a system. This concept holds significant importance in the field of thermodynamics, which focuses on the transfer of heat energy in various systems. Consequently, the change in entropy (dS) occurring during a particular thermodynamic process is of greater relevance to physicists than the absolute value of entropy itself.

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

Gibbs function (G): The Gibbs free energy represents the energy linked to a chemical reaction that is available to perform work, integrating both enthalpy (H) and entropy (S) into a unified measure.

$$G = H - TS \quad \dots\dots(5)$$

In a straightforward compressible system, the variation in Gibbs free energy (dG) is expressed as follows:

$$(dG) = Vdp - SdT \quad \dots\dots(6)$$

In alloy systems, the concepts of mixing entropy (S_M) and mixing enthalpy (H_M) are discussed, along with their interrelation to the Gibbs free energy of mixing (G_M), expressed by the equation:

$$G_M = H_M + TS_M \quad \dots\dots(7)$$

Activity (α_1): The activity (α_1) of a constituent atom can be determined based on the activity coefficient (γ) and the concentration (c), Hence :

$$a_A = c\gamma_A \quad \dots\dots(8)$$

$$a_B = (1-c)\gamma_B \quad \dots\dots(9)$$

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

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

Activity is a thermodynamic function that can be directly measured through experimental techniques, including the electromotive force method and the Knudsen effusion method. Consequently, it serves as a means to verify the accuracy of expressions derived from theoretical frameworks[2].

Concentration fluctuations in the long wavelength limit [$Sc(0)$]: The Concentration-Concentration Structure Factor $Sc(q)$ evaluated at $q=0$ pertains to

the long wavelength limit. In the context of a binary mixture, this can be articulated as

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

where $\langle (\Delta c)^2 \rangle$ denotes the mean square fluctuation in concentration. This quantity can be readily derived from statistical mechanics in relation to the Gibbs free energy G.

$$\left[(\Delta c)^2 \right] = \frac{k_B T}{\left(\frac{\partial^2 G}{\partial c^2} \right)_{T,p,N}} \quad \dots(12)$$

In theory, $S_{cc}(0)$ can be ascertained directly through small-angle diffraction experiments; however, this presents a significantly more challenging experimental issue that has yet to be effectively addressed. In an ideal scenario, where the Gibbs free energy of mixing (G_M) is considered,

$$G_M = c \ln c + (1-c) \ln(1-c) \quad \dots(13)$$

The value $S_{cc}(0)$ thus transforms into an optimal value $S_{cc}^{id}(0)$. This transformation is particularly significant for illustrating the extent of interaction within an alloy mixture.

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

Short-range order parameter (α): The Warren-Cowley short-range order parameter α_1 , which pertains to the first-neighbour shell, typically characterizes the arrangement of atoms and molecules within solids and liquids. This arrangement occurs over a limited distance that is comparable to inter-atomic separations. The parameter α_1 also indicates any specific deviation on a local length scale. These deviations can be categorized into three scenarios: $\alpha_1 = 0$ signifies a random distribution of atoms, $\alpha_1 < 0$ indicates the pairing of dissimilar atoms, while $\alpha_1 > 0$ suggests a propensity for clustering or the pairing of similar atoms. By employing a probabilistic framework, the limiting values of α_1 are demonstrated to fall within a defined range.

$$-\frac{c}{(1-c)} \leq \alpha_1 \leq 1, c \leq 0.5 \quad \dots(15)$$

$$-\frac{(1-c)}{c} \leq \alpha_1 \leq 1, c \geq 0.5 \quad \dots(16)$$

The relationship is defined as $-1 \leq \alpha_1 \leq 1$ when $c = 0.5$ for equi-atomic compositions. The minimum value $\alpha_1^{\min} = -1$, indicates a complete ordering of A-B pairs within the melt. Conversely, the maximum value, $\alpha_1^{\max} = 1$, suggests total

segregation in the melt, resulting in like atoms being nearest neighbors[4].

C. Theoretical Models

The challenge of acquiring values for certain measurable mixing properties at elevated temperatures intensifies the motivation to explore quantities such as G_M and α_1 . Additionally, understanding the behavior of alloys necessitates the development of theoretical models over time. Notable examples of these models include the Quasi-chemical model, which will be discussed in the subsequent sub-section, the Percus-Yevick (PY) hard sphere model, and Self-Association Models, which will be utilized and elaborated upon in section 3.1, among others.

Quasi-chemical model: The observation that alloys can create compounds in the solid state at specific theoretical compositions has led to the hypothesis regarding the presence of chemical complexes $A\mu B\nu$ in the liquid state. The fundamental representation of the quasichemical expression for a binary mixture includes the count of unlike atom pairs NAB , where A and B represent the constituent atoms, along with the counts of like atom pairs NAA and NBB , and the interchange energy (ω) in its corresponding relation.

$$\frac{4N_{AANBB}}{N_{AB}^2} = \eta^2 \quad \dots(17)$$

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

$$GM = G_M^{id} + G_M^{xs} \quad \dots(18)$$

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

$$G_M^{id} = RT \{ c \ln c + (1-c) \ln(1-c) \} \quad \dots(19)$$

And,

$$G_M^{xs} = RT \{ c \ln \gamma_A + (1-c) \ln \gamma_B \} \quad \dots(20)$$

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

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

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

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

The expression for the entropy of mixing (S_M) can easily be obtained from equation (18) and by using $c, R, T, \omega, \gamma_A$, etc.

$$S_M = - \left(\frac{\partial G_M}{\partial T} \right)_p \quad \dots\dots(24)$$

Then obtain,

$$S_M = S_{id} + S_0 + S_1 \quad \dots\dots(25)$$

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

$$S_0 = -\frac{1}{2} R_z \{ c \ln \gamma_A + (1-c) \ln \gamma_B \} \quad \dots\dots(27)$$

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

Now by applying equation (18) and (25), we will have the heat of mixing ($HM=GM+TSM$)

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

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

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

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

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

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,

$$\alpha_1 = \frac{\beta-1}{\beta+2} \quad \dots\dots(32)$$

Noteworthy, for $\omega < 0, \beta < 1$ and $\alpha_1 < 0$ there is a predilection for unlike atoms pairing then again, $\omega > 0, \beta > 1$ ensures $\alpha_1 > 0$ there is a preference for like atoms association as the nearest neighbors corresponding to segregation in the alloy [4].

III. METHODS

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, $n = \mu/v$
- The free energy of mixing G_M is expressed as

$$G_M = RT [c \ln c + (1-c) \ln(1-c) + c \ln(1-\beta) + \ln \gamma] + c(1-c) \gamma W \quad \dots\dots(33)$$

Where

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

The role of components' activity: Activity is a crucial parameter that can be directly measured through experimentation. The values of activities are believed to be influenced by the interactions among the various species present in the system, which subsequently affect the bond energies. Therefore, measuring activities within a category of similar systems can serve as a foundation for correlating behaviors, which may then facilitate the extrapolation of behaviors in more intricate systems. Additionally, the activity of a component in a solution serves as an indicator of its propensity to exit the solution[10].

This can be assessed using the general expression provided in equation (8).

$$RT \ln \alpha_K = \left(\frac{\partial G_M}{\partial N_K} \right)_{T,P,N}$$

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

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

And,

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

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

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

for this reason, the enthalpy of mixing H_M will be

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

The entropy of mixing: This is given as:

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

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

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

We will then have

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

Where,

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

The short-range order parameter: The Warren-Cowley short-range order parameter α_1 is expressed as:

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

Where,

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

Z is the coordination number.

IV. RESULTS

The thermodynamic characteristics and microscopic functions of the Sn-Zn binary liquid alloy have been calculated utilizing the C++ programming language. This approach is intended to simplify the complexities associated with manual calculations. C++ supports object-oriented programming principles, which facilitate generic programming even within a strongly typed language, among other advantages. The results obtained, when plotted across the entire concentration range (0.0-1.0), demonstrate a significant correlation with the experimental values. The experimental data regarding the interactive parameters and their temperature derivatives have been sourced from the American Society of Metals (ASM).

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

This parameter is maintained as a constant during the calculations. The positive value of W ensures that the attraction between dissimilar atoms (Sn-Zn) does not exceed that of similar atoms (Sn-Sn or Zn-Zn), suggesting a propensity for segregation within the Sn-Zn alloys when in a molten state.

The Gibbs free energy of mixing, G_M/RT , for the Sn-Zn alloy at a temperature of 750 K has been analyzed for deductions.

The theoretical calculations and the graph depicting the Gibbs Free Energy of mixing, G_M/RT in relation to concentration, C_{Zn} , demonstrate a notable alignment between the experimental and computed free energies, as shown in Figure 1. Any minor discrepancies observed may be attributed to the contributions arising from the entropy of mixing.

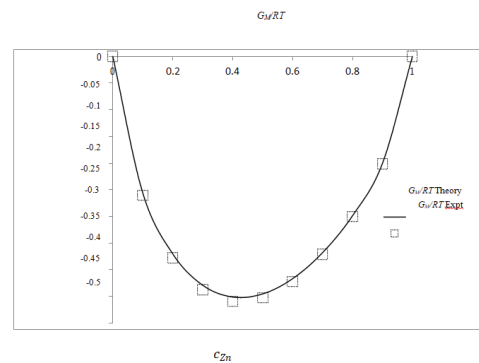


Figure 1: The graph of gibbs free energy of mixing, G_M/RT versus concentration, C_{Zn} in Sn-Zn alloy at 750 K; The Solid line represents calculated values and square boxes for experimental values.

Deductions from the activity (a) concerning the Sn-Zn alloy at a temperature of 750 K.

The calculation of the activity for the Sn-Zn liquid has been conducted utilizing Equation 33. A correlation is evident in the graph depicting the activity, comparing the computed values with the observed values (Figure 2).

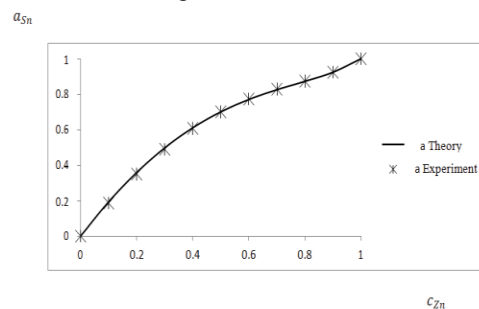


Figure 2: The Graph of thermodynamic activity, a_{zn} versus concentration, C_{zn} for Sn-Zn alloy at 750 K; The solid line for calculated values, hook for experimental values.

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 characteristics and extent of segregation in binary liquid alloys can be assessed through the values of $S_{cc}(0)$ and α_1 . The condition where $S_{cc}(0) > S_{cc}^{id}(0)$ suggests a tendency for segregation in the Sn-Zn alloy under consideration. Understanding α_1 provides immediate insight into the local atomic arrangements of Sn and Zn within the mixture, as detailed in the Short-range Order Parameter. The normalized values of this parameter (α_1) indicate the strength of local atomic order. Furthermore, the calculated, experimental, and ideal values of $S_{cc}(0)$ are illustrated in Figure 3. Across the entire concentration range, both computed and experimental values of $S_{cc}(0)$ exceed the ideal values. Additionally, all values of α_1 have been found to be positive for every composition, as shown in Figure 4. The implications of the calculated values for both $S_{cc}(0)$ and α_1 suggest that the Sn-Zn alloy in its liquid state at 750 K behaves as a segregating system.

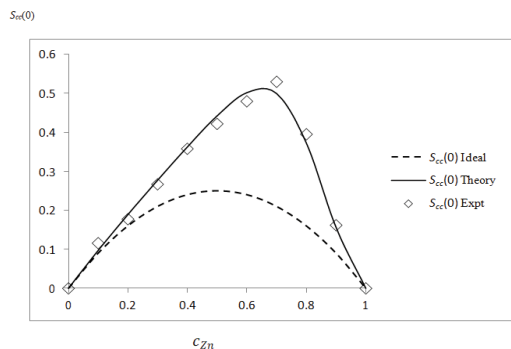


Figure 3: The graph of concentration fluctuation, $S_{cc}(0)$ versus concentration, C_{Zn} in Sn- Zn alloy at 750 K; The Solid line for calculated values, round dot line for ideal values and diamonds for experimental values.

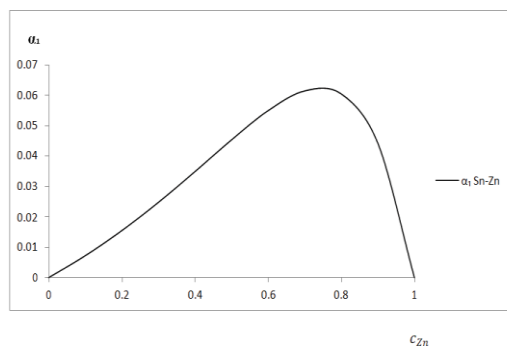


Figure 4: Calculated Warren-Cowley short-range order parameter, α_1 versus concentration, C_{Zn} for Sn-Zn alloy at 750 K.

V. CONCLUSION

A theoretical examination of the free energy of mixing, activity, concentration fluctuations in the long wavelength limit, and the Warren-Cowley short-range order parameter for the Sn-Zn alloy in its liquid state has been conducted utilizing the self-association model. The results indicate that the alloy behaves as a moderately interacting system, exhibiting a notable inclination towards the formation of homo-pairs or phase separation, characterized by a preference for like atom pairing (Sn-Sn and Zn-Zn) across all compositions.

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