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Segregating Nature of Cu-Ag Melt at Different Temperatures

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Abstract

Information about the mixing properties of the liquid state of alloys is valuable in the production of mechanical alloys. The validity of the simple theory of mixing (STM) has been established at first for Cu-Ag (Copper-Silver) binary liquid alloy at the temperature of 1423 K by comparing the experimental values obtained from the direct calorimetric measurements. Secondly, the study of the mixing behaviors of the respective alloy has been extended to elevated temperatures (1523 K, 1623 K, and 1723 K) theoretically. Modified Butler's approach and modified Kaptay's approach were used to predict the surface tension and viscosity. Theoretical analysis suggests that the Cu-Ag alloy is of the weakly interacting system. Extension of theoretical study to elevated temperature reveals that the segregating nature of alloy gradually decreases at higher temperatures. Decrement of surface tension and viscosity were observed at elevated temperatures.

Keywords: Simple Statistical Theory; Renovated Butler Model; Segregating Nature; Liquid Alloy; Modified Kaptay's Approach; Viscosity

Introduction

Most of the solid alloys are made by mixing the liquid states of the components. So the study of thermodynamic and structural properties of the liquid alloy is important to know the stability and structure of alloys. The study of the surface and viscous properties of the alloy is necessary because they also affect the performance of the alloy. Excess free energy of mixing (G_M^{XS}), the free energy of mixing (G_M), the enthalpy of mixing (H_M), excess enthalpy of mixing (H_M^{XS}), the entropy of mixing (S_M), excess entropy of mixing (S_M^{XS}), activity (a_i), concentration fluctuation in the long-wavelength limit ($S_{CC}(0)$), Warren Cowley's short-range order parameter (α_1), etc. are some parameters used to study the thermodynamic and structural properties of the liquid alloy. The different parameters used to quantify and analyze the surface and transport properties of liquid alloys are the surface tension (σ), surface concentration (X_i^S), the ratio of mutual to intrinsic diffusion coefficient $\left(\frac{D_M}{D_{id}}\right)$, viscosity ($\eta$), etc. Analyzing the above-mentioned parameters of the liquid form of an alloy, one can have the knowledge of phase separating and ordering nature of the mixture [1-6].

Cu-Ag (Copper-Silver) alloy is made by mixing the individual elements in the molten form. This alloy has a lofty form of mechanical properties than that of pure components [7]. Cu-Ag alloy has been widely used in the field of electronics, optical devices, kitchen utensils, solar cells, catalysts, antimicrobial and antiseptic applications, protective surface coatings, mechanical engineering, etc. The thermal stability of silver can be improved by mixing copper on it. Wires made from the Cu-Ag alloy can be used in electrical connections to enhance the quality of conductivity. The ductility of copper becomes higher on the addition of silver [8-18].

In this work, the simple statistical theory of mixing [2,3,19,20,21] used to predict the thermodynamic, structural, surface, and transport properties of Cu-Ag liquid alloy at 1423 K [21] has been studied at first. Extremum difference between the theoretical and experimental values of enthalpy of mixing (H_M) and entropy of mixing (S_M) are observed as 19.8259 % and 8.217218 %, respectively. In this work, these errors are lowered by changing the value of the interaction energy parameter. Extension of work to higher temperatures has been done with the newly assigned value of the interaction energy parameter. Surface tension and viscosity of the alloy are computed using the modified Butler's approach [2,20,22,23] and modified Kaptay's approach [24, 25]. In this paper, section 2, 3, and 4 deal with the theoretical formulation, results & discussion, and conclusions, respectively.

Theoretical Formulation

Thermodynamic Properties

Consider a binary liquid alloy having N_A number of A atoms and N_B number of B atoms. Let $q_A^{N_A}$ and $q_B^{N_B}$ are the partition functions of atoms, μ_A and μ_B are the chemical potentials, E is the configuration energy, K_B is the Boltzmann constant, and T is the absolute temperature. Then the grand partition function can be expressed as [2,3, 19, 20, 21]

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp\left(\frac{\mu_A N_A + \mu_B N_B - E}{K_B T}\right) \tag{1}$$

Let G_M is the free energy of mixing, G_M^{XS} is the excess free energy of mixing, X_i is the concentration of each component, and R is the universal gas constant. Then from the standard thermodynamic relation we have,

$$G_M = G_M^{XS} + RT\sum_i X_i \ln X_i \tag{2}$$

For binary liquid alloy,

$$G_M = G_M^{XS} + RT\,(X_1 \ln X_1 + X_2 \ln X_2) \tag{3}$$

$$\text{Or, } \frac{G_M}{RT} = X_1 X_2 \frac{\omega}{K_B T} + X_1 \ln X_1 + X_2 \ln X_2 \tag{4}$$

Here ω is the interaction energy.

The relation of the heat of mixing (H_M) with the free energy of mixing (G_M) is given as

$$H_M = G_M - T\left(\frac{dG_M}{dT}\right) \tag{5}$$

$$\text{Or, } H_M = RT\left[X_1 X_2 \frac{\omega}{K_B T} - X_1 X_2 \frac{1}{K_B}\frac{d\omega}{dT}\right] \tag{6}$$

Let S_M be the entropy of mixing then from the standard thermodynamic relation,

$$G_M = H_M - TS_M \tag{7}$$

$$\text{Or, } \frac{S_M}{R} = \frac{H_M}{RT} - \frac{G_M}{RT} \tag{8}$$

Using equation (4) and (6), equation (8) becomes

$$\frac{S_M}{R} = -\left(X_1 X_2 \frac{1}{K_B}\frac{d\omega}{dT} + X_1 \ln X_1 + X_2 \ln X_2\right) \tag{9}$$

The relation between activity (a_i) of binary liquid alloy with the free energy of mixing (G_M) is given as

$$RT \ln a_i = G_M + (1 - X_i)\left(\frac{\partial G_M}{\partial X_i}\right)_{N,T,P} \tag{10}$$

Using the value of free energy of mixing (G_M) in equation (10) the expression for activity (a_i) for each of the component are obtained as

$$a_1 = \exp\left[\ln X_1 + X_2^2 \frac{\omega}{K_B T}\right] \tag{11}$$

$$a_2 = \exp\left[\ln X_2 + X_1^2 \frac{\omega}{K_B T}\right] \tag{12}$$

Structural Properties

To know about the atomic arrangement inside the alloy in molten form, the study of concentration fluctuation in the long-wavelength limit (S_{CC} (0)) and Warren-Cowley short-range order parameter (α_1) is obligatory.

The relation between the free energy of mixing (G_M) and concentration fluctuation in the long-wavelength limit (S_{CC} (0)) is given as [2, 20]

$$S_{CC}(0) = K_B T \left(\frac{\partial^2 G_M}{\partial X^2}\right)^{-1}_{N,T,P} \tag{13}$$

$$\text{Or, } S_{CC}(0) = X_1 X_2 \left[1 + \frac{Z(1-\beta)}{2\beta}\right]^{-1} \tag{14}$$

Where Z=10 is coordination number and

$$\beta = [1 + 4X_1X_2\{\exp(2\omega/ZK_BT) - 1\}]^{1/2} \tag{15}$$

Concentration fluctuation in the long-wavelength limit (S_{CC} (0)) is related to Warren-Cowley short-range order parameter (α_1) through the below equation [3, 20]

$$\alpha_1 = \frac{S-1}{S(Z-1)+1} \tag{16}$$

$$\text{Where } S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)} = \frac{S_{CC}(0)}{X_1X_2} \tag{17}$$

Surface Properties

The surface tension of liquid mixture at a certain temperature T is given as [2, 20, 22, 23],

$$\sigma = \sigma_1^0(T) + \frac{RT}{A_1} \ln\left(\frac{X_1^S}{X_1}\right) + \left(\frac{G_1^{E,s} - G_1^{E,b}}{A_1}\right) \tag{18}$$

$$= \sigma_2^0(T) + \frac{RT}{A_2} \ln\left(\frac{X_2^S}{X_2}\right) + \left(\frac{G_2^{E,s} - G_2^{E,b}}{A_2}\right) \tag{19}$$

Where A_i is the hypothetical surface area of the i^{th} component in the pure liquid, X_i^S is the surface mole fraction of the ith component, X_i is the bulk mole fraction of the i^{th} component, $G_i^{E,s}$ is the partial surface excess free energy of the i^{th} component in the liquid solution and $G_i^{E,b}$ is the partial bulk excess free energy of the ith component in the liquid solution. If we assumed that partial surface excess free energy and partial bulk excess free energy has the same concentration dependence, we could write [23, 26],

$$G_i^{E,s} = 0.83 \times G_i^{E,b} \tag{20}$$

In equation (19) $\sigma_i^0(T)$ is the surface tension of the pure i^{th} component (i= A or B) of the liquid mixture given as [27]

$$\sigma_i^0(T) = \sigma_0 + (T\text{-}T_0)\frac{d\sigma}{dt} \tag{21}$$

Where σ_0 is the surface tension at melting temperature, T is the temperature of the interest, T_0 is the melting temperature, and $\frac{d\sigma}{dt}$ is the temperature coefficient of surface tension. The hypothetical molar surface area of the i^{th} component of pure liquid metal is given as

$$A_i = f\,(V_i)^{2/3}\,(N_{Av})^{1/3} \tag{22}$$

Where V_i is the molar volume of the pure metal, and N_{Av} is Avogadro's number.

The geometrical constant f is given as

$$f = \left(\frac{3f_b}{4}\right)^{\frac{2}{3}} \frac{\pi^{1/3}}{f_s} \tag{23}$$

Where f_b and f_s are the volume and surface packing fractions. Generally, we can take the value of 'f' as 1. The ideal value of surface tension is given as

$$\sigma^{id} = X_1\sigma_1^0\,(T) + X_2\sigma_2^0\,(T) \tag{24}$$

Transport Properties

Viscosity (η) and the ratio of mutual to the intrinsic diffusion coefficient $\left(\frac{D_M}{D_{id}}\right)$ are the two parameters to interpret the transport properties of alloys in the molten state. The ratio of mutual to the intrinsic diffusion coefficient $\left(\frac{D_M}{D_{id}}\right)$ of binary liquid alloys can be expressed in terms of activity (a_i) with the help of Darken's equation as [20, 22]

$$\frac{D_M}{D_{id}} = \frac{d \ln a_i}{dX_i} \tag{25}$$

Equation (25) can also be written as

$$\frac{D_M}{D_{id}} = \frac{S_{CC}^{id}\,(0)}{S_{CC}\,(0)} = \frac{1}{S} \tag{26}$$

The viscosity of liquid alloy can be obtained as [24, 25]

$$\eta = \left(\frac{hN_{Av}}{X_1V_1 + X_2V_2 + V^E}\right)\exp\left(\frac{X_1G_1^* + X_2G_2^* - (0.155 \pm 0.015)H_M}{RT}\right) \tag{27}$$

Where h is Planck's constant, V^E is the excess volume of alloy formation, which is very small and can be neglected, N_{Av} is Avogadro's number and G_i^* is the Gibbs energy of activation of the viscous flow in the pure component, which is given as

$$G_i^* = RT \ln\left(\frac{\eta_i V_i}{hN_{Av}}\right) \tag{28}$$

Where V_i is the molar volume of pure metal given as

$$V_i = \frac{m_i}{\rho_i(T)} \tag{29}$$

Here m_i is the atomic mass of components and ρ_i (T) is the density of pure metal at temperature T, which can be calculated as [27]

$$\rho_i(T) = \rho_0 + (T\text{-}T_0)\frac{d\rho}{dt} \tag{30}$$

Where ρ_0 is the density at melting temperature, T is the temperature of need, T_0 is the melting temperature, and $\frac{d\rho}{dt}$ is the temperature coefficient of density. In equation (28), η_i is the viscosity of pure components at the required temperature and is given as [27]

$$\eta_i = \eta_i^0 \exp\left(\frac{E_i}{RT}\right) \tag{31}$$

Where η_i^0 is the viscosity of pure metal at its melting temperature, and E_i is the energy per mole of a pure component. The ideal value of viscosity of the liquid mixture is given as

$$\eta_{id} = \eta_1 X_1 + \eta_2 X_2 \tag{32}$$

Results and Discussion

Thermodynamic, Structural, Surface, and Transport properties at T=1423 K

Thermodynamic Properties

The experimental values of different thermodynamic functions for Cu-Ag alloy [28] are the selected values given by Hultgren et al. by comparing additional experimental data. They have used the calorimetric measurement, compared with other measures, and made the selection of best values. They have given the phase diagram of respective alloys too. Possible errors in the selected values are mentioned as ± 0.0177 RT for Gibb's free energy of mixing (G_M) and the enthalpy of mixing (H_M), ±0.025 R for the entropy of mixing (S_M), and ±0.01 for the activity of components (a_i). The interaction energy parameter of the alloy was obtained by using experimental values of free energy of mixing (G_M) [28] and equation (4) by the method of successive approximation. The best fit parameter is found to be $\frac{\omega}{K_BT} = 1.22$. The positive value of $\frac{\omega}{K_BT}$ indicates that there is a tendency to form homo pairs in the alloy. Assuming the interaction energy parameter depends upon temperature, we have computed the value of temperature derivative of ordering energy parameter with the help of experimental values of entropy of mixing (S_M) [28] and equation (9) by the method of successive approximation. The best fit value is found to be $\frac{1}{Kg}\frac{d\omega}{dT} = -0.25$. The theoretical values of $\frac{H_M}{RT}$ were computed using equation (6). The plot of the theoretical and experimental values of $\frac{G_M}{RT}$, $\frac{H_M}{RT}$, and $\frac{S_M}{R}$ versus X_{Cu} is depicted in Figure 1.

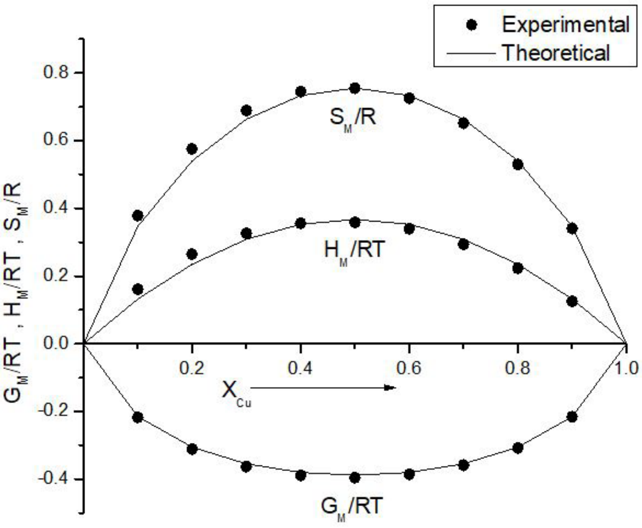

Figure 1: Free energy of mixing (G_M/RT), the heat of mixing (H_M/RT), and the entropy of mixing (S_M/R) Vs concentration of Cu (X_{Cu}) in liquid Cu-Ag alloy at 1423 K

Theoretically, computed values of $\frac{G_M}{RT}$, $\frac{H_M}{RT}$, and $\frac{S_M}{R}$ are in good agreement with experimental values. The minimum value of $\frac{G_M}{RT}$ is – 0.38815 theoretically and – 0.396 ± 0.0177 experimentally at X_{Cu}=0.5. The maximum value of $\frac{H_M}{RT}$ is 0.3675 theoretically and 0.358844 ± 0.0177 experimentally at X_{Cu}=0.5. Similarly, the maximum value of $\frac{S_M}{R}$ is 0.75564718 theoretically and 0.754873 ± 0.025 at X_{Cu}=0.5. At the temperature of 1423 K, $\frac{H_M}{RT}$ and $\frac{S_M}{R}$ are maximum, but $\frac{G_M}{RT}$ is minimum at X_{Cu}= 0.5. Hence the Cu-Ag system is found to be symmetric about equiatomic composition. The maximum error between the theoretically computed value and experimentally observed values of enthalpy of mixing (H_M) and entropy of mixing (S_M) are 17.8361 % and 8.093472 %, respectively. Positive values of $\frac{H_M}{RT}$ and $\frac{S_M}{R}$ at all concentrations and low negative values of $\frac{G_M}{RT}$ at all concentrations indicate that the liquid alloy is disordered, and the bonding is weak among the complex and the atoms. The theoretical values of activity (a_i) for each component were computed using equations (11) and (12), and presented in Figure 2 with the experimental and ideal values.

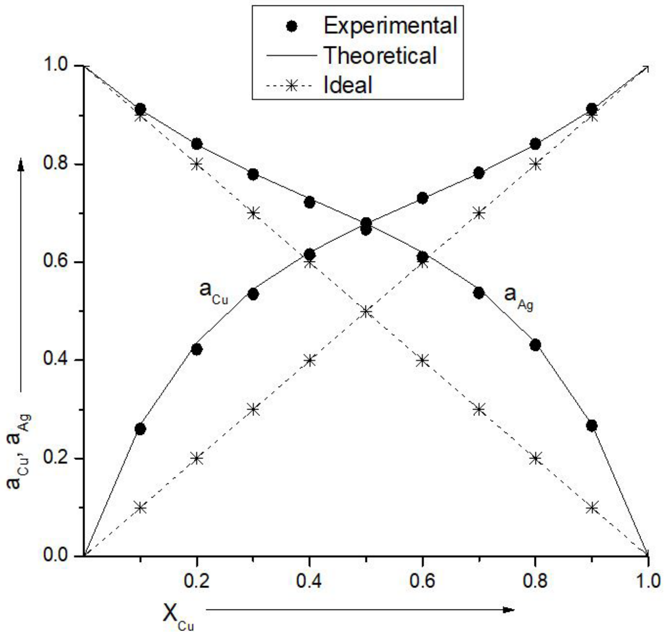

Figure 2: Theoretical, experimental, and ideal values of activity (a_i) of both Cu and Ag Vs concentration of Cu (X_{Cu}) in liquid Cu-Ag alloy at 1423 K

Structural Properties

Theoretical values of concentration fluctuation in the long-wavelength limit (S_{CC} (0)) with its ideal value (S_{CC}^{id} (0)) and Warren-Cowley short-range order parameter (α_1) were computed using equation (14), (16), and (17). Experimental values of concentration fluctuation in the long-wavelength limit (S_{CC} (0)) are obtained directly from the experimental values of activity and depicted in Figure 3.

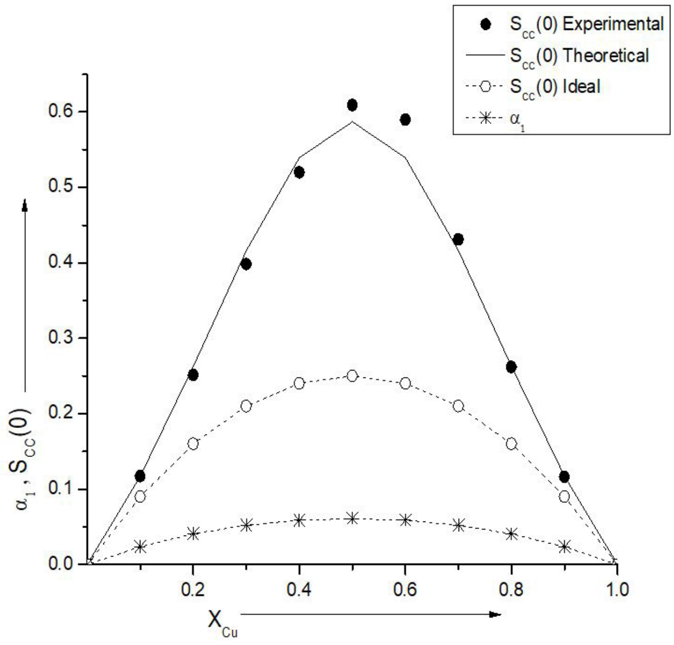

Figure 3: Theoretical, experimental, and ideal values of concentration fluctuation in the long-wavelength limit (S_{CC} (0)) and Warren-Cowley short-range order parameter (α_1) Vs concentration of Cu (X_{Cu}) in liquid Cu-Ag alloy at 1423 K

At the concentration of X_{Cu}= 0.5 and 0.6, the theoretical and experimental values of concentration fluctuation in the long-wavelength limit (S_{CC} (0)) are in poor agreement, but for other concentrations, they are in good agreement. At all concentrations, values of concentration fluctuation in the long-wavelength limit (S_{CC} (0)) are greater than their ideal values (S_{CC}^{id} (0)), and Warren-Cowley short-range order parameter (α^1) is positive, revealing the segregating nature of Cu-Ag liquid alloy at 1423 K.

Surface Properties

Surface tension (σ) with its ideal values (σ_{id}) and surface concentration (X_i^S) are computed using equation (18), (19), and (24). Table 1 represents the input parameters necessary for the calculation of surface tension. The isotherm plots of surface tension and surface concentration are portrayed in Figures 4 and 5.

Table 1: Input parameters for surface tension (σ) [23]

Metal	T_o	σ_o	$\frac{d\sigma}{dT}$	ρ_0	$\frac{d\sigma}{dt}$
	(K)	(N/m)	(N/mK)	(Kg/m³)	(Kg/m³K)
Cu	1356	1.285	-0.00013	8000	-0.801
Ag	1233.7	0.903	-0.00016	9346	-0.907

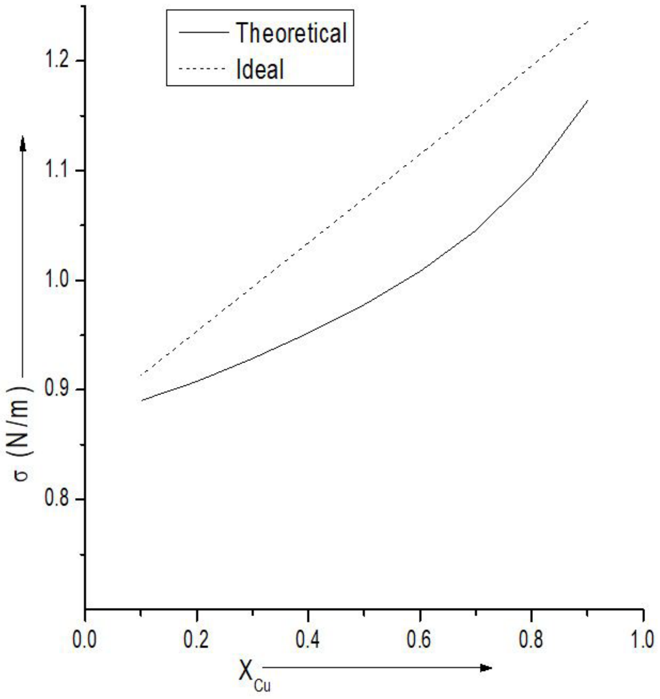

Figure 4: Theoretical and ideal values of surface tension (σ) Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at 1423 K

The surface tension of Cu-Ag liquid alloy increases with an increase in the concentration of Cu. For all concentrations, the values of surface tension are lower than that of its ideal values revealing that the Cu-Ag system is a system of a non-ideal liquid alloy at 1423 K. The negative departure of surface tension from ideality indicates the positive value of excess free energy of mixing of liquid alloy, which is in accordance with the experimentally observed values of excess free energy of mixing [28]. A comparison between the theoretical and experimental value of the surface tension is not performed due to the unavailability of concentration-dependent data

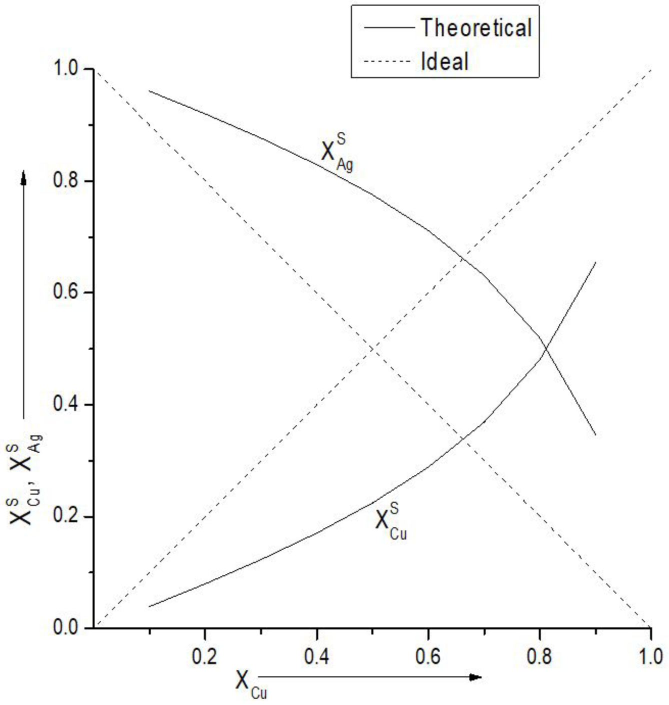

Figure 5: Theoretical and ideal values of surface excess (X_i^S) Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at 1423 K

It is found that the values of the surface concentration of Cu increase and Ag decrease with the increase in the concentration of Cu. For the entire concentration range, the surface concentration of Cu is less than that of its ideal value, but the surface concentration of Ag is greater than that of its ideal value, which indicates that Ag atoms segregate on the surface, but Cu atoms remain in a bulk region in the Cu-Ag liquid alloy at 1423 K

Transport Properties

The ratio of mutual to intrinsic diffusion coefficient $\left(\frac{D_M}{D_{id}}\right)$ and viscosity (η) are computed using equation (26) and (27). The input parameters used for the computation of viscosity are presented in Table 2

Table 2: Input parameters for viscosity (η) [23]

Metal	T_o(K)	E (J/mol)	η_o (Ns/m^2)
Cu	1356	30500	0.000301
Ag	1233.7	22200	0.0004532

The isotherm plots of the ratio of mutual to intrinsic diffusion coefficient and viscosity are portrayed in Figures 6 and 7.

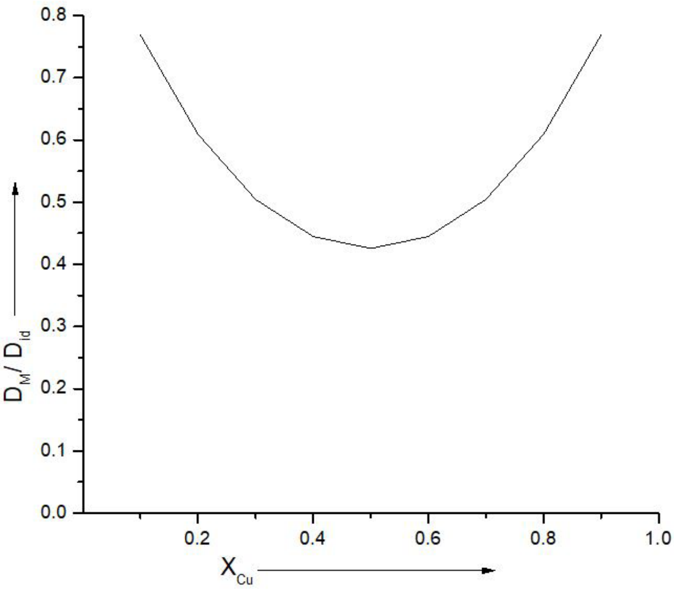

Figure 6: Computed values of the ratio of mutual to the intrinsic diffusion coefficient $\left(\frac{D_M}{D_{id}}\right)$ Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at 1423 K

Since the values of the ratio of mutual to intrinsic diffusion coefficient are less than 1 for all concentrations, Cu-Ag melt shows segregating nature at the temperature of 1423 K. Negative departure of viscosity from its ideal values at all concentrations conforms to the segregating nature of the Cu-Ag system at 1423 K. Concentration-dependent data of viscosity is not available, so the comparison with theoretically computed values is not possible.

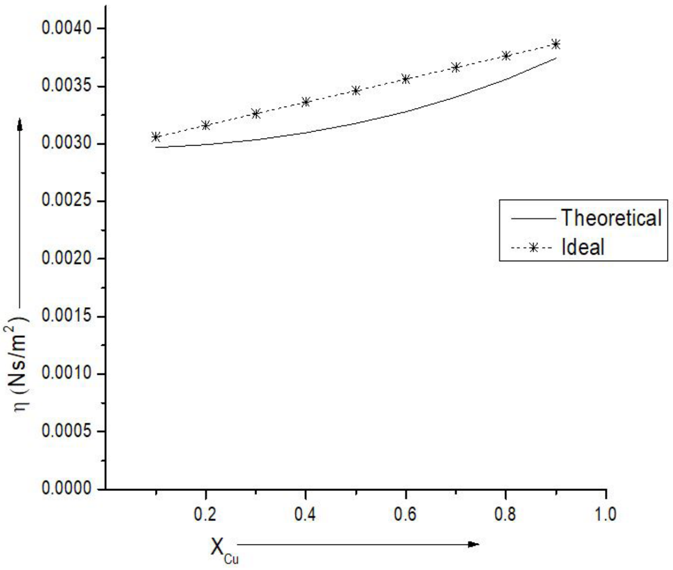

Figure 7: Theoretical and ideal values of viscosity (η) Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at 1423 K

Thermodynamic, Structural, Surface, and Transport properties at T > 1423 K

The simple theory of mixing has been extended to the temperature higher than that of the melting temperature of Cu-Ag liquid alloy (1423 K) to observe and analyze the thermodynamic, structural, surface, and transport properties. Since the value of the ordering energy parameter depends on temperature, values for the temperature higher than 1423 K have been calculated, keeping the temperature derivative of the interaction energy parameter constant. We have made the use of the following equations for the calculation of the interaction energy parameter at different temperatures [22].

$$d[\omega_0(T)] = \left(\frac{\partial \omega_0}{\partial T}\right) dT \tag{33}$$

$$\omega(T_i) = \omega_0(T) + \left(\frac{\partial \omega_0}{\partial T}\right) dT \tag{34}$$

Where T_i is the temperature of interest, and T is the melting temperature.

$$dT = T_i - T \tag{35}$$

With the use of equations (33), (34), and (35), values of interaction energy parameters at different temperatures were calculated and presented in Table 3. Due to the unavailability of experimental data for all concentrations and temperatures, the comparison between theoretical and experimental data is not possible at elevated temperatures.

Thermodynamic Properties

Theoretical computation of different thermodynamic parameters like free energy of mixing $\frac{G_M}{RT}$, the heat of mixing $\frac{H_M}{RT}$, and activities of components (a_i) at different temperatures was done and are presented in Figures 8 and 9.

Table 3: Interaction energies (ω) of Cu-Ag liquid alloy at different temperatures

Temperature (K)	ω (J/mol)
1423	14433.6
1523	14225.75
1623	14017.9
1723	13810.05

The extremum values of $\frac{G_M}{RT}$ are - 0.38815, - 0.41228, - 0.43343, and - 0.45213 at 1423 K, 1523 K, 1623 K, and 1723 K, respectively at X_{Cu}=0.5. The extremum values of $\frac{H_M}{RT}$ are 0.3675, 0.34337, 0.322213, and 0.303513 at 1423 K, 1523 K, 1623 K, and 1723 K, respectively. It is observed that the values of $\frac{G_M}{RT}$ and $\frac{H_M}{RT}$ both decrease with an increase in the temperature indicating that the segregating nature of liquid Cu-Ag alloy decreases with an increase in the temperature. For all temperatures, the liquid Cu-Ag alloy is symmetric at equiatomic composition.

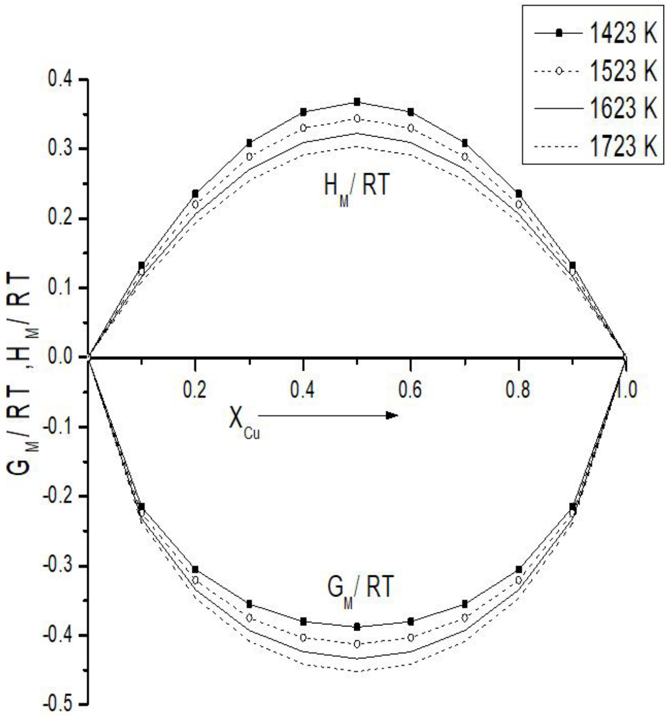

Figure 8: Free energy of mixing (G_M/RT) and heat of mixing (H_M/RT) Vs concentration of Cu (X_{Cu}) in liquid Cu-Ag alloy at different temperatures

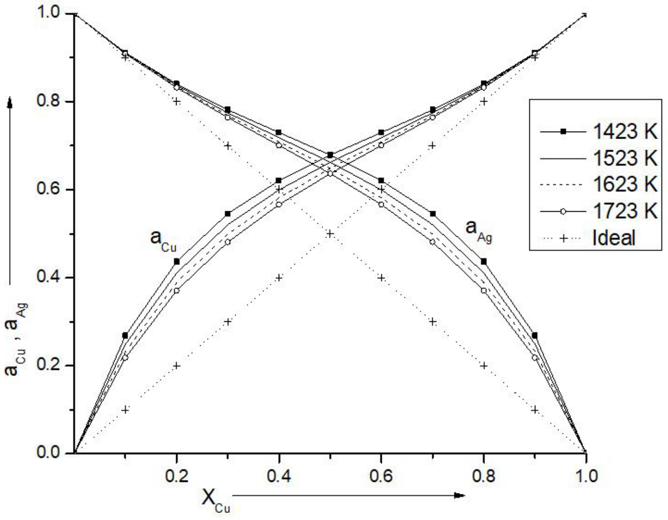

Figure 9: Activity (a_i) of each component Vs concentration of Cu (X_{Cu}) in liquid Cu-Ag alloy at different temperatures

Compound forming tendency in liquid Cu-Ag alloy increases with an increase in temperature because activities of both components are decreasing with an increase in temperature. The positive departure of activities from the ideal values was observed for both components, and they are approaching their ideal values with an increase in temperature.

Structural Properties

Theoretical computation of concentration fluctuation in the long-wavelength limit (S_{CC} (0)) and Warren-Cowley short-range order parameter (α_1) were done at different temperatures and are presented in Figures 10 and 11. For all temperatures at all concentrations, values of S_{CC} (0) are greater than their ideal values. The maximum values of S_{CC} (0) are 0.58721, 0.533429, 0.493444, and 0.431275 at 1423 K, 1523 K, 1623 K, and 1723 K, respectively at X_{Cu}=0.5. Due to an increase in temperature, values of S_{CC} (0) are approaching their ideal values indicating that the segregating nature of liquid Cu-Ag alloy decreases with an increase in temperature. The positive values of α_1 at all temperatures indicate the preference of self-association between the like atoms. Maximum values of α_1 are 0.060924, 0.056115, 0.051896, and 0.048165 at 1423 K, 1523 K, 1623 K, and 1723 K respectively at X_{Cu}=0.5. The self-associating property of liquid Cu-Ag alloy decreases with an increase in temperature.

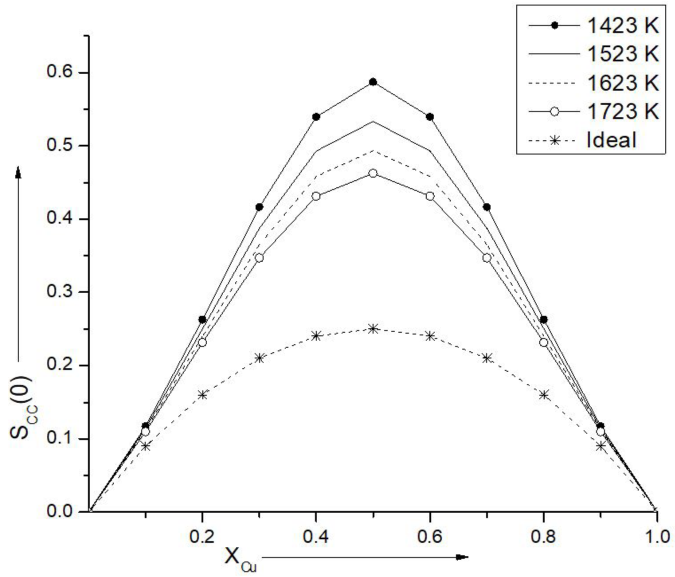

Figure 10: Concentration fluctuation in the long-wavelength limit (S_{CC} (0)) Vs concentration of Cu (X_{Cu}) in liquid Cu-Ag alloy at different temperatures

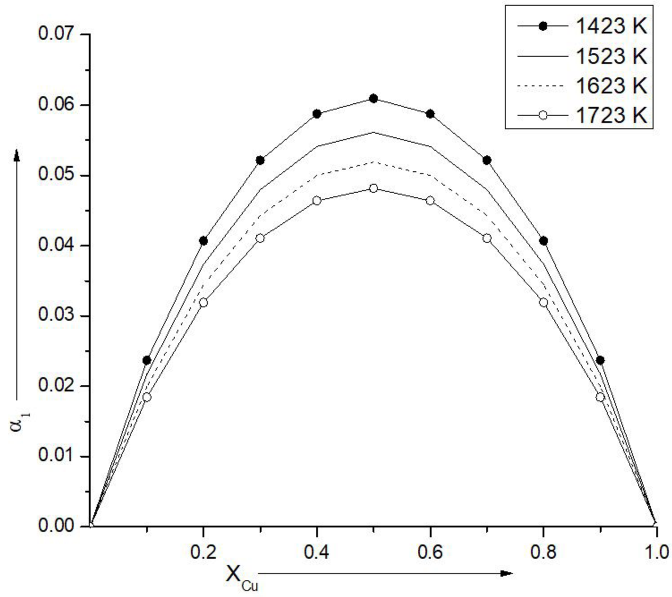

Figure 11: Warren-Cowley short-range order parameter (α_1) Vs concentration of Cu (X_{Cu}) in liquid Cu-Ag alloy at different temperatures

Surface Properties

Surface tension (σ) and surface concentration or surface excess (X_i^S) at different temperatures were computed theoretically and are depicted in Figures 12, 13, and 14. A gradual decrement in surface tension with an increase in temperature was observed. The predicted values of surface excess of Cu increase, but Ag decreases with an increase in temperature, both of them approaching their ideal values with an increase in temperature. Thus at elevated temperature, the Cu-Ag system tends to maintain equilibrium.

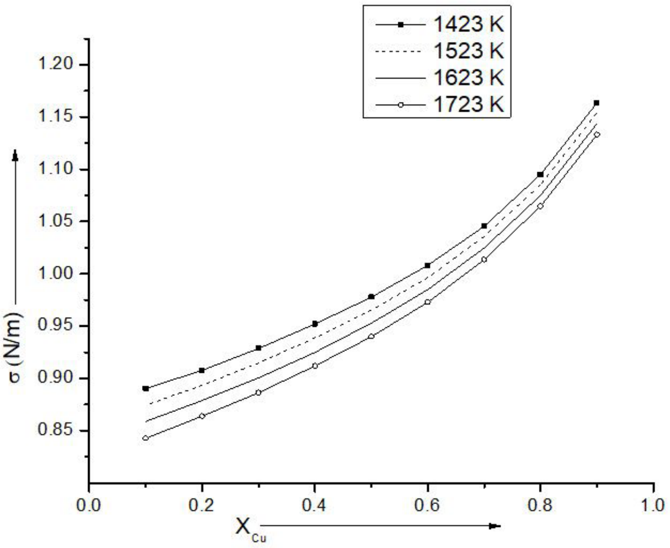

Figure 12: Values of surface tension (σ) Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at different temperatures

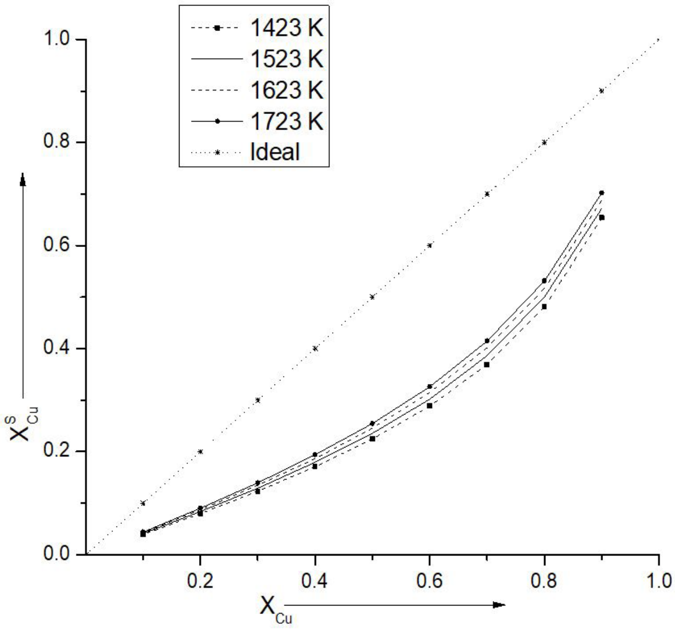

Figure 13: Surface excess of Cu (X_{Cu}^S) Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at different temperatures

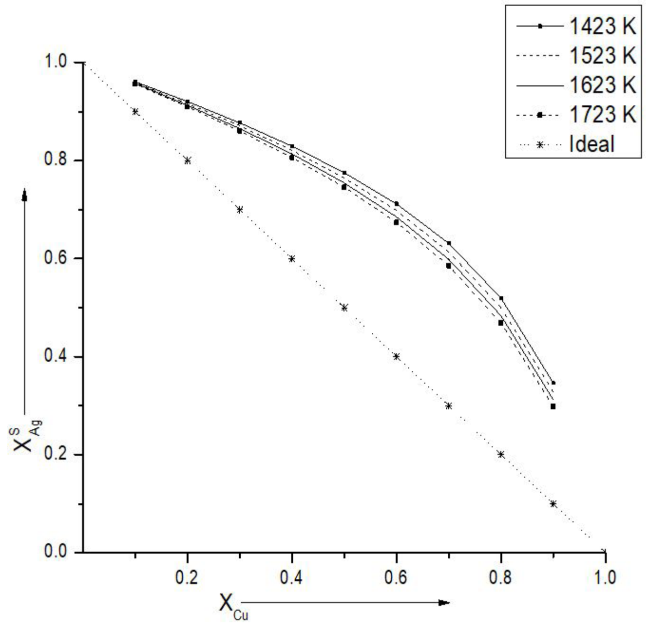

Figure 14: Surface excess of Ag ($X_{Ag}{}^S$) Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at different temperatures

Transport Properties

The ratio of the mutual to the intrinsic diffusion coefficient $\left(\frac{D_M}{D_{id}}\right)$ and viscosity (η) at different temperatures were computed. The minimum values of $\left(\frac{D_M}{D_{id}}\right)$ are 0.425742, 0.468666, 0.506643, and 0.54048 at 1423 K, 1523 K, 1623 K, and 1723 K, respectively, at X_{Cu}=0.5. An increment in the chemical order of the liquid Cu-Ag system was observed with an increase in temperature as the values of $\left(\frac{D_M}{D_{id}}\right)$ is rising with the increase in temperature. The viscosity of liquid Cu-Ag decreases with the increase in temperature, similar to most of the liquids. Figures 15 and 16 represent the transport properties of the liquid Cu-Ag system at different temperatures.

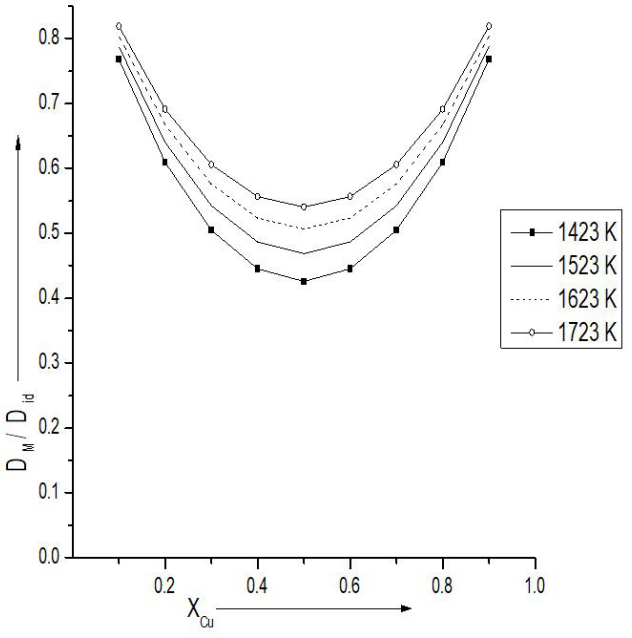

Figure 15: The ratio of the mutual to the intrinsic diffusion coefficient $\left(\frac{D_M}{D_{id}}\right)$ Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at different temperatures

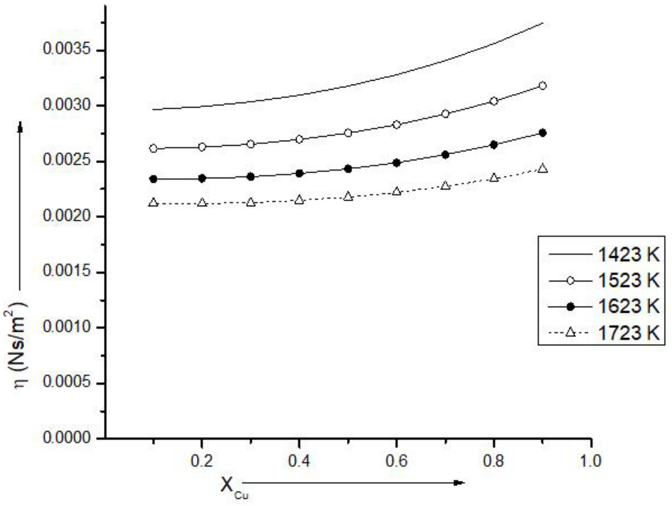

Figure 16: Viscosity (η) Vs concentration of Cu (X_{Cu}) in Cu-Ag liquid alloy at different temperatures

Conclusions

Conclusions drawn from this research work are as follows.

(i) The maximum error between the theoretically computed value and experimentally observed values of enthalpy of mixing (H_M) and entropy of mixing (S_M) at 1423 K are lowered by taking a new value for the interaction energy parameter than previous work [21].

(ii) The interaction energy is positive, indicating the homo coordinating nature of the alloy.

(iii) Thermodynamic and structural studies of the Cu-Ag system prevail that it is a weakly interacting system near the melting temperature.

(iv) Extension of study to higher temperatures reveals that the observed segregating nature of the alloy at 1423 K decreases gradually with an increase in temperature.

(v) The negative departure of surface tension and viscosity from their ideality was observed and are the supportive results for the segregating nature of the alloy.

(vi) Surface tension and viscosity both rise in the Cu-rich region.

(vii) Surface tension and viscosity both decrease with an increase in temperature.

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