Theoretical investigation of thermodynamic, transport and structural properties of Au-Ag liquid alloy at different temperature

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Abstract- Thermodynamic properties, transport properties and structural properties have been calculated using regular solution model. The interaction energy is temperature dependent and played an important role to explain the properties of Au-Ag liquid alloy at different temperatures. The theoretical values of interchange energy at different temperatures are obtained by best fit parameter approximation with the experimental values at 1350K. The study found that the alloy is ordering in nature.

Index terms - Regular solution model, Thermodynamic properties, Transport properties, Structural properties, Ordering nature, Different temperatures, order energy parameter.

1 INTRODUCTION

The properties of gold based brazing alloys have a number of uses in the construction of aero engine and space craft in nuclear engineering to increase the quality and strength of joints between metallic materials. A small fraction of gold can raise the quality of the joint between materials so it is also useful in soldering. Silver based alloy is important in brazing and welding process as alloying of silver with other elements increase its wear-resistance and hardness [1]. Au-Ag liquid alloy is used for preparation of many materials especially in jewelry.

The mixing properties of liquid alloys are important for preparation of desired materials. Thermodynamic property is important to understand the behavior of alloys and transport property is required for many metallurgical processes and heterogeneous chemical reactions. In thermodynamic properties we have calculated free energy of mixing (G_M), activity (a), entropy of mixing (S_M) and heat of mixing (H_M). And, in transport properties we have computed viscosity (η) and diffusion coefficient ratio (D_m/D_{id}). Many researchers [2], [3], [4], [5] have been working on several models to explain the mixing behavior of binary liquid alloys. We have used regular solution model [6] as the atoms of Au and Ag are all alike in shape and size i.e. atomic volume of Au/atomic volume of Ag=11.5/11.6 ≈ 1. Thus Au-Ag is suitable candidate for investigation using regular solution model. And, viscosity is studied with the help of Moelwyn-Hughes equation [7], [8]. The theoretical formulation has been presented in

section (2), result and discussion in section (3) and conclusion in section (4).

2 FORMALISM

Regular solution model is based on the crudest approximation that the constituent atoms A and B are sufficiently similar in size and shape so they are interchangeable on the lattice. And, all configurations of atoms, whether in Pure states A and B or in the solution A-B have equal energy. In this model the energetic effect has also been incorporated and it is considered that there will be contribution to potential energy from A-B pairs. The binary liquid alloy A-B of homogenous solution consists of $C_{A(A=Au)}$ ($\equiv c$) mole of A and $c_{B(A=Ag)}$ {$\equiv(1-c)$} mole of B respectively.

2.1. Thermodynamic properties

In regular solution model, the expression for the free energy of mixing (G_M) of binary liquid alloy is

$$G_M = G_M^{id} + H_M \qquad (1)$$

Where, heat of mixing (H_M) and ideal free energy of mixing (G_M^{id}) are given by

$$G_M^{id} = RT\,[c\ln c + (1-c)\ln(1-c)] \qquad (2)$$

and

$$H_M = \omega c_A c_B \qquad (3)$$

From equation (1), (2) and (3), we get

$$G_M = RT [c \ln c + (1-c)\ln(1-c)] + c(1-c).\omega \qquad (4)$$

Where, ω is interaction energy.

The expression for activities a_A of the elements A in the binary liquid alloy can be derived from the standard relation, that is

$$RT \ln a_A = G_M + (1-c)\frac{\partial G_M}{\partial c} \qquad (5)$$

$$\frac{\partial G_M}{\partial c} = RT[\ln c - \ln(1-c)] + (1-2c).\omega \qquad (6)$$

Using equation (4) and (6) in equation (5), we get

$$\ln a_A = \ln c + \frac{\omega}{RT}(1-c)^2 \qquad (7)$$

and the activity of the element B (a_B) is given by

$$\ln a_B = \ln(1-c) + \frac{\omega}{RT}c \qquad (8)$$

The temperature derivative of G_M provides an expression for integral entropy of mixing (S_M) which is given by

$$S_M = -\frac{\partial G_M}{\partial T} \qquad (9)$$

From equation (3) and (8), we get

$$\frac{S_M}{R} = -[c \ln c + (1-c)\ln(1-c)] - c(1-c).\frac{1}{R}\frac{\partial \omega}{\partial T} \qquad (10)$$

The interchange energy (ω) is temperature dependent. The necessity of taking ω as temperature dependent has been noticed by Bhatia et. al [9], Ratti and Bhatia [10], Alblas et. al [11].

The relation between free energy of mixing (G_M), entropy of mixing (S_M), and heat of mixing (H_M) is given as,

$$\frac{H_M}{RT} = \frac{S_M}{R} + \frac{G_M}{RT} \qquad (11)$$

Using equation (4), (10) and (11), we get

$$\frac{H_M}{RT} = c(1-c).\frac{\omega}{RT} + c(1-c)\frac{1}{R}.\frac{\partial \omega}{\partial T} \qquad (12)$$

2.2 Transport Properties

Diffusion coefficient is important to study mixing behavior of an alloy in microscopic level. Singh and Sommer [12] have derived a relation between diffusion coefficient and concentration fluctuation as

$$\frac{D_M}{D_{id}} = \frac{S_{CC}^{id}(0)}{S_{CC}(0)} \qquad (13)$$

Where, D_M is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal mixture given as

$$D_M = c_1 D_2 + c_2 D_1 \qquad (14)$$

Where, D_1 and D_2 are the self-diffusivities of pure components A and B respectively.

In term of energy order parameter ω, the diffusion coefficient can be expressed as [13]

$$\frac{D_M}{D_{id}} = [1 - \frac{2\omega}{RT}S_{cc}^{id}(0)] \qquad (15)$$

Viscosity is one of the important transport property of binary liquid alloy. It helps to understand the mixing behavior of binary liquid alloys at atomic level. we have used the Moelwyn-Hughes equation [7] to investigate the viscosity of Au-Ag liquid alloy which is given as

$$\eta = (c_1\eta_1 + c_2\eta_2)(1 - c_1 c_2.\frac{H_M}{RT}) \qquad (16)$$

Where, η_k (k=1, 2) is the viscosity of pure component K and for most liquid metals, it can be calculated from Arrhenius type equation [14] at temperature T as

$$\eta_K = \eta_{OK} \exp\left[\frac{E_n}{RT}\right] \qquad (17)$$

Where, η_{OK} is constant (in unit of viscosity) and E_n is the energy of activation of viscous flow for pure metal (in unit of energy per mole).

2.3 Structural Properties

The concentration fluctuation in the long wavelength limit $(S_{cc}(0))$ is used to study the nature of atomic order in binary liquid alloy [18] by using relation,

$$S_{CC}(0) = \frac{RT}{\left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}} \qquad (18)$$

From equation (4) and (18), we get

$$s_{cc}(0) = \frac{c_A c_B}{1 - 2c_A c_B . \frac{\omega}{RT}} \qquad (19)$$

The experimental determination of $S_{cc}(0)$ is derived from experimental values of the activities [17] of the constituent species of the binary liquid alloys from the relation

$$s_{cc}(0) = (1-c)a_A \left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} = c a_B \left(\frac{\partial a_B}{\partial c}\right)^{-1}_{T,P,N} \qquad (20)$$

Here, a_A and a_B are the activities of the component of A and B respectively.

The Warren-Cowley [13], [19] short range order parameter (α_1) provides insight into the local arrangement of the atoms in the molten alloys. Though it is difficult to obtain the experimental values of α_1, theoretical values of these parameters can be evaluated

$$\alpha_1 = \frac{s-1}{s(Z-1)+1} \qquad (21)$$

where, $s = \frac{S_{cc}(0)}{S_{cc}^{id}(0)}$, $s_{cc}^{id}(0) = c_A c_B$

and Z is the coordination number = 10 in our study.

2.4 order energy parameter at different temperatures

The values for the free energy of mixing (G_M) of liquid alloys at different temperatures can be calculated from equation (4) by knowing the values of ordering energy parameter (ω) at different temperatures from the relation [15], [16]

$$\omega(T) = A + BT \qquad (22)$$

Where, A and B are coefficient constants.

3. Results and discussion

From our calculation, the best fit parameters was found to be ω/RT = -0.9 and $\frac{1}{R}\frac{\partial\omega}{\partial T}$ = +0.94 and $\frac{1}{R}\frac{\partial\omega}{\partial T}$ at temperature 1350K using the best fit approximation with the experimental values of the alloy from Hultgren et.al. 1973 [17] using equations (4) and (10).

The values of A and B obtained with the help of values of ω/RT and $\frac{1}{R}\frac{\partial\omega}{\partial T}$ at temperature 1350K of the alloy Au-Ag using equation (22). By taking the values of coefficient constants A and B for the alloy, the theoretical values of interchange energy (ω) at different temperatures (i.e. 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K) are obtained and presented in the table 1.

Table 1
Estimated values of order energy parameter (ω) at different temperatures

Temperature (T)	Order energy Parameter (ω/RT)
1450K	-0.7730
1550K	-0.6625
1650K	-0.5654
1750K	-0.4794
1850K	-0.4026
1950K	-0.3338
2050K	-0.2717

Interaction energy is found to be positive at our temperatures of study which indicates Au and Ag atoms are attracted to each other in the alloy at those temperatures. Using theoretically computed interchange energy (ω) presented on table 1 , we have computed free energy of mixing (G_M), activity (a), entropy of mixing (S_M), heat of mixing (H_M), Ratio of mutual and self-diffusivity (D_M/D_{id}) and viscosity (η) at different temperatures (i.e.= 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K) using Regular solution model [6].

3.1 Free energy of mixing

The values of free energy of mixing (G_M) of the alloy at different temperatures (i.e. 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K) have been calculated by using the corresponding values of $\omega(T)$ in equation (4) over the entire range of concentration. The equation (4) has been used to compute the free energy of mixing (G_M) of Au-Ag liquid alloy at different temperatures of study in the concentration range C_{Au}=0.1 to 0.9 which is shown in fig. 1 .
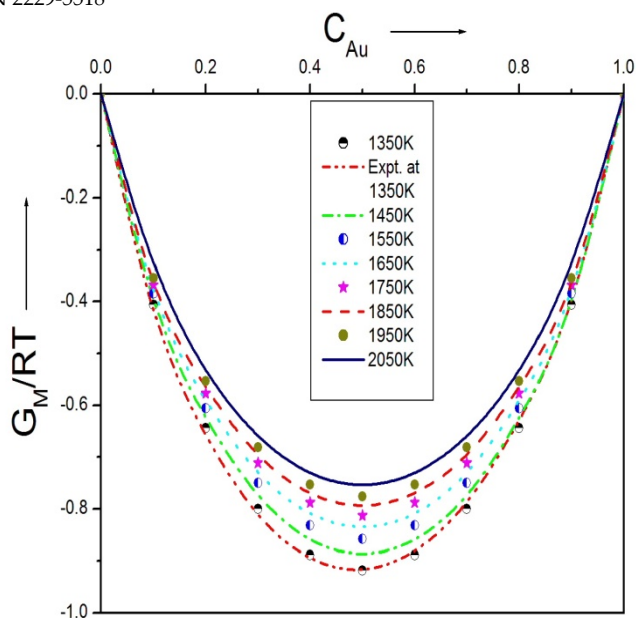
Fig.1. Graph for (G_M/RT) Versus the concentration of C_{Au} of Au-Ag liquid alloy at temperatures 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K.

At 1350K, the theoretical and experimental values [17] of G_M/RT of the alloy are in well agreement. The minimum value of G_M/RT at C_{Au}=0.5 i.e. -0.9180. The maximum discrepancy between the theoretical and experimental values of G_M/RT is 2.83% at C_{Au}=0.9. The values of free energy of mixing are found to be negative in the entire concentration range. And , at all the different temperatures (i.e. 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K) of study the minimum value is at C_{Au}=0.5 which indicates that the symmetry in free energy of mixing has been well explained by our present model. As the temperature of the alloy increases from 1350K to 2050K, the values of G_M/RT increases and vice-versa.

3.2 Entropy of mixing (S_M)

The theoretical value of $\frac{1}{R}\frac{\partial \omega}{\partial T}$ at 1350K is obtained using equation (10) by best fit method with the help of experimental values of entropy of mixing (S_M) is taken for Hultgren et. al. [17] i.e. $\frac{1}{R}\frac{\partial \omega}{\partial T} = 0.94$ and with the help of this value theoretical values of entropy of mixing is computed. The entropy of mixing of Au-Ag alloy at different temperatures (i.e 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K) are calculated using equation (10)

with the help of values of energy order parameters ω(T) presented on the table 1.
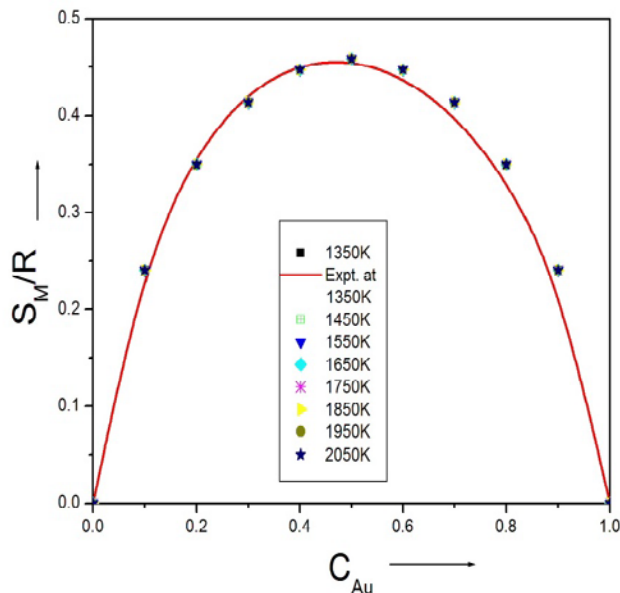

Fig. 2. Graph for S_M/R versus the concentration of C_{Au} of Au-Ag liquid alloy at temperatures 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K.

At 1350K, the values of S_M/R are found to be positive in the entire concentration range. The maximum theoretical value of S_M/R is 0.4582 at C_{Au} =0.5 while the experimental value of S_M/R is 0.4576 at C_{Au} =0.5. This explains the symmetry in entropy of mixing of Au-Ag liquid alloy at 1350K. And, at different temperatures, the values of entropy of mixing remain unchanged as the theoretical value of . $\frac{1}{R}\frac{\partial \omega}{\partial T} = 0.94$ remains constant using equation (22).

3.3 Heat of mixing (H_M)

The heat of mixing (H_M) for the alloy is computed using equation (12) using theoretical values of order energy parameter which is shown in fig, 3.
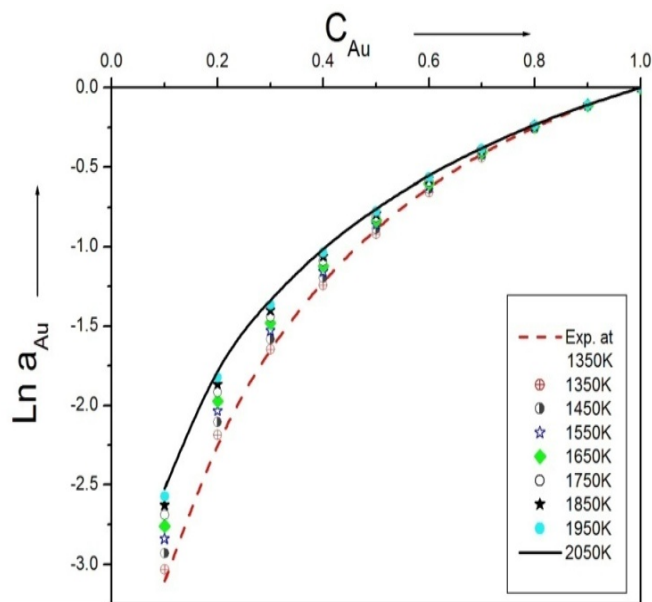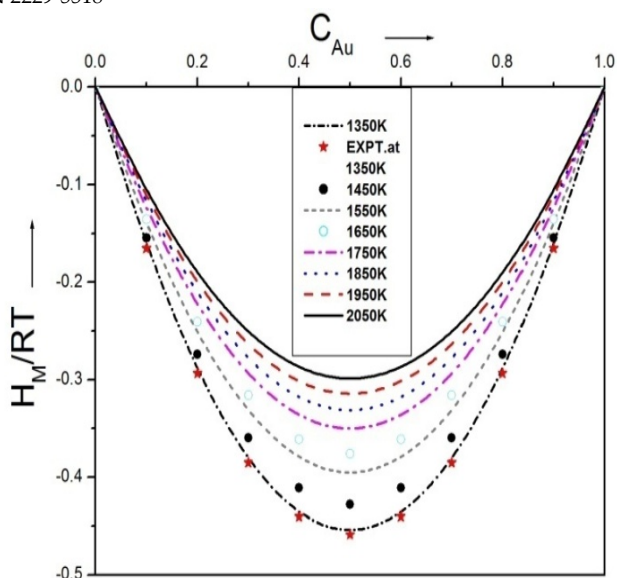
Fig. 3. Graph for H_M/RT versus the concentration of C_{Au} of Au-Ag liquid alloy at temperatures 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K.

At 1350K, it was found that the theoretical and experimental values of H_M/RT are in well agreement. The values of H_M/RT are negative in the entire concentration range i.e. C_{Au}=0.1 to 0.9 . The minimum value of H_M/RT (i.e. H_M/RT= - 0.4598 at C_{Au}=0.5). And, at different temperatures i.e. 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K the minimum value is at C_{Au} = 0.5. Thus the symmetry in heat of mixing is well explained. As the temperature of the alloy is increased from 1350K to 2050K, the values of H_M/RT increases.

3.4 Activity

We have used the equations (7) and (8) to compute the activity of Au and Ag atoms of Au-Ag liquid alloy. The graph of the activity (Ln a) is shown in fig.4 and figure (5).
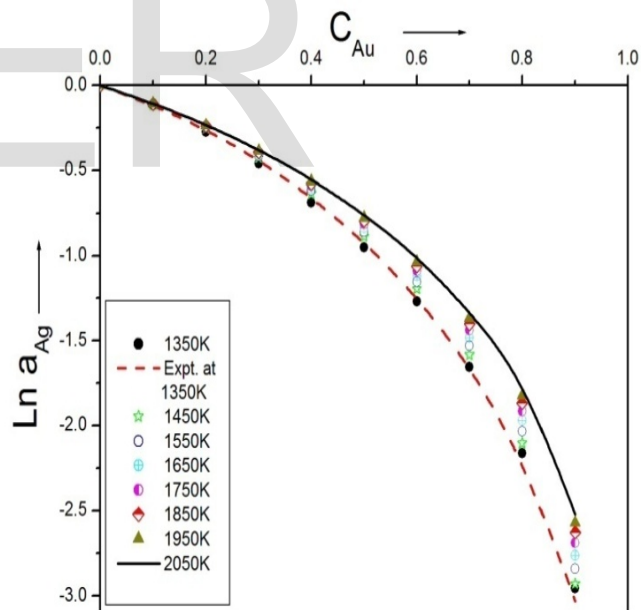

Fig. 4. Graph for Ln a_{Au} at different temperatures versus C_{Au} of Au-Ag liquid alloy at 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K.

Fig. 5. Graph for Ln a_{Ag} at different temperatures versus C_{Au} of Au-Ag liquid alloy at 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K.

At 1350K, the computed values of activity of both the components of Au-Ag alloy are in good agreement with the experimental values for whole range of concentration. For Au the disagreement between the theoretical and experimental values is maximum i.e. 6.11% at C_{Au} =0.7 while for Ag it is found to be 4.94% at at C_{Au} =0.7. And as the temperature increased from 1350K to 2050K, the values of activity (Ln a) increases.

3.5 Transport properties: chemical diffusion and viscosity

The diffusion coefficient D_M/D_{id} is calculated using equation (15) with the help of theoretical values of order energy parameters which is shown in figure (6).
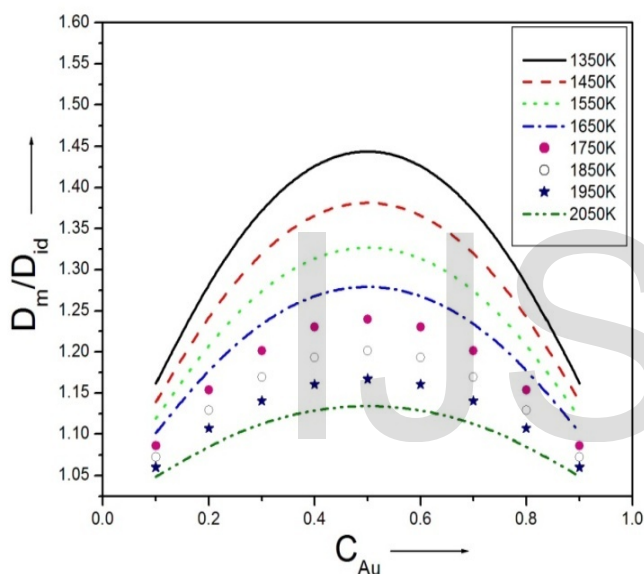

Fig. 6. Ratio of mutual and self-diffusivities, D_M/D_{id} for Au-Ag liquid alloy at temperatures 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K versus concentration of Au.

From the figure it is clear that the value of $\frac{D_M}{D_{id}} > 1$ in the entire range of concentration at different temperatures which is indicative for the presence of chemical order in the alloy. The maximum value of D_M/D_{id} is at $C_{Au} = 0.5$, confirms the ordering tendency of the atoms in Au-Ag liquid alloys is greater about equiatomic composition. And, as the temperature increases from 1350K to 2050K, the values of diffusion coefficient increases at the whole concentration range i.e. 0.1 to 0.9.

We have used equation (16) in conjugation with equation (17) to calculate viscosity. To compute viscosity of Au-Ag alloy at 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K , the viscosities of pure components Au and Ag at that temperatures are required which is computed using equation (17). The viscosity of pure component can be obtained with the help of constants η_{ok} and E for the metals [14] and is as shown in the figure (6).
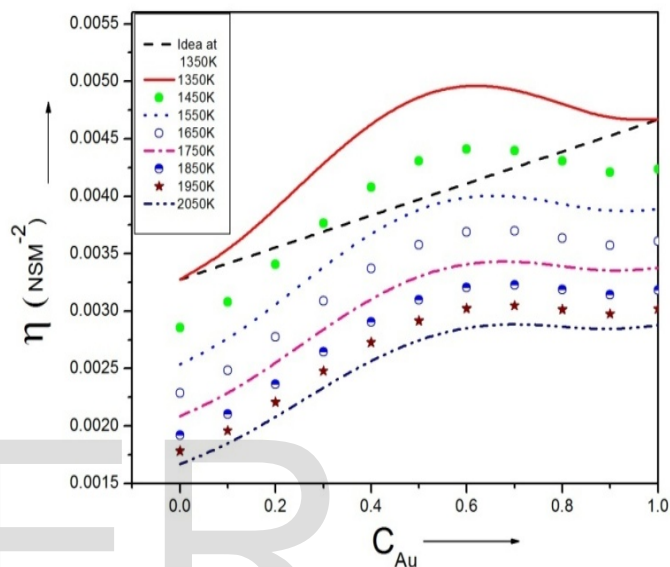

Fig. 7. Viscosity of Au-Ag liquid alloy at 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K versus concentration of Au.

At 1350K, the plot shows that viscosity of the alloy is slightly deviated from ideal values at the concentration C_{Au}=0.1 to 0.9. The viscosity of pure component of Au atom is more than the viscosity of pure component Ag at each temperatures of study. As the concentration of Au atom increases, the viscosity of the alloy increases at 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K. And, the viscosity of the alloy increases with the increase in temperature from 1350K to 2050K at each concentration range as shown in figure (7).

3.6 Structural properties

The experimental values of concentration fluctuation in the long wavelength limit ($S_{cc}(0)$) can be calculated from equation (20). The computed and experimental values of

Short range order parameter α_1 at 1350K along with different temperatures i.e. at 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K are shown in fig. 8.
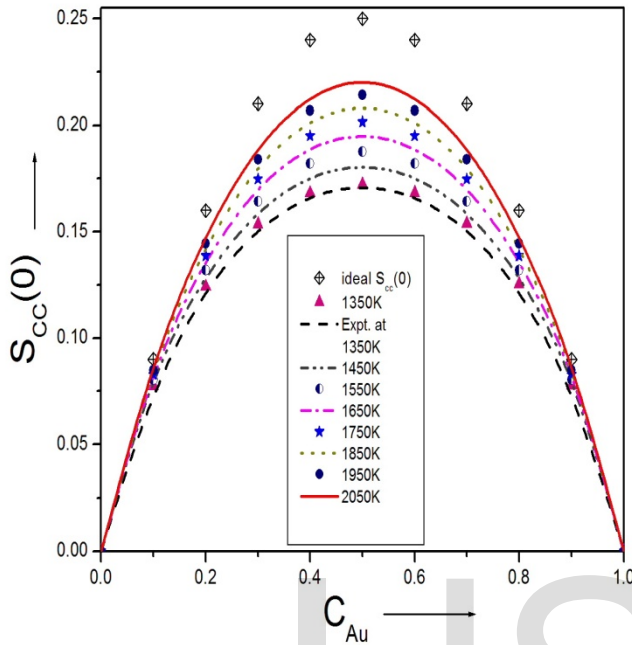

Fig. 8. Theoretical values of Concentration fluctuation of Au-Ag liquid alloy at 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K along with experimental values at 1350K and $S_{cc}^{id}(0)$.

At 1350K, the calculated values of $S_{cc}(0)$ are in well agreement with the experimental values [17]. The computed values of $S_{cc}(0)$ are less than the ideal values at all the concentrations. The computed value of $S_{cc}(0)$ is maximum at C_{Au} =0.5 i.e. 0.1724 and experimental value is also maximum at C_{Au} =0.5 i.e. 0.1722.

At different temperatures i.e. 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K the maximum value obtained at C_{Au} =0.5. Thus the symmetry in $S_{cc}(0)$ for Au-Ag liquid alloy is observed. The maximum value of $S_{cc}(0)$ is at 2050K among our temperatures of study and as the temperatures increases from 1350K to 2050K, the values are increases at each concentration.

At a given composition, Fig. 8 shows that $S_{cc}(0) < S_{cc}^{id}(0)$ throughout the entire concentration range at all

temperatures of investigation which indicates that hetero-coordination is favored in the Au-Ag alloy at these temperatures.

The Warren-Cowley chemical short-range order parameter (α_1) [13], [19] is computed from equation (21) using the theoretical values of $S_{cc}(0)$ which is shown in fig. 9 .
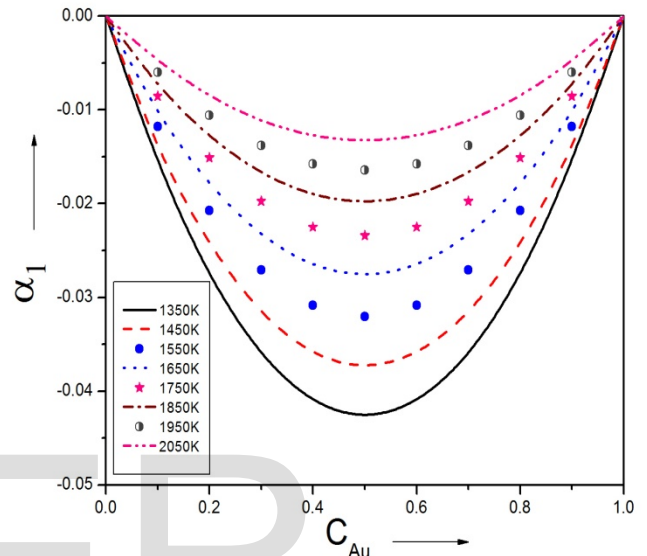

Fig. 9. Chemical short range order parameter (α_1) of Au-Ag liquid alloy at 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K with co-ordination number (Z)= 10.

The plot shows that Chemical short range order parameter (α_1) is always negative at all the concentrations which is in support of ordering nature of the alloy. Its value is minimum at C_{Au}= 0.5 at all temperature of study which indicates symmetry. The value of α_1 increases as the temperature increases from 1350K to 2050K.

4. CONCLUSION

-The regular solution model successfully explains the symmetry in the properties of mixing of Au-Ag liquid alloy.
-The Au-Ag liquid alloy is an ordered system and is weakly interacting in nature.
-The interchange energy (ω) is temperature dependent and played important role to study the properties at temperatures 1350K, 1450K, 1550K, 1650K, 1750K, 1850K, 1950K and 2050K.

-The symmetry in free energy of mixing and heat of mixing is observed and its value increases as the temperature increases in all temperatures of investigations.

-The activity of the alloy slightly increases as the temperature of study increases at each concentration range.

-The diffusion coefficient decreases as the temperature increases.

-Viscosity is temperature dependent and decreases as the temperature of study increases.

- The symmetry in Concentration fluctuation and Chemical short range order parameter is observed, and increases its value as the temperature of study increases.

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