

## A Simple Theory of Mixtures for the Study of the Temperature Dependence of Thermo-structural Properties of Al-Ga Liquid Alloy

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**ABSTRACT:** *A simple theory of mixtures for symmetric alloys was used to study the thermodynamic and structural properties of the Al-Ga alloy in the liquid state at 1023 K. The computed thermodynamic properties are in a very good agreement with the observed values and show that the alloy is weakly interacting. The computed structural properties show that the Al-Ga alloy is segregating in nature which is in agreement with the observed values. The excess free energy of mixing, activity of monomers and concentration fluctuation in the long wavelength limit was extrapolated to higher temperatures by optimising the temperature dependent parameters. As the temperature increases, the behaviour of the alloy shifts towards the ideality.*

**Keywords:** Simple theory of mixture, Al-Ga alloy, hetero-pairs, concentration fluctuation, diffusion coefficients

### 1. INTRODUCTION

Understanding the mixing behaviour of the constituents of an alloy in the liquid state is of great importance in developing the desired materials in the solid-state. The tendency to form hetero-pairs or homo-pairs in liquid alloys is also a matter of interest to researchers. The symmetric and asymmetric behaviours of an alloy also provide enormous information for further research. However, due to the state of disorder present in a liquid state, the formulation of an exact theoretical model for the liquid alloy to understand thermo-structural properties is a difficult task. To comprehend the complexities of liquid alloys, a number of models have, therefore,

been employed by researchers.<sup>1-12</sup> In the present work, a simple theory of mixture for symmetric alloy was employed to study the thermodynamic and structural properties of aluminium-gallium (Al-Ga) alloy at 1023 K in the liquid state.<sup>14,15</sup>

In the simple theory of mixtures, the heat of mixing is only related to the bond energies between adjacent atoms, and the interatomic distances and bond energies are independent of composition. The simple theory of mixture is applicable to a binary solution in which the atomic size factor of the constituents, described in the following formula, should be within 15%:<sup>16</sup>

$$\text{Atomic size factor} = \left( \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \times 100 \right)$$

In the Al-Ga alloy, the atomic size factor is very small and is less than 15%. It is a well-known fact that the atomic radius increases on moving downwards a group in the modern periodic table. Even though Al comes first and Ga in its next period, the atomic radius of Ga is less than that of Al. This interesting and exceptional fact led the authors to investigate the Al-Ga alloy. Further, if there is a large difference in the electronegativity of the constituents of a solution, charge transfer occurs, and the formation of strong ionic bonding is likely to exist. In Al-Ga alloy, the electronegativity of Al (= 1.61) and Ga (= 1.81) are comparable to each other and hence, there is less chance of forming ionic bonding between them. For this reason, a simple theory of mixture was employed to explain the mixing behaviour of the Al-Ga alloy in the liquid state.

The outline of this paper is as follows. In Section 2, the theoretical basis of our work is presented. Section 3 gives the results and discussion of this work. Finally, the conclusions are outlined in Section 4.

## 2. THEORETICAL BASIS

Consider metal A (=Al) and metal B (=Ga) mixed in the molten state. The excess Gibb's free energy of mixing ( $G_M^{XS}$ ) of the binary mixture can be expressed in a polynomial in terms of concentration as:<sup>14,15</sup>

$$G_M^{XS} = x_1 x_2 \{A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + \dots\}$$

or

$$G_M^{XS} = x(1-x)\{A_0 + A_1(1-2x) + A_2(1-2x)^2 + \dots\} \quad (1)$$

where the coefficients  $A_0, A_1, A_2, \dots$  are independent of composition but dependent on temperature  $T$  and on pressure  $P$ ,  $x = x_2$  is the concentration of B, and  $1 - x = x_1$  is the concentration A. For a symmetrical binary mixture, the coefficient  $A_1 = 0$ .<sup>17</sup> Then, Equation 1 becomes:

$$G_M^{XS} = x(1-x)\{A_0 + A_2(1-2x)^2\} \quad (2)$$

The excess entropy of mixing for the symmetrical mixture can be obtained using a standard thermodynamic relation  $S_M^{XS} = -\frac{\partial G_M^{XS}}{\partial T}$  as:

$$S_M^{XS} = -x(1-x)\left\{\frac{\partial A_0}{\partial T} + \frac{\partial A_2}{\partial T}(1-2x)^2\right\} \quad (3)$$

The heat of mixing, Gibb's free energy of mixing and entropy of mixing are related by the relation:

$$G_M^{XS} = H_M - TS_M^{XS}$$

Using this relation together with Equations 2 and 3, we have:

$$H_M = x(1-x)\left[\left\{A_0 - T\frac{\partial A_0}{\partial T}\right\} + \left\{A_2 - T\frac{\partial A_2}{\partial T}\right\}(1-2x)^2\right] \quad (4)$$

Now, the activity of monomers of the symmetrical binary mixture is given as:<sup>17</sup>

$$RT \ln(a_1/x_1) = x_2^2 [A_0 + A_2(x_2 - x_1)(x_2 - 5x_1)] \quad (5a)$$

$$RT \ln(a_2/x_2) = x_1^2 [A_0 + A_2(x_1 - x_2)(x_1 - 5x_2)] \quad (5b)$$

where  $a_1$  and  $a_2$  are the activity coefficients of monomers A and B of the binary mixture, respectively. These activity coefficients can be related to the activities of monomers A and B by the respective relations  $a_1 = x_1\gamma_1$  and  $a_2 = x_2\gamma_2$ .

The quantity that is important to understanding the ordering and segregating nature of a binary mixture, called concentration fluctuation in the long wavelength limit ( $S_{CC}(0)$ ), can be related to the Gibb's free energy of mixing as follows:<sup>2</sup>

$$S_{CC}(0) = \frac{RT}{\left(\frac{\partial^2 GM}{\partial x^2}\right)_{T,P,N}} \quad (6)$$

Therefore, using Equations 2 and 6 with  $G_M = G_M^{XS} + RT(x_1 \ln x_1 + x_2 \ln x_2)$   $S_{CC}(0)$  for a symmetrical binary mixture is given as:

$$S_{CC}(0) = \frac{x(1-x)}{1 - \frac{2x(1-x)A_0}{RT} + \frac{2x(1-x)A_2}{RT} + (24x - 24x^2 - 5)} \quad (7)$$

The  $S_{CC}(0)$  can also be related to the activity of the monomers of the binary mixture, called the observed value, is given as:<sup>17</sup>

$$S_{CC}(0) = x_2 a_1 \left( \frac{\partial a_1}{\partial x_2} \right)_{T,P,N}^{-1} = x_1 a_2 \left( \frac{\partial a_2}{\partial x_1} \right)_{T,P,N}^{-1} \quad (8)$$

To know greater insight into the atomic ordering of a binary alloy, Warren-Cowley short range order parameter ( $\alpha_1$ ) can be determined.<sup>18,19</sup> The expression for  $\alpha_1$  is given as:

$$\alpha_1 = \frac{S-1}{(z-1)S+1}, \quad \frac{S_{CC}(0)}{S_{CC}^{id}(0)} \quad (9)$$

where  $S_{CC}^{id}(0) = x_1 x_2$  and  $z$  is the coordination number.

The segregating and ordering nature of an alloy can also be judged by means of the ratio of mutual and ideal diffusion coefficients. The mutual diffusion coefficients ( $D_M$ ) and ideal diffusion coefficient ( $D_{id}$ ) are given as:<sup>20,21</sup>

$$D_M = D_{id} \frac{\partial \ln a}{\partial x} \quad (10)$$

$$D_{id} = xD_1 + (1-x)D_2 \quad (11)$$

where  $D_1$  and  $D_2$  are the self-diffusion coefficients of pure components A and B, respectively.

The mutual and ideal diffusion coefficients can be related to concentration fluctuation in the long wavelength limit as follows:<sup>20,21</sup>

$$\frac{D_M}{D_{id}} = \frac{x_1 x_2}{S_{CC}(0)} = 1 - \frac{2x(1-x)A_0}{RT} + \frac{2x(1-x)A_2}{RT} \frac{24x - 24x^2 - 5}{24x - 24x^2 - 5} \quad (12)$$

The parameters  $A_0$  and  $A_2$  can be extrapolated to different temperatures using the relation

$$A'_0 = A_0 + \frac{\partial A_0}{\partial T} dT \quad (13a)$$

$$A'_2 = A_2 + \frac{\partial A_2}{\partial T} dT \quad (13b)$$

where  $dT$  is the difference in temperature.

### 3. RESULTS AND DISCUSSION

The parameters  $A_0$  and  $A_2$  for the Al-Ga alloy at 1023 K were estimated by the least square method using the observed values of the excess free energy of mixing and Equation 2 in the concentration range 0.1 to 0.9 of Al.<sup>22</sup> The respective best fit value of  $A_0$  and  $A_2$  were found to be 1254 J mol<sup>-1</sup> and 0 at 1023 K for the Al-Ga alloy. The positive value of  $A_0$  indicates that there is a tendency of phase segregation (preferred with like atom pairing) in the Al-Ga alloy in the molten state. The computed values of the  $G_M^{XS}$  obtained from Equation 1 were plotted against  $x$  (concentration of Ga) for the Al-Ga alloy at 1023 K along with their observed values in Figure 1.

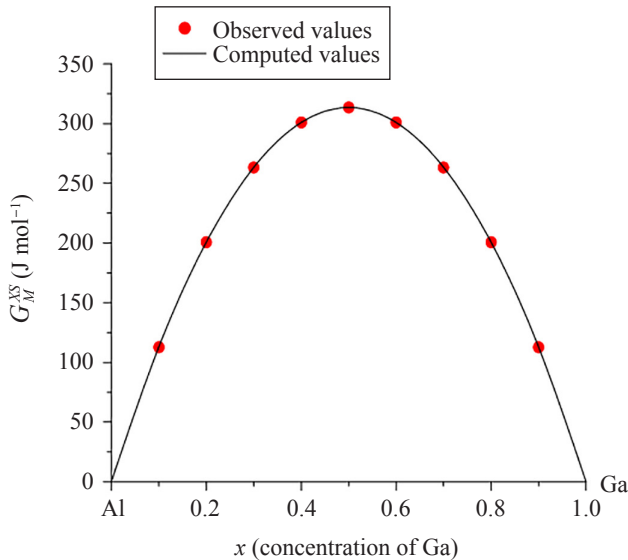


Figure 1: Excess free energy of mixing  $G_M^{XS}$  vs. concentration of Ga of liquid Al-Ga alloy at 1023 K.

The computed and observed values of  $G_M^{XS}$  for the Al-Ga alloy at 1023 K are in excellent agreement with one another at all concentrations.<sup>22</sup> Both the computed and observed values showed that the Al-Ga alloy at 1023 K is a symmetric alloy with a maximum value at equiatomic composition. The computed maximum value of  $G_M^{XS}$  ( $= 313.5 \text{ J mol}^{-1}$ ) is exactly equal to the observed maximum value ( $= 313.5 \text{ J mol}^{-1}$ ) at equiatomic compositions.<sup>21</sup> It is also worth mentioning that the maximum value of  $G_M^{XS}$ , as evident from the computed and observed values, implies that the Al-Ga alloy in the molten state at 1023 K is a weakly interacting segregating alloy. The positive value of  $G_M^{XS}$  at all compositions is also a confirmation of the phase segregating nature of Al-Ga alloy at 1023 K.

Activity, a thermodynamic quantity that can be directly obtained from experiments, can be used to compute the thermodynamic functions, such as free energy of mixing and concentration fluctuation in the long wavelength limit. The deviations of a binary solution from an ideal behaviour can be understood by means of this quantity. The magnitudes of the activities of monomers of a solution depend on the bond energies between the constituents of the mixture. The activities of Al and Ga in the Al-Ga alloy at 1023 K were computed using Equation 5 and the estimated values of  $A_0$  and  $A_2$ . The computed and observed values of the activities of Al and Ga are plotted in Figure 2. The computed and observed values of the activities of the monomers of the Al-Ga alloy at 1023 K were found to be in excellent agreement with one another.<sup>22</sup> The activity coefficients of the monomers of the Al-Ga alloy at 1023 K were found to be greater than unity (even though by a small amount) for all compositions. This clearly indicates that the Al-Ga alloy at 1023 K exhibits a positive deviation from Raoult's law. Therefore, in the case of Al-Ga alloy, less energy is required to separate the constituent atoms, i.e., the alloy is of a segregating nature.

In order to compute the entropy of mixing of the Al-Ga alloy at 1023 K in the liquid state, the temperature derivative of the energy parameter  $\frac{\partial A_0}{\partial T}$  and  $\frac{\partial A_2}{\partial T}$  were determined by the method of optimisation using the observed value of the excess entropy of mixing and Equation 3. The best fit values were  $\frac{\partial A_0}{\partial T} = -1.071 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\frac{\partial A_2}{\partial T} = -0.534 \text{ J mol}^{-1} \text{ K}^{-1}$ . The computed and observed values of the entropy of mixing for the Al-Ga alloy at 1023 K were found to agree very well with one another (Figure 3).<sup>22</sup> Both the observed and computed value showed that the entropy of mixing was symmetrical about equiatomic composition. The heat of mixing of the Al-Ga alloy at 1023 K was calculated using Equation 4 and the values of  $A_0$ ,  $A_2$ ,  $\frac{\partial A_0}{\partial T}$  and  $\frac{\partial A_2}{\partial T}$ . The computed and observed values of heat of mixing were found to be a reasonable agreement with each other (Figure 4).

Both the computed and observed values of the heats of mixing are positive at all compositions. The positive value of heat of mixing of the Al-Ga alloy is also indicative of the segregating nature of the alloy. However, the small positive value of the heat of mixing implies that the bonding strength between the like atoms is weak.

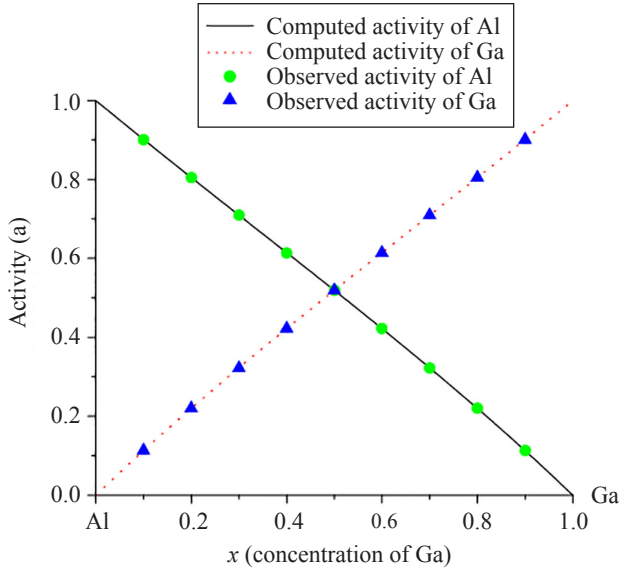


Figure 2: Activity of Al and Ga vs. concentration of Ga of liquid Al-Ga alloy at 1023 K.

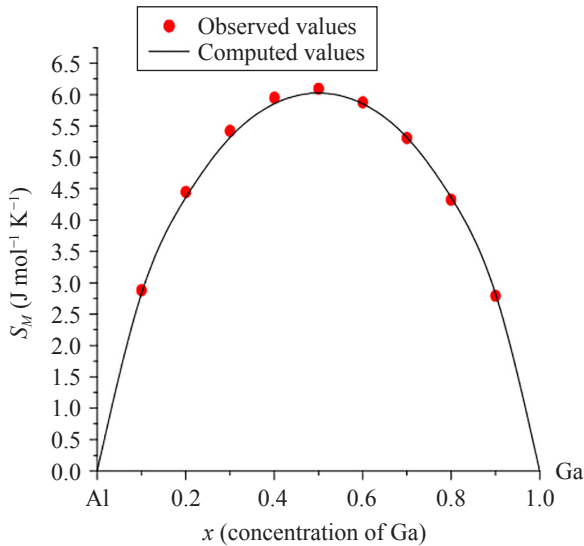


Figure 3: Entropy of mixing  $S_M$  vs. concentration of Ga of liquid Al-Ga alloy at 1023 K.

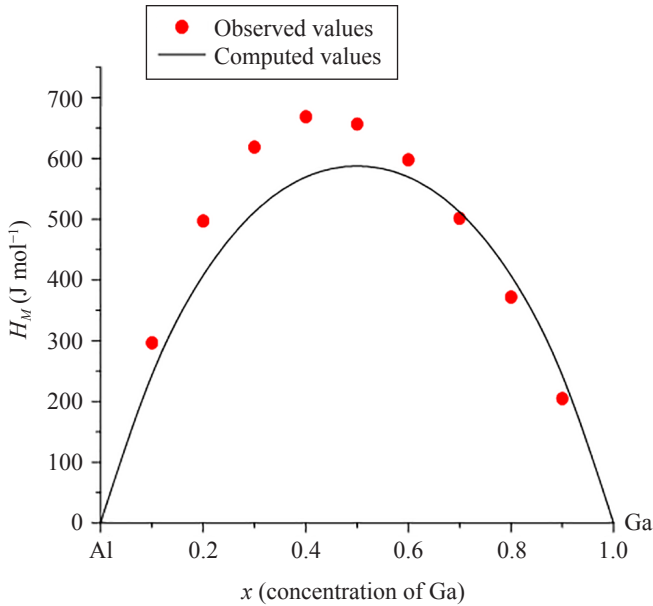


Figure 4: Heat of mixing  $H_M$  vs. concentration of Ga of liquid Al-Ga alloy at 1023 K.

In order to understand the ordering and segregating nature, the concentration fluctuation in the long wavelength limit ( $S_{CC}(0)$ ) for the Al-Ga alloy at 1023 K was computed using Equation 7. The observed value of  $S_{CC}(0)$  was calculated using Equation 9 and the observed value of activities of the monomers of the alloy.<sup>22</sup> The computed, observed and ideal value of  $S_{CC}(0)$  was plotted in Figure 5. There was excellent agreement between the computed and observed values. The computed and observed values of  $S_{CC}(0)$  for the Al-Ga alloy at 1023 K were symmetric at equiatomic composition. The computed and observed values of  $S_{CC}(0)$  were slightly greater than the ideal value at higher and lower concentration end of Al. At intermediate composition, the computed and observed  $S_{CC}(0)$  were significantly greater than the ideal value. This result implies that the Al-Ga alloy at 1023 K in the liquid state is segregating at all compositions. However, the tendency of segregation of the alloy was found to be greater in intermediate compositions. The knowledge of  $\alpha_1$  is very useful to provide immediate insight into the nature of the local arrangements of atoms in the mixture. Therefore,  $\alpha_1$  for the Al-Ga alloy at 1023 K was computed using Equation 9. For binary liquid alloy, the value of  $\alpha_1$  lies between  $-1$  and  $+1$ . It was observed that  $\alpha_1$  for the Al-Ga alloy at 1023 K was positive throughout the whole range of concentration (Figure 6). The positive value of  $\alpha_1$  provided the conformation of homocordination, i.e., like atoms tend to pair as the nearest neighbours in the Al-Ga alloy at 1023 K in the liquid state.



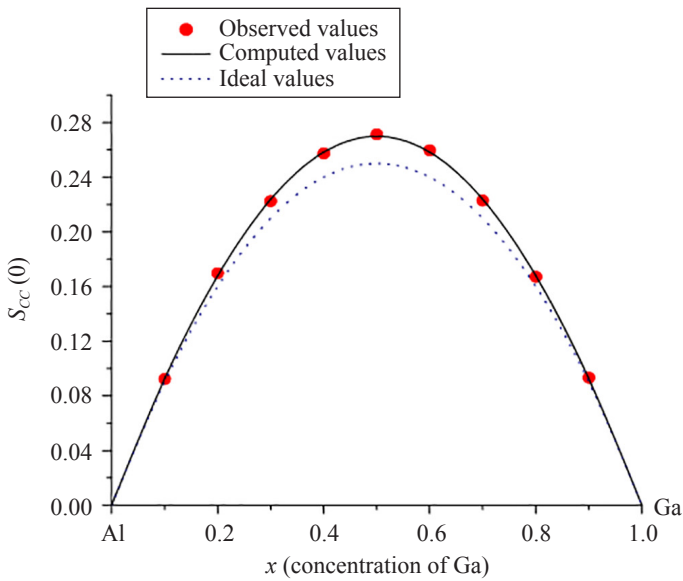


Figure 5: Concentration fluctuations in long wavelength limit  $S_{cc}(0)$  vs. concentration of Ga of liquid Al-Ga alloy at 1023 K.

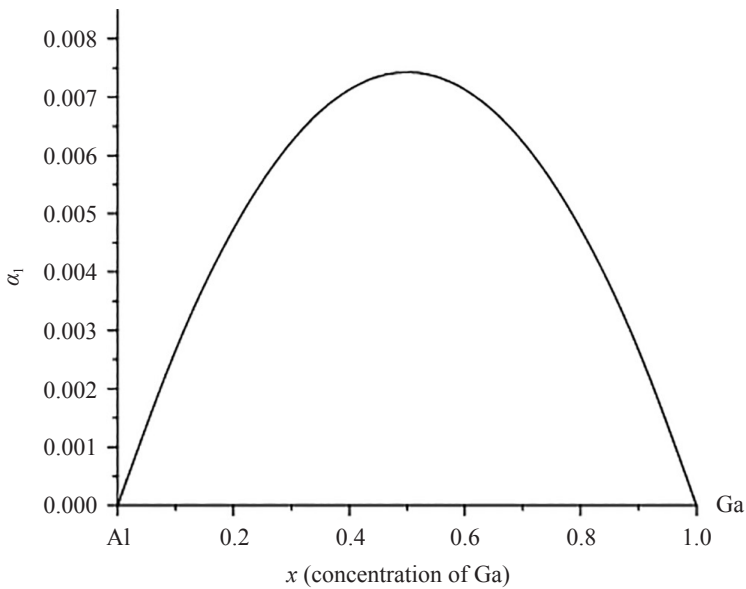


Figure 6: Short range ordering parameter  $\alpha_1$  vs. concentration of Ga of liquid Al-Ga alloy at 1023 K.

The segregating and compound forming nature of an alloy can be understood in terms of the ratio of the mutual and ideal diffusion coefficients ( $D_M/D_{id}$ ). The ratio was computed using Equation 12. This ratio for the Al-Ga alloy at 1023 K was found to be positive and less than unity. The nature of the curve of  $D_M/D_{id}$  against the concentration of Ga is upward concave (Figure 7).  $D_M/D_{id}$  indicates the mixing behaviour of alloy, i.e., the tendency for the compound formation and  $D_M/D_{id} < 1$  indicates phase separation. For ideal mixing,  $D_M/D_{id}$  approaches 1. Thus, the Al-Ga alloy is weakly segregating in nature.

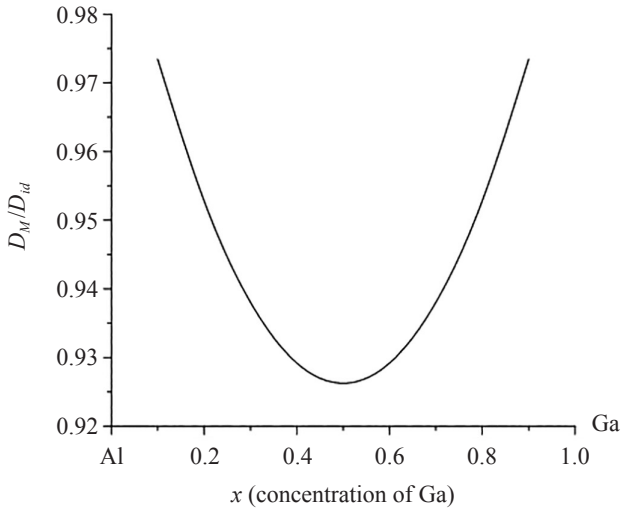


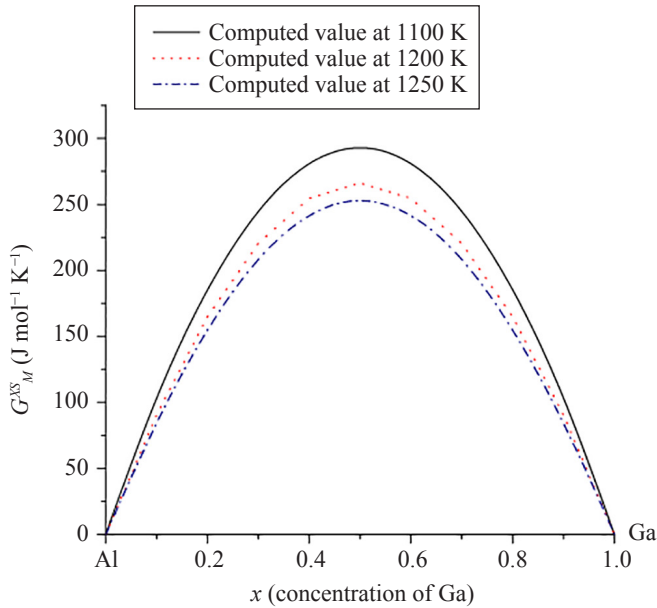
Figure 7:  $D_M/D_{id}$  vs. concentration of Ga of liquid Al-Ga alloy at 1023 K.

The parameters  $A_0$  and  $A_2$  can be computed for higher temperature using Equation 13, assuming the variation of these parameters with temperature to be linear within a certain range of temperature. The values of these parameters at different temperatures are listed in Table 1.

Using the temperature-dependent parameters and Equation 2, the excess free energy of mixing for the Al-Ga alloy at 1100 K, 1200 K and 1250 K was computed and compared in Figure 8. The positive value of excess free energy of mixing for the Al-Ga alloy was found to decrease with a rise in the temperature. This is the usual behaviour since the excess free energy of mixing must decrease and shift towards ideal nature (ideal value of excess free energy of mixing is zero) as the temperature increases. The activities of the monomers Al and Ga of Al-Ga alloy were also computed at 1100 K, 1200 K and 1250 K using temperature dependent parameters and Equation 5 (Figure 9). It was found that the activities of the monomers shifted towards the ideality as the temperature increased.

Table 1: Temperature dependent parameters.

Temperature	Parameter ( $\text{J mol}^{-1}$ )	
	$A_0$	$A_2$
1023 K	1254	0
1100 K	1171.553	-41.118
1200 K	1064.433	-94.518
1250 K	1010.883	-121.218

Figure 8: Excess free energy of mixing ( $G_M^{XS}$ ) vs. concentration of Ga of liquid Al-Ga alloy at 1100 K, 1200 K and 1250 K.

The concentration fluctuation in the long wavelength limit for the Al-Ga alloy was also computed at 1100 K, 1200 K and 1250 K using the temperature-dependent parameters listed in Table 1 and Equation 7. The computed values of  $S_{CC}(0)$  for Al-Ga alloy at different temperatures are compared in Figure 10. It was found that the  $S_{CC}(0)$  goes on decreasing as the temperature increased. This clearly indicates that the behaviour of the Al-Ga alloy shifts towards the ideality as the temperature increases. Up to the temperature 1250 K,  $S_{CC}(0)$  varied in a usual way. However, when the temperature was increased above 1250 K,  $S_{CC}(0)$  became less than the ideal value at some compositions. This is unusual behaviour which is called artifact (computational inability of a model).<sup>23–25</sup> This means the temperature dependent parameters do not vary linearly with temperature above 1250 K.

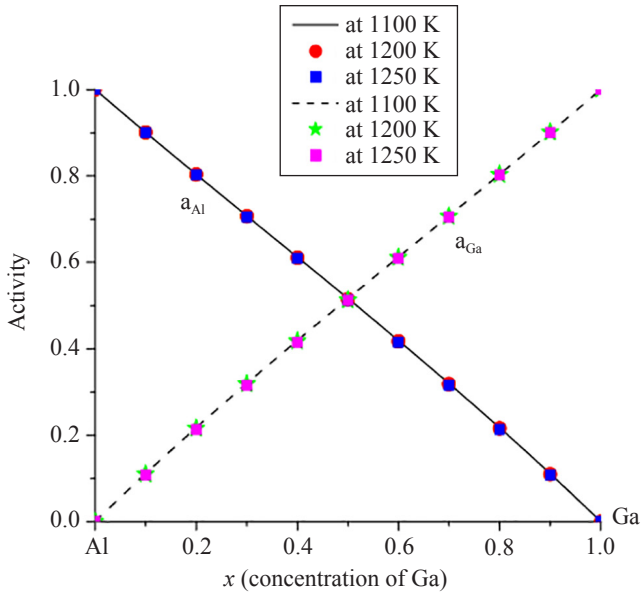


Figure 9: Activities of Al and Ga in Al-Ga alloy vs. concentration of Ga at 1100 K, 1200 K and 1250 K.

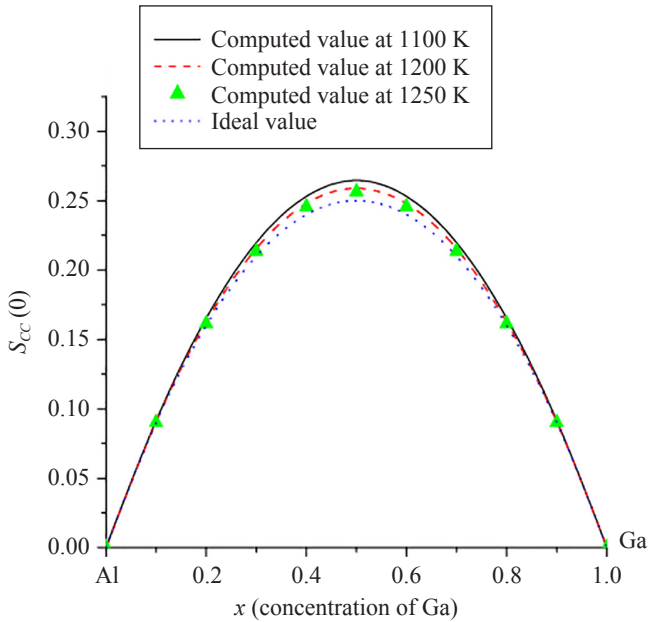


Figure 10: Concentration fluctuations in long wavelength limit  $S_{cc}(0)$  vs. concentration of Ga of liquid Al-Ga alloy at 1100 K, 1200 K and 1250 K.

#### 4. CONCLUSION

It is concluded from the study that the Al-Ga alloy is symmetric, weakly interacting and segregating in the liquid state. The excess free energy of mixing of the Al-Ga alloys decreases with a rise of temperature. The concentration fluctuation in the long wavelength limit of the Al-Ga alloys shifts towards the ideality with a rise in temperature.

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