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Calculation of Concentration-Concentration Fluctuation Scc(0) And Deviation In Scc(0) from Ideal Solution Values Using Two Atoms Cluster Model (TACM) For Li-Mg and K-Na Liquid Alloys.

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Abstract

The thermodynamic model based on cluster of two atoms is considered with the view to obtaining deviations in Scc(0) from ideal values. Concentration-concentration fluctuation; Scc(0) of two binary molten alloys was successfully calculated. Literature data for thermodynamic properties of these alloys are evaluated based on cluster of two atoms for each system with the view to obtaining concentration-concentration fluctuation; Scc(0) enumerating the low order atomic correlation in the nearest neighbour shell of liquid binary alloys with the highlights of deviation in Scc(0) of these alloys. The values of Scc(0) for Li-Mg through the entire concentration are positive but smaller than the ideal values, the values of Scc(0) for K-Na are also positive but greater than the ideal values. The indication of the deviation in Scc(0) for Li-Mg suggest hetercoordination ,the implication of the deviation in Scc(0) for K-Na suggests homocoordination in the nearest neighbour shell. The values of deviation in Scc(0) for Li-Mg alloy throughout the composition range are negative and positive for K-Na alloy. The Scc(0) and deviation in Scc(0) for Li-Mg and K-Na alloys are presented.

Keywords: Concentration-concentration fluctuation, deviation in concentration- concentration fluctuation, two atoms cluster model

1.0 Introduction

Fluctuation in concentration and subsequent effects in relation to ideal solution values have been subject of interest in liquid alloys and related disciplines [1-9]. Singh [2] selected the short range order parameter (SRO) for six binary alloys, generated values for them in conjunction with the values also generated for higher order conditional probabilities. Similar inputs such as ordering energy values and melting temperatures (both from observation), coordination numbers and Boltzmann constant were employed in the described programs for generating data in higher order conditional probabilities and SRO. Two of the alloys Li-Mg and K-Na have been considered. However, the concentration-concentration fluctuation Scc(0) of the remaining four binary alloys in the same category are not discussed in this paper.

In this research, attention is made on the calculation of the Scc(0) and the deviations in Scc(0) from the ideal values of these two alloys (K-Na & Li-Mg) using available data i.e. ordering energy values from the article on short range order for Two Atoms Cluster Model. The significance of the positive or negative sign of Scc(0) is the implication or indication of the type of atomic distribution [2].

Data on ordering energy w, temperature T, and coordination number Z for these binary alloys were used for computation via TACM and the presentation of the results of Scc(0) ,with the view to ascertainingthe extent by which it is reliable to consider this approach of calculating Scc(0) as an alternative option to the higher order model when a set of parameters is available for systems of interest when simplicity is also considered.

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The Scc(0) of eleven binary alloys of which Li-Mg & K-Na alloys were not included was generated using input parameters such as ordering energy values (computed from experimental activity ratios, a_A and a_B values, and experimental free energy of mixing values), melting temperatures, coordination number(z),and Boltzmann's constant. Substitutions were carried out in the thermodynamic expressions [3], made available by the statistical mechanical model and assigning of programs using the latter model (expressions) was subsequently addressed for generating values. Values of deviation in Scc(0) were also generated by finding the difference between the ideal values $S_{cc}^{id}(0) = c(1-c)$ and the generated Scc(0) values.

2.0 Theory

The calculation of Scc(0) is of great importance, in view of the fact that the understanding of Scc(0) will shed light on alloying behaviour in terms of compound formations, self coordination and phase segregation. Thermodynamically, the relationship between free energy of mixing; G_m and Scc(0) is given by equation (6). The following thermodynamic expressions are from statistical mechanical model [4].

$$Scc(0) = \frac{c(1-c)}{(1+(\frac{Z}{2\beta})(1-\beta))} \quad (1)$$

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

$$Where\ \eta = \exp(w/z k_B T) \quad (3)$$

$$S_{cc}^{id} = C(1-c) \quad (4)$$

$$Diff_i = S_{cc}(0) - S_{cc}^{id}(0) \quad (5)$$

In Equations (1), (3)and (5), k_B is the Boltzmann constant, T is the temperature, Z is coordination number of the alloys, $S_{cc}^{id}(0)$ is the ideal concentration-concentration fluctuation, c is the concentration of one atom and 1-c is the concentration of the other atom.

Table 1: Ordering energy w in eV of binary alloys

Alloys	Temperature(k)	Coordination Number(Z)	W(eV) (TACM)
Li-Mg	887	10.0	-0.0932
K-Na	384	10.0	+0.0335

Source[5]

In the calculation of Scc (0) for an alloy, whenever its values are greater than $S_{cc}^{id}(0)$i.e. ideal concentration-concentration fluctuation, it is an indication that such an alloy is homocoordinated system (segregated) otherwise, it is a heterocoordinated (chemically ordered) system. In an event that a given alloy has equal values at a concentration range indicates that such an alloy might be glass formed.

The choice of these two alloys Li-Mg and K-Na, is due to the fact that much work had not been done on them, that is to say they were considered in [6] without attaching the Scc (0). For the deviation in Scc(0) for each alloy we have the needed set of experimental data.

$$S_{cc}(0) = NK_BT\left(\frac{\partial^2 Gm}{\partial c^2}\right)^{-1} \quad (6)$$

3.0 Results and Discussion

Table 2: Calculated concentration-concentration fluctuation for Li-Mg alloy at 887 K using the value of ordering energy obtained from Table 1 for Two Atoms Cluster Model (TACM). The ideal values and the deviation from ideal solution values are also presented.

Concentration of lithium C_{Li}	**Calculated $S_{CC}(0)$**	**Ideal $S_{CC}(0)$**	**Deviation from ideal Scc(0) $Diff_{Li}$**
0.0	0.000	0.000	0.000
0.1	0.075	0.090	-0.015
0.2	0.125	0.160	-0.035
0.3	0.150	0.210	-0.060
0.4	0.175	0.240	-0.065
0.5	0.180	0.250	-0.070
0.6	0.176	0.240	-0.064
0.7	0.150	0.210	-0.060
0.8	0.126	0.160	-0.034
0.9	0.050	0.090	-0.040
1.0	0.000	0.000	0.000

Without necessarily attaching experimental data in the long wave length limit of Scc(0) in Table 2 which was reported complex in determination empirically in articles. The concentration-concentration fluctuation of Li-Mg thus gives additional information to available data. The deviation is illustrated in Figure 1. Apart from the fact that the calculated Scc(0) is not in good agreement with the ideal value solution, the sign of the deviation in Scc(0) is respectively negative which is in support of heterocoordination. Calculating Scc(0) in the entire region i.e. $0.1 \leq C_{Li} \leq 0.9$ has demonstrated short range order quality. The thermodynamic expression above has assisted in this computation [7].

Table 3: Calculated concentration-concentration for K-Na alloy at 384K using the value of ordering energy obtained from Table 1 for Two Atoms Cluster Model (TACM). The ideal values and the deviation from ideal solution values are presented.

Concentration of potassium C_k	**Calculated$S_{CC}(0)$**	**Ideal$S_{CC}(0)$**	**Deviation from ideal values$Diff_k$**
0.0	0.000	0.000	0.000
0.1	0.100	0.090	0.010
0.2	0.230	0.160	0.070
0.3	0.350	0.210	0.110
0.4	0.430	0.240	0.190
0.5	0.470	0.250	0.220
0.6	0.420	0.240	0.180
0.7	0.380	0.210	0.170
0.8	0.270	0.160	0.110
0.9	0.125	0.090	0.040
1.0	0.000	0.000	0.000

We have calculated the Scc(0) and its deviation for K-Na liquid alloy and observed opposite sign to that of Li-Mg liquid alloy. This is an indication that K-Na alloy is a candidate of homocoordination because its deviation in Scc(0) is positive. There is a noticeable disparity between the Scc(0) and its deviation. Although, a direct experimental determination of Scc(0) is often avoided due to complexities involved yet on the basis of this calculation we have provided useful information for K-Na liquid alloy.

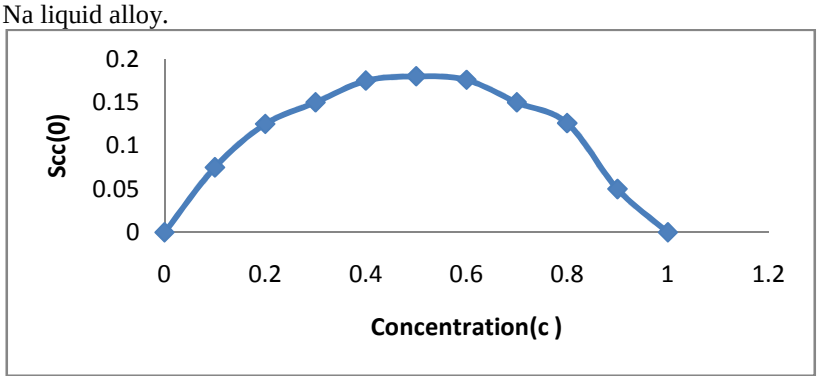

Fig.1: Graph Scc(0) Vs Concentration(c) for LiMg liquid alloy at 887k

From the plot in Figure 1, computed values of Scc(0) are positive but lower than the ideal values. The curve looks like a small hill although plotted points were spaced notwithstanding it is the right shape for positive Scc(0) yet lower than ideal situation at temperature of 887k for Li-Mg liquid alloy [8].

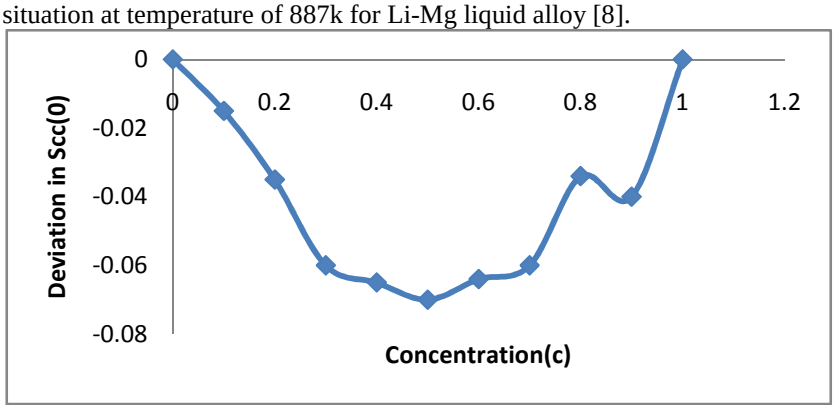

Fig. 2: Graph of Deviation in Scc(0) Vs Concentration(c)for LiMg liquid Alloy at 887k

From the plot in Figure 2, computed values of Scc(0) are positive but lower than the ideal values. The implication is shown in this plot which is displayed in valley form. From part of the curve between c=0.8 and 0.9 for deviation in Scc(0) there is a sub valley showing that there is a reduction in the significance of the values of the deviation between that range. This is also the right way for the curve to be especially when values of scc(0) fall below the ideal value solution. The only difference is that the curve supposed to be smooth (points spacing expected to be very small) but without sub valley. This curve is in support of heterocoordination [9].

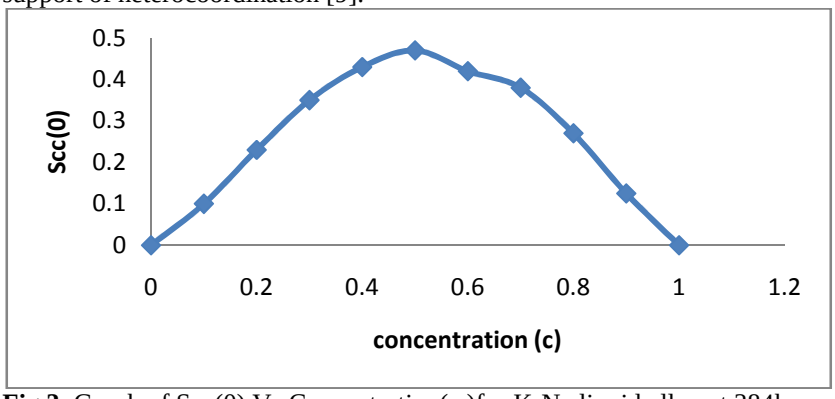

Fig.3: Graph of Scc(0) Vs Concentration(c)for K-Na liquid alloy at 384k

From the plot in Figure 3, computed values of Scc(0) are positive but higher than the ideal values. The curve looks like a small hill although plotted points were spaced notwithstanding it is the right shape for positive Scc(0) at temperature of 384k for K-Na liquid alloy. Within the range $0<c<0.5$, Scc(0) increases from 0 to 0.47 but the reverse is the case for the range $0.51<x<1.0$ where values of Scc(0) decreases from 0.47 to zero.

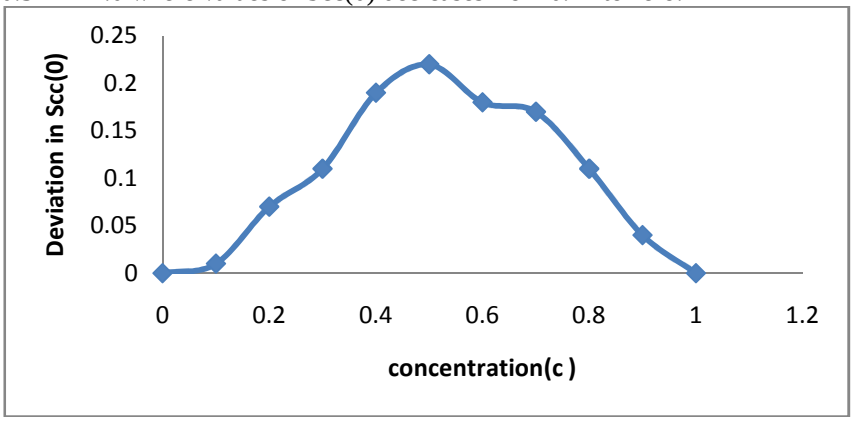

Fig. 4: Graph of Deviation in Scc(0) Vs Concentration(c)for K-Na liquid alloy at 384k

From the plot in Figure 4, computed values are positive but higher than the ideal values. The implication is shown in this plot which is displayed in hill form. From parts of the curve between c=0.2 and 0.4 and between c=0.5 and 0.7 for deviation in Scc(0) there are slight depressions showing that there are reductions in the significance of the values of the deviation between those ranges. This is also the right way for the curve to be especially when values of scc(0) rise above the ideal value solution. The only difference is that the curve is supposed to be smooth (points spacing expected to be very small) but without depression. This curve is in support of homocoordination [10].

4.0 Conclusion

The two atoms cluster model (TACM) provides a fairly good account of the thermodynamic properties of molten Li-Mg and K-Na alloys and of the fact that the ordering energy w should be temperature dependent and has been considered useful. There is evidence for preference of unlike atoms as nearest neighbour in Li-Mg melt because we observed that Scc(0) at 887 K is smaller than the ideal solution $\left[S_{cc}^{id}(0) = c(1-c)\right]$ throughout the entire concentration and therefore indicates heterocordination (unlike atoms pairing as the nearest neighbour shell).

There is also an indication for like atoms pairing as the nearest neighbour in contrast to the Li-Mg liquid alloy. K-Na alloy suggests homo-coordination or self coordination in nearest lattice sites. The computed values of Scc(0) for k-Na liquid alloy are higher than the ideal values.

This article has shed light on the nature of the deviation from the ideal behaviour in the liquid phase through the entire concentration range.

In conclusion, we would like to recommend that this model (Two Atoms Cluster Model) of approach should be seen as one reliable approach. It is better to consider this option for simplicity to any alloy of interest before higher order model (Four Atoms cluster model)if the atoms are more than two.

5.0 References

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