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Effects of Temperature on the Thermodynamic Properties of Binary Liquid Alloys

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Abstract

The conditional probability A/B or B/A, chemical short range order, SRO, concentration to concentration fluctuation in the long wave length limit, Scc(0) and activity ratios a_A and a_B have been studied as functions of composition in AuCu and CdMg molten alloys by using thermodynamic expressions. The ordering energy, w has been function of temperature and the above thermodynamic quantities were calculated at different temperatures. The study reveals that thermodynamic property,conditional probability is invariant at different temperatures. The computed activity ratios of AuCu and CdMg deviate from experimental observations throughout the entire concentration range. The values of short range order parameter (SRO)are negative for both alloys throughout the range of compositionwhich indicates heterocoordination. Also positive values of Scc(0) for both alloys yet smaller than the ideal values suggest unlike atoms pair as nearest neighbour which is in support of heterocoordination.

Keywords: Thermodynamic properties, ordering energy and temperatures.

1.0 Introduction

The diffraction experiments are very useful to yield structural information and thermodynamic properties of binary liquid alloys [1]. In most cases, obtaining the experimental data needed for the calculation of activity is not a problem (except in some uncommon cases where the experimental data for some alloys may not be available due to experimental difficulties. In principle, SRO can be experimentally determined from the knowledge of concentration-concentration partial structural factor, $S_{cc}(q)$, and the number-number partial structural factor $S_{NN}(q)$. However, these structures are not easily measurable in most diffraction experiments. Hence SRO is usually computed without necessarily making reference to its experimental values. Additionally, a direct experimental determination of Scc(0) is often avoided due to complexities involved. For this reason the option of theoretical model [2] which matches experimental observation was employed.

In this write-up measured values of ordering energy and observed activity at different temperatures were made available. In the application of the theoretical model using the observed values of ordering energy, the values of activity was calculated and compared with its experimental values at different temperatures. Other thermodynamic properties such as conditional probability, SRO and Scc(0) of these binary liquid alloys were also calculated at different temperatures using measured value of ordering energy.

Singh [3], Bhatia and Hargroove [4] in their articles discussed SRO, Scc(0) and other thermodynamic properties of some binary liquid alloys, generated values using inputs such as ordering energy values, coordination numbers, melting temperatures and Boltzmann constant employed in the described programs for generating data.

In the calculation of the bulk properties of binary alloys attention is often focused on thermodynamic properties, such as activity a_A and a_B, conditional probability A/B or B/A, short range order parameter SRO and concentration-concentration fluctuation Scc(0), free energy of mixing G_M, enthalpy of mixing H_M ,entropy of mixing $S_M$and soon for the entire concentration.

The calculations of these quantities at different temperatures involve getting the available experimental data and employing suitable theoretical model. These two candidates (Au-Cu and Cd-Mg liquid alloys)under observation are those with very small differences in the values of thermodynamic quantities at different temperatures.

Investigations of liquid metallic alloys on the basis of Quasi Lattice Model (QLM) or Statistical Mechanical Model (SMM) and their usage for generating values is also found in the work ofSingh and Sommer [5] where these models were used for the calculations of some thermodynamic properties of compound forming binarymolten alloys at their melting temperatures.

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On this observation write-up the SMM was applied to AuCu and CdMg liquid alloys for the qualitative investigation of their thermodynamic properties at different temperatures. Programs were inscribed to generate data for thermodynamic expressions as functions of concentration, c, using ordering energy values, w, coordination number, Z, Boltzmann constant, K and temperature, T presented in Table 1.

2.0 Theoretical Formulation

The basic form of the analytical expression for the binary mixture starts with the relationship between the number of unlike atom pairs N_{AB} (A and B signify constituent atoms), like atom pairs N_{AA} *and* N_{BB} and the ordering energy w, given as

$$4\frac{N_{AA}N_{BB}}{N_{AB}^2}=\eta^2 \quad (1)$$

Where $\eta = \exp(w/ZKT)$ (2)

Z is the coordination number for the first shell, w is the ordering energy, K is the Boltzmann constant and T is the temperature.

The expressions for the Thermodynamic Properties are given as

Conditional Probability of atom A having atom B as the nearest neigbour is given as

$$A/B=\frac{1}{1+\frac{1-c}{c}\sigma^{-1}\exp(\frac{w}{ZKT})} \quad (3)$$

Conditional Probability of atom B having atom A as the nearest neigbour is given as

$$B/A=\frac{1}{1+\frac{c}{1-c}\sigma\exp(\frac{w}{ZKT})} \quad (4)$$

$$\sigma=\frac{\beta-1+2c}{2\eta c} \quad (5)$$

Where $\beta=(1+4c(1-c)[(\eta)(\eta)-1])^{0.5}$ (6)

η, β, σ are thermodynamic parameters which are interwoven. C is concentration of A atom and 1-c is concentration of B atom in the mixture with the knowledge of the ordering energy (w), (A/B) and (B/A) can be determined from Equations (3) and (4).

Chemical Short Range Order,**SRO** is given as

$$(1+\frac{SRO}{c(1-c)(1-2SRO+(SRO)(SRO))})=\exp(2w/ZKT) \quad (7)$$

This is the desired relationship between the short range order and the ordering energy for the first shell. Though this connectivity is generalisable for higher shells, yet liquid alloy suffices the purpose.

Concentration –concentration fluctuation,**Scc (0)** is given as

$$Scc(0)=\frac{c(1-c)}{(1+(\frac{Z}{2\beta})(1-\beta)} \quad (8)$$

The activity, a, is given as

Activity $a=\left(\frac{1-c}{c}\right)\left(\frac{1}{\gamma^z}\right)$ (9)

$$\gamma=\frac{\beta-1+2c}{2\eta c} \quad (10)$$

Table 1: Ordering energy w in eV of binary alloys

Alloys	Temperature (^0K)	Coordination number(Z)	w(eV)
Au-Cu	800	10.0	-0.0069
Au-Cu	1550	10.0	-0.0206
Cd-Mg	543	10.0	0.0347
Cd-Mg	923	10.0	-0.0059

Source: [5]

3.0 Results and Discussion

Table 2: Conditional Probability (A/B, B/A), activity ratios, short range order and concentration concentration fluctuation of AuCu alloys at 800K, Z=10.0 (A=Au, B=Cu).

CA	**(A/B)**	**(B/A)**	**Activity Ratio Expt**	**Activity Ratio Theory**	**S.R.O** α_1	**Scc(0)**
0.1	0.1001	0.9016	178.6	9.751	-0.0018	0.009
0.2	0.2006	0.8026	45.13	4.248	-0.0032	0.155
0.3	0.3013	0.7029	7.623	2.429	-0.0042	0.202
0.4	0.4019	0.6029	1.744	1.530	-0.0048	0.229
0.5	0.5025	0.5025	0.562	1.000	-0.0050	0.238
0.6	0.6029	0.4019	0.168	0.653	-0.0048	0.229
0.7	0.7029	0.3013	0.087	0.412	-0.0042	0.202
0.8	0.8026	0.2006	0.039	0.235	-0.0032	0.155
0.9	0.9016	0.1001	0.015	0.103	-0.0018	0.009

The conditional probabilities, activity ratio, the short range order parameter and concentration concentration fluctuation of AuCu liquid alloys are tabulated in Table2.The computed values of the activity ratio are not in good agreement with the experimental observation at all concentrations. The short range order parameter SRO is negative throughout. This is indicates preference for heterocoordination in the liquid phase. Because the values of SRO for AuCu at 800K are negative, it is an indication that this candidate is in support of unlike pair as the nearest neighbor [6].

Table 3: Conditional Probability (A/B, B/A), activity ratios, short range order concentration and concentration fluctuation of AuCu alloys at 1550K, Z= 10.0 (A=Au, B=Cu).

CA	**(A/B)**	**(B/A)**	**Activity Ratio Expt**	**Activity Ratio Theory**	**S.R.O** α_1	**Scc(0)**
0.1	0.1003	0.9024	40.140	10.150	-0.0027	0.008
0.2	0.2010	0.8038	12.160	4.379	-0.0048	0.153
0.3	0.3019	0.7044	4.933	2.479	-0.0063	0.198
0.4	0.4029	0.6043	2.181	1.546	-0.0072	0.224
0.5	0.5038	0.5038	1.000	1.000	-0.0075	0.232
0.6	0.6043	0.4029	0.458	0.647	-0.0072	0.223
0.7	0.7044	0.3019	0.203	0.403	-0.0063	0.198
0.8	0.8038	0.2010	0.082	0.228	-0.0048	0.153
0.9	0.9024	0.1003	0.025	0.099	-0.0027	0.008

The conditional probabilities between 800K and 1550k for AuCu liquid alloys in Tables 2 and 3 did not show any difference. The computed values of the activity are not in good agreement with the experimental observation at almost all the concentrations except at C_{cd} =0.5 where the computed value is in perfect agreement with the observed value. The computed values of Scc(0) for AuCu at 800k and 1550K are smaller than the ideal solution$Scc^{id}(0)$= c(1-c) which therefore indicates a preference for unlike atom pairs as the nearest neighbour. For equiatomic composition, Scc(0) is about 7.2% lower than the ideal value with increase in temperature. The short range order parameter, SRO computed at different temperatures shown in Fig. 8 has been found negative for all compositions which imply local ordering. The values of SRO in AuCu at 1550K are almost two third values of SRO at 800k. Values of Scc(0) in AuCu at 1550K are almost the same at 800k. Activity ratio values in AuCu at 1550k are nearly the same with activity ratio values at 800K.

Table 4: Conditional Probability (A/B, B/A), activity ratios, short range order and concentration concentration fluctuation of CdMg alloys at 543K, Z=10.0 (A=Cd, B=Mg).

CA	(A/B)	(B/A)	Activity Ratio Expt	Activity Ratio Theory	S.R.O α_1	Scc(0)
0.1	0.1002	0.9015	222.25	9.696	-0.0017	0.089
0.2	0.2001	0.8024	61.417	4.230	-0.0030	0.156
0.3	0.3012	0.7027	17.452	2.422	-0.0039	0.202
0.4	0.4019	0.6027	4.382	1.528	-0.0045	0.229
0.5	0.5023	0.5023	0.994	1.000	-0.0047	0.389
0.6	0.6027	0.4018	0.232	0.654	-0.0045	0.229
0.7	0.7027	0.3012	0.058	0.413	-0.0039	0.202
0.8	0.8024	0.2006	0.016	0.236	-0.0030	0.155
0.9	0.9015	0.1002	0.005	0.103	-0.0017	0.089

Table 5: Conditional Probability (A/B, B/A), activity ratios, short range order and concentration concentration fluctuation of CdMg alloys at 923K, Z=10.0 (A=Cd, B=Mg).

CA	(A/B)	(B/A)	Activity Ratio Expt	Activity Ratio Theory	S.R.O α_1	Scc(0)
0.1	0.1001	0.9012	55.50	9.557	-0.0013	0.089
0.2	0.2005	0.8019	17.86	4.185	-0.0024	0.156
0.3	0.3009	0.7022	6.816	2.405	-0.0031	0.204
0.4	0.4014	0.6022	2.722	1.523	-0.0036	0.232
0.5	0.5019	0.5019	1.068	1.000	-0.0037	0.241
0.6	0.6022	0.4014	0.408	0.657	-0.0036	0.232
0.7	0.7022	0.3009	0.408	0.416	-0.0031	0.204
0.8	0.8019	0.2005	0.054	0.239	-0.0024	0.156
0.9	0.9012	0.1001	0.017	0.105	-0.0013	0.089

The conditional probabilities of CdMg between 543K and 923k did not show any difference as seen in Tables 4 and 5.The computed values of the activity are not in concerted agreement with the experimental observation at almost all the concentrations except At Ccd = 0.7 where the computed value is in agreement with the observed value. SROfor AuCu and CdMg are negative at all concentrations which imply heterocoordination in the liquid phase i.e. unlike atoms are preferred as nearest neighbour in the first coordination shell. There is little or no difference in the values of SRO computed for AuCu and CdMg in the range of temperatures from 800k to 1550k and from 543K to 923K. Between the two systems CdMg is highly heterocoordinated liquid than AuCu. It is interesting to correlate the short range order in liquid alloys with measurable thermodynamic function like activity. There is no difference between the values of activity for AuCu from 800k to 1550k and CdMg from 543k to 923k .The Computed Values of Scc(0) for both AuCu and CdMg deviate from the ideal value of Scc(0) of these two candidates under consideration. These can be determined from Tables 2 to 5.

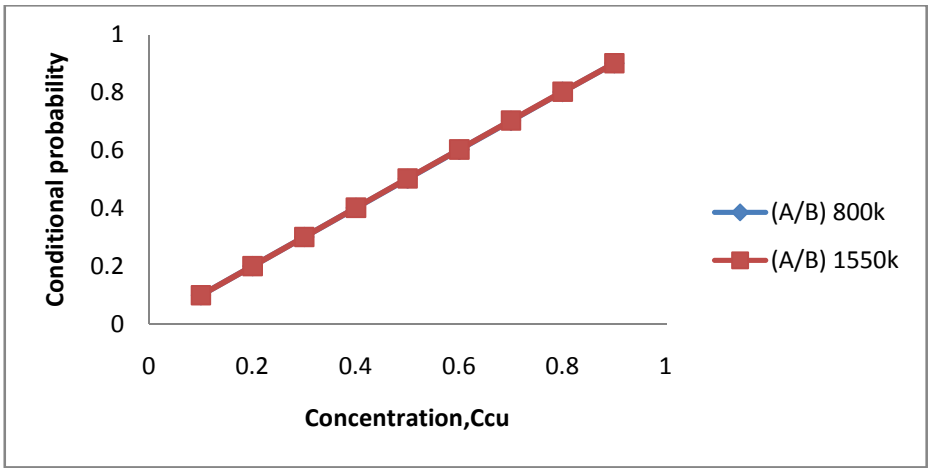

Fig.1: Graph of conditional probability against concentration at 800K and 1550K for AuCu Alloy

The conditional probability follows the same trend from 800K to 1550K. There is no difference in the linear path followed by A/B of AuCu between the temperatures [6].

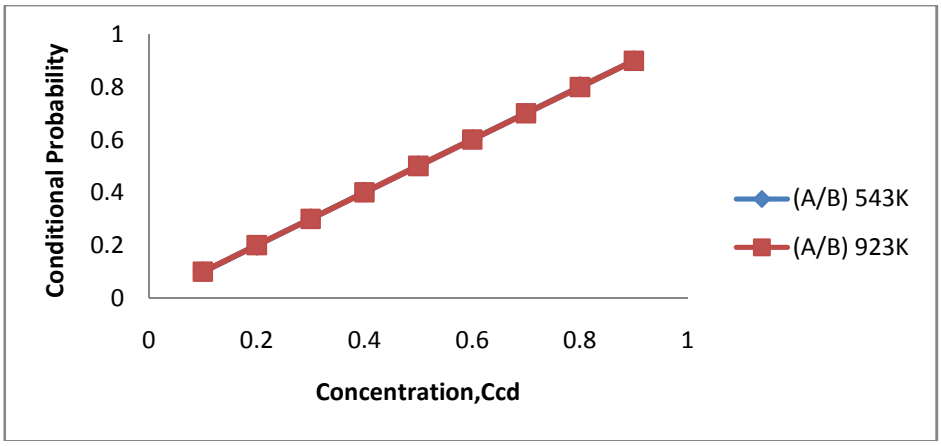

Fig.2: Graph of conditional probability against concentration at 543k and 923K for CdMg

Also the conditional probability for CdMg between 543K and 923K shows no difference. At both temperatures the linearity is the same. The gradient is the same at both temperatures. Effect of increase or change in temperature is not felt.

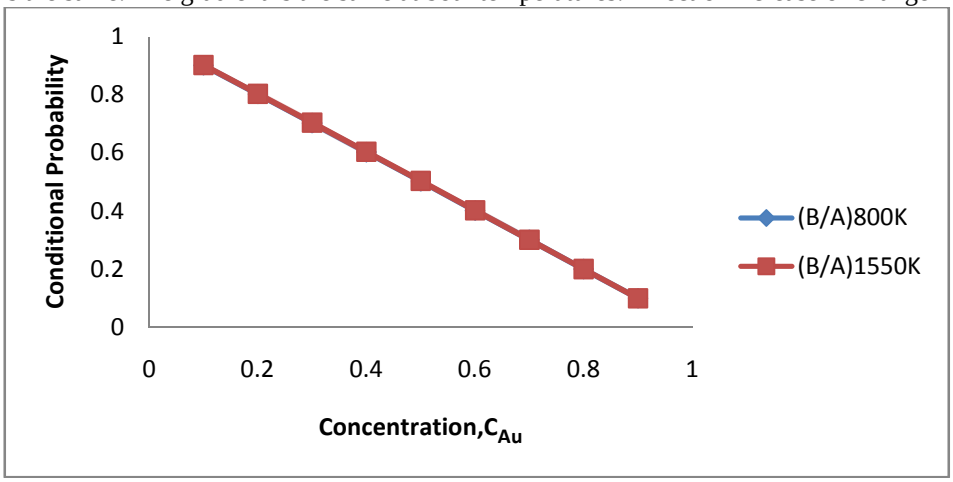

Fig. 3: Graph of conditional probability against concentration at 800k and 1550K for AuCu liquid alloy

As the other conditional probability (B/A) decreases the concentration of Au increases which is the same between 800K and 1550K.The gradient is negative in both cases. This is in agreement with the probability of atom B having atom A as the nearest neighbour in the first shell [7].

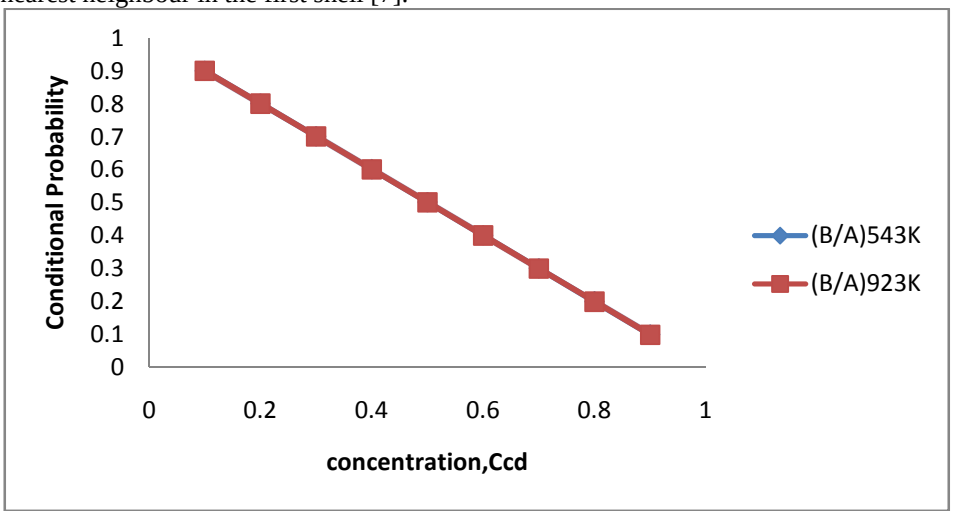

Fig. 4: Graph of conditionalprobability against concentration at 543k and 923K for CdMgliquid alloy

An increase in temperature from 543K to 923K for CdMg Liquid alloy does not show any influence on the descending slope of B/A as a function of composition of cadmium, Ccd .

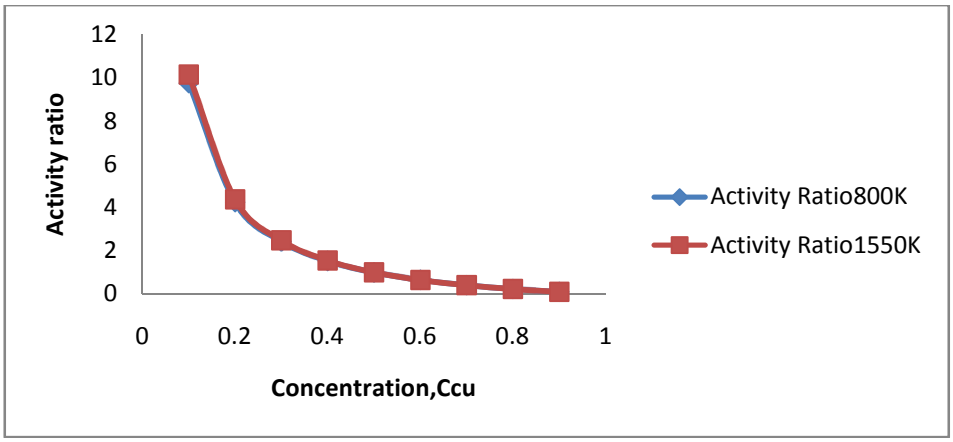

Fig.5: Graph of activity ratio against concentration at 800K and 1550k for AuCu liquid alloy

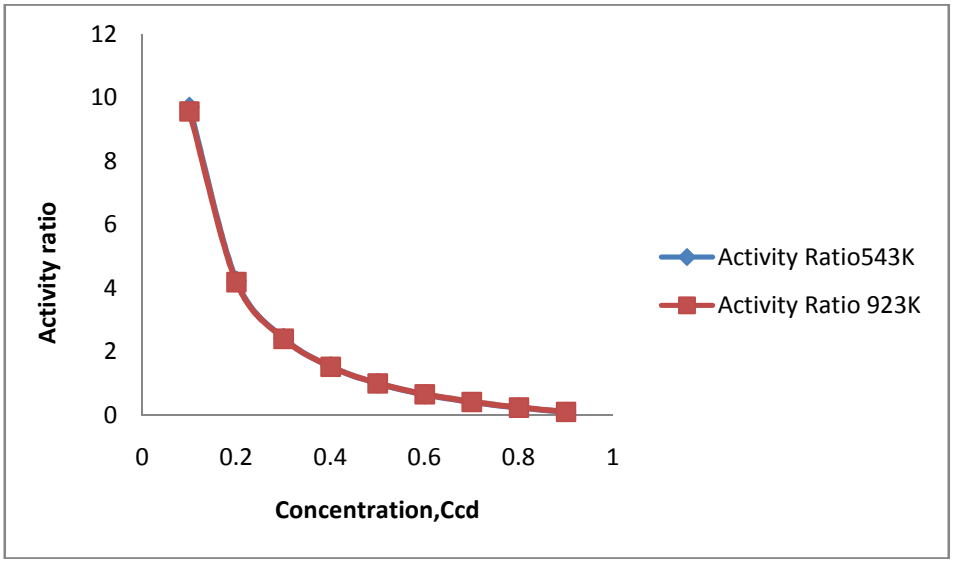

Fig.6: Graph of activity ratio against concentration at 543K and 923K for CdMg liquid alloy

Computed activities of AuCu and CdMg liquid alloy as a function of composition did not show any indication of effect of temperature change or increased temperatures from 800K to 1550k and from 543K to 923K. The descending curves are the same irrespective of the temperatures [8].

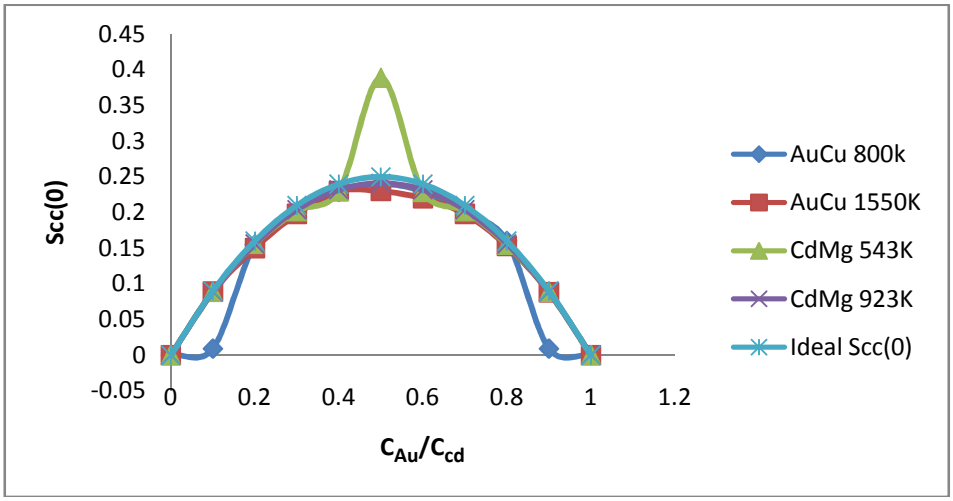

Fig. 7: Graph of Scc(0) against Concentrations of AuCu and Cd-Mg liquid alloys

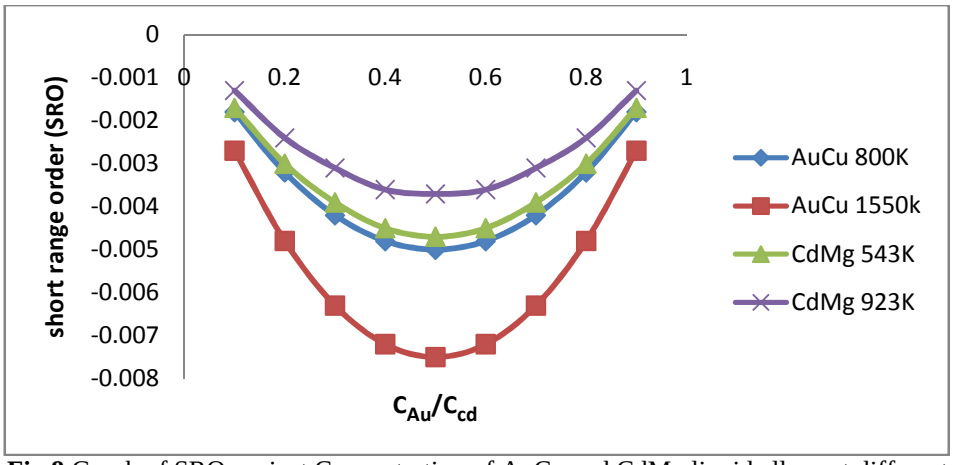

Fig.8:Graph of SRO against Concentration of AuCu and CdMg liquid alloys at different temperatures

In Fig.7 for AuCu and CdMg liquid alloys among the four values of temperatures, it is at 543K for C_{cd}= 0.5 (Scc(0)= 0.40) that the Scc(0) is the highest showing highly heterocoordination in the liquid phase. It signifies that heterocoordination is higher in CdMg than AuCu alloy. The Scc(0) for AuCu at 800k has slight deviations from ideal solution at C_{Au}= 0.1 and 0.9 [9].

The short range order computed at different temperatures has shown in Fig.8 has been found negative for all compositions which implies that the local ordering exists in the melt. Short range order at equiatomic composition is maximum for CdMg at 923K and lowest for AuCu at equiatomic composition at 1550K [10].

4.0 Conclusion

The statistical mechanical model provides a good account of the thermodynamic properties of molten AuCu and CdMg liquid alloys at different temperatures and thereis the fact that the ordering energy w is temperature dependent and thermodynamic properties are concentration dependent. There are evidences for preference of unlike atoms as nearest neighbours in both AuCu and CdMg melts which support heterocoordination in the two liquid alloys. There was like or no deviation from the ideal values but at equiatomic composition for CdMg at 543K, the deviation became obvious.

5.0 References

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