

### Calculation of Excess Stability Functions of Four Binary Alloys

O. W. Abodunrin and A. A Ajayi

*Department of Physics, Afe Babalola University, Ekiti State, Nigeria.*

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**Abstract:** The thermodynamic model based on cluster of two atoms is considered with the view to obtaining  $S_{cc}(0)$  and the excess stability function of  $S_{cc}(0)$ . Concentration-concentration fluctuation;  $S_{cc}(0)$  of four binary molten alloys were calculated. The thermodynamic properties of these alloys are evaluated based on cluster of two atoms (A & B) or (B & A). Each system has the view of obtaining concentration-concentration fluctuation;  $S_{cc}(0)$  enumerating the low order atomic correlation in the nearest neighbour shell of liquid binary alloys. The highlights of excess stability functions (ES) of  $S_{cc}(0)$  of these alloys were reported. The values of  $S_{cc}(0)$  for all these alloys are higher than the ideal solution values. The values of  $S_{cc}(0)$  for Bi-Cd alloy is close to the ideal  $S_{cc}(0)$ . The indication of the excess stability of  $S_{cc}(0)$  for some alloys is in support of homocoordination. The  $S_{cc}(0)$  and excess stability function of  $S_{cc}(0)$  for four alloys are presented.

**Keywords:** Concentration-concentration fluctuation, Excess stability function and ordering energy.

### Introduction

The neutron diffraction experiment in particular is a very useful tool to obtaining structural information and thermodynamic properties of binary liquid alloys [1]. In most cases, obtaining the experimental data needed for the calculation of specific thermodynamic properties is not a problem (except in some uncommon cases where the experimental data for some alloys may not be available due to cumbersome task involved and experimental difficulties). In principle, Short Range Order (SRO) which has relationship with Concentration-Concentration Fluctuation in the long wave length limit ( $S_{cc}(0)$ ) in the literature can be experimentally determined from the knowledge of concentration-concentration partial structural factor,  $S_{cc}(q)$ , and the number-number partial structural factor  $S_{NN}(q)$  [2]. 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  $S_{cc}(0)$  is often avoided due to complexities involved. For this reason the option of thermodynamic model which is readily used was employed.

In this study, ordering energy values were determined from  $S_{cc}(0)$ . [3] of which four alloys were considered and In the application of the thermodynamic model using the determined values of ordering energy, the values of  $S_{cc}(0)$  and ES were calculated at various temperatures [4].

The calculations of the thermodynamic quantities at different temperatures involve getting the available experimental data and employing suitable theoretical model. These four candidates Cd-Ga, Ag-Ge, Al-Au and Bi-Cd liquid alloys) under observation are those with variations in the values of thermodynamic quantities at various temperatures. To be specific application is therefore made to these alloys

which belong to hereocoordinated and self coordinated group of alloys. The alloys were preferred because all of them represents the classes of metals and semiconductors.

Investigations of liquid metallic alloys on the basis of Quasi Lattice Model (QLM) and its usage for extracting values is also found in [5-7] where this model was used for the calculations of some thermodynamic properties of compound forming binary molten alloys at their melting temperatures.

In this observation, the QLM was applied to Cd-Ga, Ag-Ge, Al-Au and Bi-Cd liquid alloys for the qualitative investigation of their thermodynamic properties. Ordering energy values determined from  $S_{cc}(0)$  are recorded in Table 1. 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.

TABLE 1. Ordering energy ( $w$ ) in eV of binary alloys

Alloy	Temperature(°K)	Z	$W_1$ (eV)
Cd-Ga	700	10.0	0.1133
Ag-Ge	1250	10.0	0.0288
Al-Au	1338	10.0	0.0980
Bi-Cd	773	10.0	0.0210

## Theory

The calculation of  $S_{cc}(0)$  needs the attachment like Excess Stability Function (ES). The variation of this quantity with composition is informative. This view provides facts that shed light on monotonous behavior of excess stability function of nearly ideal solutions with values approaching zero, although it will exhibit one or more peaks for solutions with strong chemical interactions. The positions of peaks correspond to compositions in which ordering (chemical short-range or intermediate-range) will occur. For an ideal solution  $S_{cc}(0) = X_1X_2$ , whereas for an alloy exhibiting formation,  $S_{cc}(0)$  exhibits one or more dips with values close to zero. Consequently, a maximum in ES corresponds to a minimum in  $S_{cc}(0)$ . The width and the height of the dip in  $S_{cc}(0)$  and the peaks in ES can be shown to be related to the degree and extent of stability of the complex entities. Thermodynamically, the relationship between short range order parameter: SRO, concentration - concentration fluctuation;  $S_{cc}(0)$  and other

thermodynamic properties had been sighted in the literature [8-10]. Moreover, between Es and  $S_{cc}(0)$  it is given below. The following thermodynamic expressions are from Quasi Lattice Model.

## Quasi Lattice Expressions for Various Thermodynamic Functions

### Concentration-Concentration Fluctuation in the Long Wavelength Limit

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

$$\text{where } \eta = \exp(w/ZKT) \quad (2)$$

and  $Z$  is the coordination number for the first shell,  $w$  is the ordering energy,  $K$  is the Boltzmann constant,  $T$  is the temperature,  $c$  is concentration of atom A and  $1-c$  is the concentration of atom B.

$$\text{Where } \beta = (1 + 4c(1-c)[(\eta)(\eta) - 1])^{0.5} \quad (3)$$

$\eta$  and  $\beta$  are thermodynamic parameters which are interwoven

### Excess Stability Function (ES)

$$ES = \frac{RT}{S_{cc}(0)} - \frac{RT}{c(1-c)} \quad (4)$$

### Ideal Concentration - Concentration Fluctuation in the Long Wavelength Limit

$$S_{cc}^{id}(0) = c(1-c) \quad (5)$$

$R$  is molar gas constant.

## Results

TABLE 2. Calculated experimental  $S_{cc}(0)$  and ES of Cd-Ga alloy using experimental activity. Ccd is the concentration of cadmium in the alloy at 700 °K.

Ccd	$S_{cc}(0)$	$S_{cc}(0)_{id}$	ES ( $10^{-3}$ J/mol)
0.0	0.0000	0.00	0
0.1	0.170	0.09	-30.4301
0.2	0.437	0.16	-23.0545
0.3	0.976	0.21	-21.7494
0.4	1.718	0.24	-20.8615
0.5	1.745	0.25	-20.0060
0.6	1.143	0.24	-19.1580
0.7	0.638	0.21	-18.5918
0.8	0.347	0.16	-19.6044
0.9	0.228	0.09	-39.1390
1.0	0.0000	0.00	0

TABLE 3. Calculated experimental  $S_{cc}(0)$  and ES of Ag-Ge alloy using experimental activity.  $C_{Ag}$  is the concentration of silver in the alloy at 1250 °K.

$C_{Ag}$	$S_{cc}(0)$	$S_{cc}(0)_{id}$	$ES(10^{-3} \text{ J/mol})$
0.0	0.0000	0.00	0
0.1	0.112	0.09	-22.6814
0.2	0.193	0.16	-11.1067
0.3	0.262	0.21	-9.8438
0.4	0.303	0.24	-9.084
0.5	0.288	0.25	-5.4856
0.6	0.222	0.24	3.5102
0.7	0.153	0.21	18.4363
0.8	0.104	0.16	37.9742
0.9	0.076	0.09	21.2714
1.0	0.0000	0.00	0

 TABLE 4. Calculated experimental  $S_{cc}(0)$  and ES of Al-Au alloy using experimental activity.  $C_{Al}$  is the concentration of Aluminum in the alloy at 1338 °K.

$C_{Al}$	$S_{cc}(0)$	$S_{cc}(0)_{id}$	$ES(10^{-3} \text{ J/mol})$
0.0	0.0000	0.00	0
0.1	0.180	0.09	-61.7979
0.2	0.313	0.16	-33.9859
0.3	0.372	0.21	-23.0680
0.4	0.412	0.24	-19.3508
0.5	0.422	0.25	-17.4960
0.6	0.403	0.24	-18.6982
0.7	0.251	0.21	-8.6549
0.8	0.268	0.16	-28.0182
0.9	0.151	0.09	-49.9314
1.0	0.0000	0.00	0

 TABLE 5. Calculated experimental  $S_{cc}(0)$  and ES of Bi-Cd alloy using experimental activity.  $C_{Bi}$  is the concentration of bismuth in the alloy at 773 °K.

$C_{Bi}$	$S_{cc}(0)$	$S_{cc}(0)_{id}$	$ES(10^{-3} \text{ J/mol})$
0.0	0.0000	0.00	0
0.1	0.089	0.09	-0.8023
0.2	0.166	0.16	-1.4516
0.3	0.250	0.21	-4.8961
0.4	0.296	0.24	-4.6168
0.5	0.296	0.25	-3.5459
0.6	0.256	0.24	-1.6736
0.7	0.204	0.21	0.9004
0.8	0.156	0.16	1.0310
0.9	0.065	0.09	27.4645
1.0	0.0000	0.00	0

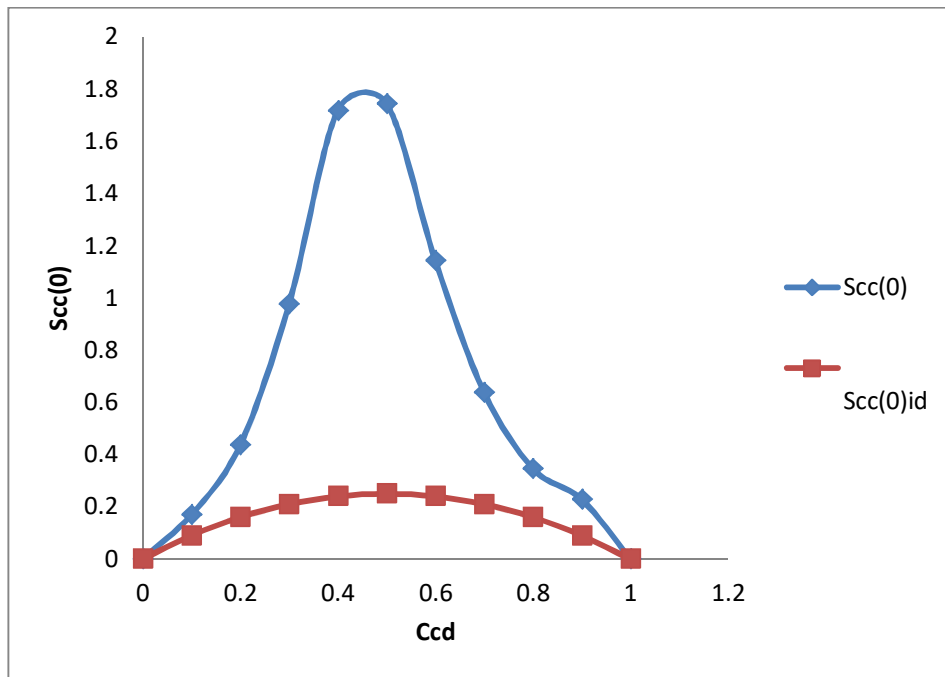


FIG. 1. Scc(0) of Cd-Ga against Concentration  $C_{cd}$ .

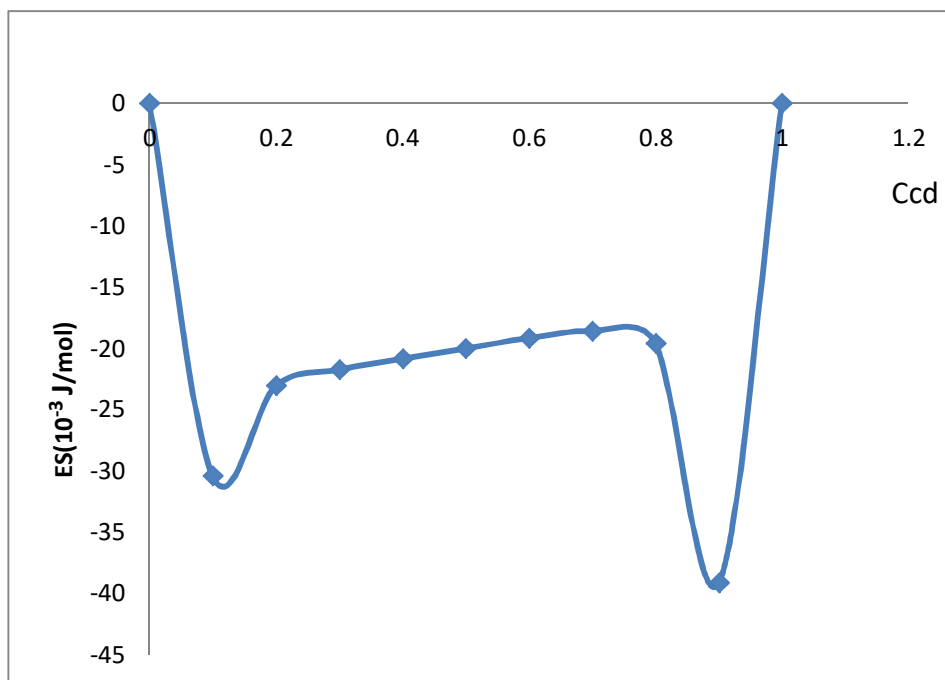


FIG. 2. ES of Cd-Ga against Concentration  $C_{cd}$ .

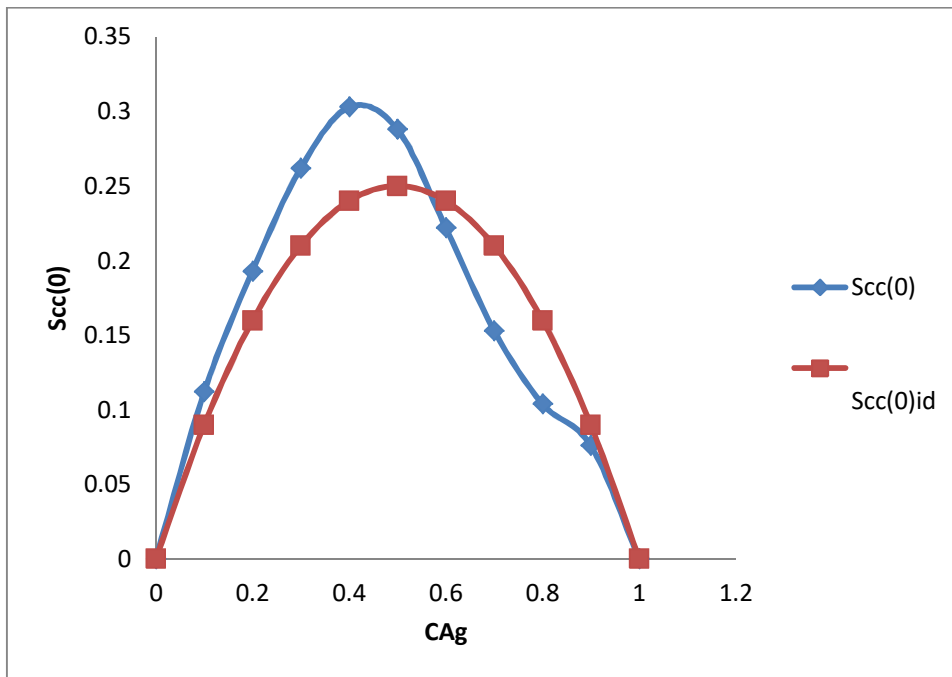


FIG. 3. Scc (0) of Ag-Ge against Concentration  $C_{Ag}$ .

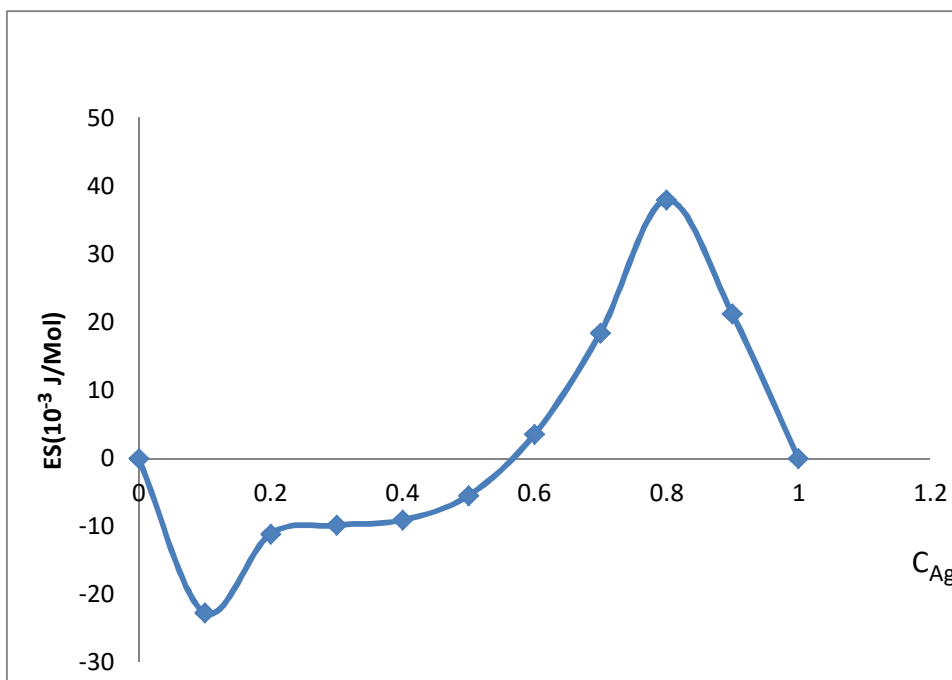


FIG. 4. ES of Ag-Ge against Concentration  $C_{Ag}$ .

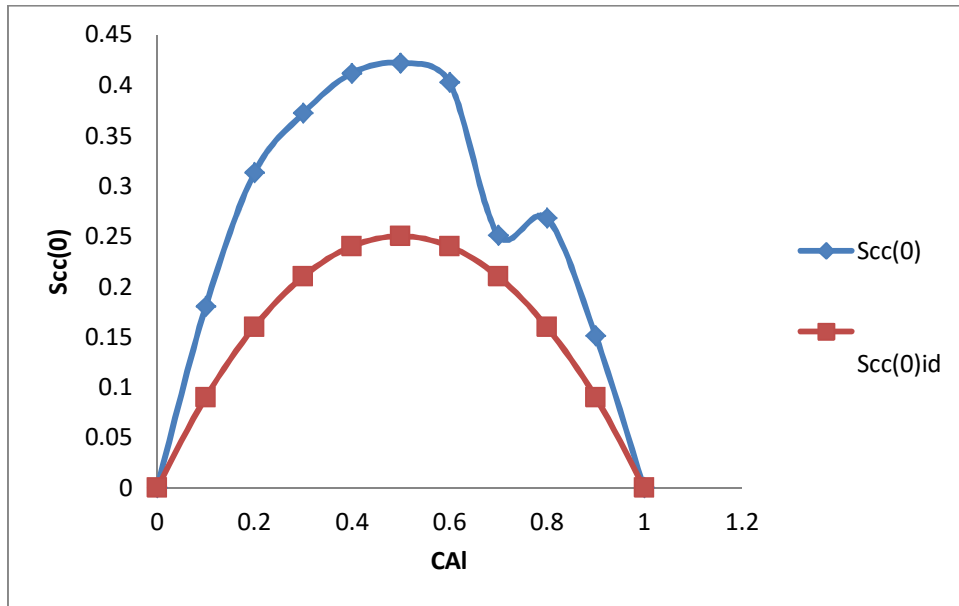


FIG. 5. Scc(0) of Al-Au alloy against Concentration  $C_{Al}$ .

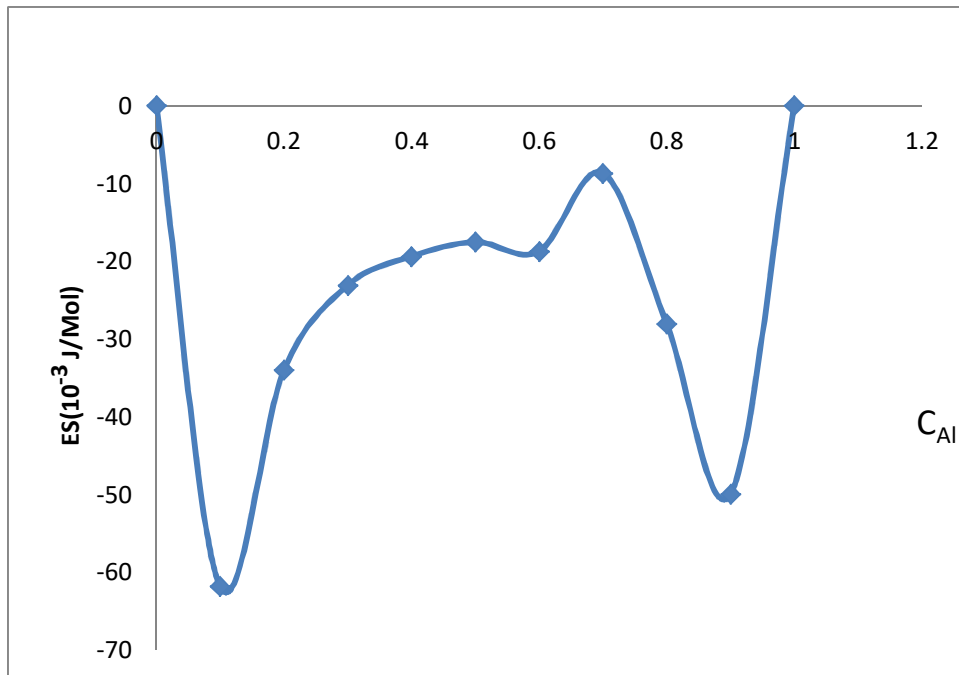
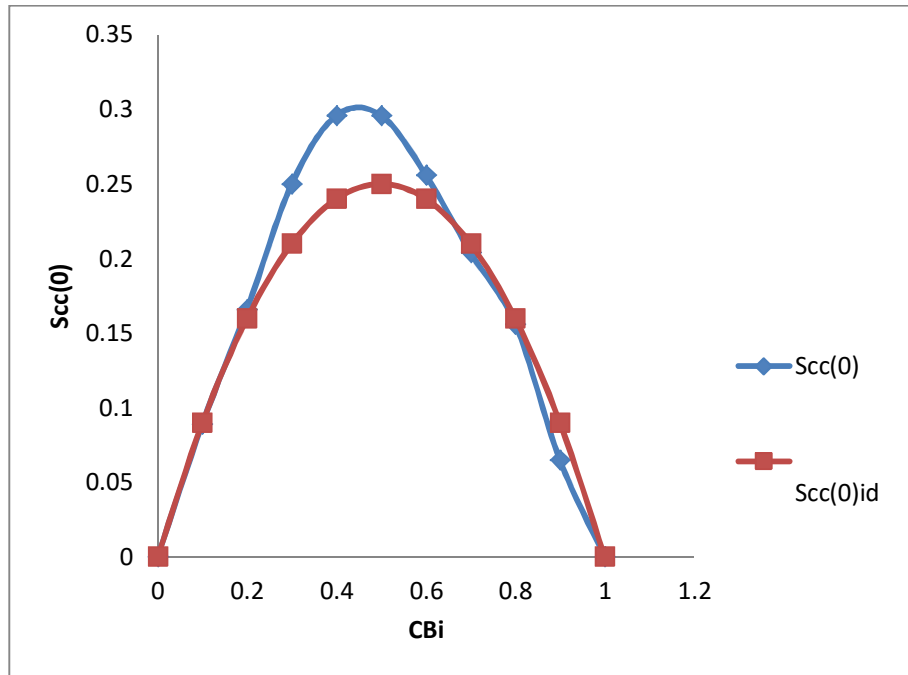
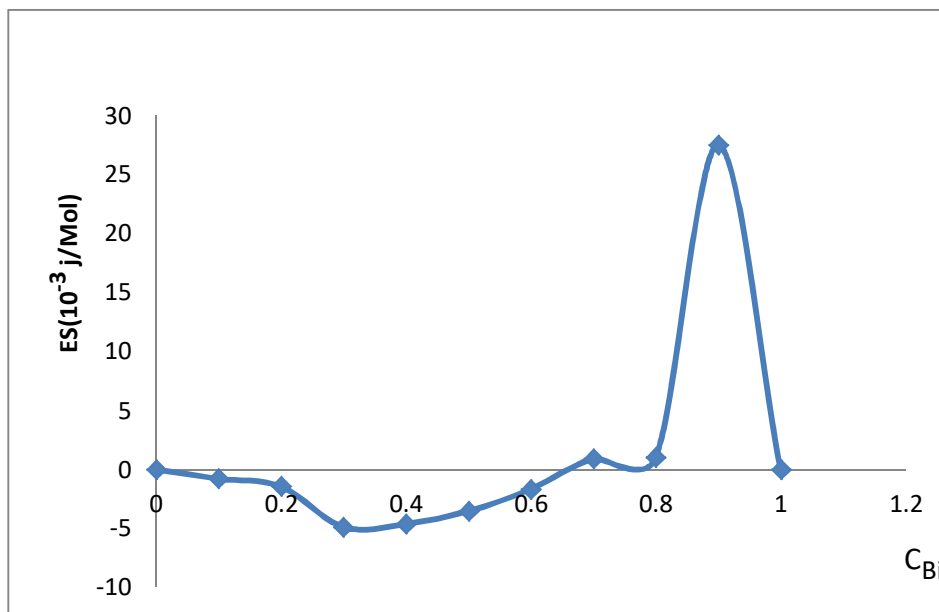


FIG. 6. ES of Al-Au alloy against Concentration  $C_{Al}$ .


 Fig. 7:  $Scc(0)$  of Bi-Cd against Concentration  $C_{Bi}$ .

 FIG. 8. ES of Bi-Cd against Concentration  $C_{Bi}$ .

## Discussion

Figs. 1, 3, 5 and 7 show the plots of concentration-concentration fluctuation  $Scc(0)$  against concentration of element for Cd-Ga, Ag-Ge, Al-Au and Bi-Cd liquid alloys at their melting temperatures. The  $Scc(0)$  of these alloys increases initially to a maximum (owing to the charge transfer between neighboring atoms) within the entire concentration range with distinct peaks at  $C_{Cd} = 0.5$ ,  $C_{Ag} = 0.4$  and  $C_{Bi} = 0.4$ , and the remaining liquid alloy has some

depression at the right side of the curve (owing to chemical alternation of positive and negative charges with length scale approximately twice the nearest neighbor distance) at  $C_{Al} = 0.7$ . In Fig. 5, the curve of  $scc(0)$  against  $C_{Al}$  of aluminum-gold alloy rises above the ideal solution curve (because of the topological short range order i.e. geometrical arrangements of atoms) it indicates homocoordination (Preference of like atoms as the nearest neighbor). Fig. 3 has ideal solution curve

intersecting with the curve of  $S_{cc}(0)$  at concentration between  $C_{Ag} = 0.5$  and  $0.6$  because of directional bonding. In Fig. 7 the calculated  $S_{cc}(0)$  is in perfect agreement with ideal solution values at points  $C_{Bi} = 0, 0.1, 0.2, 0.7, 0.8$  and  $1.0$  but observed disagreement at points  $C_{Bi} = 0.3, 0.4, 0.5, 0.6$  and  $0.9$ . This is because the there is a near cancellation of the ionic potentials while at large distances ionic potentials was screened. Fig. 7 also, has its calculated values for  $S_{cc}(0)$  of Cd-Ga above the ideal solution values which is in support of homocoordination or self coordination.

Figs. 2, 4, 6 and 8 show the plots of excess stability function versus concentration of element. The display in Fig. 2 shows an initial decrease in curve to a minimum (possibly when the disordered potential is too large) with a corresponding gradual increase and some fluctuations with concentration. The excess stability function has negative values, its falls downward to concentration  $C_{cd} = 0.1$  before ascending in a straight line between  $C_{cd} = 0.2$  and  $0.8$  eventually a repetition of what was displayed at  $C_{cd} = 0.1$  was also displayed at  $C_{cd} = 0.9$  with minimum excess stability function between  $C_{cd} = 0.8$  and  $1.0$  which was lower than what was observed at the initial stage of the curve. The excess stability function displayed in Fig. 4 shows initial decrease as the concentration increases and subsequent increase in concentration makes excess stability function reach the highest value. In Fig. 6, the display shows the short range repulsive potential which

prevented the atoms of Au and Al from reaching each other than the effective diameter thereby allowing the  $E_s$  values completely negative throughout the concentration. In Fig. 8, as the concentration increases there was corresponding decrease in excess stability function (due to interatomic potentials repelled by the central potential) between  $C_{Bi} = 0.2$  and  $0.6$  with negative significance. Sharp increase in excess stability up to maximum value (due to pair correlation function thus formed at a distance a little greater than the effective diameter) in the concentration range  $C_{Bi} = 0.8-0.9$  was observed before falling sharply to zero excess stability function at  $C_{Bi} = 1.0$ . Lastly, the peaks of excess stability function were obtained in the concentration range of between  $0.8$  for Ag-Ge and  $0.9$  for Bi-Cd except Al-Au and Cd-Ga liquid alloys.

## Conclusion

Ag-Ge and Bi-Cd liquid alloys are chemically strong interacting compounds with chemical short-range order. The dip in Al-Au liquid alloy is an indication of slight formation. The width and height of excess stability function at specific concentration for Ag-Ge is a candidate of stability possibly in excess. The narrow width and considerable height of excess stability function for Bi-Cd is described with strong stability and Cd-Ga liquid alloy are weak interacting system with intermediate-range.

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