Volume 14, Number 2, 2021. pp. 111-116

Jordan Journal of Physics

ARTICLE

Calculation of Darken Stability Functions of Al-In and Bi-Zn

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Doi:

Received on: 27/01/2020; *Accepted on: 29/07/2020*

Abstract: The thermodynamic model based on cluster of two atoms is considered with the view to obtaining Concentration-concentration fluctuation Scc(0) and the darken stability function. The thermodynamic properties of these alloys were evaluated based on cluster of two atoms (A & B) or (B & A). Each system has the view of obtaining concentration-concentration fluctuation, Scc(0) enumerating the low order atomic correlation in the nearest neighbour shell of liquid binary alloys. The highlights of reciprocals of Scc(0) of these alloys were noted . The values of Scc(0) for *Al-In* alloy throughout the entire concentration were positive and higher for activity ratio and lower than the ideal solution values for free energy of mixing at specific Al composition. The values of darken stability function of *Al-In* alloy falls below the ideal darken stability function for activity ratios and free energy of mixing . The indication of the reciprocal of Scc(0) for all the alloys is in support of homocoordinated / heterocoordination in the nearest neighbour shell. The Scc(0) and darken stability function of t Bi-Zn binary alloys were noted with fluctuations.

Keywords: Concentration-concentration fluctuation, Darken stability function, Ordering energy.

Introduction

This study focuses attention on an aspect where detailed information was not made available on the thermodynamics properties of binary liquid alloy [1]. Relevant properties include concentration-concentration fluctuation, Scc(0) and short range order parameter, SRO [2]. The Scc(0) and SRO of some binary alloys were calculated without attaching the darken stability functions i.e. 1/Scc(0) [3]. The calculated experimental concentration-concentration fluctuation, Scc (0) using ordering energy from free energy of mixing and experimental activities of eleven binary alloys were computed without attaching their darken stability functions. For these properties, data were generated using inputs such as ordering energy value, coordination number, melting temperature and Boltzmann constant. Thermodynamic expressions as functions of concentration from quasichemical model were employed in the described programs for generating data for these thermodynamic properties. The Al-In and Bi-Zn liquid alloys were selected based on the *fact* the experiment number-number partial structural factor S_{NN} (0) and concentration-concentration partial structural factor and Scc(q) were difficult to obtain from neutron diffraction experiment.

Therefore, the observation in this article focuses attention on the determination of ordering energy values of two binary liquid alloys from values of deviations in Scc(0) [3]. These ordering energy values were used in the calculation of Scc(0) and 1/Scc(0) of the two binary liquid alloys. Similar method for generating values was followed by inscribing programs which involves using inputs from Table 1. The thermodynamic expressions made available by quasichemical model which matches experimental observations for many alloys whose S_{NN} (0) are easily obtained from

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neutron experiment were used. The quasichemical model has the capacity to accommodate higher order atomic correlation forming the Four Atoms Cluster Model (FACM). This gives the advantage over other models.

The determined values of ordering energy are displayed in Table 1.

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

Alloy	Temperature (^{o}K)	Z	w_1(eV)	w_2(eV)	w_3(eV)
Al-In	1338	10.0	0.0980	0.1127	0.1130
Bi-Zn	773	10.0	0.0210	0.0206	0.0206

Theory

The calculation of Scc(0) is often attracting attachment like $(S_{cc}(0))^{-1}$. This view provides additional facts that shed light on alloying behavior in terms of compound formation [4], self coordination, phase segregation and complex concentration formation [5, 6]. Thermodynamically, the relationship between short range order parameter, SRO, concentration-concentration fluctuation, Scc(0) and other thermodynamic properties had been sighted in the literature [7-9]. Moreover, between G_m and 1/Scc(0) it is given below. The following thermodynamic expressions are from quasichemical model.

Quasichemical Expressions for Various Thermodynamic Functions

Free Energy of Mixing G_m;

$$G_m = G_m^{id} + G_m^{xs} \quad (1)$$

$$G_m^{id} = RT\{c\ln c + (1-c)\ln(1-c)\} \quad (2)$$

$$G_m^{xs} = RT\{c\ln\gamma_A + (1-c)\ln\gamma_B\} \quad (3)$$

Where G_m^{id} and G_m^{xs} are ideal and excess free energy of mixing. R is molar gas constant, T is temperature, c & 1-c represent the concentration of A and B atoms in the alloy respectively. γ_A and γ_B are the activity coefficients and stand for

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

$$\gamma_B = \left(\frac{\beta + 1 - 2c}{(1-c)(1+\beta)}\right)^{\frac{z}{2}} \quad (5)$$

$$\beta = (1 + 4c(1-c)(\eta^2 - 1))^{\frac{1}{2}}, \quad (6)$$

where $\eta = \exp(w/zk_BT)$ (7)

$$a_A = c\left(\frac{\beta - 1 + 2c}{c(1+\beta)}\right)^{\frac{z}{2}} \quad (8)$$

$$a_B = (1-c)\left(\frac{\beta + 1 - 2c}{(1-c)(1+\beta)}\right)^{\frac{z}{2}} \quad (9)$$

η and β are thermodynamic parameters which are interwoven.

The relationship between darken stability function; 1/Scc(0) and free energy of mixing G_m is given as

$$(s_{cc}(0))^{-1} = \frac{1}{N k_B T}\left(\frac{\partial^2 G_m}{\partial c^2}\right)_{T,P,N} \quad (10)$$

Also the relationship between activity (a_A or a_B) and darken stability function is given as

$$(S_{cc}(0))^{-1} = \frac{1}{(1-c)a_A}\left(\frac{\partial a_A}{\partial c}\right)_{T,P,N} = \frac{1}{C a_B}\left(\frac{\partial a_B}{\partial (1-c)}\right)_{T,P,N} \quad (11)$$

From Eqs. (1), (2), (3) to (11) N is the total number of atoms in the alloy, k_B is the Boltzmann constant, T is the temperature, p is the pressure and Z is coordination number of the alloys. The terms a_A and a_B in Eq. (11) represent the activities of atom A and atom B respectively.

The expression for the ideal darken stability function is given by

$$(S_{cc}^{id}(0))^{-1} = \frac{1}{c(1-c)} \quad (12)$$

Scc(0)1, 1/Scc(0)1, Scc(0)2 and 1/Scc(0)2 are from experimental activities, Scc(0)3 and 1/Scc(0)3 are from experimental free energy of mixing

Results and Discussion

In Fig. 1 and Table 2 it is observed that, in the range of compositions $0<C_{Al}<1.0$, the $Scc(0)\,\exp$ obtained via each of the three methods indicates the alloy is in prefect agreement. The values are greater and lower than the ideal values at $C_{Al} = 0.6$ which indicate homocoordinated and heterocoordination. although in terms of magnitude, the results Scc(0)1 and Scc(0) 3 are closer than Scc(0) 2. In addition, at the composition $C_{Al} = 0.6$, the magnitude of Scc(0) 1 is the largest of the three. Hence in the region $0 < C_{Al} < 1.0$ one can say that the usual Eqs. (10) and (11) give rise to the expected results in the Al-In liquid alloy. It is also observed from this Figure and the Table that Scc(0) 3 appears to be more reliable than the results from Scc(0)1 and Scc(0)2.

In Fig. 2 and Table 2 it is observed that, in the range of composition $0.3 \le CAl \le 0.7$, the 1/Scc(0)exp obtained via each of the three methods is in perfect agreement. In the region $0 \le CAl \le 0.2$, 1/Scc(0) 1 is closest to the ideal darken stability function (1/Scc(0)id) and in the region $0.8 \le CAl \le 1.0$, 1/Scc(0)2 is the closest to the ideal darken stability function.

TABLE 2. Calculated experimental concentration-concentration fluctuation and darken stability function of Al-In alloy. C_{Al} is the concentration of Aliminium in the alloy.

C_{Al}	Scc(0)1	Scc(0)2	Scc(0)3	Scc(0)id	1/Scc(0)1	1/Scc(0)2	1/Scc(0)3	1/Scc(0)id
0.0	0.000	0.000	0.000	0.00	0.0000	0.000	0.000	0.0000
0.1	0.150	0.204	0.162	0.09	6.667	4.901	6.172	11.1111
0.2	0.417	0.382	0.424	0.16	2.398	2.618	2.358	6.2500
0.3	0.997	1.035	0.974	0.21	1.003	0.966	1.027	4.7619
0.4	2.234	2.282	2.050	0.24	0.448	0.438	0.488	4.1667
0.5	5.864	5.239	8.053	0.25	0.171	0.191	0.124	4.0000
0.6	70.437	-128.993	-23.186	0.24	0.014	-0.008	-0.043	4.1667
0.7	6.775	5.922	3.550	0.21	0.148	0.169	0.282	4.7619
0.8	0.692	3.735	0.713	0.16	1.445	0.268	1.403	6.2500
0.9	0.237	0.189	0.289	0.09	4.219	5.291	3.460	11.1111
1.0	0.0000	0.000	0.000	0.00	0.000	0.0000	0.0000	0.0000

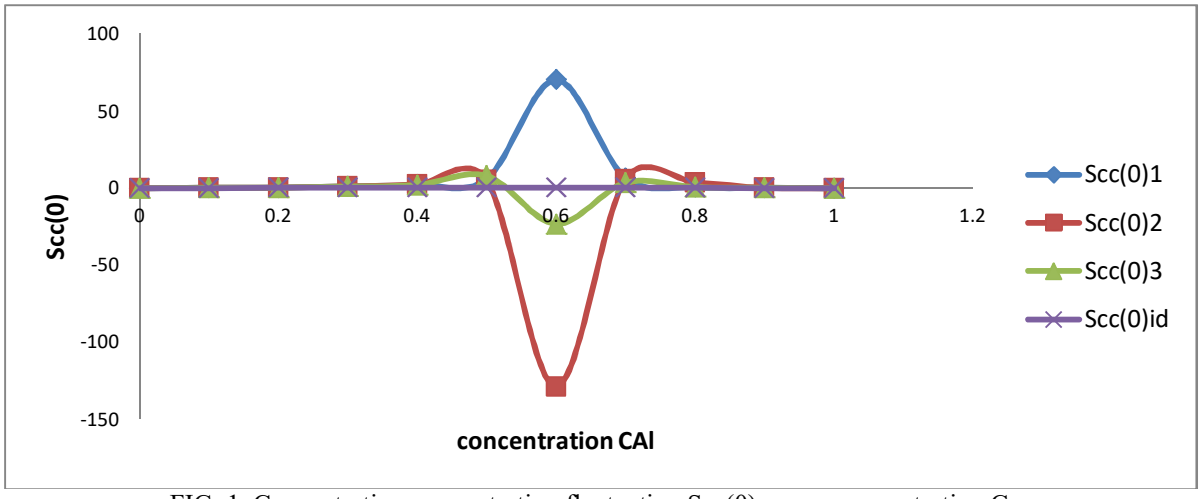

FIG. 1. Concentration-concentration fluctuation Scc(0) versus concentration C_{Al}.

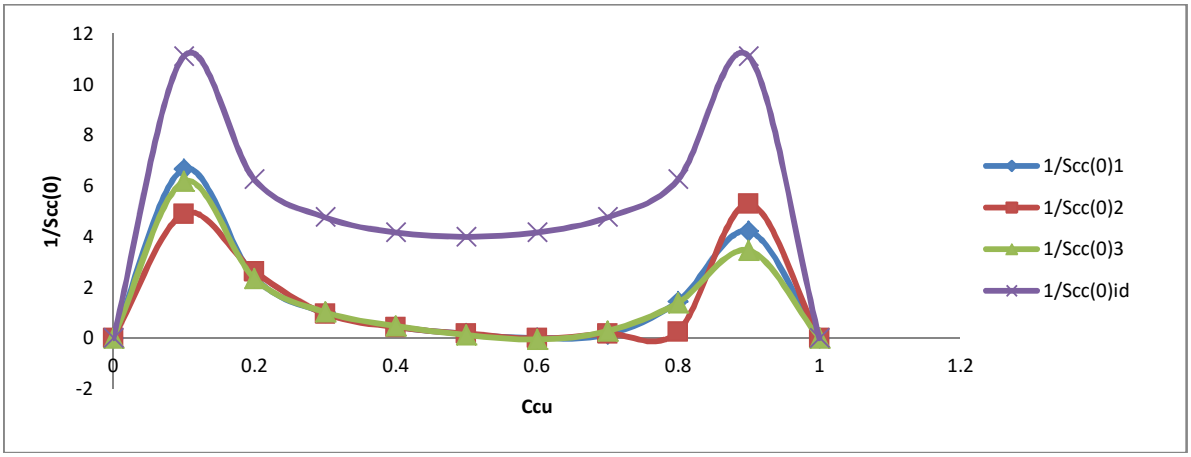

FIG. 2. Darken stability function versus concentration C_{Al}.

In Fig. 3 and Table 3 based on observation, in the range of composition $0.2 \le CBi \le 0.5$, the $Scc(0)\exp$ obtained via each of the three methods are in not perfect agreement and indicate the alloy to be homocoordinated and heterocoordination because its values are lower and greater than the ideal values. Although in terms of magnitude, the results Scc(0)2 and Scc(0)3 are closer than Scc(0)1 in the range 0.4 < C_{Bi} < 1.0. In addition, at the composition C_{Bi} = 0. 2, the magnitude of Scc(0)1 is the largest of the three. Hence in the region $0<C_{Bi}<1.0$ it is observed that the usual Eqs. (10) and (11) give rise to the expected results in the Bi-Zn liquid alloy. It is also observed from this Figure and Table that Scc(0)2 appears to be more reliable than the results from Scc(0)1 and Scc(0)3.

Table 3: Calculated experimental concentration-concentration fluctuation and darken stability function of Bi-Zn alloy. C_{Bi} is the concentration of bismuth in the alloy.

C_{Bi}	Scc(0)1	Scc(0)2	Scc(0)3	Scc(0)id	1/Scc(0)1	1/Scc(0)2	1/Scc(0)3	1/Scc(0)id
0.0	0.000	0.000	0.000	0.00	0.000	0.000	0.000	0.0000
0.1	0.837	0.442	8.315	0.09	1.195	2.262	0.120	11.1111
0.2	22.459	-5.384	-4.99	0.16	0.045	-0.171	-0.200	6.2500
0.3	2.593	1.935	1.894	0.21	0.386	0.513	0.528	4.7619
0.4	8.756	0.754	0.759	0.24	0.114	1.318	1.318	4.1667
0.5	0.482	0.503	0.513	0.25	2.075	1.988	1.949	4.0000
0.6	0.395	0.385	0.386	0.24	2.532	2.597	2.591	4.1667
0.7	0.301	0.292	0.281	0.21	3.322	3.559	3.559	4.7619
0.8	0.14	0.198	0.195	0.16	7.143	5.050	5.128	6.2500
0.9	0.133	0.099	0.135	0.09	7.519	10.101	7.4070	11.1111
1.0	0.000	0.000	0.000	0.00	0.000	0.000	0.000	0.0000

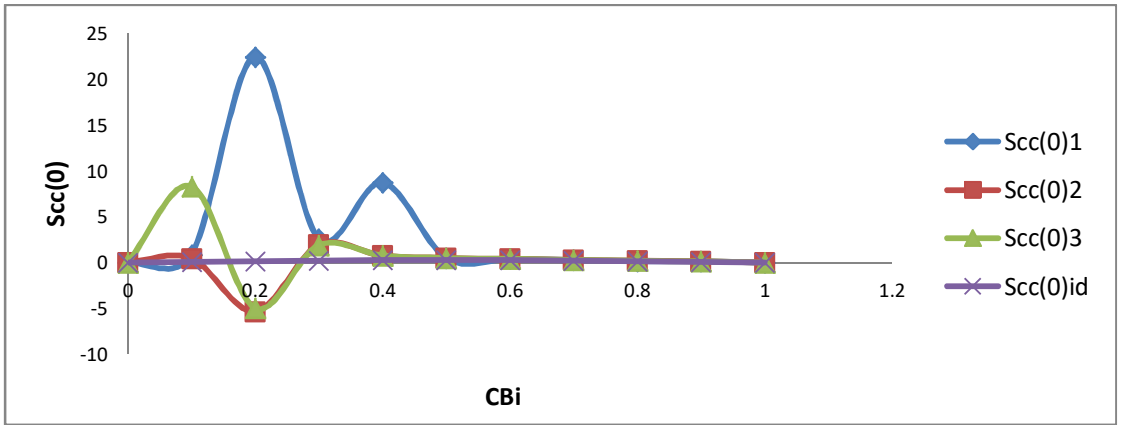

FIG. 3. Concentration-concentration fluctuation Scc(0) versus concentration C_{Bi}.

In Fig. 4 and Table 3 in the range of composition $0 \leq CBi \leq 1.0$, the 1/Scc(0)exp obtained via each of the three methods is not in perfect agreement because of the regions $0.3 \leq CBi \leq 0.5$ and $0 \leq CBi \leq 0.2$. At $C_{Bi} = 0.1$, the three approaches are below the ideal darken stability function. In the region At $C_{Bi} = 0.8$, only 1/Scc(0) 1 is above the darken stability function. At $C_{Bi} = 0.9$, only 1/Scc(0) 2 is close the ideal darken stability function.

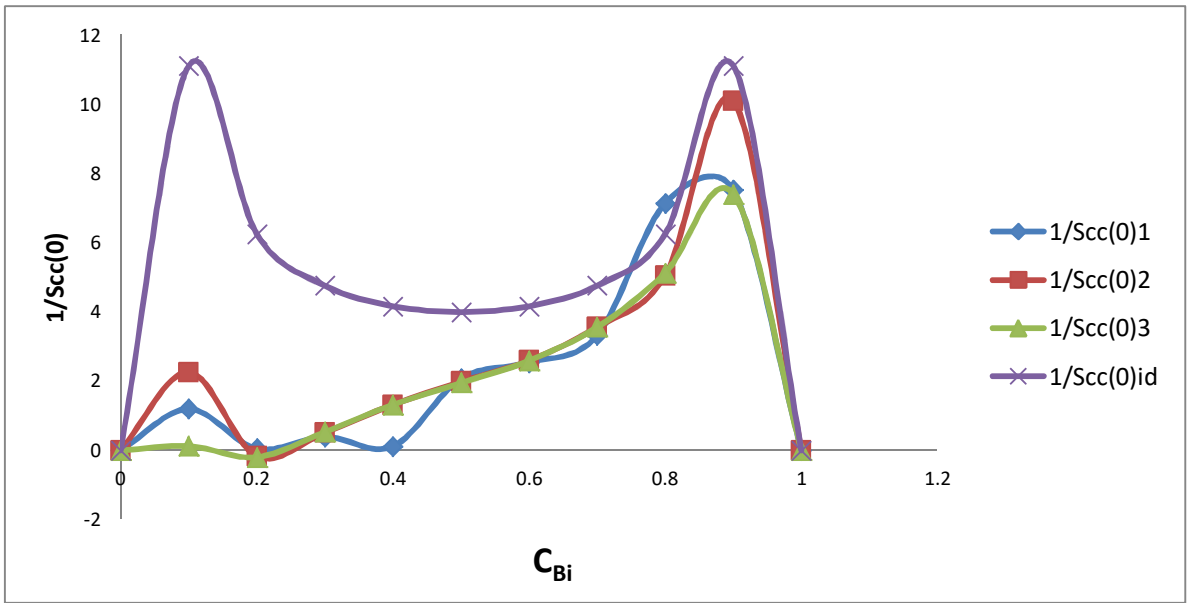

FIG. 4. Darken stability function versus concentration C_{Bi}.

Lastly, the darken stability functions for the three approaches are in not good agreement with the ideal darken stability function. This is in support of homocoordination and heterocoordination. The success of Eqs. (10) and (11) depends upon the true knowledge of the ordering energy w.

Concluding Remarks

This study has revealed, contrary to the belief that the Scc(0)exp of liquid binary alloys can be computed via the experimental activities and experimental free energy of mixing using Eqs. (10) and (11) within a given set of data for experimental a_A, a_B and G_M from common source (as different sets of data for a system may not be available, or if available may not necessarily agree throughout the entire composition) that:

(1) There are no instance where the Scc(0)exp obtained via each of the three methods agrees completely throughout the entire composition for the two Alloys.

(2) There is one instance where Scc(0)exp obtained via each of the three methods have partial agreement instead of complete agreement (this is Al-In). The equality sign in Eqs. (10) and (11) is suggested equivalent sign.

In Conclusion, it is recommend that whenever Scc(0)exp is needed, the common approach of obtaining it via experimental activity a_A should be seen as the best reliable method among the three.

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