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## Calculation of experimental concentration–concentration fluctuations of liquid binary alloys using experimental free energy of mixing and experimental activities

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We have calculated the experimental concentration–concentration fluctuations ( $S_{cc}^{\text{exp}}(0)$ ) of 11 binary liquid alloys using the methods of experimental free energy of mixing and the experimental activities. We observed that contrary to the belief that  $S_{cc}^{\text{exp}}(0)$  can be obtained via any of these methods, it was only two of the alloys that had a satisfactory entire composition agreement between the three methods. In most of the alloys it was partial agreement. This indicates that there is a limit to the extent the  $S_{cc}^{\text{exp}}(0)$  obtained via the two methods involving Gibbs–Duhem integration should be taken as an alternative to that obtained via activity measured directly. Thus, whenever the result of  $S_{cc}^{\text{exp}}(0)$  obtained via the latter disagrees with other thermodynamic results, the option of substituting the model or alloy in use should be preferred to re-calculating the  $S_{cc}^{\text{exp}}(0)$  using either experimental activity or experimental free energy of mixing obtained by Gibbs–Duhem integration.

**Keywords:** concentration–concentration fluctuations; experimental activities; experimental free energy of mixing

### 1. Introduction

Within the last couple of decades, much work has been done by various researchers on calculating the properties of binary liquid alloys. More often than not, researchers have always been interested in the bulk, surface and transport properties of binary liquid alloys. On the basis of such calculations, binary alloys have been classified or grouped as: chemically ordered (or heterocoordinated), segregated (or homocoordinated), strong, weak, regular, asymmetric, symmetric etc. [1,2].

In the calculation of bulk properties of binary liquid alloys, attention is often focused on thermodynamic properties, such as free energy of mixing,  $G_M$ , activity, ( $a_A$  for A-atom or  $a_B$  for B-atom in an A–B alloy), short-range order parameter,  $\alpha_1$ , concentration–concentration fluctuations,  $S_{cc}(0)$ , enthalpy of mixing,  $H_M$ , and entropy of mixing,  $S_M$ . The calculations of these quantities involve getting experimental data about them and employing suitable theoretical models.

In most cases, obtaining the experimental data needed for the calculation of  $G_M$ ,  $a_A$ ,  $H_M$  and  $S_M$  is not a problem (except in some uncommon cases where the

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experimental data for one or two of these may not be available due to experimental difficulties). In principle,  $\alpha_1$  can be experimentally determined from knowledge of the concentration–concentration partial structure factor,  $S_{cc}(q)$ , and the number–number partial structure factor,  $S_{NN}(q)$ . However, these structure factors are not easily measurable in most diffraction experiments [3]. Hence,  $\alpha_1$  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 [4,5], yet it is an accepted tradition to obtain  $S_{cc}^{\text{exp}}(0)$  via either the experimental  $G_M$ , or the experimental  $a_A$  or  $a_B$  [1,5–7]. Further, we noticed that while most researchers do employ the experimental  $a_A$  option in their calculations of  $S_{cc}^{\text{exp}}(0)$ , Awe *et al.* [7], Bhatia [8] and Odusote *et al.* [9] have reported, independently, that they used experimental  $G_M$  to obtain  $S_{cc}^{\text{exp}}(0)$  for Bi–Pb, Sb–Sn, Na–K, Al–Zn and Bi–In liquid alloys, which are in agreement with the expectations outlined in [1,5–7].

The focus of this study, therefore, is to compute the  $S_{cc}^{\text{exp}}(0)$  of some alloys via the experimental  $G_M$  on one hand, and, on the other hand, to obtain two other  $S_{cc}^{\text{exp}}(0)$  via the experimental  $a_A$  and the experimental  $a_B$ , and then compare the three results of  $S_{cc}^{\text{exp}}(0)$ , with a view to ascertain to what extent is it safe to consider one of these three approaches of calculating  $S_{cc}^{\text{exp}}(0)$  as an alternative option to the others when a set of experimental  $a_A$ ,  $a_B$  and  $G_M$  are available for a system of interest.

In doing the aforementioned, we made use of the available experimental data on Ag–Al at 1273 K, Ag–Ge at 1250 K, Al–Au at 1338 K, Al–In at 1173 K, Au–Ni at 1150 K, Bi–Cd at 773 K, Bi–Zn at 873 K, Cd–Ga at 700 K, Cu–Pb at 1473 K, In–Na at 713 K, and Na–Pb at 700 K, which were taken from Hultgren *et al.* [10].

In the next section, we shall discuss the theory behind the calculation of  $S_{cc}(0)$  from  $G_M$ ,  $a_A$  and  $a_B$ . This shall be followed by a discussion of the results obtained from our calculations. The last section bears concluding remarks.

## 2. Theory

The calculation of  $S_{cc}(0)$  is of great importance, in view of the fact that an understanding of  $S_{cc}(0)$  will shed light on alloying behaviour in terms of compound formation and phase segregation [6,11]. Thermodynamically, the relationship between  $G_M$  and  $S_{cc}(0)$  is given by Singh [2], Singh and March [5], Bhatia [7], Bhatia and Thornton [12] and Singh *et al.* [13]:

$$S_{cc}(0) = Nk_B T \left( \frac{\partial^2 G_M}{\partial c^2} \right)_{T,P,N}^{-1} \quad (1)$$

The relationship between activity ( $a_A$  or  $a_B$ ) and  $S_{cc}(0)$  is given by [5–7]:

$$S_{cc}(0) = (1 - c) a_A \left( \frac{\partial a_A}{\partial c} \right)_{T,P,N}^{-1} = c a_B \left[ \frac{\partial a_B}{\partial (1 - c)} \right]_{T,P,N}^{-1} \quad (2)$$

In Equations (1) and (2),  $N$  is the total number of atoms in the alloy,  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $P$  is the pressure. The terms  $a_A$  and  $a_B$  in Equation (2) represent the activities of atoms  $A$  and  $B$ , respectively. Also in this

equation,  $c$  and  $(1 - c)$  stand for the concentration of atoms  $A$  and  $B$  in the alloy, in that order. The expression for the ideal  $S_{cc}(0)$  is given by [2]:

$$S_{cc}^{\text{id}}(0) = c(1 - c). \quad (3)$$

In the calculation of  $S_{cc}(0)$  for an alloy, whenever its values are greater than  $S_{cc}^{\text{id}}(0)$ , it is an indication that such an alloy is a homocoordinated system; otherwise, it is a heterocoordinated system [5]. In the event that for a given alloy, its values of  $S_{cc}(0)$  equal  $S_{cc}^{\text{id}}(0)$  at a composition range, which is usually far beyond stoichiometric composition, it is an indication that such an alloy might be a glass former [2,13].

We have employed Equations (1) and (2) in our computation of the  $S_{cc}^{\text{exp}}(0)$  for each of the 11 alloys of interest. Usually, these two equations are employed in the computation of both the calculated concentration–concentration fluctuations,  $S_{cc}^{\text{cal}}(0)$  (by making use of the expressions for  $G_M$  or  $a_A$  or  $a_B$  of the chosen model of interest) and the  $S_{cc}^{\text{exp}}(0)$  [2]. The latter is obtained in this work by making use of the experimental values of  $G_M$ ,  $a_A$  and  $a_B$ , taken as a set, for each alloy of interest from the tabulated data in [10] via numerical programmes, where each of  $G_M$ ,  $a_A$  and  $a_B$  is written as a polynomial and then employed in Equations (1) and (2).

Additionally, we used the technique of singular value decomposition (SVD), as in [15], in our polynomial fits. This technique is quite suitable to fit a set of data points  $(x_i, y_i)$  to a model which is not just a linear combination of 1 and  $x$  (i.e.  $a + bx$ ), but rather a linear combination of any  $M$  specified functions of  $x$ . This function could be a polynomial of degree  $M - 1$  (as in our fittings for  $S_{cc}^{\text{exp}}(0)$ ), or could be sines and cosines. SVD takes care of difficulties in least squares problems, such as overdetermination (i.e. number of data points greater than number of parameters), underdetermination (i.e. existence of ambiguous combinations of parameters) and the like. In using SVD we ensured that for the nine experimental data points of  $a_A$  or  $a_B$  or  $G_M$ , we used an eight order polynomial fit.

Our choice of the 11 alloys of interest is primarily on the premise that for each alloy we have the needed set of experimental data. Also, the 11 alloys represent in a way the various classes of binary alloys. The results obtained are shown both in tables and figures presented and discussed in the next section.

### 3. Results and discussion

In Figure 1 and Part A of Table 1 we observe that, in the range of composition  $0.4 \leq C_{\text{Ag}} \leq 0.8$ , the  $S_{cc}^{\text{exp}}(0)$  obtained via each of the three methods indicates that the alloy is heterocoordinated, although in terms of magnitude, the results  $S_{cc}^{\text{exp1}}$  and  $S_{cc}^{\text{exp2}}$  are closer than  $S_{cc}^{\text{exp3}}$ . In addition, at the composition  $C_{\text{Ag}} = 0.1$ , while the results from  $S_{cc}^{\text{exp2}}$  and  $S_{cc}^{\text{exp3}}$  indicate heterocoordination, the result  $S_{cc}^{\text{exp1}}$  indicates homocoordination. At the composition  $C_{\text{Ag}} = 0.9$ , the results  $S_{cc}^{\text{exp1}}$  and  $S_{cc}^{\text{exp3}}$  indicate homocoordination, although their magnitude difference is quite large, while the value for  $S_{cc}^{\text{exp2}}$  is negative. Hence, it follows that only in the region  $0.4 \leq C_{\text{Ag}} \leq 0.8$  we can say that the usual Equations (1) and (2) give rise to the expected results in the Ag–Al liquid alloy. It is also observed from this figure and table that  $S_{cc}^{\text{exp3}}$  appears to be more reliable than the results from the two activities (i.e.  $S_{cc}^{\text{exp1}}$  and  $S_{cc}^{\text{exp2}}$ ) if the value at  $C_{\text{Ag}} = 0.9$  is thrown out, and this will qualitatively agree with earlier results for this alloy at a temperature of 1173 K, as in [17,18].

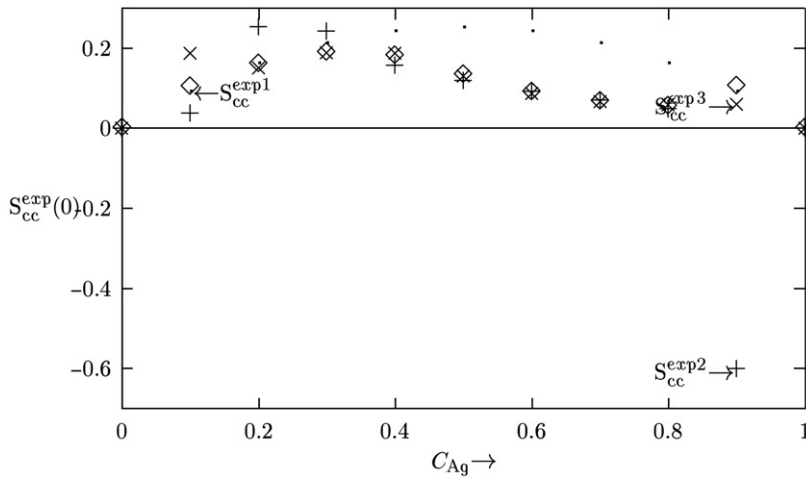


Figure 1. Experimental concentration–concentration fluctuations,  $S_{cc}^{\text{exp}}(0)$  vs. concentration for Ag–Al liquid alloy at 1273 K. The  $\bullet$  represents the ideal values, the  $\diamond$  represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{\text{exp1}}$ ), the  $+$  represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{\text{exp2}}$ ), while the  $\times$  represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{\text{exp3}}$ ).  $C_{Ag}$  is the Ag concentration in the alloy.

Table 1. Calculated experimental concentration–concentration fluctuations for Ag–Al, Al–Au and Al–In alloys using the experimental activities and free energy of mixing obtained from [10]. Diff( $i$ )  $i = 1, 2, 3$  is the difference between  $S_{cc}^d$  and respective  $S_{cc}^{\text{exp}(i)}$  ( $S_{cc}^{\text{exp1}}$ ,  $S_{cc}^{\text{exp2}}$  and  $S_{cc}^{\text{exp3}}$  represent values obtained from activity components  $a_A, a_B$  and free energy of mixing,  $G_M$  respectively).  $C_{Al,Ag}$  is the concentration of aluminium and silver in their respective alloys.

$C_{Al,Ag}$	Part A: Ag–Al at 1273 K			Part B: Al–Au at 1338 K			Part C: Al–In at 1173 K		
	Diff1	Diff2	Diff3	Diff1	Diff2	Diff3	Diff1	Diff2	Diff3
0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.1	−0.013	0.052	0.030	0.090	0.077	0.071	0.060	0.114	0.072
0.2	0.000	−0.094	0.102	0.153	0.138	0.132	0.257	0.222	0.264
0.3	0.021	−0.033	0.144	0.162	0.181	0.182	0.787	0.825	0.764
0.4	0.060	0.082	0.152	0.172	0.208	0.213	1.997	2.042	1.810
0.5	0.117	0.131	0.119	0.172	0.218	0.219	5.614	4.989	7.803
0.6	0.150	0.147	0.053	0.163	0.205	0.200	−170.197	−129.233	−23.426
0.7	0.144	0.139	0.022	0.141	0.138	0.157	5.965	5.712	3.340
0.8	0.105	0.111	0.009	0.108	0.127	0.102	0.532	0.575	0.553
0.9	−0.015	0.690	−0.097	0.061	0.097	0.047	0.147	0.099	0.199
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

It has been reported in [1] that Ag–Ge does not belong exclusively to either short-range ordered alloy or segregating systems and it is of interest to note that our results for this alloy, as shown in Part A of Table 2 and Figure 2, are in agreement with this. In fact, there is a reasonable level of agreement between the three methods of

Table 2. Calculated experimental concentration–concentration fluctuations for Ag–Ge and Bi–Cd alloys using experimental activities and free energy of mixing obtained from [10]. Diff(i)  $i = 1, 2, 3$  is the difference between  $S_{cc}^{id}$  and respective  $S_{cc}^{exp(i)}$  ( $S_{cc}^{exp1}$ ,  $S_{cc}^{exp2}$  and  $S_{cc}^{exp3}$  represent values obtained from activity components  $a_A$ ,  $a_B$  and free energy of mixing,  $G_M$  respectively).  $C_{Ag,Bi}$  is the concentration of silver and bismuth in their respective alloys.

$C_{Ag,Bi}$	Part A: Ag–Ge at 1250 K			Part B: Bi–Cd at 773 K		
	Diff1	Diff2	Diff3	Diff1	Diff2	Diff3
0.0	0.000	0.000	0.000	0.000	0.000	0.000
0.1	0.022	0.020	0.034	−0.001	0.000	−0.021
0.2	0.033	0.031	0.029	0.006	0.007	0.010
0.3	0.052	0.051	0.050	0.040	0.041	0.041
0.4	0.063	0.065	0.065	0.056	0.056	0.057
0.5	0.038	0.037	0.036	0.046	0.045	0.045
0.6	−0.018	−0.018	−0.021	0.016	0.017	0.017
0.7	−0.057	−0.055	−0.058	−0.006	−0.006	−0.002
0.8	−0.056	−0.058	−0.055	−0.004	−0.009	−0.008
0.9	−0.014	−0.004	−0.014	−0.025	−0.008	−0.029
1.0	0.000	0.000	0.000	0.000	0.000	0.000

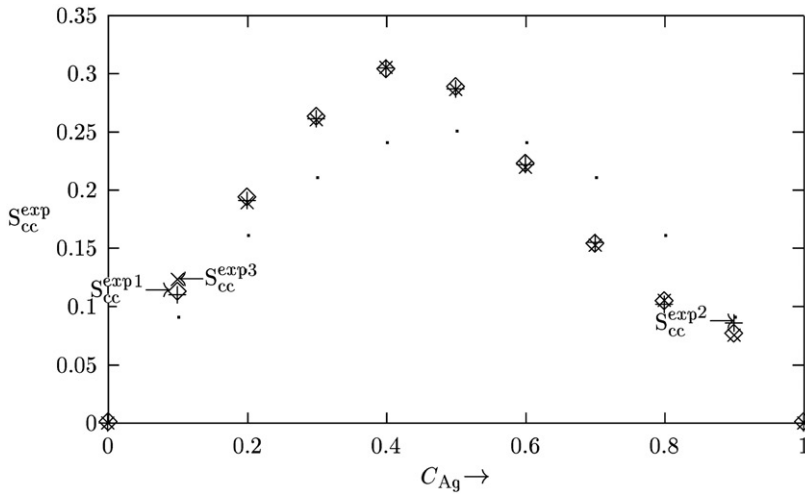


Figure 2. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp3}(0)$  vs. concentration for Ag–Ge liquid alloy at 1250 K. The  $\bullet$  represents the ideal values, the  $\diamond$  represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{exp1}$ ), the  $+$  represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the  $\times$  represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Ag}$  is the Ag concentration in the alloy.

calculating  $S_{cc}^{exp}(0)$ , both in the region  $0 \leq C_{Ag} \leq 0.6$  where the segregating attribute is exhibited, and in the region  $0.6 \leq C_{Ag} \leq 1.0$  where short-range order quality is demonstrated. Hence, it can be said that the usual Equations (1) and (2) lead to the expected results throughout the entire composition of Ag in the Ag–Ge system.

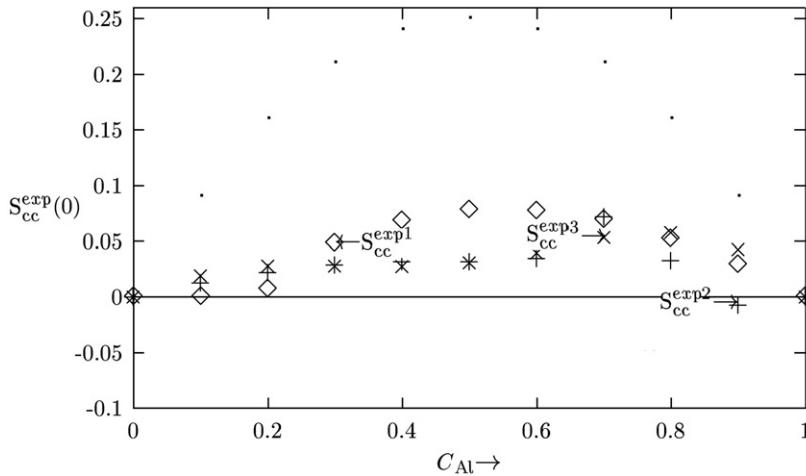


Figure 3. Experimental concentration–concentration fluctuations,  $S_{cc}^{\text{exp}}(0)$  vs. concentration for Al–Au liquid alloy at 1338 K. The  $\bullet$  represents the ideal values, the  $\diamond$  represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{\text{exp1}}$ ), the  $+$  represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{\text{exp2}}$ ), while the  $\times$  represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{\text{exp3}}$ ).  $C_{Al}$  is the Al concentration in the alloy.

In Part B of Table 1 and Figure 3 we observe that the large negative deviation of each of the three plots ( $S_{cc}^{\text{exp1}}$ ,  $S_{cc}^{\text{exp2}}$  and  $S_{cc}^{\text{exp3}}$ ) from the  $S_{cc}^{\text{id}}$  is a confirmation that Al–Au is a strongly interacting alloy, as reported in [5]. Also, we observe that with the exception of concentration  $C_{Al}=0.9$  where the value of  $S_{cc}^{\text{exp2}}$  is negative, the three methods are in good agreement, although in the region  $0 \leq C_{Al} \leq 0.6$  the values of  $S_{cc}^{\text{exp2}}$  and  $S_{cc}^{\text{exp3}}$  are closer than  $S_{cc}^{\text{exp1}}$ , while in the rest of the composition the values of  $S_{cc}^{\text{exp1}}$  and  $S_{cc}^{\text{exp3}}$  are closer than that of  $S_{cc}^{\text{exp2}}$ . Consequently, we can say that the usual Equations (1) and (2) give rise to the expected results, to some extent, in Al–Au system.

With the exception of the composition  $C_{Al}=0.6$ , the  $S_{cc}^{\text{exp}}(0)$  we computed for Al–In via the three methods, as shown Figure 4 and Part C of Table 1, indicates that this alloy is a segregating system in agreement with [1]. A closer look at the magnitude of each of the plots of  $S_{cc}^{\text{exp1}}$ ,  $S_{cc}^{\text{exp2}}$  and  $S_{cc}^{\text{exp3}}$  shows that Equations (1) and (2) in this alloy only hold satisfactorily in the composition  $0 \leq C_{Al} \leq 0.4$  and  $0.8 \leq C_{Al} \leq 1.0$ , since in these composition ranges the values of  $S_{cc}^{\text{exp1}}$ ,  $S_{cc}^{\text{exp2}}$  and  $S_{cc}^{\text{exp3}}$  are equivalent. However, in the composition  $0.4 < C_{Al} < 0.8$  there is pronounced disparity in the values of  $S_{cc}^{\text{exp1}}$ ,  $S_{cc}^{\text{exp2}}$  and  $S_{cc}^{\text{exp3}}$ . Hence, we can say that in Al–In, Equations (1) and (2) hold to some extent.

We observe in Figure 5 and Part A of Table 3 that there is a good level of agreement between the results obtained via the three methods for Au–Ni in the composition range  $0.4 \leq C_{Au} \leq 1.0$ , while in the composition  $0.1 \leq C_{Au} \leq 0.3$  there are some significant disparities. Hence, we can say that Equations (1) and (2) significantly give identical results in Au–Ni, in the range  $0.4 \leq C_{Au} \leq 1.0$  only.

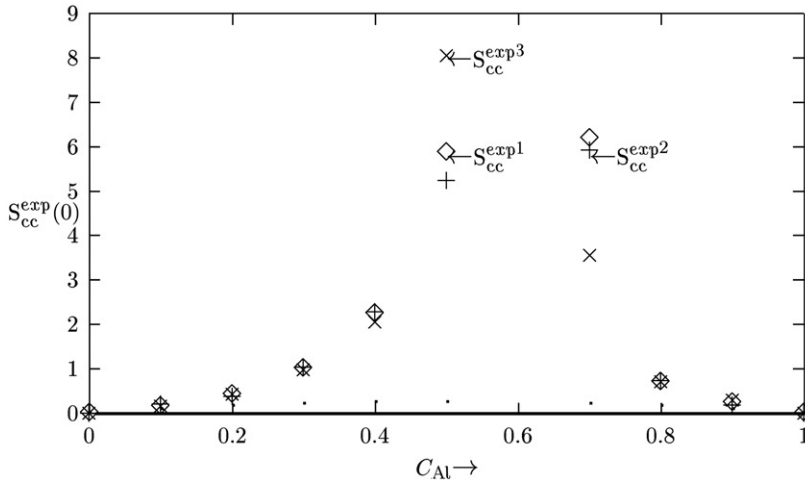


Figure 4. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for Al–In liquid alloy at 1173K. The • represents the ideal values, the ◇ represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{exp1}$ ), the + represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the ✕ represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Al}$  is the Al concentration in the alloy.

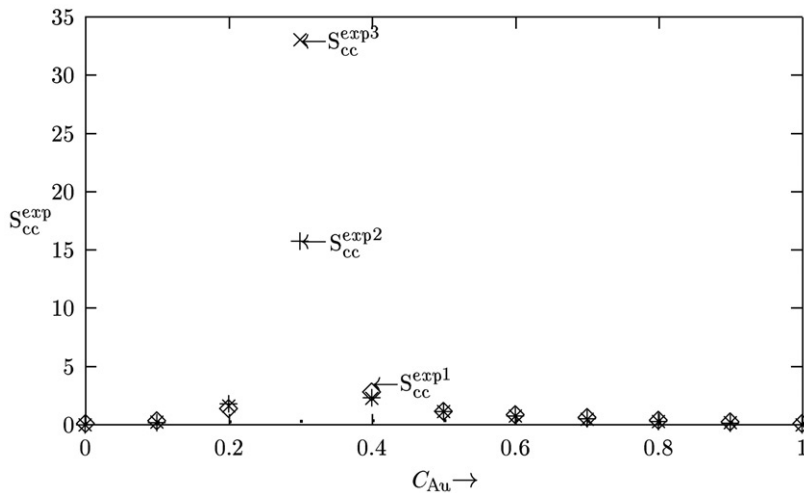


Figure 5. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for Au–Ni liquid alloy at 1150 K. The • represents the ideal values, the ◇ represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{exp1}$ ), the + represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the ✕ represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Au}$  is the Au concentration in the alloy.



Table 3. Calculated experimental concentration–concentration fluctuations for Au–Ni, Bi–Zn and Cd–Ga alloys using experimental activities and free energy of mixing obtained from [10]. Diff(i)  $i = 1, 2, 3$  is the difference between  $S_{cc}^{id}$  and respective  $S_{cc}^{exp(i)}$  ( $S_{cc}^{exp1}$ ,  $S_{cc}^{exp2}$  and  $S_{cc}^{exp3}$  represent values obtained from activity components  $a_A, a_B$  and free energy of mixing,  $G_M$  respectively).  $C_{Au,Bi,Cd}$  is the concentration of gold, bismuth and cadmium in their respective alloys.

$C_{Au,Bi,Cd}$	Part A: Au–Ni at 1150K			Part B: Bi–Zn at 873K			Part C: Cd–Ga at 700K		
	Diff1	Diff2	Diff3	Diff1	Diff2	Diff3	Diff1	Diff2	Diff3
0.0	0.000	0.000	0.00	0.000	0.000	0.000	0.000	0.000	0.000
0.1	0.142	0.097	0.125	0.747	0.352	8.225	0.080	0.061	0.117
0.2	1.121	1.658	1.433	22.299	−5.544	−5.150	0.277	0.290	0.292
0.3	514.087	15.538	32.858	2.383	1.725	1.684	0.766	0.720	0.682
0.4	2.452	2.064	2.036	0.516	0.514	0.517	1.478	1.480	1.246
0.5	0.775	0.900	0.868	0.232	0.255	0.263	1.495	1.636	1.529
0.6	0.508	0.538	0.521	0.155	0.145	0.146	0.903	0.886	0.995
0.7	0.335	0.311	0.284	0.091	0.082	0.071	0.428	0.410	0.432
0.8	0.116	0.135	0.133	0.024	0.038	0.035	0.187	0.203	0.182
0.9	0.074	0.032	0.085	0.043	0.009	0.045	0.138	0.122	0.113
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

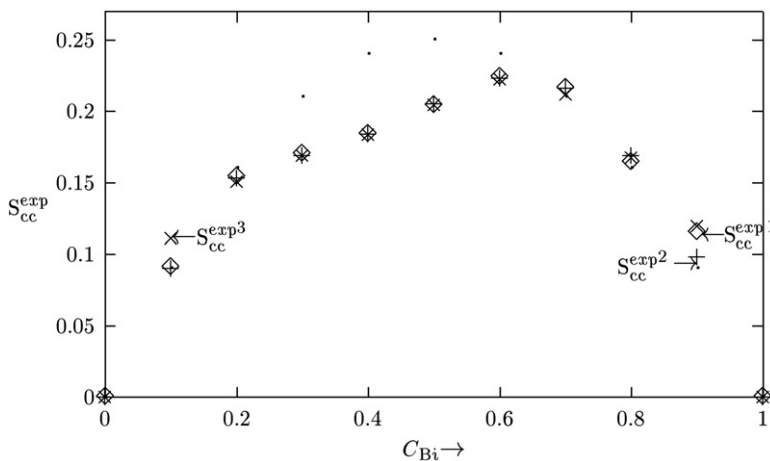


Figure 6. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for Bi–Cd liquid alloy at 773 K. The  $\bullet$  represents the ideal values, the  $\diamond$  represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{exp1}$ ), the  $+$  represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the  $\times$  represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Bi}$  is the Bi concentration in the alloy.

A comparison of the results of  $S_{cc}^{exp}(0)$  obtained for Bi–Cd via the three methods as shown in Figure 6 and Part B of Table 2 indicates that Equations (1) and (2) give us identical results in Bi–Cd throughout the entire composition of Bi in Bi–Cd system. The slight disparities in the values of  $S_{cc}^{exp1}$ ,  $S_{cc}^{exp2}$  and  $S_{cc}^{exp3}$  at  $C_{Bi} = 0.9$  in our opinion are ignorable.

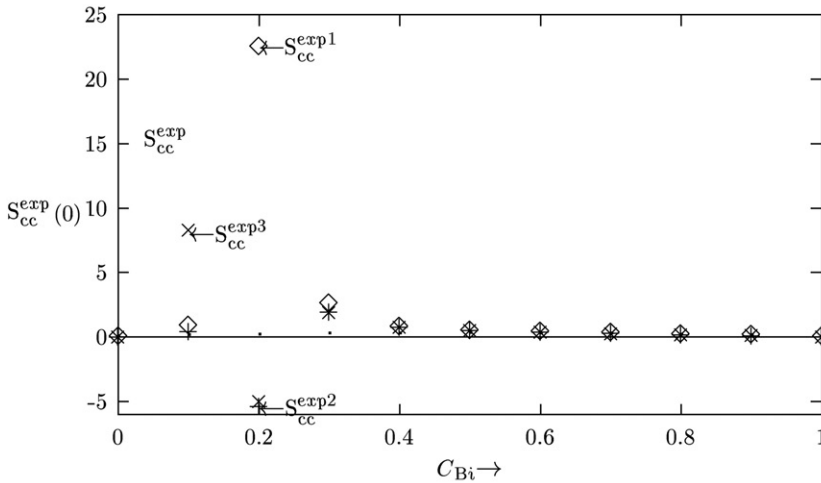


Figure 7. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for Bi–Zn liquid alloy at 873 K. The  $\bullet$  represents the ideal values, the  $\diamond$  represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{exp1}$ ), the  $+$  represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the  $\times$  represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Bi}$  is the Bi concentration in the alloy.

In Figure 7 and Part B of Table 3 we observe that there is a good level of agreement in the  $S_{cc}^{exp}(0)$  obtained via the three methods in the composition range  $0.4 \leq C_{Bi} \leq 1.0$ , while there is significant disparity in the results in the range of composition  $C_{Bi} < 0.4$ . Although, a comparison of these results with that obtained at 900 K by Singh and Sommer in [18] shows that  $S_{cc}^{exp1}$  is more reliable than either  $S_{cc}^{exp2}$  or  $S_{cc}^{exp3}$ , we do observe that Equations (1) and (2) only give significantly similar results in Bi–Zn in the composition range  $0.4 \leq C_{Bi} \leq 1.0$ .

As shown in Part C of Table 3 and Figure 8, we observe that in Cd–Ga, except in the composition  $C_{Cd} = 0.4$  and  $C_{Cd} = 0.5$ , there is good level of agreement between the results obtained via the three methods. This implies that in the Cd–Ga alloy, Equations (1) and (2) hold significantly in virtually the entire composition of Cd in Cd–Ga. In addition, Singh and Sommer [1] stated that Cd–Ga is a segregating system characterised by liquid miscibility gaps like Al–In, Bi–Zn and Cu–Pb. The evidence of segregation can be seen in Figure 8 and Part C of Table 3, where the computed  $S_{cc}^{exp}(0)$  is clearly greater than  $S_{cc}^{id}$  throughout the entire composition of Cd in the Cd–Ga system.

With the exception of the composition range  $0.4 \leq C_{Cu} \leq 0.7$ , in Figure 9 and Part A of Table 4 we notice that there is a good level of agreement between the three results  $S_{cc}^{exp1}$ ,  $S_{cc}^{exp2}$  and  $S_{cc}^{exp3}$  in the rest of the composition of Cu in the Cu–Pb system. This indicates that Equations (1) and (2) give identical results in the Cu–Pb system provided we exclude the composition range  $0.4 \leq C_{Cu} \leq 0.7$ . It is of interest to note that the results for  $S_{cc}^{exp1}$  and  $S_{cc}^{exp2}$  agree with that of Singh and Mishra in [19].

A look at Figure 10 and Part B of Table 4 show that in the composition range  $0.4 \leq C_{In} \leq 0.7$ , the results obtained from each of the three methods are equivalent.

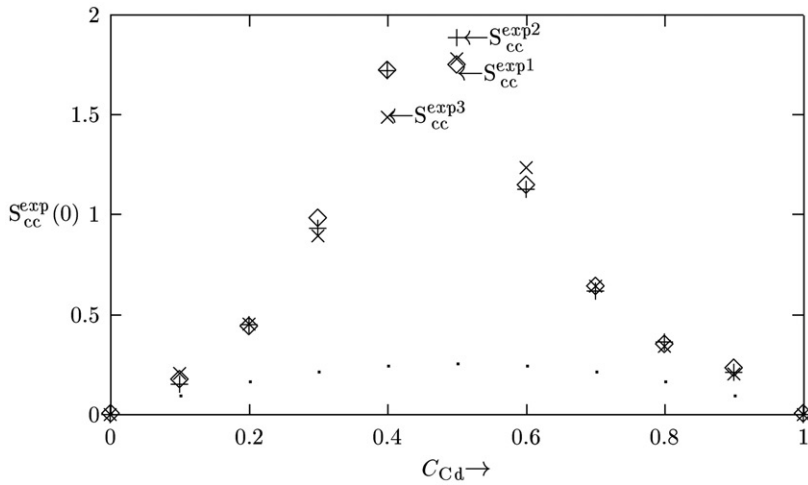


Figure 8. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for Cd–Ga liquid alloy at 700 K. The • represents the ideal values, the ◇ represents the experimental values of concentration fluctuations obtained via activity A of the component atom, (i.e.  $S_{cc}^{exp1}$ ), the + represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the × represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Cd}$  is the Cd concentration in the alloy.

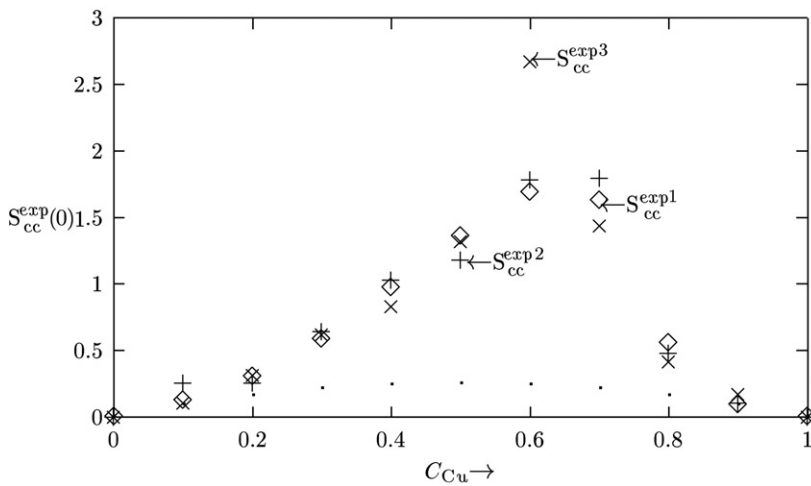


Figure 9. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for Cu–Pb liquid alloy at 1473 K. The • represents the ideal values, the ◇ represents the experimental values of concentration fluctuations obtained via activity A of the component atom, (i.e.  $S_{cc}^{exp1}$ ), the + represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the × represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Cu}$  is the Cu concentration in the alloy.

Table 4. Calculated experimental concentration–concentration fluctuations for Cu–Pb, In–Na and Na–Pb alloys using experimental activities and free energy of mixing obtained from [10]. Diff(i)  $i = 1, 2, 3$  is the difference between  $S_{cc}^{id}$  and respective  $S_{cc}^{exp(i)}$  ( $S_{cc}^{exp1}$ ,  $S_{cc}^{exp2}$  and  $S_{cc}^{exp3}$  represent values obtained from activity components  $a_A, a_B$  and free energy of mixing,  $G_M$  respectively).  $C_{Cu,In,Na}$  is the concentration of Copper, Indium and Sodium in their respective alloys.

$C_{Cu,In,Na}$	Part A: Cu–Pb at 1473K			Part B: In–Na at 713K			Part C: Na–Pb at 700K		
	Diff1	Diff2	Diff3	Diff1	Diff2	Diff3	Diff1	Diff2	Diff3
0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.1	0.034	0.165	0.017	130.327	-0.131	-0.040	0.128	0.022	-0.018
0.2	0.142	0.097	0.152	-0.102	-0.231	-0.220	0.109	0.104	0.091
0.3	0.372	0.433	0.410	0.019	0.058	0.025	0.139	0.152	0.150
0.4	0.728	0.791	0.592	0.134	0.134	0.136	0.188	0.183	0.186
0.5	1.107	0.929	1.067	0.171	0.164	0.170	0.205	0.198	0.203
0.6	1.446	1.543	2.432	0.166	0.166	0.165	0.198	0.197	0.199
0.7	1.415	1.587	1.225	0.133	0.139	0.134	0.172	0.181	0.175
0.8	0.392	0.319	0.256	0.078	0.056	0.081	0.130	0.448	0.130
0.9	-0.001	0.015	0.081	0.034	0.058	0.012	0.071	0.089	0.063
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

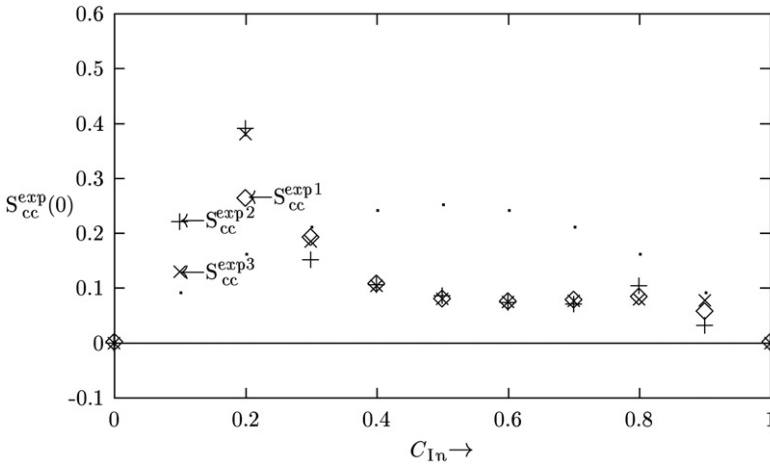


Figure 10. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for In–Na liquid alloy at 713 K. The • represents the ideal values, the  $\diamond$  represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{exp1}$ ), the + represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the  $\times$  represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{In}$  is the In concentration in the alloy.

However, outside this composition range there exists a significant disparity in the results. Thus, it can be said that Equations (1) and (2) hold for the composition range  $0.4 \leq C_{In} \leq 0.7$  in In–Na liquid alloy.

Figure 11 and Part C of Table 4 reveal that the results obtained via the three methods are equivalent in the entire composition of Na in the Na–Pb system except

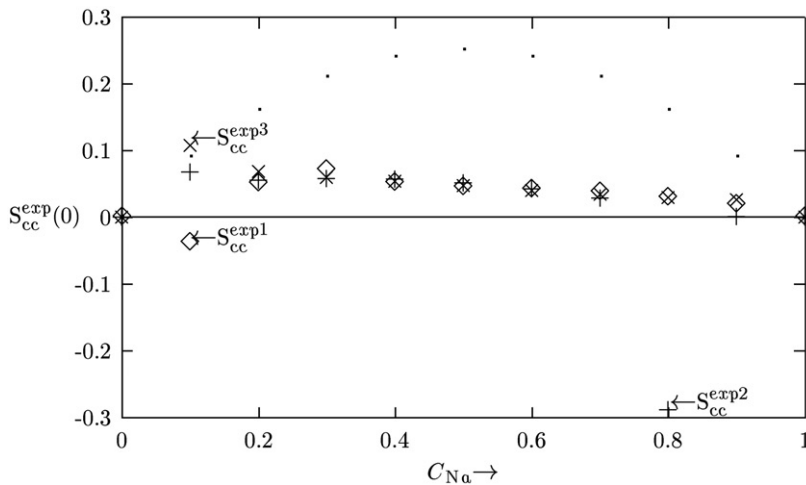


Figure 11. Experimental concentration–concentration fluctuations,  $S_{cc}^{exp}(0)$  vs. concentration for Na–Pb liquid alloy at 700 K. The  $\bullet$  represents the ideal values, the  $\diamond$  represents the experimental values of concentration fluctuations obtained via activity A of the component atom (i.e.  $S_{cc}^{exp1}$ ), the  $+$  represents the experimental values of concentration fluctuations obtained via activity B of the component atom (i.e.  $S_{cc}^{exp2}$ ), while the  $\times$  represents the experimental values of concentration fluctuations obtained via the free energy of mixing,  $G_M$  (i.e.  $S_{cc}^{exp3}$ ).  $C_{Na}$  is the Na concentration in the alloy.

at  $C_{Na}=0.1$  and  $C_{Na}=0.8$ , where the values of  $S_{cc}^{exp1}$  and  $S_{cc}^{exp2}$  are, respectively, negative. Being so, it follows that Equations (1) and (2) hold in the Na–Pb system, with the exception of composition  $C_{Na}=0.1$  and  $C_{Na}=0.8$ . We observe that there is a strong deviation from the ideal mixture in this alloy, as reported in [5].

#### 4. Concluding remarks

This study has revealed, contrary to the belief that the  $S_{cc}^{exp}(0)$  of liquid binary alloys can be computed via the experimental free energy of mixing or experimental activities using Equations (1) and (2) within a given set of data for experimental  $G_M$ ,  $a_A$  and  $a_B$  obtained from a 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 [5]) that:

- (1) There are only two instances where the  $S_{cc}^{exp}(0)$  obtained via each of the three methods agrees completely throughout the entire composition (these are Ag–Ge and Bi–Cd in Figure 2 and Figure 6, respectively).
- (2) There are nine instances where  $S_{cc}^{exp}(0)$  obtained via each of the three methods have partial agreement instead of complete agreement (these are Ag–Al, Al–Au, Al–In, Au–Ni, Bi–Zn, Cd–Ga, Cu–Pb, In–Na and Na–Pb in Figures 1, 3–5, 7–10 and 11, respectively). Hence, in our view the partial agreement might suggest that there are instances where the equality signs in Equations (1) and (2) would be better taken as equivalence.

- (3) There are two instances where  $S_{cc}^{\text{exp}}(0)$  obtained via activity  $a_A$  appear to be more reliable than via activity  $a_B$  or via  $G_M$  (these are Bi–Zn and Cu–Pb in Figures 7 and 9, respectively).
- (4) There is only one instance where  $S_{cc}^{\text{exp}}(0)$  obtained via activity  $a_B$  appears to be more reliable than via activity  $a_A$  or  $G_M$  (this is in Ag–Al in Figure 1).
- (5) There are no instances where  $S_{cc}^{\text{exp}}(0)$  obtained via  $G_M$  appears to be more reliable than via either of the two activities.

Although our observations, as presented in (1)–(5) above, have been based on what resulted from our use of a given set of data for each alloy and not differing sets of data, we are hopeful that this is in no way a strong constraint against the reliability of our observations due to the following reasons:

- (i) Different sets of data for a system may not be available and where available may not necessarily agree throughout the entire composition, as in [5].
- (ii) The set of data used for all the alloys we worked on was taken from a well cited source [10] that has been referenced for decades.
- (iii) The essence of this work is to find out to what extent the results obtained from Equations (1) and (2) agreed within a given set of data, as expected in [1,2,6,7,16].

In conclusion, we would like to recommend that whenever  $S_{cc}^{\text{exp}}(0)$  is needed, the common practice of obtaining it via experimental activity  $a_A$  should be seen as the only reliable method. This is because experimental activity  $a_A$  is obtained directly from experiments [20,21], unlike the other two methods, whose results could be influenced by Gibbs–Duhem integration. In addition, whenever the  $S_{cc}^{\text{exp}}(0)$  obtained via experimental activity  $a_A$  does not agree with other thermodynamic result(s), it is better to consider the option of substituting the theoretical model in use or the alloy of interest than to re-calculate  $S_{cc}^{\text{exp}}(0)$  via either experimental activity  $a_B$  or experimental  $G_M$ .

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