THE STUDY OF CONDITIONAL PROBABILITIES AND THERMODYNAMIC PROPERTIES OF NA-K AND GA-ZN LIQUID ALLOYS

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ABSTRACT
A model based on the calculation of conditional probabilities has been used to gain further insight into the study of energetics of Na-K and Ga-Zn liquid alloys. The model refers to as four atom cluster model enables us to observed feature of these alloys. Our calculations yield for both alloys, agreement with the experiment about the concentrations at which segregation occurs in both alloys.also the degree of segregation in Na-K is larger than Ga-Zn.
Keywords: Ordering Energy, activity, chemical short-range order, Four-atom cluster model.

INTRODUCTION
The study of thermodynamics quantities and by extension ordering phenomena has engaged the attention of physicist for the past few years. These investigations were initially mainly from the point of view of experiment and theoretical formulations/models [1-3]. In recent times, computer simulations have further helped to gain more insight into the problem. Depending on the intricacies of the models, one usually ends up with some parameters to be fitted to some experimental data [4].

For binary alloys, severe limitations in explaining results usually come up in situations were there in formation of complexes and ideal one has to seek recourse to computationally more demanding Car-Parrinello type of simulations. The present paper is an attempt to explain ordering phenomena in Na-K and Ga-Zn alloys using the Singh [2] model. The model has been used to a large extent [4, 12] in explaining the thermodynamics properties of molten alloys with considerable success. On the other hand, the thermodynamic model can readily be used to extract the microscopic chemical structure of such liquid alloys [3].

Singh and Mishra [1] formulated a model based on a cluster of two-atom interacting via pairwise interaction. They were able to obtain analytical expressions for conditional probabilities (i/j), the probability of finding i atom as the nearest neighbour of a given j atom in terms of activities and ordering energy. From their calculations it was possible for them to obtain activity ratio, excess free energy of mixing, concentration-concentration fluctuation in the long wavelength limit and chemical short-range order parameter for some liquid binary alloys.

Singh [2] extended the model to a cluster of four atoms with a view to obtain higher order conditional probabilities enumerating the atomic distributions in the nearest neighbour shell.

The four-atom cluster model referred herein as FACM has been used in this work. To achieve these, the essential interaction parameters for the model has been chosen to reproduce experimental excess free energy of mixing., concentration-concentration fluctuation in the long wavelength limit, the pairwise conditional probabilities and short range order parameter for three binary systems.. The binary systems chosen are Na-K (at 384K) and Ga-Zn (at 750K).

The choice of these two alloys is based on the premise that they represented different classes of binary liquid alloys and the required experimental data on thermodynamic properties for these alloys are available [6].

In addition the alloys or the individual constituent elements of our chosen candidates are known for their industrial relevance, some of the important uses of these materials are:

- Gallium is useful as thermometric liquid and doping semiconductors and production of solid-state devices like transistors while Zinc is used to produce die-castings [7].
- Sodium is used as a heat transfer fluid in some types of nuclear reactor and inside the hollow valves of high performance internal combustion engine while potassium is used to fit glass which is much stronger than regular glass and Na-K is used as heat transfer medium and can also be used as a desiccant for producing dry and air free solvent [7].

In the next section the formalism of the FACM is discussed, the results are discussed in section 3 while final section gives a summary of the conclusion.

BASIC FORMALISM OF FOUR-ATOM CLUSTER MODEL

If the existence of a binary alloy consisting of N atoms of which $N_A = N_C$ are A atoms and $N_B = N(1-c)$ are B atoms is assumed, then, the grand partition function Ξ

$$\Xi = \sum q_A^{N_A}(T) q_B^{N_B}(T) e^{\beta(\mu_A N_A + \mu_B N_B)} e^{-\beta E} \qquad \text{Where} \quad \beta = \frac{1}{k_B T} \qquad (2.1)$$

$q_i(T)$ are the partition functions of atoms i (A or B) associated with inner and vibrational degrees of freedom, μ_A and μ_B are chemical potentials of A and B atoms E is the configurational energy where E_i (i=1,2) are the configurational energies of domain i and E_{12} take into account of the interaction between atoms of cluster and the remainder in order to solve equation (2.1) above the following assumptions were necessary [2]: These are (1) that the interactions between the atoms are of short range order and effective between nearest neighbours only and (2) The atoms are located on the site of a lattice and each site has Z nearest neighbours. The whole set of lattice is further divided into a small cluster of just a few lattice sites and the remainder. To facilitate the cluster were referred by suffix 1 (or domain1) and the remainder by suffix 2 (or domain2).

In line with the aforementioned assumptions, we could define parameter P_{ij} and ε_{ij} (the bond energies for i-j nearest neighbour bonds such that

$$P_{ij} = e^{-\beta \varepsilon_{ij}}, \qquad (i, j = A, B) \qquad (2.2)$$

Further simplification [2] will give rise to an expression of the form

$$\sigma^{12} - B\,\sigma^9 - B_2 \sigma^6 - B_3 \sigma^3 - B_4 = 0 \qquad (2.3)$$

$$\sigma = \frac{\phi_B}{\phi_A}\left(\frac{P_{AA}}{P_{BB}}\right) \tag{2.4}$$

$$B_1 = \frac{(1-3x)}{\eta^3} \tag{2.5}$$

$$B_2 = \frac{3x(1-x)}{\eta^4} \tag{2.6}$$

$$B_3 = 3x^2\frac{(1-x/3)}{\eta^4} \tag{2.7}$$

$$B_4 = x^3 \tag{2.8}$$

$$x = \frac{c_B}{c_A} = \frac{1-c}{c}, \qquad \eta = \exp\left(\frac{\beta\omega}{z}\right) \tag{2.9}$$

Where $\omega = Z(\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2)$ is usually called interchange energy for the alloy.

An expression which connects activity a to σ was obtained [2] and is given in equation (2.10) below

$$c_A f_1(a,\sigma) = c_B f_2(a,\sigma) \tag{2.10}$$

Where

$$f_1(a,\sigma) = a^4\sigma^{4(Z-3)} + \frac{3a^3\sigma^{3(Z-3)}}{\eta^3} + \frac{3a^2\sigma^{2(Z-3)}}{\eta^4} + \frac{a\sigma^{(Z-3)}}{\eta^3} \tag{2.11}$$

$$f_2(a,\sigma) = \frac{a^3\sigma^{3(Z-3)}}{\eta^3} + \frac{3a^2\sigma^{2(Z-3)}}{\eta^4} + \frac{3a\sigma^{(Z-3)}}{\eta^3} + 1 \tag{2.12}$$

So if σ is known then activity a can be obtained from equation (2.10) above

Even in the framework of this model, the probability of finding an A atom or B atom on any lattice site still depends on the nature of atoms already present on the neighbouring sites. We define (A, A, A, A) as the probability that all four lattices sites of the cluster are occupied by atoms A and similarly others. Some other probability say (i, j, k, l) can further be reduced [1] to higher-order conditional probabilities (HOCP) (i/iji) (the probability of finding I atom on a given lattice site while the other sites in the cluster are occupied by i, j and i atoms) similarly others. With this in mind, one can express the probability P_{AB} using the laws of probabilities as,

$$P_{AB} = (A/B) = \left(\frac{(A/BB)}{(B/AB)+(A/BB)}\right) \tag{2.13}$$

Where (A/BB) and (B/AB) is defined in terms of (HOCP) as follows

$$(A/BB) = \left(\frac{(A/BBB)}{(B/ABB)+(A/BBB)}\right) \tag{2.14}$$

$$(B/AB) = \left(\frac{(A/AAB)}{(B/AAB)+(A/BBB)}\right) \tag{2.15}$$

The relevance of eqn (2.14) and (2.15) to this model is that they can be expressed in terms of a and σ. [8]

$$(A/BBB) = \frac{1}{1+a\sigma^{(Z-3)}\exp(3\beta\omega/Z)} \tag{2.16}$$

$$(A/ABB) = \frac{1}{1+a\sigma^{(Z-3)}\exp(\beta\omega/Z)} \tag{2.17}$$

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$$(A/AAB) = \frac{1}{1 + a\sigma^{(Z-3)}\exp(-\beta\omega/Z)} \qquad (2.18)$$

Further note that from the simple rules of probabilities

$$(B/ABB) = 1 - (A/ABB) \text{ and } (B/AAB) = 1 - (A/AAB) \qquad (2.19)$$

With the knowledge of eqs. (2.16)-(2.18) we can then obtain the value of P_{AB} defined in eq. (2.13).

The Warren-Cowley short range order parameter α_1 for the first coordination shell could be defined as [9]

$$\alpha_1 = 1 - \frac{P_{AB}}{c} \qquad (2.20)$$

Where P_{AB} is the probability that of finding A atom as nearest neighbour to B atom. Bhatia and Singh [10] showed that the boundaries value of α_1 lie in the range

$$\frac{-c}{1-c} \quad \leq \quad \alpha_1 \quad \leq \quad 1 \qquad c \leq \frac{1}{2} \qquad (2.21)$$

$$\frac{1-c}{-c} \quad \leq \quad \alpha_1 \quad \leq \quad 1 \qquad c \geq \frac{1}{2} \qquad (2.22)$$

For equiatomic concentration $\left(c = \frac{1}{2}\right)$ α_1 attain its lower and upper limit values i.e. $-1 \leq \alpha_1 \leq 1$. The Lower limit i.e. $\alpha_1^{\min} = -1$ means total order as A-B pairs of atoms as nearest neighbour, whereas $\alpha_1^{\max} = 1$ suggests segregation leading to the formation of a-rich phase and b- rich phase in the binary alloys.

Using the standard thermodynamic relation an analytic expression for the energy of mixing known as Gibb's free energy of mixing could easily be obtained [1]. An expression for G_m^{xs} as given by Fowler and Guggenheim [11] For convenience it can be recorded as;

$$\frac{G_m^{XS}}{Nk_BT} = c\ln\gamma_A + (1-c)\ln\gamma_B \qquad (2.23)$$

Where $a_A = c\gamma_A$ $\quad a_B = (1-c)\gamma_B$

$$\gamma_A = \left(\frac{\beta - 1 + 2c}{c(\beta+1)}\right)^{Z/2} \quad \text{and} \quad \gamma_B = \left(\frac{\beta + 1 - 2c}{(1-c)(\beta+1)}\right)^{Z/2} \qquad (2.24)$$

note $\beta^2 = 1 + 4c(1-c)(\eta^2 - 1)$

G_m referred to as Free energy of mixing is given as

$$G_m = G_m^{id} + G_m^{xs} \qquad (2.25)$$

where $\qquad\qquad G_m^{id} = Nk_BT(c\ln c + (1-c)\ln(1-c)) \qquad (2.26)$

The concentration-fluctuation $S_{cc}(0)$ in the long wavelength limit from a theoretical point of view is more interesting since any deviation from the ideal value of concentration fluctuation is significant in trying to explain the degree of interaction of binary mixtures. The rule is that $S_{cc}(0) << S_{cc}^{id}(0)$ is an indication of strong association or the existence of chemical complexes, while $S_{cc}(0) >> S_{cc}^{id}(0)$ implies a tendency for segregation or phase separation.

The concentration- concentration fluctuations in the long wavelength limit can be obtained from equation (2.25) by using the thermodynamic relations

$$S_{cc}(0) = (RT)^{-1}\left(\frac{\partial^2 G_m}{\partial c^2}\right)_{T,P,N} = (1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} = ca_B\left(\frac{\partial a_B}{\partial(1-c)}\right)^{-1}_{T,P,N} \tag{2.27}$$

The equation (2.27) above shows the concentration fluctuation obtained from observed or experimental activity data and the concentration-fluctuation obtained with these equations is referred to as experimental concentration-fluctuation. This is done in such a way that the experimental activity were fitted to suitable polynomials of varying degrees until computed values were found to be in good agreement with experiments and the required derivatives were taken.

The theoretical concentration-fluctuation is being computed using equation (2.28) below

$$S_{cc}(0) = \frac{c(1-c)}{1 + \frac{Z}{2}\left(\frac{1}{\beta} - 1\right)} \tag{2.28}$$

Note that when $\omega \to 0, \beta \to 1$ and $S_{cc}(0) = c(1-c) = S_{cc}^{id}(0)$

This is known as concentration fluctuation for ideal solution.

Concentration fluctuation is usually understood in terms of deviation from its ideal value given by equation (2.28) above.

Concentration fluctuation is a response function and stability requires it to be positive [8]. A strong response to a concentration-concentration stimulus shows that the system is near phase separation (PS) while weak one indicates compound formation (CF). Put in another form it can be written as

$$S_{cc}(0) = \begin{cases} < S_{cc}^{id}(0) & Heterocoordination\,(CF) \\ > S_{cc}^{id}(0) & Homocoordination\,(PS) \end{cases}$$

RESULTS AND DISCUSSIONS.

The various expressions developed in chapter two are utilized here to compute the concentration dependence of activity ratio (a), conditional probabilities (A\B) and the short range order parameter (α_1) and as well compute their other thermodynamics quantities like excess free energy of mixing $\left(\frac{G_m^{xs}}{RT}\right)$ and concentration fluctuation ($S_{cc}(0)$) using the optimized value of ordering energy or interchange energy ω obtained from the model. The experimental values used in this work have been taken from [6]. Usually in liquid alloy coordination number Z varies from 8-12 [2] but in our calculations it was fixed to 12. It was observed that our choice of Z does not have any significant effect on our results

Table 3.1 below shows that the optimized values of ω for the three alloys.

Table 3.1 SHOWING COORDINATION NUMBER (Z) AND ORDERING ENERGY (ω)

ALLOYS	Z	TEMP(K)	ω(eV)
Ga-Zn	12	750	0.036
Na-K	12	384	0.031

Activity ratio

$$C_{Ga}C_k \rightarrow$$
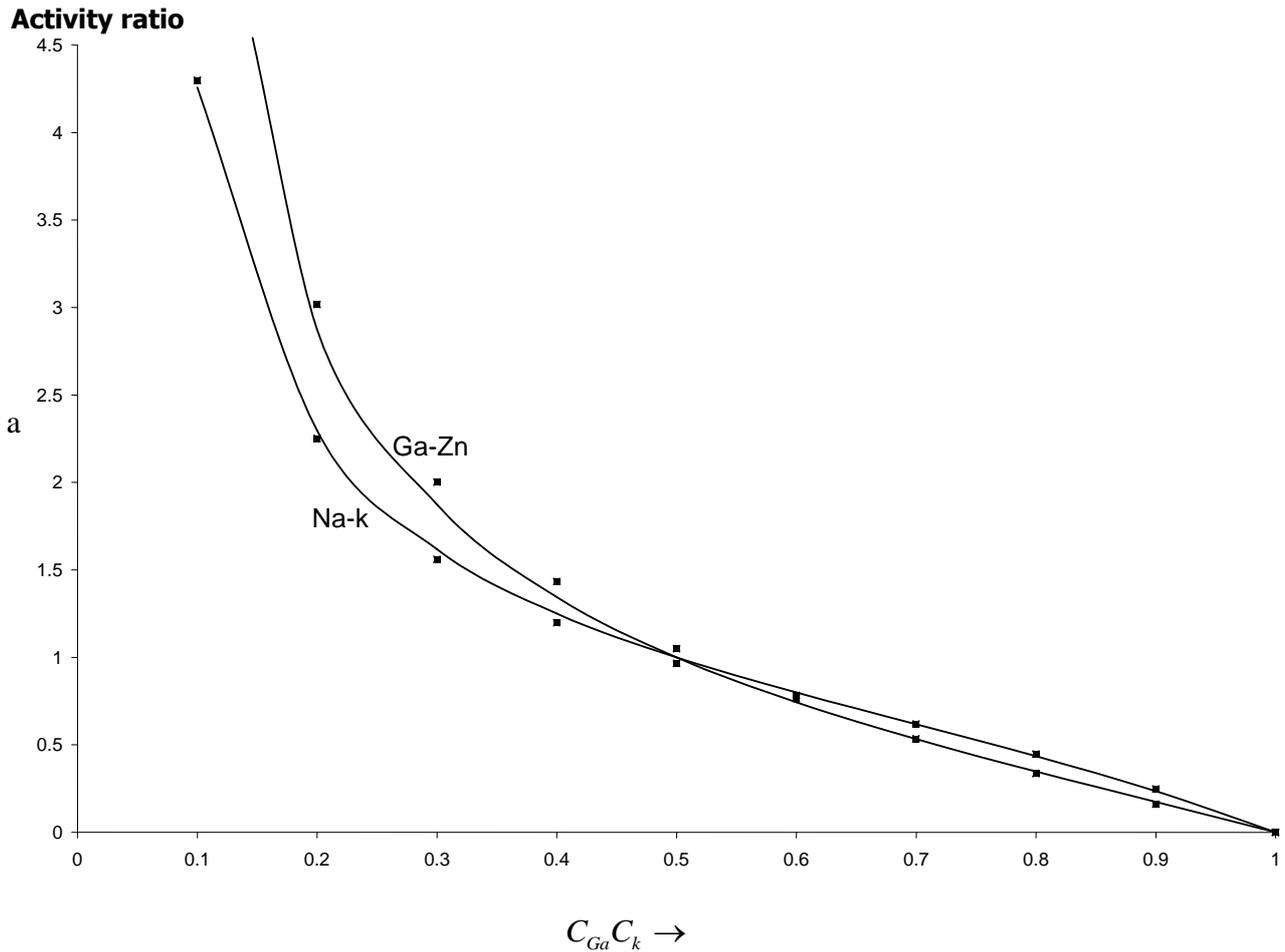
Fig 3.1a   **The graph of activity ratio a vs bulk concentration of Na-K and Ga-Zn alloys Experimental results [6] (Solid dots) and Calculated results (Solid lines)**

Conditional Probability

Table 3.2 Conditional Probabilities for atomic distribution in the nearest neighbour shell

C	Ga-Zn Alloy	Na-K Alloy
0.1	0.09912	0.09846
0.2	0.19687	0.19452
0.3	0.29384	0.28924
0.4	0.39061	0.38364
0.5	0.48778	0.47871
0.6	0.58592	0.57546
0.7	0.68562	0.67491
0.8	0.78747	0.77811
0.9	0.89207	0.88614
1.0	1.00000	1.00000

Short Range Order
The expression for α_1 is given by equation (2.20). The results obtained are shown in fig 3.2
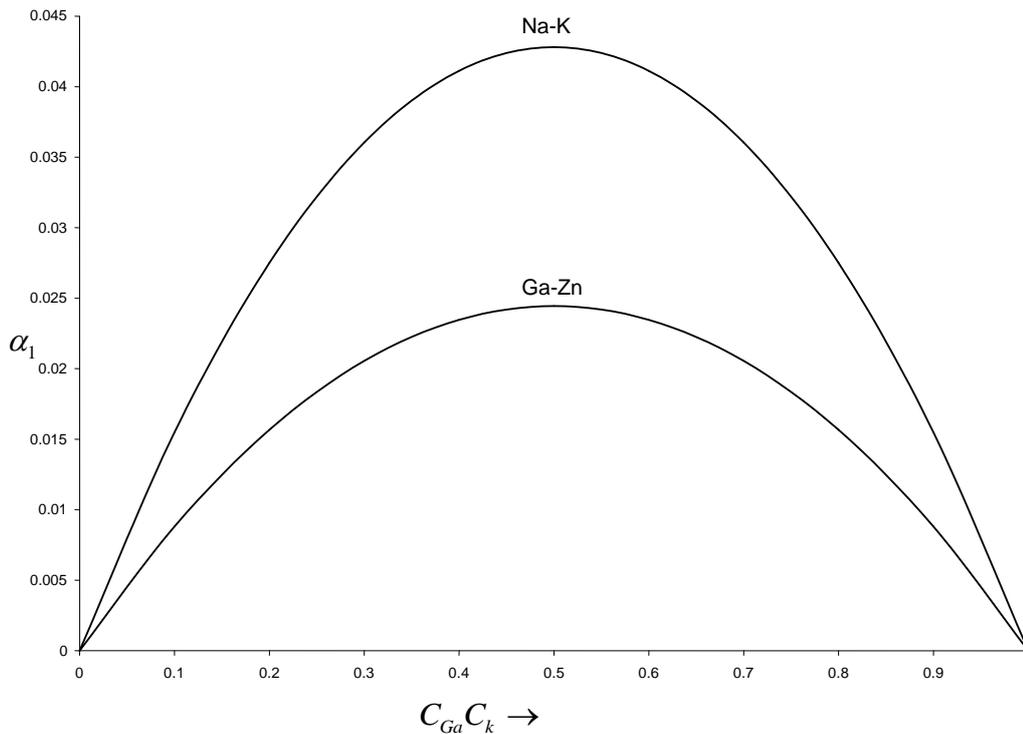
Fig 3.2 Calculated Warren-Cowley short range order parameter α_1 vs. buk concentration for Na-K, and Ga-Zn liquid alloys at 384K and 750K respectively.
Fig 3.2 shows that α_1 for Na-K and Ga-Zn alloys are positive at every composition which indicate tendency of like atoms pairing in the first coordination shell. So therefore they are segregating alloy or homocoordinated system. It could also be said from the figure 3.2 above that the degree of segregation in Na-K alloy is larger than Ga-Zn alloy.

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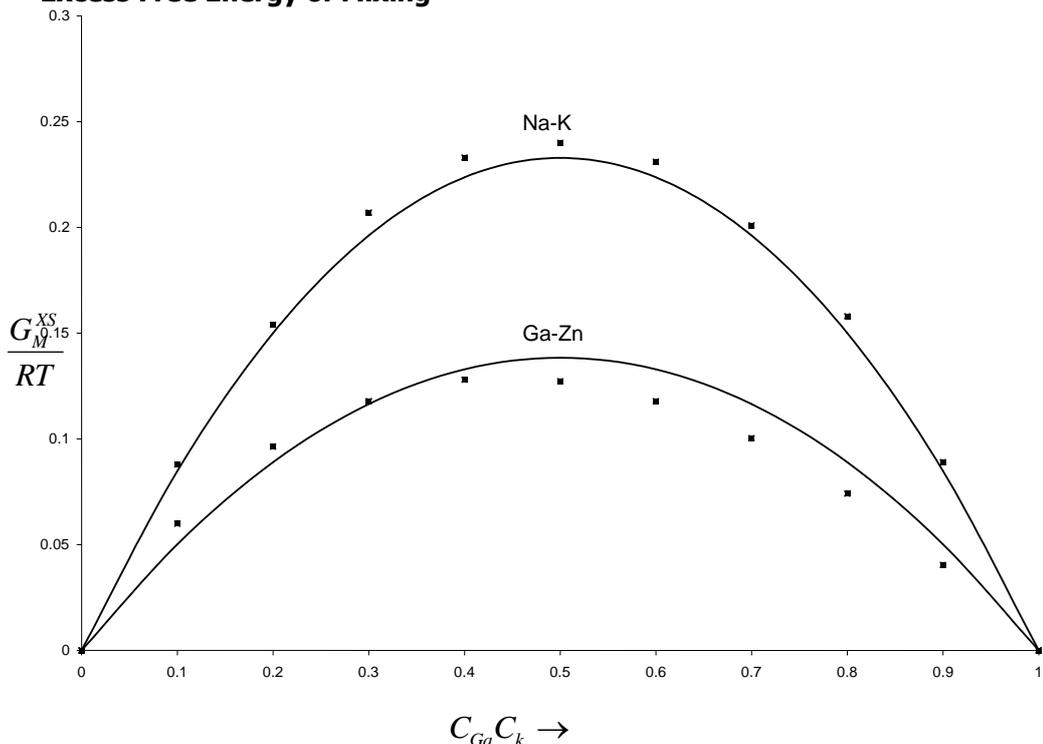**Excess Free Energy of Mixing**

Fig 3.2 The graph of free energy of mixing vs bulk concentration of Na-K and Ga-Zn alloys Experimental results [6] (Solid dots) and Calculated results (Solid lines)
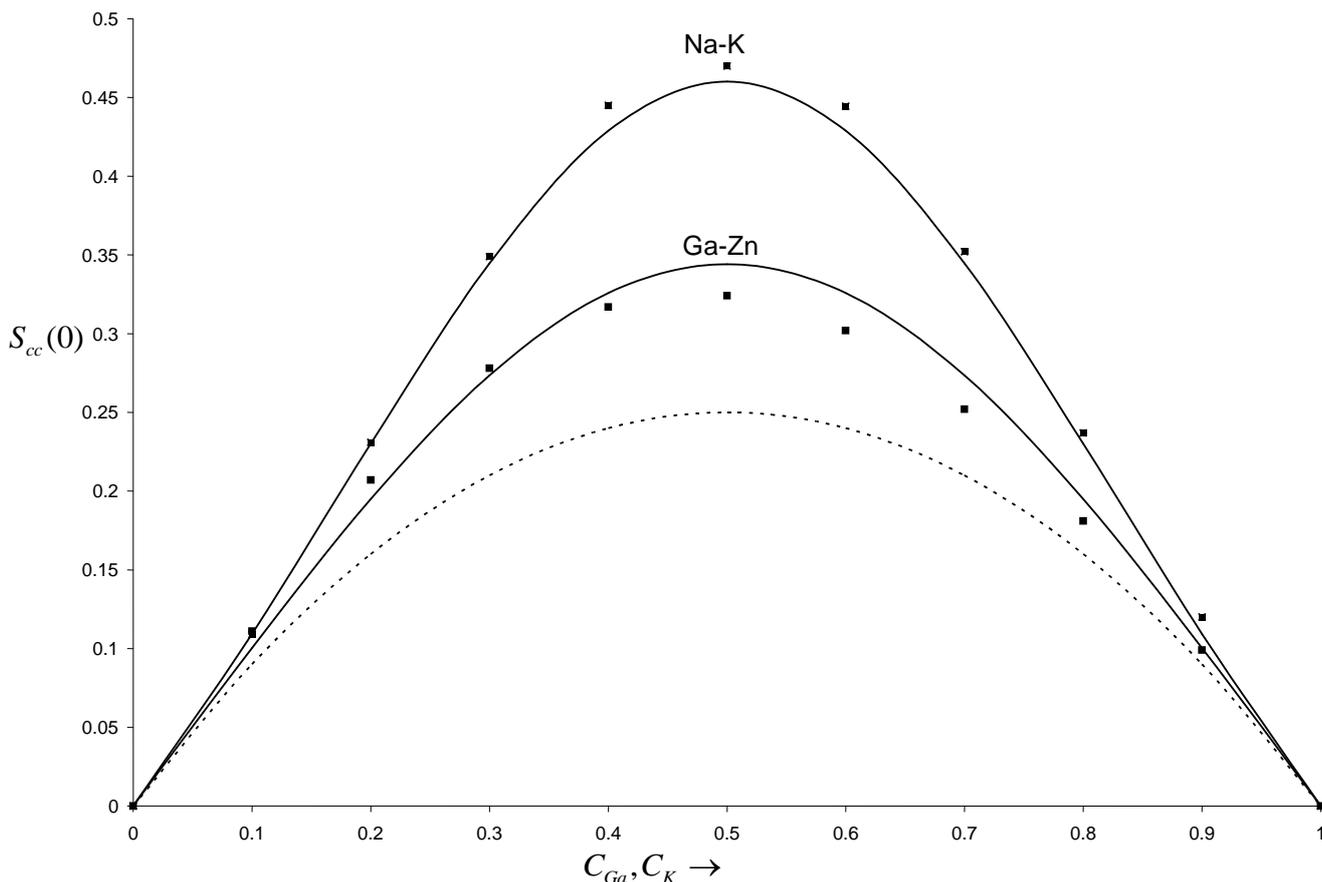
Concentration Fluctuation ($S_{CC}(0)$)

Fig 3.3 The graph of Concentration fluctuation vs. concentration of Na-K and Ga-Zn alloys

> **Experimental results [6,] (Solid dots), Calculated results (Solid lines) ideal values (dots lines).**
> **The results of Gibb's free energy of mixing and concentration fluctuation are also in agreement with our earlier submission that Na-K and Ga-Zn alloys are segregating alloys and that the degree of segregation in Na-K alloy is larger than that of the Ga-Zn alloy.**

CONCLUSIONS

The conditional probabilities and thermodynamic properties of Na-K and Ga-Zn liquid alloys have been determined using FACM. With the fitted values of the ordering or interchange energy ω for the model, the sign of the ordering energy ω obtained for the two alloys indicate that Ga-Zn and Na-K are segregating alloys (they exhibit tendency for phase separation) in ascending order.

The study of energetics effect of the alloys as indicated by our calculations of Gibb's excess free energy and concentration fluctuation corroborate our earlier observation from ordering energy that Ga-Zn and Na-K liquid alloy at 384 and 750 respectively are segregating systems in ascending order. The results obtained from the computation of the warren-cowley short range order parameter α_1 for the two alloys also support our earlier submission.

Our study has confirmed that the thermodynamic properties of binary molten system can be well modeled using the four atom cluster model and results obtained are comparable to those from complex forming theories with more parameters as earlier observed by Akinlade [12] and thus gives a better approach to the processes of compound formation or phase separation in molten binary systems.

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