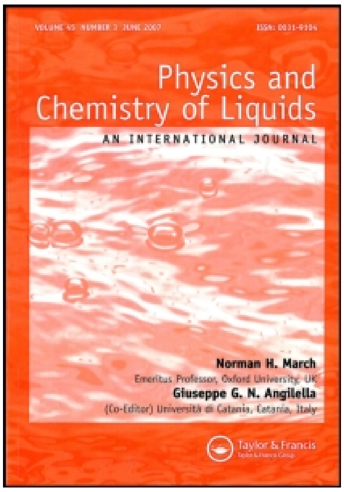

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THERMODYNAMIC INVESTIGATION OF ATOMIC ORDER IN MOLTEN K-Bi ALLOYS

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The assymmetry observed in the concentration dependence of the thermodynamic properties of K-Bi is investigated using an empirical model which assumes a process of heterocoordination. The model is further used to explain the concentration dependence of some thermodynamic properties viz.: free energy of mixing, heat of mixing and the excess entropy of mixing.

Our calculations in most cases yield qualitative agreement with experiment for all quantities investigated and are also used to supplement experimental data. We conclude by stating that the formation of the complex K_3 Bi is of a weak nature in the liquid phase. Compound formation persists at all concentrations but the K-rich end of the phase diagram is more ordered.

KEY WORDS: Order parameter, concentration fluctuation, compound formation.

1. INTRODUCTION

The calculation of thermodynamic properties of binary molten alloys for which there is formation of complexes have been relatively difficult using standard pseudopotential formalism. The usual solution is to use the computationally involved formulations of the Car-Parrinello[1] type. In recent times a number of models have been introduced for such systems[2]. Here, we intend to use the quasilattice model (QLM); this model essentially assumes the existence of privileged groups of complexes $A_\mu B_\nu$ in the molten state, (μ, ν being small numbers which denote the number of A and B atoms respectively in the complex). The compound forming alloys that have been studied are characterized by the formation of compounds at one, or more stoichometric composition, say $C_c = \mu/\mu + \nu$, this information being important in determining values for μ and ν which may also be verified from the fact that $S_{cc}(0)$ has a dip at C_c. An investigation of the stability and thermodynamic properties is initiated by studying the concentration fluctuations $S_{cc}(0)$; this is of immense help in understanding the segregation and extent of local order in binary molten alloys. $S_{cc}(0)$ is also being used[3] to shed light on the phenomenon of easy glass formation where glasses are obtained by quenching the molten alloys.

Here, we study the behavior of an alkali-pnictide alloy, specifically K-Bi. This alloy is interesting for several reasons, one of which is that its excess entropy at 65.5% has a value of ≈ -14 Jmol^{-1}K^{-1} at 873 K[4], one of the most negative entropies measured for liquid alloys. The model used requires for good interpretation, an input of several observable thermodynamic properties of the alloy being investigated. For K-Bi, the fact that all the required inputs are documented for a limited concentration range in ref.[4] makes it an interesting candidate for theoretical investigation. The main line of approach is to determine appropriate values of parameters to model the observed data and then to use those values to predict the results for the other concentration ranges.

The asymmetry in the alloys observed through thermodynamics and structure cannot be ascribed solely to a size effect ($\Omega_{Na}/\Omega_{Bi} \approx 2.2$) though the electronegativity difference of 1.1 on the Pauling scale is moderately high and one can deduce that it is an ionic alloy.

In this paper, the calculated results from the quasilattice model of G_M/RT, H_M/RT, S_M/RT and the $S_{cc}(0)$ for liquid K-Bi alloys are all compared with experiment and useful deductions highlighted. In all cases, the agreement between theory and experiment for calculated quantities was found to be quite satisfactory.

The plan of the present paper is as follows: in the next section we give a summary of the essential equations required for the present calculations. In section 3 we present our results and discussion of calculated thermodynamic quantities, the concentration-concentration fluctuations in the long wavelength limit $S_{cc}(0)$ and the Warren-Cowley[5,6] short-range order parameter α_1. The parameter α_1 is usually a valuable way of illustrating the nature of ordering in liquid alloys. The last section is a summary of the conclusions deduced from the present calculations.

2. THEORY

The theoretical formulations of the QLM has been discussed extensively in the literature[2]; essentially, one starts by assuming that for the particular case of K-Bi, the binary alloy contains in all N atoms, of which N_c are K atoms and $N(1\text{-}c)$ are Bi atoms. Evidence from resistivity measurements[10] indicates that the most stable intermetallic compound occurs at the composition K_3Bi and we assume that this also occurs in the liquid state close to the melting temperature.

On the assumption of this complex K_3Bi, the binary alloy can be assumed to consist of n_1 individual K atoms, n_2 individual Bi atoms and n_3 complexes. From the conservation of atoms, one has

$$n_1 = N_c - 3n_3, \quad n_2 = N(1-c) - n_3 \tag{1}$$

and thus $N = n_1 + n_2 + 4n_3$.

For a ternary mixture in which the constituent atoms are randomly distributed, one can express[7] from a knowledge of the partition function, the Gibbs free energy of mixing of the binary alloys as;

$$G_M = -n_3 g + RT[G_1 - G_2] \tag{2}$$

where

$$G_1 = \left[n_1 \ln\frac{n_1}{N} + n_2 \ln\frac{n_2}{N} + n_3 \ln\frac{4n_3}{N}\right] + \frac{1}{\Psi}\sum_{i<j}\sum n_i n_j V_{ij} \tag{3}$$

and

$$G_2 = \left[\frac{1}{2}Zq_3n_3\ln\frac{4}{q_3} + \frac{1}{2}Z\Psi\ln\frac{\Psi}{N}\right] \tag{4}$$

In Eqns. (3) and (4) $\Psi = n_1 + n_2 + q_3n_3$ and q_3 can be expressed as

$$q_3 = 4 - \frac{6}{Z} \tag{5}$$

Z being the coordination number. Equation (2) as it stands is rather too complicated for easy application. What one does essentially is to use one of the limiting cases, specifically the $Z \to \infty$ limit which corresponds to the Flory's formula; this leads to an expression for G_M that is given by;

$$G_M = -n_3g + RT\left[n_1\ln\frac{n_1}{N} + n_2\ln\frac{n_2}{N} + n_3\ln\frac{4n_3}{N}\right] + \sum_{i<j}\sum\frac{n_in_jV_{ij}}{N} \tag{6}$$

In Eqn. (6), the first term $-n_3g$ represents the lowering of the free energy of mixing due to the formation of complexes K_3Bi, with g representing the free energy of formation of the complex. The V_{ij}'s $(i, j = 1, 2, 3)$ are average interaction energies and by definition independent of concentration, although they may depend on temperature and pressure. With c denoting the concentration of the K atom in the liquid alloy, the equilibrium values of n_3 at a given temperature and pressure can be obtained from the condition

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,N,c} = 0. \tag{7}$$

From Eqns. (6) and (7), the equilibrium value of n_3 is given by the equation

$$\frac{n_1^3n_2^2}{n_3N^3} = 4e^{-3}e^{(Y-g/RT)}, \tag{8}$$

where

$$Y = \frac{[(n_1 - 3n_3)V_{13} + (n_2 - n_3)V_{23} - (3n_2 + n_1)V_{12}]}{RT} \tag{9}$$

From standard thermodynamic relationship, one can write S_{cc} (0) as:

$$S_{cc}(0) = \frac{RT}{(\partial^2G_M/\partial c^2)_{T,P,N}} \tag{10}$$

It can easily be shown[2] that one can write an expression $S_{cc}(0)$ for of the form

$$S_{cc}(0)=\frac{\zeta cc}{1+\Upsilon\zeta cc} \tag{11}$$

where

$$\zeta cc=N\left[\sum_{i=1}^{3}\frac{(n_i')^2}{n_i}-\frac{\frac{1}{2}Z\delta^2(n_3')^2}{\Psi}\right]^{-1}, \tag{12}$$

$$\Upsilon=\frac{2}{N\Psi RT}\sum_{i<j}\sum V_{ij}\left[n_i'n_j'+\frac{\delta n_3'}{\Psi}(n_i'n_j+n_in_j')+\frac{\delta^2(n_3')^2}{\Psi^2}n_in_j\right] \tag{13}$$

and $\delta=6/Z$, the prime on n denotes its derivative with respect to c.

A measure of the tendency to compound formation or phase separation in a liquid alloy is given by the Warren-Cowley short-range order parameter (α_1)[5,6]. This is an important indicator of the degree of ordering in a binary alloy. For nearest neighbour site α_1 can be defined as:

$$\alpha_1=1-\left(\frac{A/B}{(1-c)}\right) \tag{14}$$

where (A/B) is the conditional probability of finding a B atom nearest to a given A atom. It can easily be shown that the limiting values of α_1 lie in the range

$$\frac{-c}{(1-c)}\leqslant\alpha_1\leqslant 1 \quad c\leqslant\frac{1}{2} \tag{15}$$

$$\frac{-(1-c)}{c}\leqslant\alpha_1\leqslant 1 \quad c\geqslant\frac{1}{2} \tag{16}$$

For equiatomic composition $(c=1/2)$, one has $-1\leqslant\alpha_1\leqslant 1$. The minimum possible value of α_1 i. e. $\alpha_1^{\min}=-1$ represents the complete ordering of pairs of nearest neighbour atoms in the A-B configuration whereas $\alpha_1^{\max}=+1$ suggests segregation leading to the formation of A-A pairs or B-B pairs in the alloy. $\alpha_1=0$ corresponds to a random distribution. A more convenient expression for α_1 from a computational point of view is given by[8]

$$\alpha_1=\frac{(S-1)}{S(Z-1)+1}, \tag{17}$$

where

$$S=\frac{S_{cc}(0)}{c(1-c)}, \tag{18}$$

Z being the coordination number of the alloy. These are the essential equations for this model.

3. RESULTS AND DISCUSSION

In applying the QLM, the first step is to determine the interaction parameters g and V_{ij}'s. For this, one proceeds by solving Eqn. (8) for n_3 using Eqn. (1) and then applies expression (6) to fit G_M such that the fitted parameters reproduces as well as can be expected the experimentally measured values. Using this procedure, we obtained the following values for the interaction energies;

$$\frac{g}{RT}=5.5 \quad \frac{V_{12}}{RT}=-9 \quad \frac{V_{13}}{RT}=-45.0 \quad \frac{V_{23}}{RT}=0. \tag{19}$$

Graphs of n_1, n_2 and n_3 are given in Figure 1, while the experimental and fitted values of G_M/RT are given in Figure 2. It is quite obvious that our fitted G_M/RT gives an excellent description of the experimental data.

We have also used the Flory's formula Eqn. (6) to evaluate the concentration dependence of the heat of mixing H_M and the entropy of mixing S_M. Using the nomenclature adopted in this paper, one obtains H_M by starting from the standard

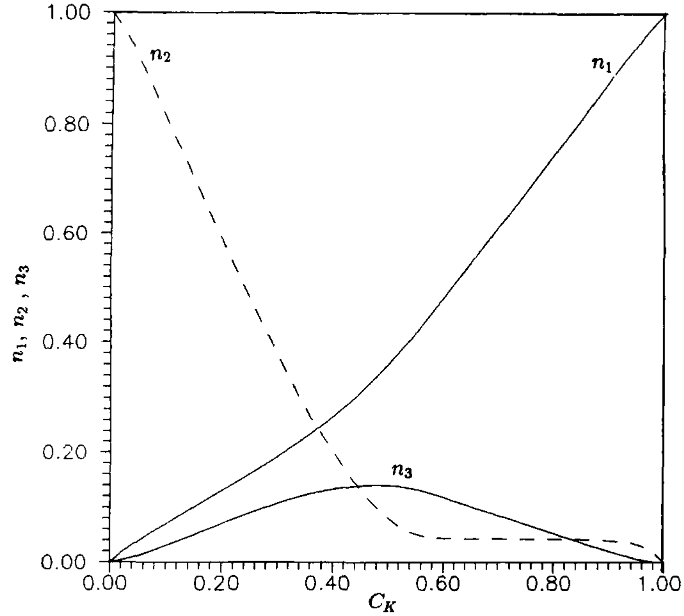

Figure 1 Concentration dependence of n_1, n_2 and n_3 for Ki-Bi molten alloy at 873 K.

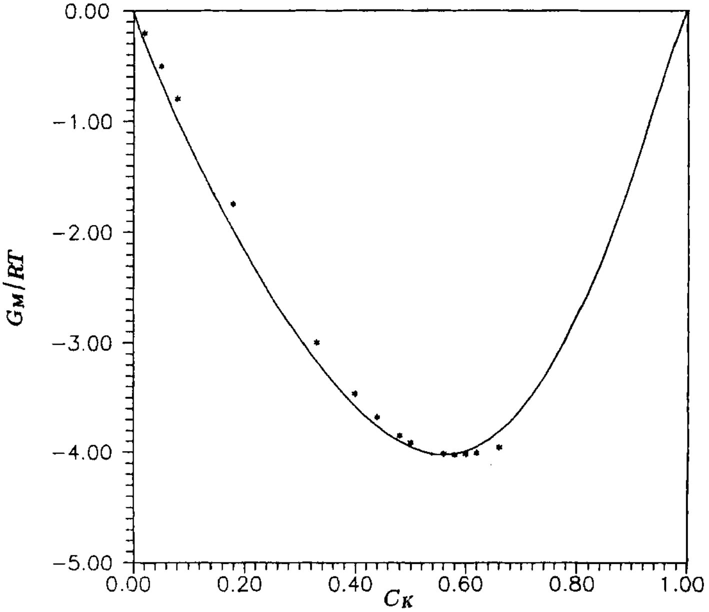

Figure 2 Experimental (stars) and theoretical (solid lines) free energy of mixing G_M/RT.

thermodynamic expression

$$H_M = G_M - T(\partial G_M/\partial T)_{P,C,N}. \tag{20}$$

From Eqns. (6) and (20), one obtains

$$H_M = -n_3\left(g - T\frac{\partial g}{\partial T}\right) + \sum_{i<j}\sum n_i n_j\left(V_{ij} - T\frac{\partial V_{ij}}{\partial T}\right) \tag{21}$$

from which the entropy of mixing can be determined using;

$$S_M = \frac{(H_M - G_M)}{T} \tag{22}$$

It thus follows that by fitting H_M, one can quantify the variation of the interaction parameters with temperature. Equation (21) was used to fit experimental values of H_M and the values obtained for the temperature derivative of the interaction parameters are:

$$\frac{\partial g}{\partial T} = -14.0R \quad \frac{\partial V_{12}}{\partial T} = 0. \quad \frac{\partial V_{13}}{\partial T} = 5.0R \quad \frac{\partial V_{23}}{\partial T} = -R \tag{23}$$

i. e. most of the interaction parameters are significantly temperature dependent. A perusal of the graphs for H_M/RT and S_M/R, with experiment, Figures 3 and 4 this

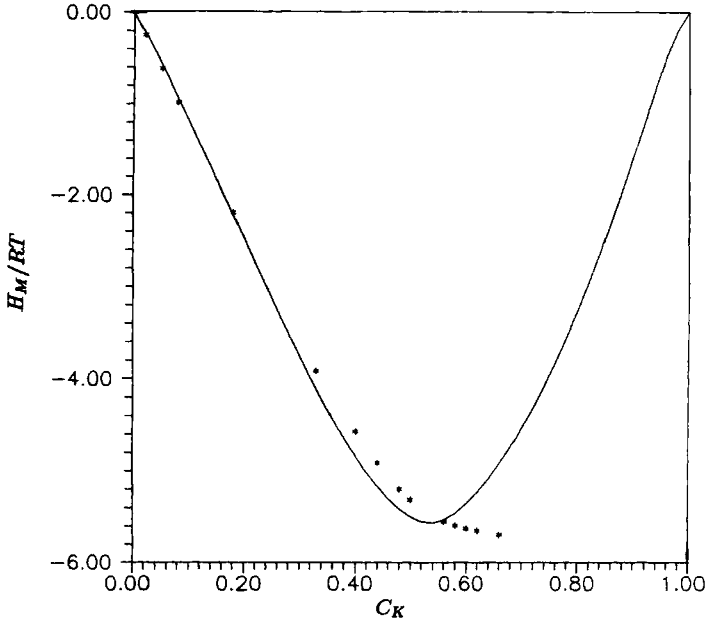

Figure 3 Computed (solid lines) and observed (stars) values of the heat of formation H_M/RT.

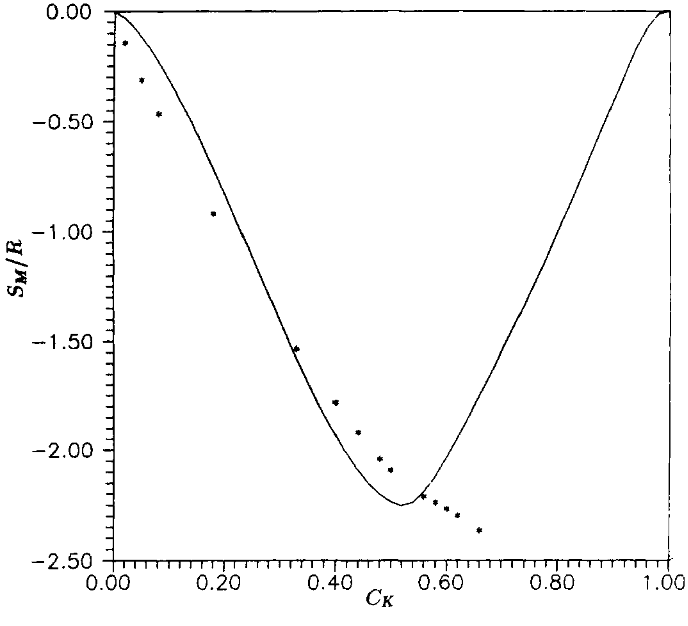

Figure 4 Computed (solid lines) and observed (stars) values of the entropy of mixing S_M/R.

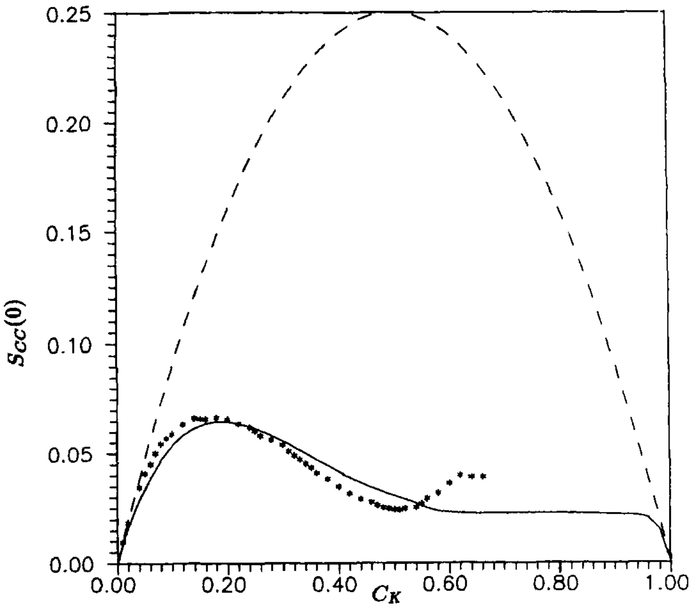

Figure 5 Experimental (stars) and calculated (solid lines) $S_{cc}(0)$ for K-Bi molten alloy, also the ideal values (dashes).

would however contravene the QLM, since the model assumes that the parameters are independent of concentration.

In conclusion one can say that by incorporating the temperature dependence of the interaction parameters, it is possible to give a fair description of the heat of mixing and excess entropy of mixing for K-Bi liquid alloys.

From the point of view of ordering in the liquid K-Bi alloy, the first interesting parameter investigated was $S_{cc}(0)$. Ordering in liquid alloys can be measured from the departure of $S_{cc}(0)$ from the ideal value given by $S_{cc}^{id}(0) = c(1-c)$.

Basically $S_{cc}(0) < S_{cc}^{id}(0)$ is an indication of heterocoordination (preference of unlike atoms to pair as nearest neighbours) while $S_{cc}(0) > S_{cc}^{id}(0)$ implies a tendency for homocoordination (preference for like atoms to pair as nearest neighbours) also called phase separation. The position of the $S_{cc}(0)$ versus c curve yields information on the nature of the complex while its depth signifies strength.

Figure 5 shows a plot of $S_{cc}(0)$ experimental and that derived from Eqn. (11). We have used $z = 12$ since this value is about the order of magnitude expected in liquid binary alloys[9]. From Figure 5 one observes that the calculated $S_{cc}(0)$ is in qualitative agreement, upto $C_K \approx 0.58$ where experimental data indicates a minima while for our calculations there is none observed. We ascribe this discrepancy to the fact there is some form of contradiction, G_M is calculated in the Flory $Z \to \infty$ limit while we have used a finite Z for $S_{cc}(0)$. The calculations are reasonable anyway, and they indicate that K-Bi is compound forming throughout the concentration range.

In order to quantify the degree of ordering in the liquid alloy, we have calculated α_1 using Eqn. (17). Essentially, negative values of α_1 can be interpreted as evidence of

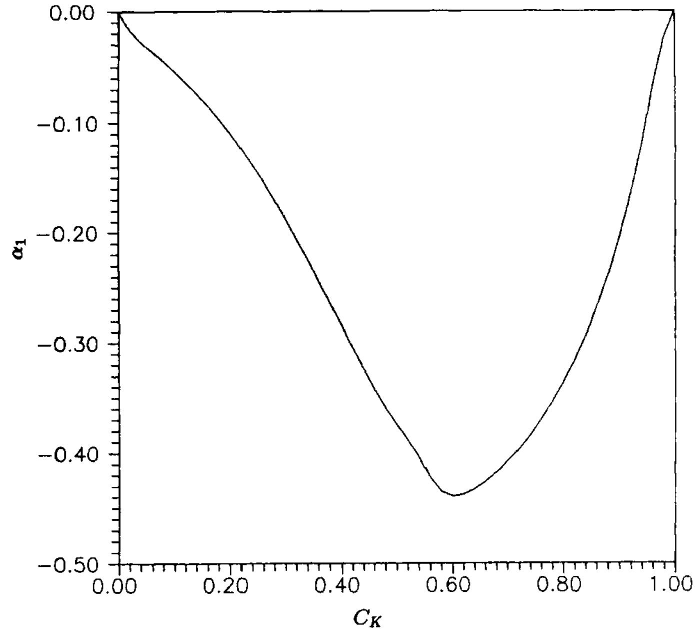

Figure 6 Ordering parameter α_1 for K-Bi as calculated using QLM.

compound formation while positive values indicate a tendency for segregation or phase separation. In practice one can calculate α_1 from measurements of $S_{cc}(q)$ and $S_{NN}(q)$; these measurements are however quite difficult in liquid alloys for which there is tendency for compound formation. For K-Bi molten alloy, there are no experimental values for α_1, however, the graph we have is for $Z = 12$, we note that the effect of Z is to increase the depth of α_1 versus concentration curve, the effect of phase separation or compound formation is not affected. A perusual of Figure 6 indicates interestingly, maximum ordering at about 60% K. Thus by starting with the K_3Bi complex, we still make an observation which is in agreement with experimental resistivity measurements which indicate a weak hump[6] at the same concentration. In general, negative values for α_1 throughout the concentration range indicates compound formation throughout the concentration range as is observed experimentally.

4. CONCLUSIONS

In the present work, a simple model has been used to study the concentration dependence of the thermodynamic properties and ordering phenomena in K-Bi molten alloys. From our calculations we conclude that:

(i) The thermodynamic properties of K-Bi molten alloys exhibit marked deviation from ideal solution behaviour.

(ii) The observed concentration dependent asymmetries can be successfully reproduced by considering the existence of chemical complexes K_3Bi in the molten phases.

(iii) Though the concentration-concentration fluctuations in the long wavelength $S_{cc}(0)$ are lower than the ideal values at all concentrations, it does not exhibit a distinctive minimum at the stoichometric composition; this could be explained on the basis that the formation of the complex K_3Bi is of a weak nature in the liquid phase. Heterocoordination persists at all concentrations but the K-rich end of the phase diagram is more ordered.

(iv) Most of the energy parameters of K-Bi are strongly temperature dependent.

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