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THE STUDY OF THERMODYNAMIC PROPERTIES OF LIQUID NaCs ALLOYS

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ABSTRACT:- *We report detailed thermodynamic properties of Na in molten Na-Cs alloys obtained by using the simple theoretical model of Heterocordination. This model has been utilized to determine the free energy of mixing, concentration fluctuations in the long wavelength limit Scc (0), the Warren Crowley short-range order parameter, heat of mixing, entropy of mixing and diffusion coefficient. From these thermodynamic quantities we find that Na-Cs exhibits strong deviation from ideality at all the composition, therefore, it is truly a demixing liquid alloy. This conclusion was justified by the plot of Scc (0), which showed that its values are far greater than the ideal values. Qualitative agreement between the calculated and the experimental quantities for most of the thermodynamics properties was also obtained for the liquid alloys. These liquid alloys further exhibit a high asymmetry in their thermodynamics properties such as the Gibbs free energy and its diffusion.*

Key words: *Resistance, length, iron content, firing time, firing temperature, particle size*

INTRODUCTION

There has been growing interest in the calculating the properties of Na - Cs alloys. (Bhatia and March 1975; Visser *et al*, 1980; Singh 1981). These model calculations have primarily been concerned with the incipient phase separation in the Na-rich part of the phase diagram. Two origins for the effect have been used. Foremost is the size difference between Na and Cs. (Yih *et al* 1982). A number of recent calculations have revealed considerably improved understanding of the thermodynamics of molten alloys containing strongly interacting metals (Ashcroft and Stroud 1978; Hoshino and Young 1980).

Na-Cs are alkali metals and their alloys have very interesting properties in the liquid state. They occur together in group 1A of the periodic classification, are strong reducing agents, volatile, can be distilled out of the reaction mixtures and obtained as pure products, and are of bright silvery luster characteristics of metals. Na is used as coolant in the valves of internal combustion engines and in nuclear reactors. The cesium is the most metallic and can be used as reductants in laboratory and industrial processes (Fischer *et al*, 1967). Various properties of Na-Cs liquid alloy show anomalous behaviors as functions of concentration. The thermodynamics data also reveal anomalous behavior (e.g., the entropy lies below the ideal mixing value, and Scc (0) lies below the ideal value $c(1 - c)$, the Gibbs energy of mixing is small and less than the ideal magnitude (Yih *et al*, 1982).

The thermodynamic properties of the alloys are important for an improvement in the understanding of the transport properties of these materials, which often form liquid semiconductors (Cutler, 1977). The present interest in these alloys is based on the unavailability of recent experimental results on their thermodynamic properties. The experimental results available are only for a limited concentration range of $0 < c < 0.3$ (Yih *et al*, 1982), where c denotes the concentration of the **A** atom in the alloy. These limitations in the experimental results are due to the nature of the alloys. In this present study we calculate all the investigated quantities for the whole concentration range. An empirical approach which is based on the complex formation model of Bhatia and Singh (1980) using the quasi- lattice approximation has been used in the present work, because of its success in explaining concentration dependence of excess-free energy of mixing and other thermodynamics properties of binary molten alloys.

The layout of our paper is as follows: An introduction; Critical discussion of the complex formation model as applied to Gibb's energy and activity; Results for the concentration -concentration fluctuations Scc (0), the Warren -Cowley short range order parameter and calculation of diffusion coefficients; Discussion of enthalpy and entropy of mixing; Conclusions.

FORMALISM

The fundamental idea is that the properties of a compound forming **A-B** alloy can be explained on the basis of a quasi-lattice model in which the alloy is treated as a mixture of **A** atoms, **B** atoms and $A_\mu B_v$, complexes, all in chemical equilibrium with one another. All the atoms are assumed to be located on the lattice sites.

We assumed that the binary **A-B** alloy consists of pseudoternary mixture $N_A = Nc$, and $N_B = N(1-c)$ g moles of **A** and **B** atoms, and a type of chemical complex. Here μ and v are assumed to be integers, c is the atomic faction of **A** atoms and N is the Avogrado's number. From the complex formation model (Bhatia and Singh, 1980), we assume that the complex Na-Cs is a stable compound in the solid state and also exists as stable compound in the liquid state.

For the present case of Na-Cs, it follows that it consists of n_1 atoms of Na, n_2 atoms of Cs and n_3 moles of the complex NaCs. Thus $\mu = 1$ and $v = 1$. From the conservation of atoms, one has

$$n_1 = c - n_3, n_2 = (1-c) - 3n_3, n = n_1 + n_2 + n_3 = 1 - 3n_3 \quad (1)$$

In the equation, c is taken to be the atomic fraction of Na atoms. The Gibbs free energy of mixing of the binary alloy can be expressed as

$$G_M = -n_3 g + \Delta G \quad (2)$$

Here g is the formation of the complex and the first term in the equation represents the lowering of the free energy due to the formation of complexes in the alloy. ΔG represents the free energy of mixing of the ternary mixture of fixed n_1, n_2 and n_3 whose constituents Na, Cs and NaCs are assumed to be interacting weakly with each other.

The Gibbs free energy of mixing of the binary alloy can be expressed as

$$G_M = -n_3 g + RT(n_1 1\mathrm{n}\ n_1 + n_2 1\mathrm{n}\ n_2 + n_3 1\mathrm{n}\ 4n_3) + \sum_{i \angle j}\sum n_i n_j v_{ij} \quad (3)$$

where 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.

The equilibrium values of n_3 at a given temperature and pressure are obtained from the condition

$$(\delta G_M / \delta n_3)_{T,P,C} = 0 \quad (4)$$

From Eqs. (3) and (4), the equilibrium values of n_3 are given by the equation

$$n_1 n_2 = 2n_3 \exp(-1) \exp\left(Y - \frac{g}{RT}\right) \quad (5)$$

Where

$$Y = \left[(n_1 - n_3)V_{13} + (n_2 - n_3)V_{23} - (n_2 + n_1)V_{12}\right] / RT \quad (6)$$

The expression for the Gibbs free energy of mixing, Eq (3), can be used to obtain an expression for the thermodynamic activity i.e.,

$$RT\ \mathrm{In}\ \alpha_A = \left[G_M + (1-c)(\delta G_M / \delta c)_{T,P,N}\right] / N \quad (7)$$

from which one can write

$$\mathrm{In}\ \alpha_A = 1 - n + 1\mathrm{n}\ n + 1\mathrm{n}\ n_1 + (n_3 V_{13} + n_2 V_{12}) / RT - \sum_{i \angle j}\sum n_i n_j V_{ij} / RT \quad (8)$$

In order to fit parameters for g and V_{ij}, the first thing to do is to calculate the value of g at the chemical concentration $c = \mu / (\mu + v)$ using as a starting point, $g \approx -(\mu + v) G_M$. The energy parameters v_{12} v_{13} and v_{23} are then adjusted in order to reproduce as closely as possible the experimentally measured composition dependence of the Gibbs energy of mixing. Using the above method, we determine the energy parameters for Na-Cs alloys as,

$$g / RT = -1.41, V_{12} / RT = 2, V_{13} / RT = 0, V_{23} / RT = 0 \quad (9)$$

Figure 1 shows that the interaction parameters as given above yield an excellent fit of G_M/RT for liquid Na-Cs alloys at 383 K. We note that the only physically meaningful parameter is *g/RT* because it is a measure of the formation of the complex in the alloy. It is obvious that its value (-0.45 at $C_{Na} = 0.5$) is very low compared with 2.80 for Fe-Al (Akinlade *et al*, 2000) and 47.8 for K-Te (Akinlade, 1994). This is an indication that Na-Cs is a weakly interacting system.

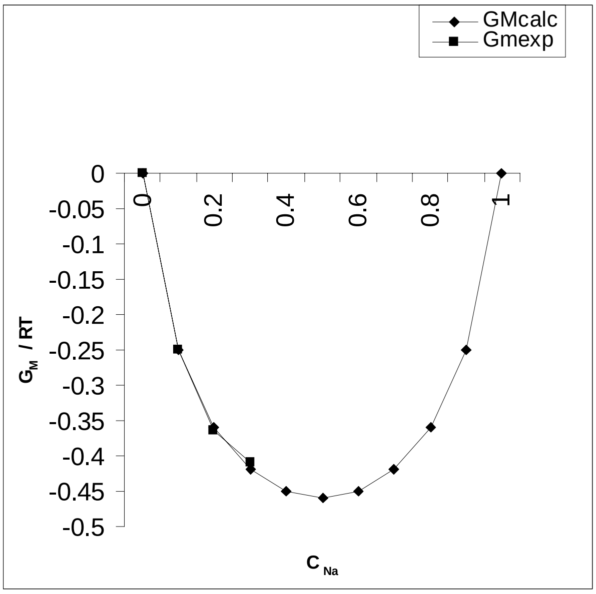

Figure 1. Concentration dependence of the free energy for Na-Cs at 383K

Using the interaction parameters given in Eq. (9) together with Eq. (5) one can obtain numerical values of n_3, the number of chemical complexes, and thus the values of n_1 and n_2 from Eq. (1) above. Utilizing the same values of the interaction parameters we show in Figure 2 a comparison of the experimental and computed values of the activity. It is quite clear that our model parameters give an excellent fit to this quantity.

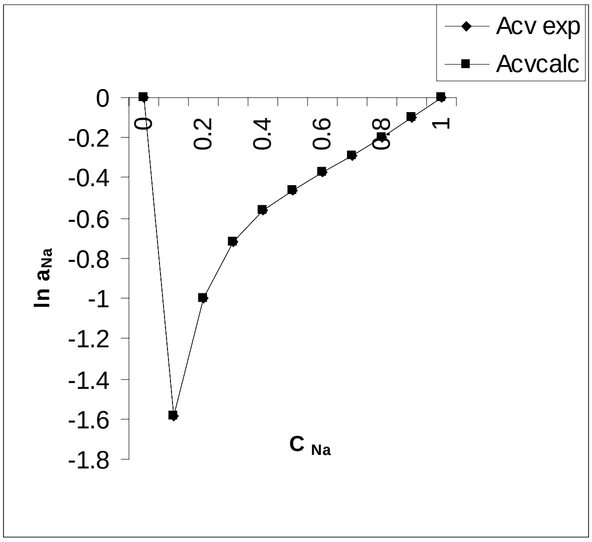

Figure 2. Thermodynamic activity versus concentration for Na-Cs alloys at 383K

RESULTS AND DISCUSSIONS

Concentration fluctuations, chemical short range-order parameter, and chemical diffusion

Our main aim was to investigate the phenomenon of ordering in the binary alloys. The first parameter investigated is the concentration-concentration fluctuation in the long wavelength limit $S_{cc}(0)$. This quantity is of good interest because any deviation from ideal value $S_{cc}^{id}(0) = c(1-c)$ is significant in describing the nature of ordering in a molten alloy. Because $S_{cc}(0)$ is a response function, stability requires it to be positive. A strong response to a concentration-concentration stimulus shows that the system is near phase separation (PS), while a weak one indicates a nearness to compound formation (CF), in other words, $S_{cc}(0) < S_{cc}^{id}(0)$ implies a tendency for heterocoordination (CF) (preference of unlike atoms to pair as nearest neighbours), while $S_{cc}(0) > S_{cc}^{id}(0)$ implies homocoordination (PS) ((preference of unlike atoms as nearest neighbours). For a demixing system, $S_{cc}(0) >> S_{cc}^{id}(0)$. From a theoretical point of view, $S_{cc}(0)$ is important because it is possible to relate it to thermodynamic quantities via the equation

$$S_{cc}(0) = RT\left(\delta^2 G_M / \delta c^2\right)^{-1}_{T,P} \tag{10}$$

The long wavelength limit of the concentration-concentration structure factors $S_{cc}(0)$ can be determined from equations (3) and (13) respectively. Bhatia and Singh (1980) provided a more reliable expression for $S_{cc}(0)$ which involves n_i, its derivative with respect to concentration, v_{ij} and its coordination number Z, thus,

$$S_{cc}(0)^{-1} = \Lambda + Y \tag{11}$$

where

$$\Lambda = \left(\sum_{i=1}^{3} \frac{(n_i)^2}{n_i} - \frac{\frac{1}{2} Z\delta^2 (n_3')^2}{\Phi} \right) \tag{12}$$

and

$$Y = \frac{2}{\Phi RT} \sum \sum_{i<j} v_{ij} \left(n_i' n_j' + \frac{\delta n_3' \left(n_i' n_j + n_i n_j' \right)}{\Phi} \right) + \frac{\delta^2 (n_3')^2 n_i n_j}{\Phi} \tag{13}$$

In the above equation

$$\delta = 6/Z \text{ and } \Phi = 1 - \delta n_3 \tag{14}$$

and the prime on the n' s refers to their first derivative with respect to c.

We note that the Flory approximation for $S_{cc}(0)$ (which is the approximation we have used to express G_M can be obtained simply by putting $Z = \infty$ in the expression above. It follows that by the time the Gibbs's energy of mixing is correctly fitted one would have determined all the parameters needed to compute $S_{cc}(0)$. In the present calculation we have used typical value $Z = 2$ for our calculations.

As for the experimental values of $S_{cc}(0)$ this has been determined from activity data (Yih *et al*, 1982), with the aid of the equation

$$S_{cc}(0) = (1-c)\alpha_A \left(\frac{\delta \alpha_A}{\delta c} \right)^{-1}_{T,P,N} = c\alpha_B \left(\frac{\delta \alpha_B}{\delta (1-c)} \right)^{-1}_{T,P,N} \tag{15}$$

Essentially, all that is required is to perform a polynomial fit to, the experimental data and then taking an analytic derivative as given in equation 15. Values obtained this way are called experimental values of $S_{cc}(0)$.

Figure 3 shows the computed and experimental value of $S_{cc}(0)$ as well as the ideal values. We notice that the alloy Na-Cs is compound forming over the whole composition range, this is because $S_{cc}(0)$ is less than the ideal values at all compositions. Also we notice that experimental and computed values are not in good agreement. This might be due to the fact that G_M is calculated in the $Z = \infty$ limit, while a finite Z is used to compute $S_{cc}(0)$. In addition, the choice of NaCs complex gave the best fits available thermodynamic information and we could not achieve better fits using order complexes.

In order to fit the degree of order in the liquid alloy, (Warren, 1969) and (Cowley, 1950), the short range order parameter α_1 can be determined from knowledge of the concentration-concentration $S_{cc}(q)$ and the number-number structure factors $S_{NN}(q)$. However, in most diffraction experiments these quantities are not easily measurable. On the other hand α_1 can be estimated from knowledge of $S_{cc}(0)$ (Singh *et al*, 1992).

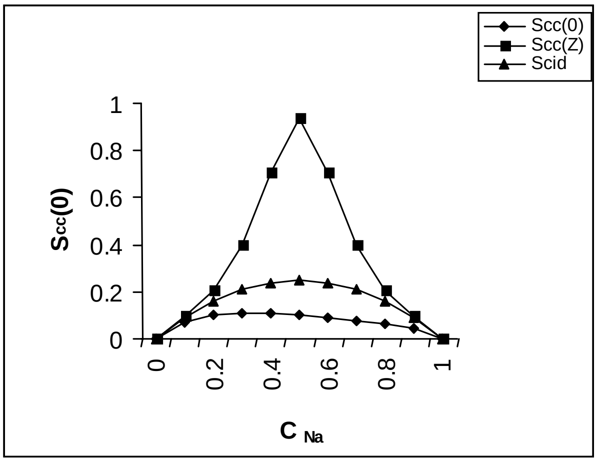

Figure 3: Concentration - concentration fluctuation S_{cc} *(0)*, as a function of concentration in Na-Cs alloys at 383K. S_{cc} *(0)* are the experimental values, S_{cc} *(Z)* the calculated values, and the S_{cid} the ideal values

The knowledge of α_1 provides an immediate insight into the nature of the local arrangements of atoms in the mixture. For nearest neighbour sites, it can be defined as

$$\alpha_1 = 1 - P_{AB} / (1-c) \tag{16}$$

where P_{AB} is the conditional probability of finding **B**-atom next to a given **A** atom. In terms of the unlike atoms equation (16) can be expressed as

$$\alpha_1 = \frac{S-1}{S(Z+1)+1}, S = \frac{S_{cc}(0)}{c(1-c)} \tag{17}$$

Z being the coordination number of the alloy. From a simple probabilistic approach, one can show that the limiting values of α_1 lie in the range

$$\frac{-c}{(1-c)} \le \alpha_1 \le 1, c \le \frac{1}{2} \tag{18}$$

$$\frac{-(1-c)}{c} \le \alpha_1 \le 1, c \ge \frac{1}{2} \tag{19}$$

At equiatomic composition, one has $-1 \le \alpha_1 \le 1$ the minimum possible value of α_1 is $\alpha_1^{\min} = -1$ and implies complete ordering of unlike atoms as nearest neighbours. On the other hand the maximum value $\alpha_1^{\min} = 1$ implies total segregation leading to phase separation $\alpha_1 = 0$ corresponds to a random distribution of atoms.

From Figure 4, which shows the variation of α_1 with composition, we observe that it is positive throughout, showing that Na-Cs is a segregating systems over the whole concentration range and symmetric as a function of concentration. In addition, α_1 is positive throughout with a value much less than 1, this indicates that Na-Cs is a weakly ordered system. We note that varying the value of Z does not have any effect on the position of the minima of α_1; the only effect is to vary the depth while the overall features remain unchanged.

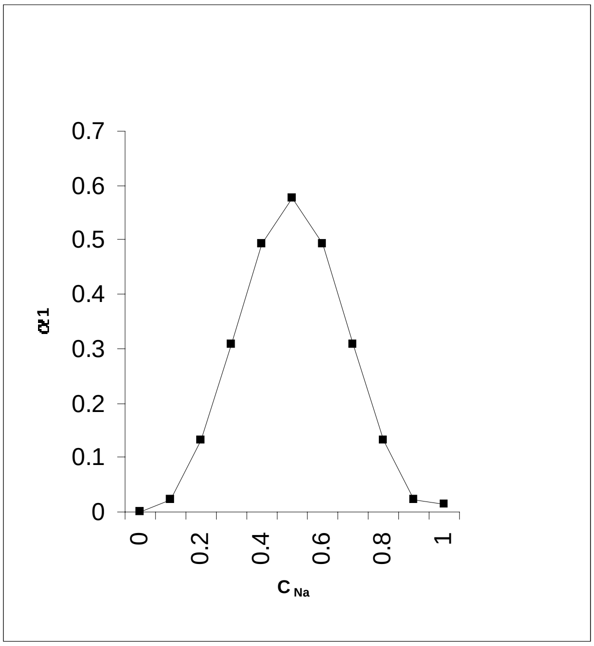

Figure 4: Warren-Cowley short-range order parameter α_1 for Na-Cs at 383K

A great amount of understanding at the microscopic level of atomic interactions in a binary liquid alloy can be gained from knowledge of the dynamic properties of the alloys. Using the thermodynamic equation for diffusion (Darken, 1967), an expression can be found that relates diffusion and S_{cc} *(0)* (Singh *et al*, 1992) thus one can write,

$$\frac{D_M}{D_{id}} = \frac{c(1-c)}{S_{cc}(0)} \tag{19}$$

Here, D_M is the chemical or interdiffusion coefficient and D_{id} is given as

$$D_{id} = cD_B + (1-c)D_A \tag{20}$$

where D_A and D_B are observed tracer diffusion coefficients. With regards to D_M / D_{id}, we note that it approaches 1 for ideal mixing, is greater than 1 for an ordered alloy, and is less than 1 for a segregating systems. The ratio is a better measure of order because it does not have a direct *Z* dependence and thus does not involve discrepancies that could come into play because of the dependence of the results on this quantity. Figure 5, which is a plot of this quantity, shows the existence of maxima at $c_{mm} \approx 0.3$. *D* is close to 1 and is quite asymmetric.

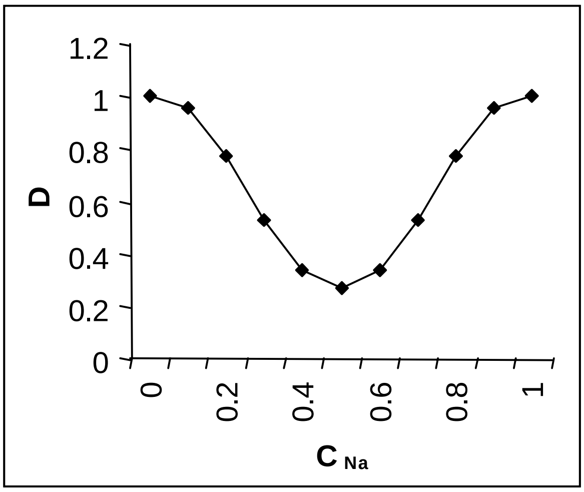

Figure 5 Computed values of the Diffusion D for Na-Cs alloys at 383K

Comparing our structural analysis to that of Yih *et al*, 1982, we state that our thermodynamic calculation does indicate the clear preference for a stable NaCs cluster at a temperature of 383K. We tried all other possibilities but could not achieve any better fits using other complexes. On the other hand, the structural analysis (Yih *et al*, 1982) reveals that the preferred complex at 383K in the melt is NaCs. It may, however, be noted that the stoichometric composition of these two complexes are quite close to each other.

Enthalpy and Entropy of Formation

Within the complex formation model, the evaluation of the enthalpy of mixing is very important because it gives an indication of the temperature dependence of the interaction parameters. The enthalpy of formation H_M can be obtained from the standard thermodynamic expression

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_p \tag{21}$$

From the expression for G_M in Eq. (3), we obtain

$$H_M = -n_3\left(g - T\frac{\partial g}{\partial T}\right) + \sum\sum_{i<j} n_i n_j \left(v_{ij} - T\frac{\partial v_{ij}}{\partial T}\right) \tag{22}$$

and thus the entropy of mixing

$$S_M = \left(H_M - G_M\right)/T \tag{23}$$

From the expression for H_M, it is obvious that in order to obtain a good fit to this quantity, we have to incorporate the temperature dependence of the interaction parameters; any other approximation would be incorrect. Using Eq. (23), we have ascertained the variation in temperature parameters from the observed (Yih T. S. et al 1982) values of H_M, the results are

$$\begin{aligned} &\partial g/\partial T = -0.93,\ \partial v_{12}/\partial T = 0, \\ &\partial v_{13}/\partial T = 0.01,\ \partial v_{23}/\partial T = 0.01 \end{aligned} \tag{24}$$

From the values above, we can deduce that apart from *g*, all the energy parameters have positive temperature coefficients. The fitted results for H_M/RT and the resulting values of S_M/R are shown in Figures 6 and 7 respectively.

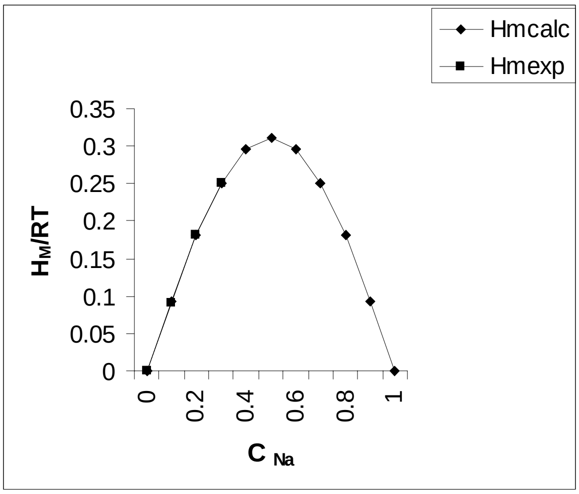

Figure 6 H_m/RT as a function of concentration in Na-Cs alloys at 383K

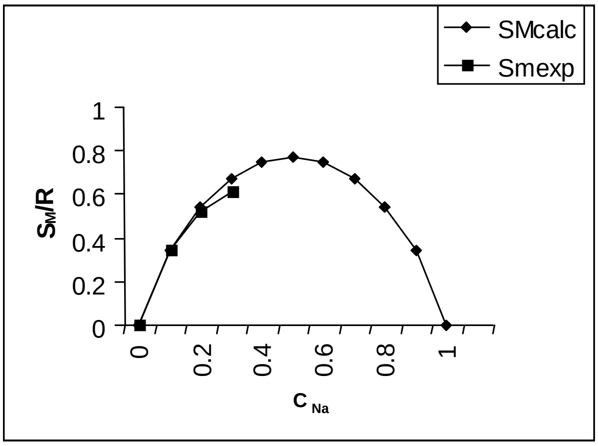

Figure 7: Computed and Experimental values of the entropy of mixing S_m/R for Na-Cs at 383K

It is clear that there is symmetry in measured and observed values of entropy. H_M is positive at all compositions indicating that the NaCs alloys are symmetric and positive (typical of a segregating system) even though its free energy of mixing indicates a very weakly interacting system. Basically, however, the values of experimental and theoretical values obtained using the interaction parameters and their temperature dependence are in very good agreement with experimental data.

SUMMARY AND CONCLUSION

In the present paper we have used the complex formation to obtain the parameters, which fit the experimentally measured G_m/RT values for Na-Cs by assuming the formation of NaCs chemical complex. The concentration dependence of their various thermodynamics quantities has been interpreted. The fitted parameters have been used to compute $S_{cc}(0)$ and the Warren-Cowley short-range order parameter α and Diffusion coefficient. A qualitative agreement has been obtained in most cases for the calculated quantities. The Na-Cs is a weakly hetercoordinated system.

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