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Thermodynamic and structural properties of K-Na liquid alloy

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Abstract
The deviation from ideal mixture behavior and concentration dependent symmetry in thermodynamic and structural properties of K-Na liquid alloy is investigated within a simple statistical model. The concentration dependence of the free energy of mixing, heat of mixing, entropy of mixing, concentration fluctuation in the long wavelength limit, Warren-Cowley short range order parameter, ratio of diffusion coefficients of Potassium-sodium alloy at 384 K and activity of the components has got special attention to show a tendency of like atom pairing in the mixture.

Key words: liquid alloy; simple statistical model; thermodynamic properties; diffusion coefficient

1. Introduction

The properties of mixing of some binary alloys such as, free energy of mixing, heat of mixing, entropy of mixing are symmetrical about the equiatomic composition [1] even though there is large size difference. Such behaviour of these liquid alloys is least understood and demands extensive theoretical investigations. Since long theoreticians [2-8] are trying to interpret the physical properties of liquid alloys so that their alloying behaviour could adequately be understood.

In the present work we intend to explain the alloying behaviour (the free energy of mixing (G_M), heat of mixing (H_M), entropy of mixing (S_M)) of potassium-sodium liquid alloy on the basis of simple statistical model. Thermodynamic parameters give us an idea about the stability and bonding strength of the constituent species of the alloy, whereas structural parameters provide the idea about ordering and segregating nature of the alloy. Some of the properties of mixing of K-Na alloys are symmetrical about equiatomic composition despite the large size difference of Na and K [1].

The outline of the paper is follows: In section 2, general formalism about the theory is presented. Section 3 deals with the result and discussion and conclusion are presented in section 4.

2. Formalism

Simple statistical model developed by Singh and Mishra [8] for the binary liquid alloys is a model in which grand partition function is used. The grand partition function is solved by assuming that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not .The grand partition function for simple binary liquid alloys can be generalized as

$$\Xi = \sum_{E} q_A^{N_A}(T)\, q_B^{N_B}(T) \exp\left(\frac{\mu_A N_A + \mu_B N_B - E}{k_B T}\right) \tag{1}$$

where $q_i^{N_i}$ are the partition functions of atoms ($i = A$ or B) associated with inner and vibrational degree of freedom. q_i is the same whether the atom i is located in the pure state or in alloy. μ_A and μ_B are the chemical potentials; E is the configurational energy; k_B, the Boltzmann constant and T, the absolute temperature. The standard thermodynamical relation for free energy of mixing is [8]

$$G_M = G_M^{XS} + Nk_B T \sum_i C_i \ln C_i \tag{2}$$

But excess of free energy of mixing is

$$\frac{G_M^{XS}}{Nk_B T} = \int_0^C \ln \sigma^z \, dC = C_A \ln \gamma_A + C_B \ln \gamma_B \tag{3}$$

where

$$\sigma = (\beta + 2C - 1)\exp(-w/zk_B T)/2C \tag{3(a)}$$

$$\gamma_A = \left[(\beta - 1 + 2C_A)/C_A(1+\beta)\right]^{z/2} \tag{3(b)}$$

$$\gamma_B = \left[(\beta + 1 - 2C_A)/C_B(1+\beta)\right]^{z/2} \tag{3(c)}$$

$$\beta = \left\{1 + 4C_A C_B\left[\exp(2w/zk_B T) - 1\right]\right\}^{1/2} \tag{3(d)}$$

Using the relations (2) and (3), the free energy of mixing will be

$$G_M = Nk_B T[C(1-C)\frac{w}{k_B T} + C\ln C + (1-C)\ln(1-C)$$

Or,

$$\frac{G_M}{RT} = C(1-C)\frac{w}{k_B T} + C\ln C + (1-C)\ln(1-C) \tag{4}$$

The Warren-Cowley chemical short range order parameter α_1 for the first coordination shell [9,10] in term of w is

$$\frac{\alpha_1}{(1-\alpha_1)^2 C_A C_B} = \exp(2w/zk_B T) - 1 \tag{5}$$

For the equiatomic composition ($C_A = C_B = \frac{1}{2}$), relation (3) reduces to

$$\frac{G_M^{XS}}{Nk_BT} = \ln 2^{z/2}[1+\exp(-w/zk_BT)]^{-z/2} \quad (6)$$

From Eq. (4), the concentration fluctuation in the long wavelength limit becomes

$$S_{cc}(0) = Nk_BT(\frac{\partial^2 G_M}{\partial C^2})^{-1}_{T,P,N} = C_AC_B[1+(z/2\beta)(1-\beta)]^{-1} \quad (7)$$

From Eqs. (5) and (7), it follows that

$$\alpha_1 = (S-1)/[S(z-1)+1] \quad (8)$$

where, $$S = \frac{S_{cc}(0)}{C_AC_B} = \frac{S_{cc}(0)}{S^{id}_{cc}(0)}$$

and z represents the number of atoms in the first coordination shell and is called coordination number.

The heat of mixing of binary liquid alloys can be obtained using the standard thermodynamic relation (4):

$$H_M = G_M - T(\frac{\partial G_M}{\partial T})_{N,P}$$
$$= RT[C(1-C)\frac{w}{k_BT} - C(1-C)\frac{1}{k_B}\frac{dw}{dT}] \quad (9)$$

The entropy of mixing is

$$S_M = -(\frac{\partial G_M}{\partial T})_{N,P} = \frac{H_M - G_M}{T} \quad (10)$$

The activity of binary liquid alloys, ai, can be related to the free energy of mixing by the relation

$$Nk_BT\ln a_i = (\frac{\partial G_M}{\partial N_i})_{T,P,N} \quad (11)$$

The mixing behavior of the alloy forming molten metals can also be studied at the microscopic level in terms of coefficients of diffusion. The Scc(0) and diffusion coefficients can be related using Darken thermo dynamic equation for diffusion [11] as follows:

$$\frac{D_M}{D_{id}} = \frac{S^{id}_{cc}(0)}{S_{cc}(0)} \quad (12)$$

Here D_{id} is the intrinsic diffusion coefficient for an ideal mixture and D_M is the chemical or mutual diffusion coefficient given by

$$D_M = C_AD_B + C_BD_A \quad (13)$$

where D_A and D_B are the self-diffusion coefficients of pure components A and B respectively.

3. Results and Discussion

3.1 Thermodynamic properties

The energy parameter used for the calculation for K-Na liquid alloys at 384K has been determined from experimental value of G_M^{XS} and H_M for equiatomic composition (C =1/2), using the equations (6) and(9) which are found as

$$\frac{w}{k_B T} = 0.989 \quad \text{and} \quad \frac{1}{k_B}\frac{dw}{dT} = 0.077$$

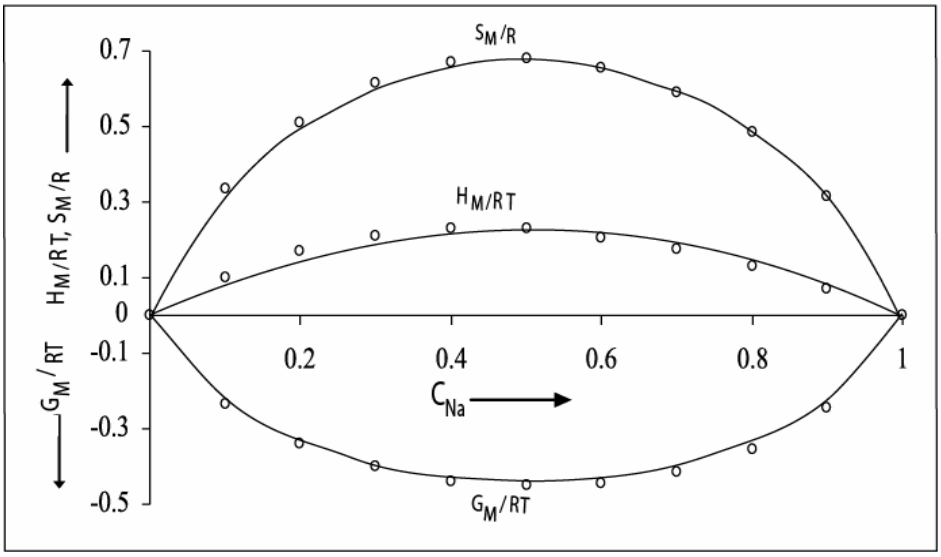

Fig. 1 : Free energy of mixing (G_M/RT) , Heat of mixing (H_M/RT) and Entropy of mixing (S_M/R) versus concentration of Na (C_{Na}) : Theoretical - solid curve; Experimental - circles.

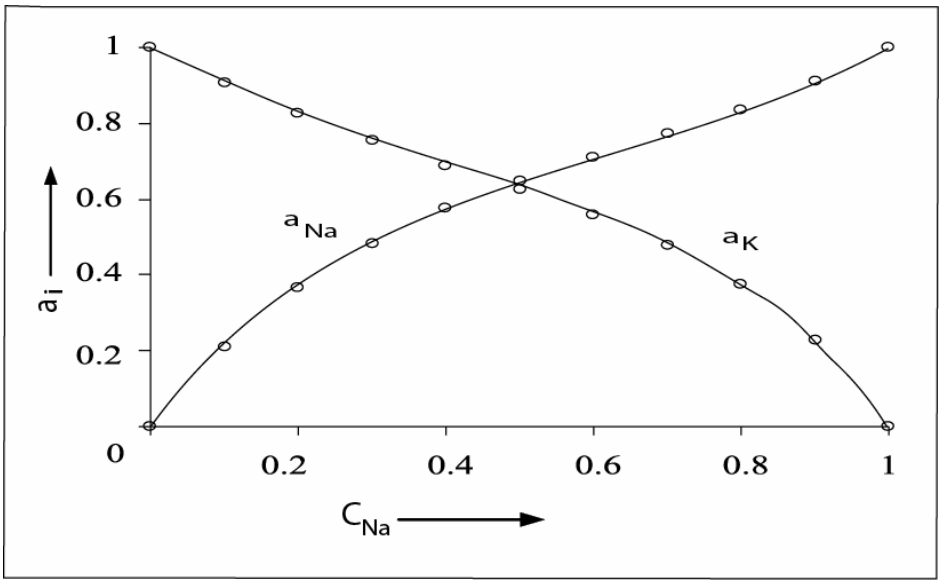

Fig. 2 : Chemical activities (a_i) versus concentration of Na (C_{Na}) : Theoretical - solid curve; Experimental - circles.

The free energy of mixing, heat of mixing and entropy of mixing for K-Na liquid alloy at 384K have been computed from equations (4), (9) and (10). The plot of G_M/RT, H_M/RT and S_M/R versus C_{Na} are depicted in Fig. 1. The theoretical and experimental values of G_M/RT, H_M/RT and S_M/R are in good agreement in all concentrations of Na. G_M/RT is minimum but H_M/RT and S_M/R are each maximum at C_{Na} =0.5, which show that K-Na liquid alloy is symmetric about equiatomic concentration. We have used the same values of the energy parameters in Eq. (11) for the evaluation of chemical activities of the components of the alloy. There is well agreement between experimental and theoretical values of the activities of the components K and Na of the alloy (Fig. 2).

3.2 Structural properties (Microscopic properties)

Using the estimated energy parameter, the theoretical values of $S_{cc}(0)$ are computed from Eq. (7). Fig. 3 shows a plot of the theoretical and experimental values of $S_{cc}(0)$ along with the ideal values. The theoretical values of $S_{cc}(0)$ are in good agreement with the experimental values of $S_{cc}(0)$. The result can be used to understand the nature of atomic order in binary liquid alloys. At a given composition if $S_{cc}(0) < S_{cc}^{id}(0)$, ordering in liquid alloy is expected while $S_{cc}(0) > S_{cc}^{id}(0)$ gives the indication of tendency of segregation.

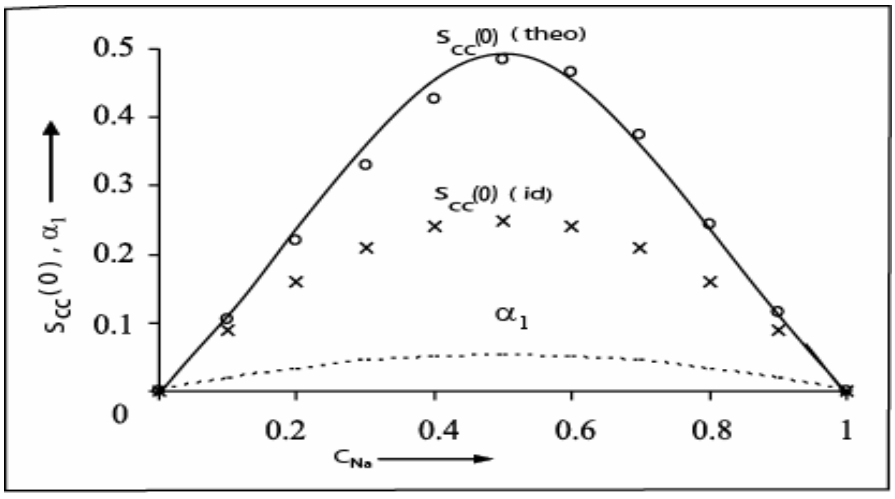

Fig. 3 : Concentration fluctuation ($S_{cc}(o)$) versus concentration of Na (C_{Na}) : Theoretical - solid curve; Experimental – circles; Ideal- crosses and Warren –Cowley SRO parameter (α_1) versus concentration of Na (C_{Na})

The knowledge of α_1 provides an immediate insight into the nature of the local arrangement of atoms in the mixture. The minimum possible value of α_1 is -1 and it indicates complete ordering of unlike atom pairing at nearest atoms. On the other hand the maximum value of α_1 is +1, which implies complete segregation leading to phase separation and α_1= 0 corresponds to a random distribution of atoms. Figure 3 shows that α_1 is positive, maximum at C_{Na} =0.5 and $S_{cc}(0) > S_{cc}^{id}(0)$ throughout whole concentration range of Na, showing that K-Na liquid alloy at 384K is segregating.The $S_{cc}(0)$ are used in Eq. (12). to evaluate the ratio of the mutual and

intrinsic-diffusion coefficients, $\frac{D_M}{D_{id}}$. The value of $\frac{D_M}{D_{id}}$ is less than 1 in the entire range of concentration (Fig.4) which is indicative for the phase separation in the mixture.

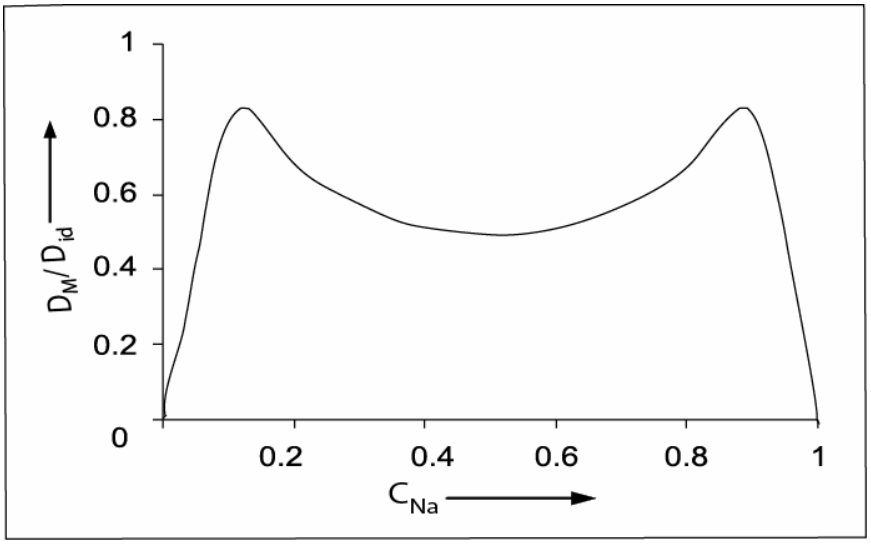

Fig. 4 : Diffusion coefficient ratio (D_M/D_{id}) versus concentration of Na (C_{Na})

4. Conclusion

The thermodynamic and structural properties of the regular K-Na alloy at 384K in liquid state are examined on the basis of simple statistical model. The analysis suggests that there is a tendency of like atom pairing in K-Na alloy in the whole range of concentration.

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