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ENTROPY OF MIXING OF TWO LEAD BASED BINARY LIQUID ALLOYS: A STATISTICAL MECHANICAL STUDY

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ABSTRACT
The thermodynamic properties of the lead based binary liquid alloys are often found to vary considerably from the ideal values. Here two such alloys—lithium-lead and sodium-lead—have been considered. Efforts are made to compute their entropies of mixing at different concentrations of the constituent species by using Flory's model. In this course the temperature dependence of the interchange energy has also been introduced. The results indicate that the size effect in the present alloys may not be an important factor for shaping the entropy of mixing as for other thermodynamic calculations.

Key words: Flory's model, Size effect, Interchange energy, Free energy of mixing, Heat of mixing.

INTRODUCTION

The concentration dependent thermodynamic properties of the lead based binary liquid alloys are interesting in many ways. The observed free energy of mixing and heat of mixing are asymmetric around equiatomic composition [2, 4, 5, 7]. In case of Li-Pb and Na-Pb liquid alloys the entropy of mixing (S_M) versus concentration (c) curves are clearly S-shaped. In these alloys the associative tendency between the unlike atoms is strong and the first principle statistical mechanical or pseudopotential type calculation of the physical properties is difficult [1, 8, 11]. Here Flory's model [3] has been applied for the computation of S_M for different concentrations of the ingredients. It is a statistical model for the binary liquid alloys based on the size effect.

MATERIALS AND METHOD

FORMULATION

Flory's expression for the free energy of mixing of a binary mixture consisting of Nc mole of species A and N(1–c) mole of species B is given by [3]

$$G_M = RT[c\ln c + (1–c)\ln (1–c) + c\ln (1–u) – \ln (1–uc)] + wc(1–c)/(1–uc), \quad \text{(i)}$$

where $u = 1 – (V_A / V_B)$, (ii)

V_A and V_B being the atomic volumes of species A and B respectively, R the universal gas constant, T the absolute temperature and 'w' the interchange energy.

Envisaging this interchange energy to be a function of temperature, the formula for the heat of mixing becomes

$$H_M = [wc(1–c)/(1–uc)] – [Tc(1–c)/(1–uc)]dw/dT + (du/dT)[RT^2c(1–c)/(1–uc)][\{u/(1–u)\} – (w/RT)c/(1–uc)], \quad \text{(iii)}$$

where $du/dT = (\gamma_B – \gamma_A)V_A/V_B$,

γ_A and γ_B being the volume expansivities of pure species A and B respectively.

Now, considering the standard thermodynamic relation

$$S_M = (H_M – G_M)/T, \quad \text{(iv)}$$

the entropy of mixing can be calculated on using equations (i) and (iii).

RESULT AND DISCUSSION

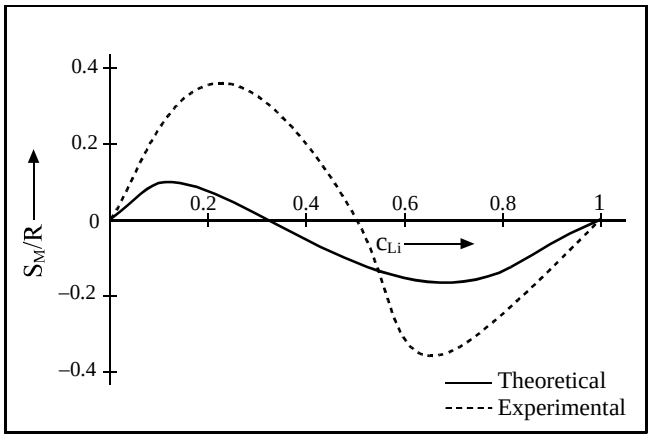
Lithium-Lead Liquid Alloy

For the purpose of equation (ii) considering A≡Li and B≡Pb one has $V_A/V_B = 0.741$ at 932 K. [9]. After finding 'u' the value of interchange energy has been determined with the help of equation (i) on using the observed data of G_M at 932 K. for different concentrations of lithium [10] and by applying the method of successive approximations. The value of w/RT used in the present work is –8.8. With this interchange energy the values of free energy of mixing have been computed at 932 K. in the concentration range from 0.1 to 0.9 by using equation (i).

Then equation (iii) has been used to ascertain the variation of interchange energy with temperature in the light of observed values of H_M at 932 K. [10] for different concentrations of lithium. In the present work the value of (1/R)dw/dT is 2.4. With this value of the temperature derivative of interchange energy the heat of mixing has been computed at 932 K. in the concentration range of lithium from 0.1 to 0.9 on using equation (iii).

Finally, the entropy of mixing of the Li-Pb liquid alloys has been calculated at 932 K. by using equation (iv) for different concentrations of lithium from 0.1 to 0.9.

Plot of S_M/R versus c_{Li} at 932 K. is shown in Figure–1 for both the computed and observed values.



Figure–1: S_M/R-c_{Li} curve for Li-Pb liquid alloys at 932 K.

The S-shaped curve shows that theoretically for $c_{Li}<0.31$, S_M is positive and for $c_{Li}>0.31$, S_M is negative. The maximum in S_M occurs at $c_{Li} = 0.1$ and the minimum at $c_{Li} = 0.65$, giving rise to some discrepancies with the experimental values.

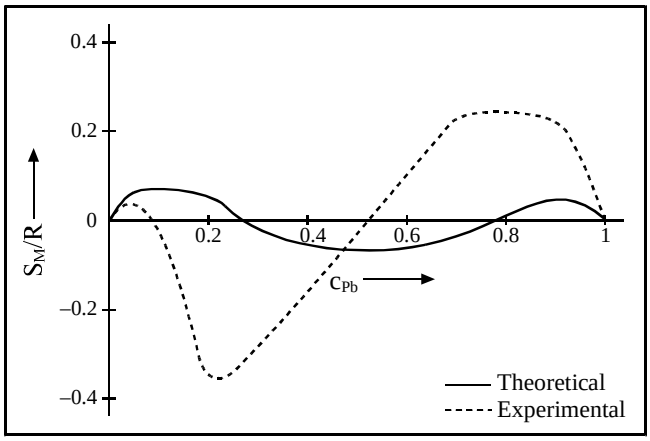
Sodium-Lead Liquid Alloy

In order to use equation (ii) considering A≡Na and B≡Pb one obtains $V_A/V_B = 0.718$ at 700 K. [6]. After finding the value of 'u' there comes the question of ascertaining the value of interchange energy. For this purpose experimental values of G_M at 700 K. [6] for different concentrations of lead are used in equation (i) for application of the method of successive approximations. The value of w/RT taken into account for the present work is –6.5. With this value of interchange energy the free energy of mixing of Na-Pb liquid alloys has been computed at 700 K. on using equation (i) for different concentrations of lead ranging from 0.1 to 0.9.

For the computation of the heat of mixing the value of the temperature derivative of interchange energy is needed. For this purpose the experimental values of H_M at 700 K. for different concentrations of lead from 0.1 to 0.9 [6] have been taken into account. Then using equation (iii) the successive approximations method has been applied like before. The value of (1/R)dw/dT ascertained in this way is 3. With this figure of the temperature derivative of interchange energy the heat of mixing of Na-Pb liquid alloys has been computed at 700 K. by using equation (iii) for different concentrations of lead.

At last, the theoretical values of the entropy of mixing of sodium-lead liquid alloys have been found out at 700 K. in the concentration range of lead from 0.1 to 0.9 on using equation (iv).

Plot of S_M/R versus c_{Pb} at 700 K. is shown in Figure–2 for both the computed and observed values.



Figure–2: S_M/R-c_{Pb} curve for Na-Pb liquid alloys at 700 K.

The computed value of S_M is positive for $c_{Pb}<0.28$, negative for $0.28<c_{Pb}<0.78$ and again positive for $c_{Pb}>0.78$. But the experimental values show that S_M is positive for $c_{Pb}<0.09$, negative for $0.09<c_{Pb}<0.51$ and then positive for $c_{Pb}>0.51$.

CONCLUSION

In spite of some discrepancies between the computed and experimental values of the entropy of mixing of lithium-lead and sodium-lead liquid alloys, the nature of its variation with concentration is explained to a great extent by the present model.

The study of entropy of mixing indicates that Li-Pb liquid alloys are structurally disordered for lower concentration of Li and become ordered in the higher concentration range of lithium. The discrepancies between the computed and observed values of entropy of mixing of the present alloys may be due to the formation of different complexes.

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