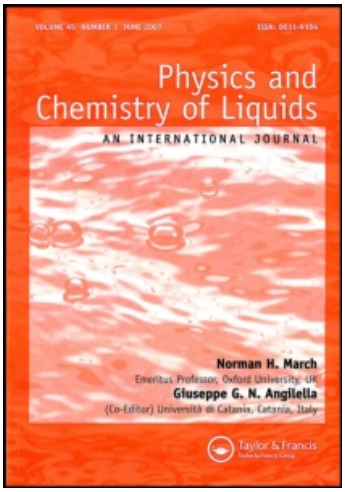

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Improved Flory Formula for the Entropy of Mixing of Binary Liquids

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IMPROVED FLORY FORMULA FOR THE ENTROPY OF MIXING OF BINARY LIQUIDS

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A simple model for the entropy of mixing of the compound forming binary alloys is proposed. It is shown that the entropy of the associates is proportional to the relative volume contraction of the liquid alloys.

KEY WORDS: Volume contraction, Flory model.

1 INTRODUCTION

The thermodynamic properties of certain alloys exhibit strong deviations from ideal behaviour around compound forming composition. These effects are attributed to the existence of chemical complexes (or associates) with a finite life time by Hoshino and Young[1]. Hafner *et al.*[2] assumed repulsive Yukawa tails between like ions and attractive ones between unlike ions, known as hard sphere-Yukawa (HSY) system. They applied this model to calculate thermodynamic as well as the structural properties for the whole composition range for various liquid alloys having chemical short-range order.

On the other hand, there has been no application of the simple hard sphere mixture theory[3] and Flory's formula[4,5] to explain thermodynamic behaviour of compound forming alloys. Recently we have shown that the hard sphere system is one of the simple model to deal with the problem which has been proved successful for several compound forming alloys[6,7]. From the thermodynamic point of view the concept of association in liquid alloys has a great importance to describe the thermodynamic function of compound forming alloys[8]. This associative tendency is always accompanied by the large volume contraction. In this paper we show that there is an intimate connection between the entropy of the associate and volume contraction of the binary liquid alloys. Therefore, we examine the Flory's formula for the entropy of mixing by introducing a term pertaining to the entropy of the associates. We find that the resulting Flory's expression exhibit consistently good values for thermodynamic functions, including entropy of mixing and volume of mixing for binary liquid alloys.

2 FORMULATION

According to Flory[4], the entropy of mixing is given by

$$\frac{\Delta S_F}{NK_B} = -\sum_{i=1}^{2} C_i \ln \phi_i$$

where ϕ_i is the volume fraction and is given by

$$\phi_i = C_i\Omega_i/\Omega_{\text{ideal}}$$

C_i $(i = 1, 2)$ is the atomic concentration of the species i and is constrained by the relation $\sum_i C_i = 1$. Now equation is rewritten as

$$\frac{\Delta S_F}{NK_B} = \ln\left(\frac{\Omega_{\text{ideal}}}{\Omega_1^{C_1} \cdot \Omega_2^{C_2}}\right) - S_c \tag{2}$$

with

$$S_c = C_1 \ln C_1 + C_2 \ln C_2$$

Up to now, no volume contraction has been considered explicitly and Eq. (2) cannot describe the behaviour of compound forming alloys. In fact, in liquid binary alloys, where the size effects are significant, the volume of mixing plays a significant role[6,7]. Therefore we introduce the concentration dependent effective volume instead of Ω_{ideal} in Eq. (2) in the following manner.

$$\Omega_F = \Omega_{\text{ideal}} + C_1C_2\Delta\Omega_0 \tag{3}$$

with

$$\Omega_{\text{ideal}} = C_1\Omega_1 + C_2\Omega_2$$

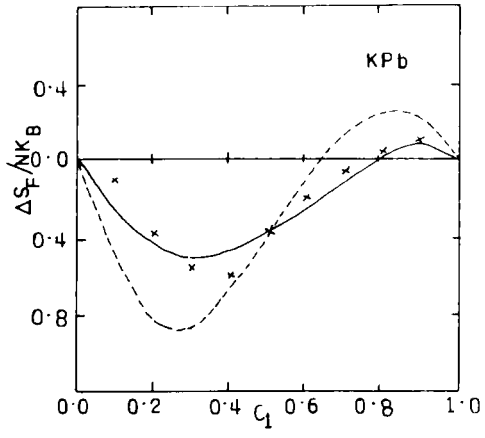
Ω_1 and Ω_2 are the atomic volume of pure liquid metals. $\Delta\Omega_0$ is a disposable parameter.

To get an idea of the relation of entropy of associate to the volume contraction, we look at the behaviour of simple metals at the melting point. It is known that there is a direct correlation between the change of volume and the entropy change upon melting[9,10] which may be written as

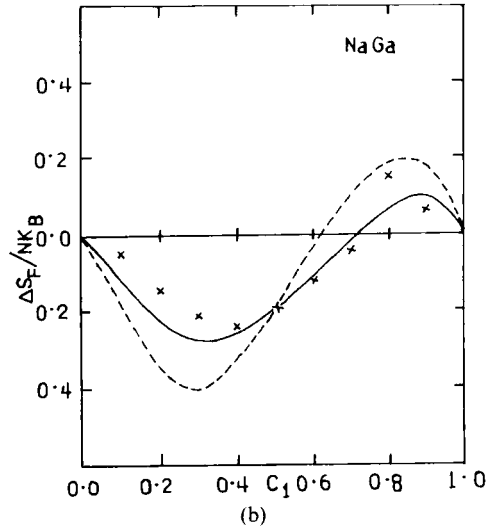
$$\frac{\Delta S^{\text{fus}}}{NK_B} = \ln 2 + 10\left(\frac{\Delta\Omega}{\Omega}\right)^{\text{fus}} \tag{14}$$

The term ln 2 has been attributed to vibrating vacancies in the solid[11]. Second term of Eq. (4) refers to the entropy of the reference state of the associates. Therefore, we adopt the following relation for the entropy change due to formation of the associates on mixing

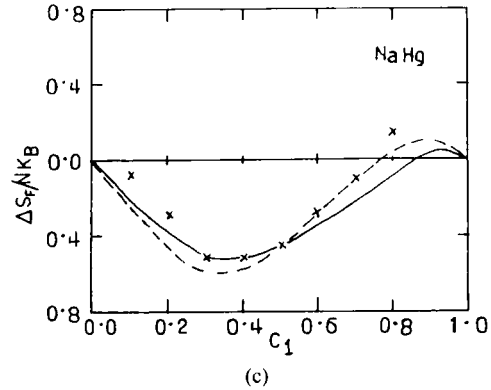
$$\frac{\Delta S}{NK_B} = f(\Delta\Omega/\Omega) = 10(\Delta\Omega/\Omega) \tag{5}$$



(a)



(b)



(c)

Figure 1(a–c) Concentration dependence of the entropy of mixing ΔS_F of the liquid alloys KPb, NaGa and NaHg; modified Flory's formula (———) hard sphere mixture theory (- - - - -); experimental values (× - × - ×); from Ref. 12 for KPb and NaHg and Ref. 13 for NaGa.

where $(\Delta\Omega/\Omega)$ is the relative change of the volume upon mixing of the liquid metals. The expression for Flory's formula Eq. (2) can now be written as

$$\frac{\Delta S_F}{NK_B} = \ln\left(\frac{\Omega_F}{\Omega_1^{C_1}\Omega_2^{C_2}}\right) - S_c + 10\left(\frac{\Delta\Omega}{\Omega_F}\right) \tag{6}$$

3 RESULTS AND DISCUSSION

The entropy of mixing calculations require the volume of mixing, a concentration dependent value, as input information. In the present work, the atomic volume (Ω_F) of the liquid mixture at equiatomic concentration is so fitted as to satisfy Eq. (6) with the experimental value of the entropy of mixing. That leads to an evaluation of the atomic volume of mixing $(C_1C_2\Delta\Omega_0)$ from Eq. (3) and hence the effective volume at different concentrations. We now present our results for the entropy of mixing by using modified Flory's expression (Eq. 6) for some compound forming alloys like NaGa, KPb and NaHg. The computed values are displayed in Figures 1(a-c) and are compared with those obtained by the hard sphere mixture theory[6,7]. Our values are in good agreement with the experimental values[12,13] and show much improvement over hard sphere mixture theory particularly toward heavier metal side. Looking to the magnitude of the different contributions in Eq. (6); we find that the term $10(\Delta\Omega/\Omega_F)$ plays a major role in deciding the shape of the entropy of mixing curve showing thereby that the compound formation in these alloys is obtained due to the formation of the associates that leads to a considerable change in volume. In view of our

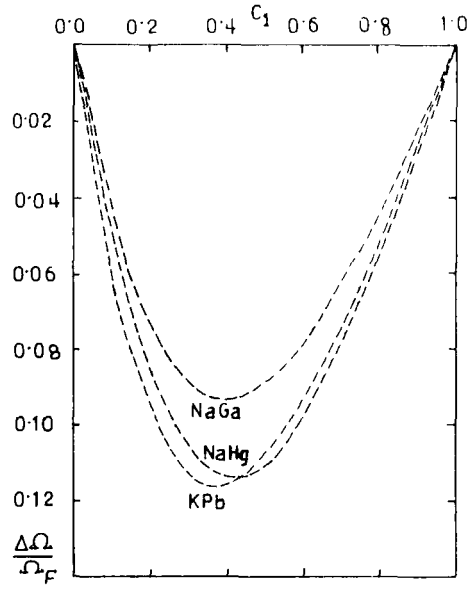


Figure 2 Concentration dependence of the fractional change in volume $(\Delta\Omega/\Omega_F)$ using modified Flory's formula for KPb, NaGa and NaHg alloys.

previous work[14] in which Flory's formula leads to a disasterous value of the volume of mixing, we display the volume of mixing curves in Figure 2 which were found quite reasonable.

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