

Energy Disorder in Liquid Fe-Si Alloy

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Abstract

The observed asymmetry in the properties of mixing of Fe-Si alloy in molten state is successfully explained on the basis of regular associated solution model. We have determined the free energy of mixing, heat of mixing and entropy of mixing of Fe-Si alloys in molten state at 1873 K. The analysis suggests that heterocoordination leading to the formation of complex Fe_2Si is likely to exist in the liquid and is of a strongly interacting nature. The theoretical analysis reveals that the pairwise interaction energies between the species depend considerably on temperature.

Keywords: Liquid alloy; clusters; thermodynamic properties

1. Introduction

The asymmetric behaviour of mixing properties of the binary alloys may be attributed to the strong interactions present in it [2, 3]. Large negative excess free energy of mixing, entropy of mixing and heat of mixing with a sharp change in slope near compound forming concentrations are the characteristics of the compound forming alloys [4,5]. The formation of compound in solid state led many theoreticians [6-8] to believe that chemical complexes might exist in molten state. These complexes are given different names, such as ‘pseudomolecules’, ‘clusters’, ‘complexes’ etc. Various models based on the above assumptions [8-10] are being used to understand the alloying behaviour of binary alloys. We intend to use regular associated model to explain the alloying behaviour of Fe-Si alloys in molten state at 1873K. The phase diagram suggests that Fe_2Si complexes exist in solid state [1].

In the next section, the basic expression for the formalism used in the calculation is presented. Section 3 gives the results and discussion of this work and the conclusions are outlined in section 4.

2. Formalism

Let there be three species in equilibrium in the liquid alloy, namely, monomers A(=Fe), B(= Si) and A_pB (= Fe_2Si) molecules in the respective concentrations n_A, n_B , and n_{ApB} moles. Considering a solution of n_1 atoms of A and n_2 atoms of B, the formation of n_{ApB} complex requires $n_1 = n_A + p_{ApB}$ and $n_2 = n_B + n_{ApB}$ for conservation of mass in the partially associated solution. When there is association, the thermodynamic behaviour of complexes A and B components is governed

by their true mole fractions x_A, x_B and x_{ApB} rather than their gross mole fraction x_1 and x_2 , where

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2} \quad (1)$$

$$x_A = \frac{n_A}{n_A + n_B + n_{ApB}}, \quad x_B = \frac{n_B}{n_A + n_B + n_{ApB}} \quad \text{and} \quad x_{ApB} = \frac{n_{ApB}}{n_A + n_B + n_{ApB}} \quad (2)$$

Using equations (1) and (2) the two sets of mole fractions are related to each other by the relations

$$x_A = x_1 - p x_2 x_{ApB}, \quad x_B = x_2 - (1 - p x_2) x_{ApB} \quad (3)$$

Progonine and Defay [11] have shown that in associated solutions, the gross chemical potentials of components 1 and 2 are equal to the chemical potentials of the monomeric species A and B. Following Jordan [7] the activity coefficients \tilde{a}_A, \tilde{a}_B and \tilde{a}_{ApB} of monomers and complex can be expressed in terms of pairwise interaction energies through

$$RT \ln \gamma_A = x_B^2 \omega_{12} + x_{ApB}^2 \omega_{13} + x_B x_{ApB} (\omega_{12} - \omega_{23} + \omega_{13}) \quad (4a)$$

$$RT \ln \gamma_B = x_{ApB}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{ApB} (\omega_{23} - \omega_{13} + \omega_{12}) \quad (4b)$$

$$RT \ln \gamma_{ApB} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_B x_{ApB} (\omega_{13} - \omega_{12} + \omega_{23}) \quad (4c)$$

where ω_{12}, ω_{13} and ω_{23} are interaction energies for the species A, B ; A, A_pB and B, A_pB respectively, T the temperature and R stands for the universal gas constant.

The equilibrium constant for the reaction $A_pB \rightleftharpoons pA+B$ is given by

$$k = \frac{x_A^p x_B \tilde{a}_A^p \tilde{a}_B}{x_{ApB} x_{ApB}} \quad (5)$$

Thus, using equation (3), (4) and (5), one gets

$$\ln k = h \left(\frac{x_A^p x_B}{x_{ApB}} \right) + \frac{\omega_{12}}{RT} [p x_B (1 - x_B) + x_A] + \frac{\omega_{13}}{RT} [p x_{ApB} (1 - x_A) - x_A] + \frac{\omega_{23}}{RT} [x_{ApB} (1 - p x_B) - x_B] \quad (6)$$

Now using the equations listed above the integral excess free energy ΔG^{xs} is given by

$$\Delta G^{XS} = \frac{1}{(1+pX_{ApB})} (x_A x_B \omega_{12} + x_A x_{ApB} \omega_{13} + x_B x_{ApB} \omega_{23}) + \frac{RT}{(1+pX_{ApB})} \times (x_A \ln x_A + x_B \ln x_B + x_{ApB} \ln x_{ApB}) - RT(x_1 \ln x_1 + x_2 \ln x_2) + \frac{x_{ApB}}{(1+pX_{ApB})} RT \ln k \quad (7)$$

Once the expressions for ΔG [$=\Delta G^{XS}+RT(x_1 \ln x_1 + x_2 \ln x_2)$] is obtained, other thermodynamic and microscopic functions follow readily. Heat of mixing and entropy of mixing are related to ΔG through standard thermodynamic relations

$$\Delta H = \Delta G - T \left(\frac{\partial \Delta G}{\partial T} \right)_{T,P} \quad (8)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (9)$$

where $C (= x_{Fe})$ is concentration of A component in the alloy. Using equation (7) in equation (8), we obtained expressions for ΔH as

$$\Delta H = \frac{1}{(1+pX_{ApB})} (x_A x_B \omega_{12} + x_A x_{ApB} \omega_{13} + x_B x_{ApB} \omega_{23}) - \frac{T}{(1+pX_{ApB})} \times \left(x_A x_B \frac{\partial \omega_{12}}{\partial T} + x_A x_{ApB} \frac{\partial \omega_{13}}{\partial T} + x_B x_{ApB} \frac{\partial \omega_{23}}{\partial T} \right) - \frac{x_{ApB}}{(1+pX_{ApB})} RT^2 \frac{d \ln k}{dT} \quad (10)$$

The pairwise interaction energies and equilibrium constant are determined by the following method:

In a regular associated solution $x_1 \gamma_1 = x_A \gamma_A$ and $x_2 \gamma_2 = x_B \gamma_B$, where γ_1 and γ_2 are respective gross activity coefficients of components 1 and 2. Thus

$$\ln \gamma_1 = \ln \gamma_A + \ln \frac{\gamma_A}{x_A} \quad (11a)$$

and

$$\ln \gamma_2 = \ln \gamma_B + \ln \frac{\gamma_B}{x_B} \quad (11b)$$

The pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution can be written as [8]

$$\ln \gamma^\circ = \frac{\omega_{12}}{RT} \quad (12a)$$

$$k \exp(\omega_{13} / RT) = \frac{\gamma_1^\circ \gamma_2^\circ}{\gamma_1^\circ - \gamma_2^\circ} \quad (12b)$$

Where γ_1° and γ_2° are activity coefficients of component A and that of B at zero concentrations.

Solving equations (4a) and (4b) we obtain

$$\frac{\omega_{23}}{RT} = \frac{x_B \ln \left(\frac{a_2}{x_B} \right) + (1-x_B) \ln \left(\frac{a_1}{x_A} \right) - x_B (1-x_B) \frac{\omega_{12}}{RT}}{x_{ApB}^2} \quad (13)$$

$$\frac{\omega_{13}}{RT} = \frac{x_A \ln \left(\frac{a_1}{x_A} \right) + (1-x_A) \ln \left(\frac{a_2}{x_B} \right) - x_A (1-x_A) \frac{\omega_{12}}{RT}}{x_{ApB}^2} \quad (14)$$

Using equations (6), (13) and (14), we can derive

$$\ln k + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{ApB}} \right) \ln \left(\frac{a_1}{x_A} \right) + \frac{x_B}{x_{ApB}} \left[\ln \left(\frac{a_2}{x_B} \right) - \frac{\omega_{12}}{RT} \right] + \ln \left(\frac{a_1^p a_2}{x_{ApB}} \right) \quad (15)$$

3. Results and Discussion

The mole fraction x_{Fe_2Si} of complex Fe_2Si is determined using experimental data of activity [1] and equations (12) and (15) employing the iterative procedure. The compositional dependence of various species (figure 1) shows that the maximum association occurs at 69 at. pct. of Fe. At this composition and 1873 K, about 39 mol pct. of the liquid alloy is associated.

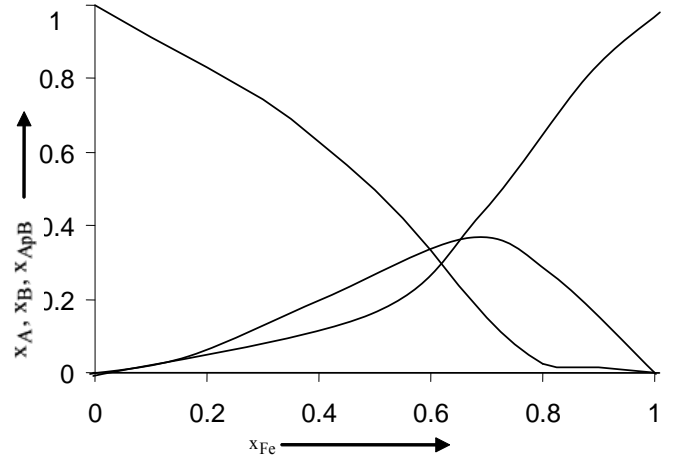


Figure-1

Compositional dependence of mole fractions x_A (A=Fe), x_B (B=Si) and x_{ApB} ($A_pB=Fe_2Si$) versus x_{Fe} (concentration of Fe) at 1873K

The equilibrium constant and pairwise interaction energies are estimated from the equations (6), (11a), (14), (15) and observed data for integral excess free energy of mixing [1]. The equilibrium constant and interaction energies for the alloy Fe_2Si in liquid state at 1873 K are found to be

$$k = 4.139 \times 10^{-3}, \omega_{12} = -64170 \text{ J mol}^{-1}, \omega_{13} = -14720 \text{ J mol}^{-1} \text{ and } \omega_{23} = -45500 \text{ J mol}^{-1}$$

All the interaction energies are large negative value and show that Fe and Si atoms are strongly attracted to each other and to the complex.

Theoretical calculation of free energy of mixing for Fe-Si liquid alloy shows that Fe-Si alloy in liquid state is strongly interacting system. Figure 2 shows very good a good agreement between calculated and experimental free energy of mixing.

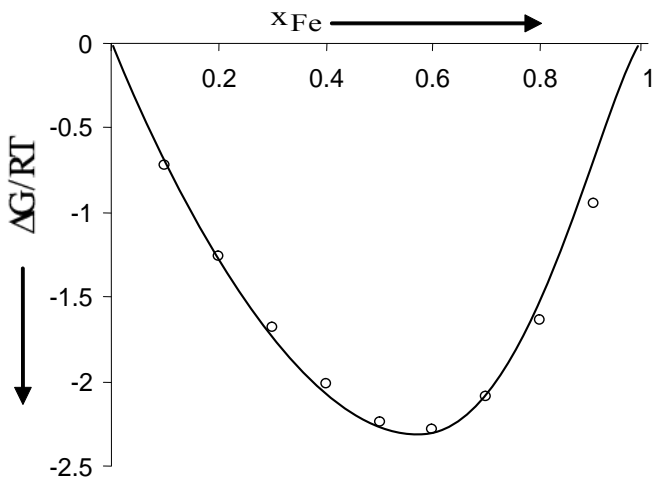


Figure-2

Free energy of mixing ($\Delta G/RT$) versus x_{Fe} of liquid Fe-Si solution (1873K); (—) theory, (○) experiment [1]

We have observed that if the interaction energies are supposed to be independent of temperature, i.e.,

$\frac{\partial \omega_{12}}{\partial T} = 0$ etc., then ΔH and ΔS so obtained are in poor agreement with experimental data. This simply suggests importance of the dependence of interaction energies on temperature. On using equation (10) and observed values of ΔH [1] we have chosen the following values for the given parameters as the best fit values for the heat of formation of Fe_2Si complex.

$$\frac{\partial \omega_{12}}{\partial T} = -45, \quad \frac{\partial \omega_{13}}{\partial T} = \frac{\partial \omega_{23}}{\partial T} = 0 \quad \text{and} \quad RT^2 \frac{\partial \ln k}{\partial T} = 185000 \pm 2500 \text{ J mol}^{-1}$$

It is found from the analysis that the heat of mixing is negative at all concentration. Our theoretical calculation shows that the minimum value of the heat of mixing is -2.585 at $x_{Fe} = 0.55$. Further it is observed that the concentration dependence of asymmetry in ΔH can be explained only when one considers the temperature dependent of the pairwise interaction energies. Figure 3 and 4 show the comparison between the experimental and calculated values of heat of mixing and entropy of mixing.

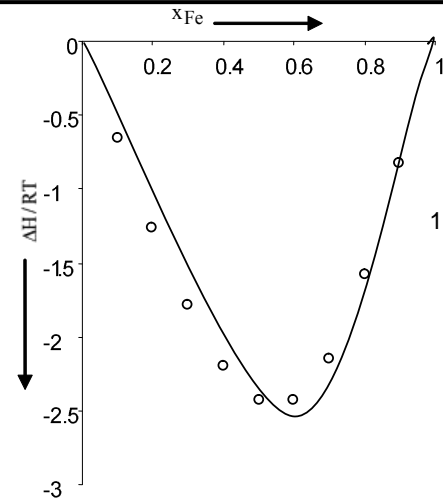


Figure -3

Heat of mixing ($\Delta H/RT$) versus x_{Fe} of liquid Fe-Si solution (1873K); (—) theory, (○) experiment [1]

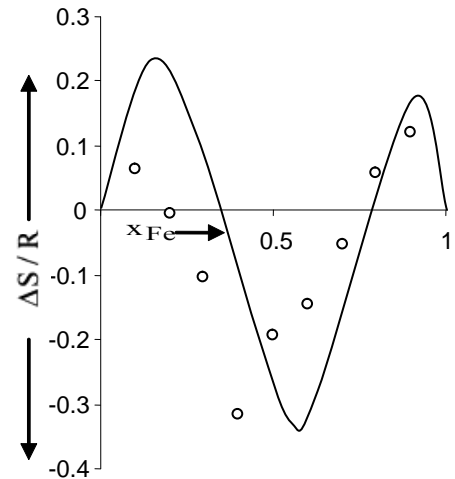


Figure-4

Entropy of mixing ($\Delta S/R$) versus x_{Fe} , (1873K); (—) theory, (○) experiment [1]

4. Conclusion

In present work, we have used regular associated solution model to obtain equilibrium constant, pairwise interaction energies for Fe_2Si liquid alloy at 1873K. The knowledge of nature and extent of interaction energies between the components and complex have been used for the estimation of thermodynamic properties of Fe_2Si alloy in liquid state. The analysis also shows that the Fe-Si system is strongly interacting heterocoordination system. The pairwise interaction energies of this system depend on temperature.

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