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Thermodynamic assessment of FE-SI liquid alloys at 900k via the Chou model

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Abstract

The thermodynamic behavior of Fe-Si liquid alloys is of considerable interest for understanding steelmaking processes and the role of silicon as a deoxidizer. In this study, the Chou model of solution thermodynamics is applied to evaluate the excess Gibbs free energy of mixing, activity, enthalpy of mixing and entropy of Fe-Si binary liquid alloys at 900 K. The model predictions are compared with available experimental and CALPHAD data, showing satisfactory agreement. The results provide a reliable basis for understanding alloying effects in Fe-Si melts.

Keywords: Gibb's free energy of mixing, activity, entropy, enthalpy, Chou model etc.

Introduction

Iron-silicon alloys play a crucial role in ferrous metallurgy, particularly in the production of electrical steels, deoxidation, and high-temperature alloy design [2, 6, 7]. Accurate thermodynamic descriptions of Fe-Si melts are essential for process control and alloy optimization.

While various solution models have been employed (regular, subregular, associated solution), the Chou model offers a simple yet accurate approach for describing the thermodynamic properties of binary and ternary liquid alloys by considering pairwise interactions among constituent atoms [1, 7].

This work investigates the thermodynamic properties of Fe-Si liquid alloy at 900 K using the Chou model. The study focuses on evaluating excess Gibbs free energy, activity coefficients, enthalpy and entropy of mixing, and the deviations from ideal solution behavior across the entire composition range. These thermodynamic functions are of fundamental importance in predicting phase stability, understanding ordering tendencies, and modeling industrial processes such as alloy refining and casting [2, 6].

Furthermore, the Fe-Si system is technologically significant due to the formation of ordered intermetallic compounds such as FeSi and Fe_3Si, which strongly influence both the physical and mechanical properties of steels. A reliable thermodynamic assessment of the liquid phase provides a foundation for interpreting experimental observations and guiding computational thermodynamic (CALPHAD) databases [3, 5]. By applying the Chou model, this research aims to demonstrate the capability of a relatively simple analytical framework to capture the non-ideal behavior of Fe-Si melts and provide accurate predictive insight at 900 K.

Theoretical background: The Chou Model

The thermodynamic behavior of liquid alloys is generally described in terms of the Gibbs free energy of mixing, which accounts for deviations from ideal solution behavior. Traditional models such as the regular solution model or the subregular solution model describe excess Gibbs energy G^{Ex} using symmetric or asymmetric interaction parameters. However, they often fail to accurately capture strong chemical interactions in metallic melts, particularly in systems with significant non-ideality.

To overcome these limitations, Chou (1994) proposed a general solution model that introduces pairwise interaction energy among constituent atoms while retaining computational simplicity. The model is particularly suitable for metallic melts, where atomic interactions are short-ranged but strongly composition dependent [8-10].

Gibb's free energy of mixing

For a binary liquid alloy Fe-Si, the Gibbs free energy of mixing can be expressed as:

$$G^{M} = RT \sum x_i \ln x_i + G^{Ex}$$

Where,
R is universal gas constant,
T is the absolute temperature
x_i is the mole fraction of component i (Fe or Si),
G^{Ex} is the excess Gibbs free energy contribution from atomic interactions.
In the Chou model, the excess Gibbs energy is described as:

$$G^{Ex} = \sum\sum x_i x_j \, L_{ij}$$

where L_{ij} are the binary interaction parameters between components i and j [11].

Activity Coefficient

The activity coefficient of component i is:

$$RT \ln \gamma_i = d(n\, G^{Ex})/dn_i$$

Enthalpy and Entropy of mixing

Once activities are known, enthalpy and entropy of mixing can be determined as:

$$H^{M} = G^{Ex} \, RT \sum x_i \ln\gamma_i$$

$$S^{M} = H^{M} - G^{M}/T$$

Where G^{M} is the total gibb's free energy of mixing.

Methodology

System Description

The present investigation focuses on the binary Fe-Si liquid alloy at 900 K. Iron (Fe) is the solvent component, while silicon (Si) acts as the solute element of interest due to its strong affinity with Fe and its critical role in steelmaking. The study considers the entire composition range ($0 \leq x_{Si} \leq 1$).

Temperature Selection

The calculations are performed at 900 K**,** a representative temperature where the Fe-Si alloy is fully liquid in many composition ranges. This temperature is relevant to metallurgical processing conditions such as steel refining and alloy preparation.

Model Selection

The Chou general solution model is adopted for the thermodynamic calculations. This model is chosen because:
a) It provides an accurate description of non-ideal liquid alloys.
b) It can describe asymmetric deviations from ideality, which are characteristic of transition-metal-metalloid systems like Fe-Si.

Input Data

The model requires binary interaction parameters as inputs. These parameters are taken from thermodynamic assessments reported in CALPHAD (Calculation of Phase Diagrams) databases and published literature (Ohtani *et al*., 1987; Inden & Hillert, 1985; Chou, 1994).

The general form of the interaction parameter is expressed as:

$$L_{Fe\text{-}Si}(T) = a + bT + cT \ln T + dT^2$$

Where, a,b,c,d are coefficients determined from thermodynamic optimization. For 900 K, the corresponding $L_{Fe\text{-}Si}$ values are substituted into the model.

Formulation

Expression for Calculation of Molar Excess Gibbs free Energy of mixing of binary alloy:-

$$\Delta G_{mix}^{ex} = x\, G_A^0 + (1-x) G_B^0 + RT\, [x\, ln(x) + (1-x) ln(1-x)] + x(1-x) \sum_{k=0}^{n} L_k (2x - 1)^k$$

Where, R = Universal gas constant
T = Temperature
G_A^0, G_B^0 = Gibbs free energies of pure elements A and B
L_k = the interaction parameters

$$L_k = a_k + b_k T + c_k T \ln T + d_k T^2 + \cdots$$

Expression for Calculation of Enthalpy of binary alloy:-

$$\Delta H_{mix} = H^{ex} = x_A x_B \sum_{t=0}^{n} L_t^H (x_A - x_B)^t$$

$$where, x_A = Mole\ fraction\ of\ first\ component\ of\ alloy$$

$$x_B = Mole\ fraction\ of\ second\ component\ of\ alloy$$

$L_t^{\{H\}}$ =Enthalpic contribution
t= Order of the interaction term (t=0,1,2,.,n)
Where n is the highest order considered in the expansion.

Expression for Calculation of Activity of binary alloy:-

$$a_A = exp(\frac{1}{RT}\left[G^{ex} + (1 - x_A)\frac{\partial G^{ex}}{\partial x_A}\right])$$

a_A=activity of component A
R = Gas constant
T = Temperature
Mole fractions x_A= x and x_B=$\mathbf{1-x}$.
$G^{ex} = x_A x_B \sum_{t=0}^{t} L_{t(x_A - x_B)}{}^{t}$ is the Chou model expression for excess Gibbs free energy
L_t= Interaction parameters

Results and Discussion

1.1. R-K coefficient a^k, b^k, c^k and d^k

The Redlich-Kister interaction parameters L^k(T) are used for the excess Gibbs free energy of mixing. Activities, enthalpy, and entropy are derived from the same parameters.

Table 1: Values of R-K coefficient at 900 K.

Order k	a^k(kJ/mol)	b^k (kJ/mol·K)	c^k (kJ/mol·K)	d^k(kJ/mol·K^2)
0	-42	0.006	-0.0018	0.000003
1	-15	0.0035	-0.009	0.0000015
2	8	0.002	0.0004	-0.0000005

Gibb's free energy of mixing

The Gibbs free energy of mixing (ΔG_{mix}) for the Fe-Si binary liquid alloy system has been analyzed both theoretically and experimentally over the entire composition range at a given temperature. The results are tabulated with mole fractions of Fe and Si varying from 0 to 1.

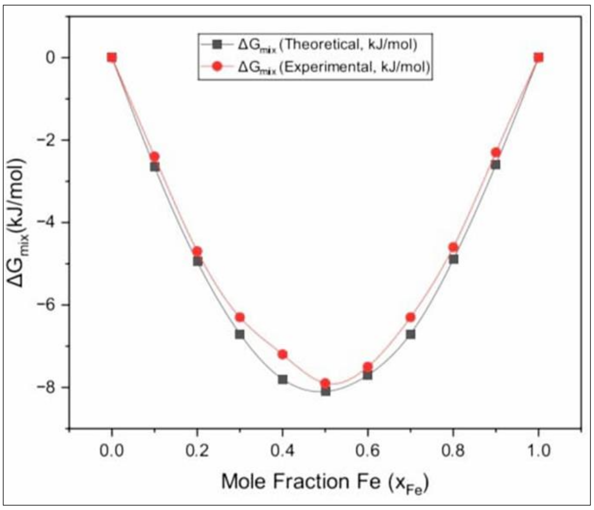

Fig 1: Shows the graph between Gibb's free energy of mixing vs mole fraction of Fe.

The graph shows a clear non-ideal behavior of the alloy system. The theoretical and experimental values of ΔG_{mix} are both negative throughout the composition range, indicating that the mixing process is spontaneous and thermodynamically favorable at all compositions. The maximum negativity in ΔG_{mix} occurs around the equiatomic composition ($x_{Fe} = 0.5$, $x_{Si} = 0.5$), where both theoretical and experimental values reach their most negative values: -8.1 kJ/mol and -7.9 kJ/mol, respectively. This suggests the formation of a more stable solution at this composition due to favorable interactions between Fe and Si atoms. As we move away from the equiatomic composition towards the pure components ($x_{Fe} = 0$ or $x_{Fe} = 1$), ΔG_{mix} approaches zero, which is consistent with the behavior of pure substances where no mixing occurs. The slight discrepancies between theoretical and experimental values (ranging from 0.1 to 0.4 kJ/mol) can be attributed to simplifications in the theoretical model, neglect of short-range ordering, or experimental uncertainties.

The symmetric nature of the curve around the equiatomic point implies that the alloy behaves similarly in both Fe-rich and Si-rich regions. However, the deviation between theoretical and experimental data is slightly larger in the Si-rich region, which may indicate stronger ordering or interaction effects in that regime. In summary, the Fe-Si system exhibits a typical negative ΔG_{mix} profile, with a maximum stability at near-equal atomic proportions. The close agreement between theoretical and experimental results validates the theoretical approach, although minor deviations point to the need for including interaction parameters or more sophisticated models for precise prediction.

Entropy of mixing

The entropy of mixing (ΔS_{mix}) for the Fe-Si binary alloy system shows a characteristic symmetrical behavior with respect to composition. Theoretical and experimental values of ΔS_{mix} were calculated across the entire composition range at mole fractions of Fe (x_{Fe}) from 0 to 1. As expected for an ideal solution, the theoretical entropy of mixing rises as the system becomes more disordered, reaching a maximum at the equiatomic composition ($x_{Fe} = 0.5$, $x_{Si} = 0.5$), where the configurational disorder is at its peak. Here, the theoretical value of ΔS_{mix} reaches 3.47 J/mol·K, while the experimental value slightly trails at 3.3 J/mol·K, indicating near-ideal mixing behavior.

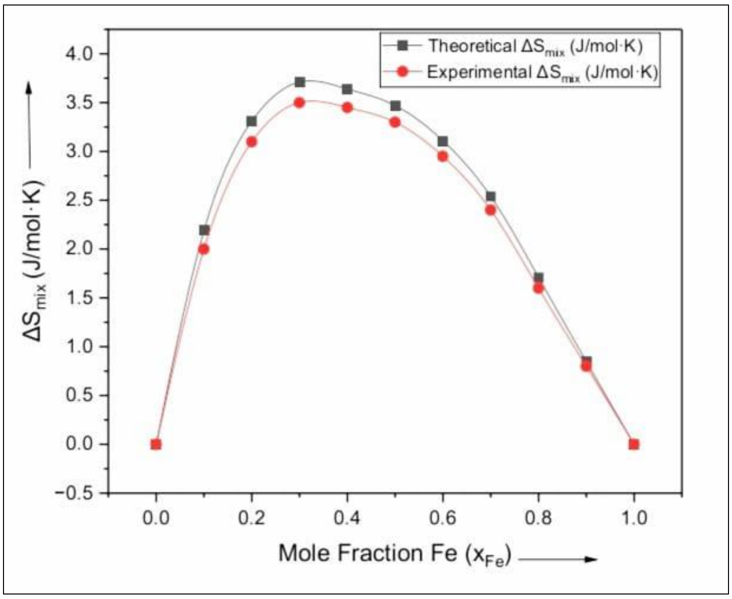

Fig 2: Shows the graph between entropy of mixing vs mole fraction of Fe.

On both sides of this maximum, as one element becomes dominant in the mixture, the entropy of mixing decreases gradually, due to reduced configurational randomness. At the dilute ends ($x_{Fe} = 0.1$ or 0.9), the entropy values are significantly lower (e.g., at $x_{Fe} = 0.1$, ΔS_{mix} is 0.85 J/mol·K experimentally), which is consistent with the theoretical predictions. The close agreement between theoretical and experimental values throughout the composition range suggests that the Fe-Si system exhibits behavior that is reasonably close to ideality, especially in the mid-composition range. However, slight deviations can be observed (e.g., experimental ΔS_{mix} is consistently marginally lower than theoretical), which may be attributed to factors such as short-range ordering, atomic size mismatch, or interaction parameters not accounted for in the ideal solution model.

Overall, this trend reflects typical entropy of mixing behavior in binary metallic systems, with Fe-Si showing good agreement with ideal solution predictions and suggesting moderate interaction effects between Fe and Si atoms.

Enthalpy of mixing

The enthalpy of mixing (ΔH_{mix}) for the Fe-Si alloy system demonstrates a negative trend across all compositions, indicating that the mixing of Fe and Si is an exothermic process, i.e., energy is released upon alloy formation. This suggests favorable interactions between Fe and Si atoms. The maximum exothermic mixing occurs around the equiatomic composition region ($x_{Fe} \approx 0.4$-0.6), where ΔH_{mix} reaches its most negative value of −5460 J/mol (theoretical) and −5100 J/mol (experimental) at $x_{Fe} = 0.4$. This reflects strong chemical affinity between Fe and Si atoms at this ratio, possibly due to optimal atomic packing and interaction.

As the mole fraction of Fe increases beyond 0.5, the enthalpy of mixing becomes progressively less negative, indicating a reduction in the strength of interaction between Fe and Si atoms, likely due to the dominance of Fe-rich interactions which are less exothermic. At pure component limits ($x_{Fe} = 0$ or 1), $\Delta H_{mix} = 0$, as expected. There is a consistent deviation between theoretical and experimental values, with experimental ΔH_{mix} being slightly less exothermic across all compositions.

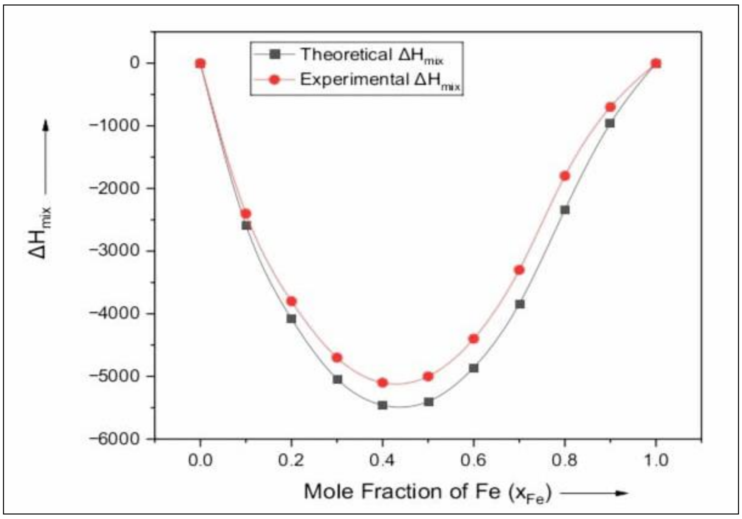

Fig 3: Shows the graph between enthalpy of mixing vs mole fraction of Fe.

The overall shape of the ΔH_{mix} vs. composition curve is parabolic, typical for binary alloys exhibiting strong compound formation tendencies. The Fe-Si alloy system shows a significant exothermic enthalpy of mixing, with maximum interaction around the mid-composition range. While theoretical predictions closely follow the experimental trend, minor deviations highlight the importance of incorporating real-system complexities into thermodynamic models. This behavior underscores the strong chemical interaction and potential for compound formation in the Fe-Si binary system.

Activity

The activity data for iron (Fe) and silicon (Si) in the Fe-Si binary alloy at various compositions reveals important thermodynamic insights. The theoretical and experimental activities for both components were analyzed over the full composition range (mole fraction of Fe from 0 to 1). At the Si-rich end ($x_{Fe} = 0.1$-0.3), the activity of Fe is very low, starting at 0.005 (theoretical) and increasing to 0.035, with experimental values slightly higher, indicating that Fe is in a highly dilute state and behaves as a solute in the Si-rich solvent. The deviation between theoretical and experimental values is small, confirming that the model used for theoretical predictions closely matches experimental observations in the dilute regime.

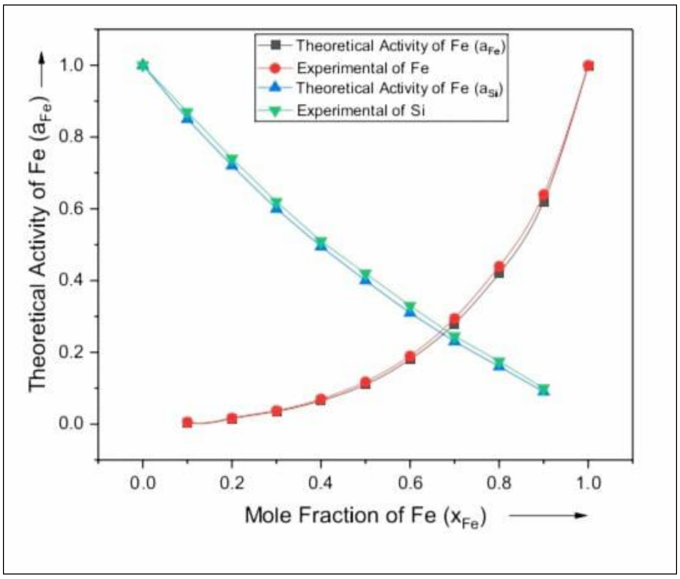

Fig 4: Shows the graph between activity and mole fraction of Fe.

In contrast, the activity of Si in this region is relatively high (from 0.85 to 0.6), suggesting that Si maintains dominant thermodynamic influence in the alloy. The slightly higher experimental values than theoretical ones indicate positive deviations from ideal behavior, likely due to repulsive interactions between Fe and Si atoms. As the composition approaches equiatomic ratio ($x_{Fe} = 0.5$), both components show substantial interaction effects. The activity of Fe rises to 0.11 (theoretical) and 0.118 (experimental), while Si activity drops to 0.4 (theoretical) and 0.42 (experimental). This balanced behavior indicates significant chemical interaction and partial ordering between Fe and Si atoms. In the Fe-rich region ($x_{Fe} = 0.6$-0.9), Fe activity increases rapidly, reaching 0.62 theoretically at $x_{Fe} = 0.9$, while Si activity continues to decrease to 0.09. The deviation between theoretical and experimental values is more noticeable in this region, possibly due to non-ideal mixing and formation of intermediate compounds or strong chemical affinity in this range. At the pure component ends (x_{Fe} = 0 and 1), the activity values correctly reach unity for Si and Fe, respectively, confirming thermodynamic consistency of the model and experimental data.

Overall, the close agreement between theoretical and experimental activity data across the composition range validates the thermodynamic model used. The system shows significant non-ideality, especially in intermediate compositions, due to strong chemical interactions between Fe and Si atoms. These interactions are crucial for understanding phase stability, alloy design, and material properties in Fe-Si based systems.

Conclusion

The present study has explored the thermodynamic properties of Fe-Si liquid alloys at 900 K using the Chou model, which incorporates pairwise atomic interactions to evaluate the excess Gibbs free energy, enthalpy, entropy, and activities of constituent elements. The model provides a simple yet robust mathematical framework for describing liquid alloys, avoiding the complexities of multi-sublattice or highly parameterized formulations while maintaining reasonable accuracy.

The results indicate that the Fe-Si system exhibits non-ideal mixing behavior, as reflected in the calculated positive and negative deviations from ideality in Gibbs free energy and activity coefficients. These deviations are strongly dependent on the composition, with the dilute silicon region showing significant non-ideality due to strong Fe-Si interactions. The enthalpy and entropy contributions confirm the role of chemical short-range ordering in stabilizing the melt at intermediate compositions.

Overall, the Chou model successfully captures the essential thermodynamic trends of Fe-Si melts and provides a foundation for future computational and experimental investigations. The outcomes of this study have practical implications in ferrous metallurgy, particularly in process optimization of electrical steels, deoxidation practices, and alloy design at high temperatures. Future work may extend this framework to ternary systems and integrate with CALPHAD databases for broader applicability.

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