

Article

Dissociation Behavior of the Congruently Melting FeSi Compound in the Fe–Si System: A Bjerrum–Guggenheim Thermodynamic Analysis

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Abstract

This study presents a thermodynamic analysis of the dissociation and association behavior of the Fe–Si system using the Bjerrum–Guggenheim osmotic coefficient. An equilibrium thermodynamic approach was applied to evaluate the Gibbs free energy, equilibrium constant, and degree of association of the congruently melting compound FeSi over a wide temperature range. The Fe–Si system was analyzed across three characteristic crystallization regions: Fe-rich, FeSi, and Si-rich. It was established that the Fe-rich region exhibits behavior approaching ideality with a nearly linear dependence of the osmotic coefficient, whereas the Si-rich region is characterized by strong deviations from ideality due to intensive association processes. The FeSi crystallization region represents a transitional regime in which association and dissociation processes occur simultaneously. The formation and partial dissociation of $[\text{Fe}_x\text{Si}_y]$ clusters significantly affect the thermodynamic behavior of the melt. It was shown that accounting for FeSi dissociation leads to a linearization of the osmotic coefficient dependence and improves the accuracy of thermodynamic description. The proposed analytical approximations demonstrate high correlation coefficients ($R^2 \approx 0.99$), confirming the reliability of the developed approach. The results provide a consistent thermodynamic framework for describing phase transformations and structural evolution in Fe–Si melts and can be applied to the optimization of metallurgical processes involving silicon-containing alloys.

Keywords: Fe–Si system; thermodynamic analysis; dissociation; association; osmotic coefficient; Bjerrum–Guggenheim; FeSi; metallic melts



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1. Introduction

The iron–silicon (Fe–Si) system plays a key role in modern metallurgy, particularly in the production of ferrosilicon and silicon-containing steels. The thermodynamic properties of Fe–Si melts determine the features of phase transformations, the nature of the formed compounds, and, consequently, the technological parameters of metallurgical processes.

Thermodynamic analysis is widely used to describe phase equilibria and transformations in metallurgical systems. The effectiveness of thermodynamic modeling has been demonstrated for complex systems such as Fe–Ni–CO and oxide systems [1,2], as well as

for hydrogen reduction of iron-bearing materials followed by phase separation [3]. The combination of thermodynamic analysis with pilot-scale experimental studies provides a more comprehensive understanding of metallurgical system behavior [4].

Thermodynamic approaches are also successfully applied to the analysis of multicomponent alloys. In particular, phase equilibria and phase diagrams have been constructed for systems such as Fe–Cr–Si–B [5], Fe–Si–Al [6], and Fe–Ca–Si–Al [7]. These studies confirm the applicability of thermodynamic models for describing phase equilibria in complex multicomponent systems. Further development of these approaches has been presented in studies devoted to the thermodynamic substantiation of iron–silicon-based systems [8].

Classical and modern methods for calculating phase diagrams and thermodynamic properties are based on fundamental works on the CALPHAD approach [9], binary phase diagram analysis [10,11], and experimental studies of Fe–Si systems and silicon-containing alloys [12]. Advances in thermodynamic modeling and phase diagram construction are also presented in the works of Voronin [13] and Zakharov [14].

Despite the considerable amount of research, the behavior of the Fe–Si system in the liquid state, particularly with respect to association and dissociation processes of intermediate compounds, remains insufficiently understood. The congruently melting compound FeSi is a key element of the system; however, its thermodynamic stability and the nature of interactions between components in the melt require further investigation.

Modern concepts of the structure of silicon melts and silicide systems are based on the formation of local structural units and associates [15,16], as well as on the application of cluster models of liquids [17,18]. In this context, the consideration of thermal dissociation processes of compounds, as described in classical works [19–21], is essential for a more accurate description of deviations from ideal behavior.

Modern CALPHAD-based thermodynamic assessments of the Fe–Si system provide detailed descriptions of phase equilibria and thermodynamic properties of the liquid phase, including activities of components and enthalpy of mixing. These studies enable accurate prediction of liquidus and solidus boundaries and are widely used for validation of thermodynamic models. In particular, improved agreement between calculated and experimental data for activities and mixing enthalpies has been achieved in CALPHAD assessments of Fe–Si and related systems [9,11,22–25].

In the present work, the Fe–Si system is analyzed using an approach based on the Bjerrum–Guggenheim osmotic coefficient, which allows accounting for association and dissociation processes in the melt. The aim of this study is to investigate the thermodynamic behavior of the Fe–Si system with consideration of FeSi dissociation and to analyze the features of different crystallization regions.

2. Materials and Methods

2.1. Thermodynamic Framework

The dissociation behavior of the FeSi compound in the Fe–Si system was investigated using an equilibrium thermodynamic approach based on the concept of monovariant phase equilibria. This approach establishes a relationship between the Gibbs free energy change, the equilibrium constant, and the degree of association/dissociation of the compound.

The theoretical basis of the method involves the use of the Bjerrum–Guggenheim osmotic coefficient to evaluate deviations from ideality in phase-equilibrium systems. This approach has been successfully applied to the analysis of binary systems, such as Cr–Si (Baisanov), as well as more complex multicomponent systems based on iron and silicon [26].

The methodology for calculating and analyzing phase equilibria is based on modern thermodynamic approaches, including the CALPHAD method [9], thermodynamic model-

ing of phase diagrams [13], generalized lattice models [14], and thermodynamic modeling of metallurgical reduction processes [27].

A modified Schröder–Le Chatelier equation was used to describe crystallization lines (liquidus and solidus), taking into account the dependence of phase transformation temperatures on the system composition.

In the present study, the modified Schröder–Le Chatelier equation is expressed as:

$$\ln(x) = -\Delta H/R(1/T - 1/T_m)$$

where x is the mole fraction of the component, ΔH is the enthalpy of fusion, T is the temperature, and T_m is the melting temperature.

2.2. Thermodynamic Data

Thermodynamic data for the components of the Fe–Si system and the FeSi compound were taken from reference sources [27]. Standard values of enthalpy (ΔH°), entropy (ΔS°), and temperature-dependent coefficients were used to calculate the molar Gibbs free energy as a function of temperature.

The change in standard Gibbs free energy was determined using temperature-dependent thermodynamic functions of the system components. The obtained values were further used to calculate the equilibrium constant and to analyze the thermodynamic behavior of the system.

The thermodynamic parameters used in the calculations are summarized in Table 1. The coefficients A , B , and C correspond to parameters of temperature-dependent functions used to describe the molar Gibbs free energy of the system components in the following form:

$$G(T) = A + BT + C \ln(T)$$

Table 1. Standard thermodynamic parameters used for the calculation of Gibbs free energy in the Fe–Si system.

Phase	T (K)	ΔH° (J/mol)	ΔS° (J/(mol·K))	A	B	C
FeSi	298	−80,332.8	50.2	10.6	3.6	−0.20
FeSi	1680	68,617.6	40.8	19.5	—	—
Fe	298	0	24.2	17.5	24.8	—
Fe	1033	5104	4.9	37.7	—	—
Fe	1185	912.1	0.8	7.7	19.5	—
Fe	1667	1108	0.7	43.9	—	—
Fe	1811	13,811	7.6	43.5	—	—
Si	298	0	18.8	23.7	3.3	−4.3
Si	1703	50,210	29.5	27.2	—	—

These coefficients represent an analytical approximation of thermodynamic data and were used to evaluate the temperature dependence of the Gibbs free energy.

2.3. Calculation Procedure

The dissociation of the FeSi compound can be written as: $\text{FeSi} \rightleftharpoons \text{Fe} + \text{Si}$

The change in standard Gibbs free energy (ΔG°) was calculated as a function of temperature using standard thermodynamic relationships [28]. The equilibrium constant (K) was determined according to:

$$K_p = e^{(-\frac{\Delta G^\circ}{RT})}$$

where K_p is the equilibrium constant, ΔG° is the Gibbs free energy change (J/mol), R is the universal gas constant ($R = 8.314 \text{ J/(mol·K)}$), and T is the absolute temperature (K).

The thermodynamic quantities presented in Tables 2, 4 and 5 were evaluated using the following relationships. The parameters of the osmotic coefficient approximation are summarized in Table 3.

Table 2. Calculated thermodynamic parameters for the Fe-rich crystallization region of the Fe–Si system.

T	ΔG° (J/mol)	K_p	α	$X_{Fe}^{(L)}$	Φ''_{Fe}
1033	−33,833	9.460	0.0000	1.0000	0.0000
1185	−33,346	9.365	0.1617	0.9851	0.6752
1413	−33,075	9.311	0.3068	0.9747	0.6183
1548	−32,805	9.258	0.4340	0.9671	0.6472
1600	−32,534	9.204	0.5833	0.9597	0.6675
1667	−32,263	9.149	0.6828	0.9553	0.7294
1683	−31,993	9.095	0.7828	0.9512	0.7871
1703	−31,722	9.040	0.8834	0.9475	0.8418
1811	−31,451	8.985	0.9845	0.9440	0.8942

Table 3. Parameters of analytical approximations for the Bjerrum–Guggenheim osmotic coefficient in different crystallization regions of the Fe–Si system.

System	Crystallization Region	Phase	A	B	C	R
FeSi	Fe-rich	δ -Fe (Φ')	13.38	−12.24	−	−0.9978
FeSi	Fe-rich	δ -Fe (Φ'')	1.87	−1.47	−	−0.9995
FeSi	Fe-rich	α_2 -Fe (Φ')	24.47	−25.42	−	−0.9907
FeSi	Fe-rich	α_2 -Fe (Φ'')	0.99	−0.42	−	−0.9010
FeSi	Fe-rich	α_1 -Fe (Φ')	70.07	−81.53	−	0.9905
FeSi	Fe-rich	α_1 -Fe (Φ'')	−0.63	1.57	−	−0.9801
FeSi–Fe	FeSi region	FeSi (Φ')	1.84	−1.59	−	−0.9920
FeSi–Si	FeSi region	FeSi (Φ')	1.55	−1.24	−	−0.9967
Si–Fe	Si-rich	Si (Φ')	−0.788	0.3504	−1.358	−

The degree of association (α) represents the fraction of atoms involved in associated cluster structures in the melt and was determined using the method proposed by Temkin and Shvartsman, based on the relationship between the equilibrium constant and the extent of association in the melt.

The mole fraction of iron in the liquid phase $X_{Fe}^{(L)}$ was calculated from phase equilibrium conditions for the corresponding temperature and composition.

The Bjerrum–Guggenheim osmotic coefficient (Φ) was introduced as a thermodynamic parameter characterizing deviations from ideal solution behavior in the melt.

In the present study, the Bjerrum–Guggenheim osmotic coefficient is not used in the classical sense of membrane osmosis, but as a formal thermodynamic parameter derived from statistical thermodynamics. It is introduced to describe deviations from ideal solution behavior in terms of activity–composition relationships.

Unlike classical activity coefficients, the osmotic coefficient provides a convenient framework for analyzing association–dissociation processes through the shape of the Φ –activity dependence. In this approach, Φ reflects interparticle interactions and structural ordering in the melt and can be directly related to phase equilibrium conditions.

Therefore, the use of the osmotic coefficient allows a unified semi-empirical description of thermodynamic behavior in Fe–Si melts, particularly in systems where cluster formation and dissociation processes are significant.

In the present study, Φ is defined through the relationship between component activities and mole fractions in the liquid and solid phases:

$$\Phi = \ln(a^L/a^S)/\ln(x^L/x^S)$$

where a^L and a^S are the activities of the component in the liquid and solid phases, and x^L and x^S are the corresponding mole fractions.

This expression provides a quantitative measure of deviation from ideal solution behavior, for which $a = x$ and $\Phi = 1$.

For practical calculations, the dependence of the osmotic coefficient on component activity was approximated using a polynomial expression:

$$\Phi = A_\Phi + B_\Phi \ln(a) + C_\Phi (\ln(a))^2$$

where A_Φ , B_Φ , and C_Φ are empirical coefficients of the osmotic-coefficient approximation. The coefficients for different crystallization regions are summarized in Table 3. These parameters should not be confused with the coefficients A, B, and C listed in Table 1, which are used to describe the temperature dependence of the Gibbs free energy.

The thermodynamic description of phase equilibrium is based on a modified form of the Schröder–Le Chatelier equation:

$$\ln(a) = -\frac{\Delta H_m}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) + \ln(\Phi)$$

where ΔH_m is the enthalpy of melting, T_m is the melting temperature of the component, R is the universal gas constant, and T is the absolute temperature.

The resulting values of ΔG° , K_p , α , liquid-phase mole fraction, and Φ calculated using these relationships are presented in Tables 2, 4 and 5 for the corresponding crystallization regions.

In this formulation, the osmotic coefficient acts as a correction term accounting for non-ideality, allowing the extension of the classical Schröder–Le Chatelier equation to real metallic systems.

Thus, the proposed approach provides a semi-empirical thermodynamic framework for describing phase equilibria and enables the analysis of association–dissociation processes in Fe–Si melts.

The dependence of Φ on component activity was determined using calculated thermodynamic parameters. For systems approaching ideal behavior, linear approximations were applied, whereas for systems exhibiting association or dissociation, second-order polynomial functions were used.

The shape of the Φ dependence was interpreted as follows: a convex profile corresponds to dissociation processes, whereas a concave profile indicates association and cluster formation.

The calculated thermodynamic parameters and osmotic coefficient values were processed using the least-squares method. Correlation coefficients (R^2) were determined to assess the reliability of the obtained relationships.

2.4. Temperature Range and Phase Regions

The calculations were carried out over a temperature range from 298 to 3000 K, covering all major phase transformations in the Fe–Si system.

The temperature range was divided into the following intervals: 298–1033 K, 1033–1185 K, 1185–1667 K, 1667–1683 K, 1683–1703 K, 1703–1811 K, and 1811–3000 K.

These intervals correspond to characteristic phase transitions of the components of the Fe-Si system and the intermediate compound FeSi [10–12].

The analysis was performed separately for different crystallization regions of the Fe-Si system, which made it possible to evaluate the features of the dissociation behavior of the compound under various thermodynamic conditions.

2.5. Application of the Bjerrum–Guggenheim Coefficient

The Bjerrum–Guggenheim osmotic coefficient (Φ) was used to characterize deviations from ideal solution behavior and to analyze interparticle interactions and structural ordering in the melt.

The dependence of Φ on component activity was determined using calculated and literature data. The obtained relationships were approximated using:

- linear functions for systems approaching ideal behavior,
- second-order polynomial functions for systems exhibiting association or dissociation.

The shape of the Φ -activity dependence was interpreted as follows: a convex curve corresponds to dissociation processes, whereas a concave curve indicates association and cluster formation [17,18].

2.6. Data Processing

The calculated thermodynamic parameters and osmotic coefficient values were processed using the least-squares method.

Correlation coefficients were evaluated, and the reliability of the obtained relationships was assessed.

The results were interpreted in terms of phase stability, structural transformations, and cluster formation processes in Fe–Si melts [19,29].

3. Results and Discussion

3.1. Features of the Fe–Si Phase Diagram

The phase diagram of the Fe–Si system (Figure 1) plays a key role in understanding phase transformations and structural features of iron–silicon melts.

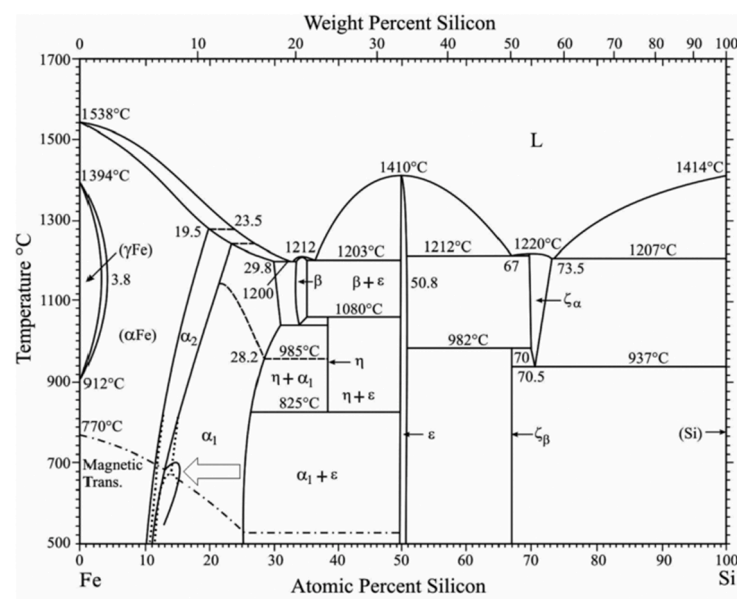


Figure 1. Phase diagram of the Fe–Si system.

It includes a number of intermediate phases, such as Fe_3Si , Fe_2Si , Fe_5Si_3 , FeSi , FeSi_2 , and Fe_2Si_5 , as well as solid solutions based on α -Fe and γ -Fe.

The FeSi compound is of particular interest because it melts congruently and represents a stable intermediate phase in the system. Its behavior near the melting temperature provides important information about the thermodynamic stability and structural organization of the melt.

For the purposes of the present thermodynamic analysis, the Fe–Si phase diagram can be conventionally divided into three characteristic crystallization regions: the Fe-rich region, the FeSi crystallization region, and the Si-rich region.

Each of these regions is characterized by specific thermodynamic conditions and interaction mechanisms between components, which determine the degree of association and dissociation of the FeSi compound.

In the Fe-rich region, solid solutions based on α -Fe and γ -Fe predominate, where ordering processes (α_1 and α_2 phases) may occur. Phase transformations in this region are associated with changes in the crystal structure of iron and its interaction with silicon [29,30].

In the FeSi crystallization region, the formation of the congruently melting compound FeSi dominates. The stability of this phase is determined by the balance between association processes (formation of clusters such as $[\text{Fe}_x\text{Si}_y]$) and dissociation processes in the melt.

In the Si-rich region, the system is characterized by the presence of silicon-based phases and a strong tendency toward the formation of complex structural units in the melt [15,16].

The phase diagram used in this study is based on literature data and thermodynamic analysis [9–12,14], which provide a reliable description of phase equilibria and temperature–composition relationships for the Fe–Si system.

In addition, methods for constructing liquidus and solidus lines, including approaches for describing eutectic systems [31], were taken into account, which enhances the reliability of thermodynamic modeling.

3.2. Fe-Rich Region

The Fe-rich region of the Fe–Si system corresponds to low silicon concentrations and is characterized by the crystallization of iron-based solid solutions. For the purposes of the present analysis, this region is treated as extending up to approximately 0.34 at.% Si, depending on the phase boundaries shown in the phase diagram.

In this region, phase transformations are primarily governed by structural changes in iron and its interaction with small amounts of silicon [30,32].

The calculated thermodynamic parameters for this region, including the Gibbs free energy change (ΔG°), equilibrium constant (K_p), degree of association (α), mole fraction of iron in the liquid phase $X_{\text{Fe}}^{(L)}$, and the Bjerrum–Guggenheim osmotic coefficient Φ_{Fe}'' , are presented in Table 2.

The temperatures listed in Table 2 correspond to characteristic phase transformation points and representative temperatures within the Fe-rich crystallization region.

As follows from the obtained data, the Gibbs free energy values remain negative over the entire temperature range, indicating the thermodynamic favorability of associated states in the system.

At the same time, a gradual decrease in the equilibrium constant (K_p) with increasing temperature is observed, reflecting a reduction in the stability of these associated structures.

The degree of association (α) increases with temperature and approaches unity, indicating a transition toward a more ordered state. Simultaneously, the mole fraction of iron in the liquid phase $X_{\text{Fe}}^{(L)}$ decreases, reflecting gradual enrichment of the melt with silicon and redistribution of components between phases.

The dependence of the Bjerrum–Guggenheim osmotic coefficient on component activity in the Fe-rich region is shown in Figure 2.

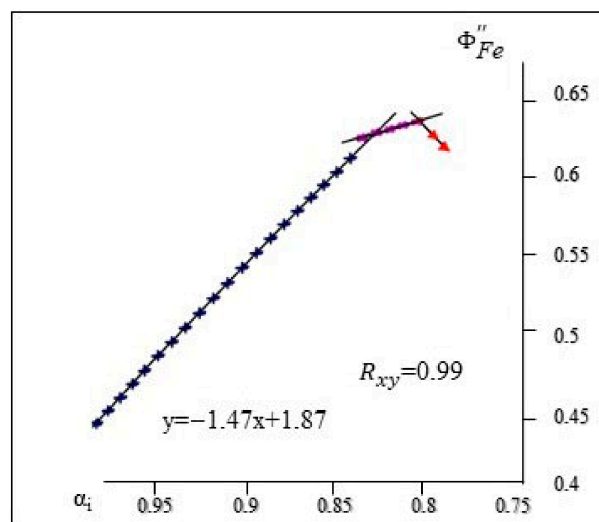


Figure 2. Dependence of the Bjerrum–Guggenheim osmotic coefficient (Φ_{Fe}) on the activity of iron (a_{Fe}) in the Fe-rich region of the Fe–Si system. Solid line represents the linear approximation; symbols correspond to calculated data; arrows indicate the direction of deviation from ideal behavior.

As shown, the Φ –activity relationship is close to linear, indicating behavior approaching ideality for the Fe-rich side, where iron is the dominant component of the system, although deviations from ideal behavior remain for the minor component (Si). The high correlation coefficient ($R \approx 0.99$) confirms the validity of the linear approximation and suggests relatively weak interparticle interactions in this region.

Slight deviations from linearity indicate the presence of structural transformations in the system. These deviations occur near characteristic temperatures and can be associated with second-order phase transitions related to ordering processes in iron [30,33].

The presence of multiple characteristic points indicates that the ordering behavior in the Fe-rich region is more complex than predicted by idealized models.

Thus, the Fe-rich region is characterized by behavior approaching ideality for the Fe-rich side, with localized deviations associated with ordering processes. These effects influence phase stability and govern the evolution of the system during crystallization.

3.3. FeSi Crystallization Region

In the FeSi crystallization region, the thermodynamic stability of cluster formations of the type $[Fe_xSi_y]$ strongly depends on temperature and system composition. The most stable associates are formed near the melting temperature of the congruently melting FeSi compound, which determines the nature of interactions between components in the melt.

For this region, the dependences of the Bjerrum–Guggenheim osmotic coefficient on component activity were constructed. The obtained relationships exhibit significant deviations from ideal behavior, caused by association processes and the formation of cluster structures [17,18].

As shown in Figure 3a, the Φ –activity relationship in the FeSi crystallization region is distinctly nonlinear, indicating the formation of variable-composition associates and the presence of strong interparticle interactions in the melt.

When the degree of dissociation of the FeSi compound is taken into account (Table 3), a linearized relationship is obtained (Figure 3b) with a high correlation coefficient ($R \approx 0.99$). This demonstrates that accounting for dissociation processes significantly improves the accuracy of the thermodynamic description of the system. Here, Φ' and Φ'' de-

note the osmotic coefficient calculated without and with consideration of dissociation processes, respectively.

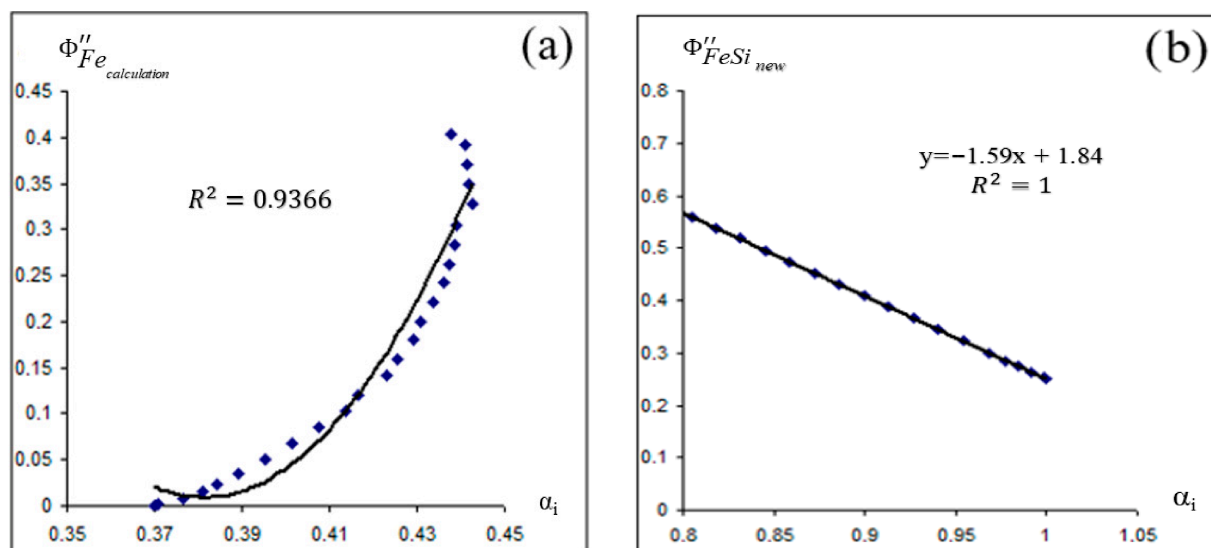


Figure 3. Dependence of the Bjerrum–Guggenheim osmotic coefficient on component activity in the FeSi crystallization region of the Fe–Si system: (a) nonlinear dependence; (b) linearized dependence accounting for dissociation.

The results indicate that, in the FeSi region, the system undergoes a transition from an associated state of the melt to a partially dissociated state, which is reflected in the change in the shape of the Φ –activity dependence.

The calculated thermodynamic parameters for the FeSi crystallization region over the entire temperature range are presented in Table 4. The extended dataset enables a more detailed analysis of the evolution of thermodynamic characteristics.

Table 4. Calculated thermodynamic parameters for the FeSi crystallization region of the Fe–Si system.

T (K)	ΔG° (J/mol)	K_p	A	$X_{Fe}^{(L)}$	Φ''_{Fe}
1683	18,401	0.26846	0.46005	0.36982	0.0000
1682	18,480	0.26673	0.45596	0.37092	0.0014
1677	18,878	0.25820	0.44216	0.37641	0.0086
1672	19,275	0.24992	0.39764	0.38090	0.0159
1667	19,672	0.24186	0.36282	0.38448	0.0235
1660	20,221	0.23105	0.32822	0.38909	0.0343
1650	21,002	0.21633	0.29132	0.39532	0.0504
1640	21,780	0.20243	0.26291	0.40146	0.0671
1630	22,555	0.18931	0.23982	0.40762	0.0847
1620	23,327	0.17694	0.21969	0.41359	0.1029
1610	24,096	0.16528	0.19650	0.41656	0.1210
1600	24,861	0.15429	0.18293	0.42316	0.1410
1590	25,623	0.14395	0.16448	0.42532	0.1599
1580	26,382	0.13421	0.15076	0.42926	0.1801
1570	27,138	0.12505	0.13635	0.43092	0.1998
1560	27,891	0.11644	0.12486	0.43387	0.2207
1550	28,640	0.10835	0.11409	0.43615	0.2417
1540	29,359	0.10096	0.10419	0.43752	0.2625
1530	30,129	0.09362	0.09465	0.43863	0.2836
1520	30,868	0.08693	0.08595	0.43884	0.3043
1510	31,604	0.08067	0.07973	0.44262	0.3285
1500	32,337	0.07480	0.07211	0.44164	0.3488

Table 4. Cont.

T (K)	ΔG° (J/mol)	K_p	A	$X_{Fe}^{(L)}$	Φ''_{Fe}
1490	33,067	0.06930	0.06562	0.44151	0.3702
1480	33,793	0.06416	0.05960	0.44085	0.3913
1473	34,516	0.05970	0.05387	0.43770	0.4032

Analysis of the obtained results shows that, with increasing temperature, dissociation processes of the FeSi compound become more pronounced, leading to changes in interparticle interactions and melt structure. Conversely, with decreasing temperature, the associated state becomes thermodynamically more stable.

An increase in the standard Gibbs free energy (ΔG°) with decreasing temperature reflects changes in the thermodynamic balance between association and dissociation processes in this crystallization region. At the same time, the equilibrium constant (K_p) decreases significantly, indicating a change in thermodynamic behavior within the FeSi crystallization region. This trend is accompanied by changes in the degree of association (α), reflecting the evolving stability of FeSi-related clusters in the melt.

Simultaneously, a pronounced nonlinear increase in the osmotic coefficient (Φ) is observed, indicating significant deviations from ideal behavior and the presence of competing association and dissociation processes.

A characteristic feature of this region is the coexistence of associated clusters and dissociated species in dynamic equilibrium, which determines the complex nature of interparticle interactions and thermodynamic behavior of the system.

Thus, the FeSi crystallization region represents a transitional regime between near-ideal behavior (Fe-rich region) and strongly associated behavior (Si-rich region), in which both association and dissociation processes simultaneously occur and govern the thermodynamic properties of the system.

The obtained results are consistent with CALPHAD-based thermodynamic assessments of the Fe–Si system, particularly in terms of phase stability and trends in component activities. The calculated behavior of the osmotic coefficient and the degree of association agrees with established thermodynamic descriptions of liquid Fe–Si alloys, including the position of phase boundaries and general features of liquidus and solidus lines, confirming the validity of the proposed approach.

These findings are further supported by modern thermodynamic studies of Fe–Si and related liquid alloy systems, including CALPHAD-based assessments and recent investigations of mixing enthalpy in liquid phases [22,23].

3.4. Si-Rich Region

The structure of liquid alloys in the Si-rich region of the Fe–Si system near the liquidus line has been investigated in previous studies [15,16]. It has been shown that at temperatures close to the liquidus, interactions between atoms of the same type predominate, especially at small overheating above the liquidus line.

With increasing temperature, interactions between atoms of different types become more significant, leading to increased structural complexity of the melt and the formation of stable associated states.

The dependence of the Bjerrum–Guggenheim osmotic coefficient on component activity for the α -Si crystallization region is shown in Figure 4a.

As follows from Figure 4a, a pronounced nonlinear increase in the osmotic coefficient is observed with decreasing temperature from the melting point of silicon (~1685 K) to the eutectic temperature (~1481 K). This behavior indicates intensive formation of $[Fe_xSi_y]$ associates in the melt [17,18].

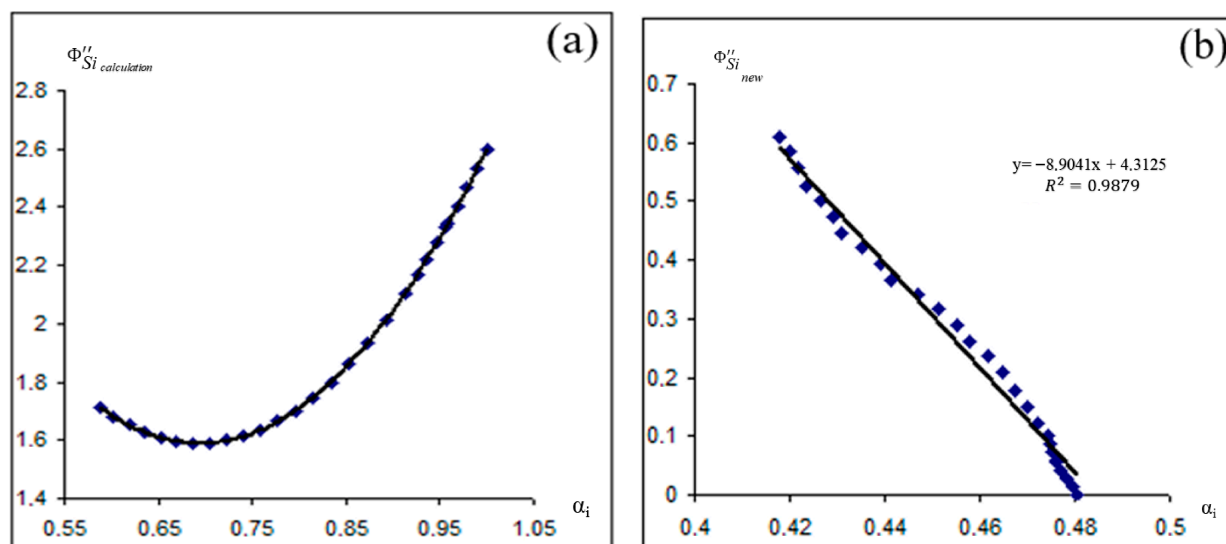


Figure 4. Dependence of the Bjerrum–Guggenheim osmotic coefficient on component activity in the Si-rich region of the Fe–Si system: (a) nonlinear dependence; (b) linearized dependence accounting for dissociation.

The calculated thermodynamic parameters for this region are presented in Table 5.

Table 5. Calculated thermodynamic parameters for the Si-rich crystallization region of the Fe–Si system.

T (K)	ΔG° (J/mol)	K_p	A	$X_{Si}^{(L)}$	Φ''_{Si}
1703	−25,082	5.8796	0.9245	0.48038	0.0000
1698	−25,216	5.9666	0.9216	0.47960	0.0142
1693	−25,349	6.0551	0.9168	0.47830	0.0284
1688	−25,481	6.1451	0.9120	0.47698	0.0426
1683	−25,612	6.2366	0.9091	0.47618	0.0568
1682	−25,679	6.2734	0.9085	0.47602	0.0596
1677	−26,014	6.4608	0.9055	0.47520	0.0739
1672	−26,347	6.6547	0.9034	0.47463	0.0882
1667	−26,680	6.8552	0.9023	0.47432	0.1027
1660	−27,148	7.1499	0.8941	0.47204	0.1224
1650	−27,816	7.5962	0.8867	0.46998	0.1509
1640	−28,479	8.0745	0.8773	0.46732	0.1791
1630	−29,140	8.5873	0.8687	0.46485	0.2073
1620	−29,798	9.1374	0.8579	0.46176	0.2351
1610	−30,452	9.7280	0.8450	0.45801	0.2623
1600	−31,103	10.3624	0.8349	0.45502	0.2899
1590	−31,751	11.0442	0.8227	0.45137	0.3168
1580	−32,396	11.7775	0.8084	0.44703	0.3429
1570	−33,038	12.5667	0.7901	0.44136	0.3673
1560	−33,776	13.5203	0.7826	0.43901	0.3948
1550	−34,311	14.3324	0.7705	0.43520	0.4207
1540	−34,943	15.3199	0.7576	0.43105	0.4460
1530	−35,571	16.3856	0.7515	0.42906	0.4739
1520	−36,197	17.5364	0.7443	0.42669	0.5013
1510	−36,819	18.7800	0.7340	0.42328	0.5272
1500	−37,438	20.1250	0.7295	0.42179	0.5559
1490	−38,053	21.5805	0.7239	0.41992	0.5842
1481	−38,665	23.1078	0.7173	0.41767	0.6088

Analysis of the data in Table 5 shows that the Gibbs free energy values remain negative and decrease with decreasing temperature, indicating high thermodynamic stability of the associated state.

At the same time, the equilibrium constant (K_p) increases, confirming the dominance of association processes. Although the degree of association (α) slightly decreases, its values remain high, indicating the preservation of structural ordering in the melt.

The osmotic coefficient exhibits a pronounced nonlinear dependence, reflecting significant deviations from ideal behavior and confirming the formation of stable silicon-rich clusters.

When FeSi is considered as the main structural unit of the melt, a linearized dependence is obtained (Figure 4b) with a high correlation coefficient ($R^2 \approx 0.99$), confirming the adequacy of the proposed thermodynamic model.

The obtained results are consistent with classical concepts of thermal dissociation and structural transformations in condensed systems [19,29].

Thus, the Si-rich region is characterized by a strongly associated state of the melt with pronounced deviations from ideal behavior, completing the transition from the Fe-rich region through the transitional FeSi region to the structurally complex Si-rich region.

The obtained results are consistent with general thermodynamic expectations and complement existing CALPHAD-based descriptions rather than replacing them. The proposed approach provides additional insight into structural transformations and association–dissociation behavior in Fe–Si melts within its defined scope.

4. Conclusions

1. An equilibrium thermodynamic approach based on the Bjerrum–Guggenheim osmotic coefficient was applied to analyze the dissociation behavior of the Fe–Si system. The proposed method allows the description of phase behavior in condensed metallic systems beyond classical dissociation models.
2. It was established that the thermodynamic behavior of the Fe–Si system changes systematically with composition. The Fe-rich region is characterized by behavior approaching ideality for the Fe-rich side, where iron is the dominant component, whereas the Si-rich region exhibits strong deviations associated with intensive interparticle interactions.
3. The FeSi crystallization region represents a transitional regime in which both association and dissociation processes occur simultaneously. The formation and partial dissociation of $[\text{Fe}_x\text{Si}_y]$ clusters determine the thermodynamic properties of the melt.
4. The analysis of the osmotic coefficient showed that a linear dependence corresponds to systems approaching ideal behavior, while nonlinear (concave) behavior indicates the presence of association processes and cluster formation.
5. It was demonstrated that accounting for the dissociation of FeSi leads to linearization of the osmotic coefficient dependence and significantly improves the accuracy of thermodynamic description ($R^2 \approx 0.99$).
6. The obtained results provide a consistent thermodynamic framework for describing phase transformations and structural evolution in Fe–Si melts. The proposed approach can be applied to the analysis and optimization of metallurgical processes involving silicon-containing alloys and may be extended to multicomponent systems.

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