A procedure was developed to calculate the position of lines of monovariant phase equilibria for crystallization areas of congruently melting compounds through the dissociation degree of a chemical compound. The relevant mathematical apparatus was recommended to describe analytically the lines and surfaces of crystallization phases using the Bjerrum-Guggenheim coefficient. The iron-silicon phase diagram demonstrated that the osmotic coefficient of Bjerrum-Guggenheim (its linear dependence) can be as an assessment criterion of the composition of melts.

**Key words:** Fe-Si system, crystallization phase, mathematical equations, dissociation degree, Bjerrum-Guggenheim coefficient.

## INTRODUCTION

At the modern stage of a fundamental understanding of the melting processes, the approach to which is based on the analysis of phase diagrams of the alloys and interaction of the components with each other [1-3], it is important to perform some fundamental studies in the physicochemical analysis, which would give rise to serious generalizations and scientifically based practical recommendations.

The extensive thermodynamic information that can be taken from the phase diagram is practically not used due to the relatively weak substantiated analysis of phase equilibria. Referring to our long experience in the mathematical description of lines of monovariant phase equilibria based on the Bjerrum-Guggenheim ($\Phi_i$) concept, we drew attention to the anomalous behavior of this coefficient near the melting temperature of a congruent compound [4].

Using the developed procedure to describe lines of monovariant phase equilibria through the osmotic coefficient of Bjerrum-Guggenheim, we obtained an accurate mathematical formula as modified Le-Chatelier-Shreder equation that described the real position of the liquidus and solidus lines on the phase diagram [4].

However in the areas of congruently melting compounds, the dependence diagrams of $\Phi_i$ from the ratio of component activities $a_1^L/a_1^S$ did not lie on the line the recalculating of the compositions to particular systems (quasi-systems).

The study of complex systems with various chemical transformations, accompanied by a change in composition, requires the introduction of new variable values characterizing these changes. One of the characteristics is a process completion rate.

The process completion rate can be shown with the dissociation degree. The dissociation degree $\alpha$ is a ratio of the number of dissociated substance moles in equilibrium to the total number of substance moles before dissociation:

\[
\alpha = \frac{d n_i}{n_i^0}, \tag{1}
\]

where $d n_i$ – dissociated moles of substance; $n_i$ – the total number of his moles.

Calculation of position of the lines of monovariant phase equilibria through the dissociation degree of a chemical compound as an example a congruently melting compound AB will be studied:

\[
AB = A + B. \tag{2}
\]

The number of substance moles in the equilibrium state of the system should be calculated:

\[
n_{AB} = z_{AB} - \alpha \tag{3}
\]
\[
n_A = z_A + \alpha \tag{4}
\]
\[
n_B = \alpha \tag{5}
\]

where $n_{AB}, n_A, n_B$ – a number of substance moles of AB, A, B in the equilibrium state; $z_{AB}, z_A, z_B$ – a number of substance moles of AB and A in initial state; $\alpha$ - dissociation degree.

The total number of moles of AB, A and B in the mixture will be calculated:

\[
\Sigma n = z_{AB} - \alpha + z_A + \alpha = l + \alpha \tag{6}
\]

The mole fraction of each mixture component will be as:
The phase diagram of the two-component Fe – Si system is shown in Figure 1. In crystallization, FeSi is thermodynamically stable or cluster strength \([FexSiy]\) is different \([7]\). Thus, the clusters formed at melting of the congruently melting compound FeSi are solid.

The dependence diagrams of the osmotic coefficient of Bjerrum-Guggenheim \((\Phi)\) on activity \((a)\) are set up. Figure 2a (system FeSi-Fe) shows that the formation of FeSi associates is characteristic for this crystallization area. While taking into account the dissociation degree of FeSi (Table 1), new diagrams of the osmotic coefficient of Bjerrum-Guggenheim (Figure 2b, equation (7)) were obtained.

Table 1 demonstrates the calculated thermodynamic data for the second crystallization area of the FeSi-Si quasi-system.

The phase diagram of composition – temperature of the two-component Fe – Si system is shown in Figure 1. In crystallization, FeSi is thermodynamically stable or cluster strength \([Fe_{Si_{1}}]\) is different \([7]\).

Thus, the clusters, formed at melting of the congruently melting compound FeSi, are solid.

The dependence diagrams of the osmotic coefficient of Bjerrum-Guggenheim for FeSi-Fe quasi-system are shown in Figure 1. In crystallization, FeSi is thermodynamically stable or cluster strength \([Fe_{Si_{1}}]\) is different \([7]\).

Thus, the clusters, formed at melting of the congruently melting compound FeSi, are solid.

The dependence diagrams of the osmotic coefficient of Bjerrum-Guggenheim \((\Phi)\) on activity \((a)\) are set up. Figure 2a (system FeSi-Fe) shows that the formation of FeSi associates is characteristic for this crystallization area. While taking into account the dissociation degree of FeSi (Table 1), new diagrams of the osmotic coefficient of Bjerrum-Guggenheim (Figure 2b, calculation by equation (7)) with correlation dependence \(R=0.987\) were obtained.

Table 1 demonstrates the calculated thermodynamic data for the second crystallization area of the FeSi-Si quasi-system.

The dependence diagrams of the osmotic coefficient of Bjerrum-Guggenheim are shown in Figure 3a, b. The convexity of the diagram (Figure 3a) demonstrates that the presence of congruently chemical compound FeSi in the melting is characteristic for this crystallization area.

According to our developed procedure, a new diagram (Figure 3b) with a correlation dependence of
0.9982 was obtained by taking into account the dissociation degree of the compound.

**CONCLUSIONS**

Thus, the Gibbs energies of the dissociation reaction of the stable chemical compound FeSi, equilibrium constant along the line of monovariant phase equilibrium and the dissociation degree of the congruently melting compound FeSi were calculated. It was found that for the Fe-Si binary system the dissociation degree FeSi is 45%, which indicates a very good dissociation of this compound up to the eutectic temperature [4].

This system is characterized by a smooth run of the liquidus curve at the melting temperature of the congruently melting compound FeSi in compliance with the conclusions of N.S. Kurnakov on dissociation of the congruent compound in the melting [2, 8].
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