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ESTIMATION OF DISSOCIATION DEGREE OF CONGRUENTLY MELTING COMPOUNDS THROUGH OSMOTIC COEFFICIENT OF BJERRUM-GUGGENHEIM

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Preliminary Note – Prethodno priopćenje

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 analyticallythe 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, crystalization phase, mathematical equations, dissocitaion 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 (Φ_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 Φ_i from the ratio of component activities a_1^L/a_1^S did not lie on lineatthe recalculating of the compositions to particular systems (quasi-systems).

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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 shownwith the dissociation degree. The dissociation degree α is a ratio of the number of dissociated substance moles in equilibrium to the total number of substance moles before dissociation:

$$\alpha = \frac{dn_i}{n_i^0}, \quad (1)$$

where dn_i – dissociated moths 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:

$$AB = A + B. \quad (2)$$

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

$$n_{AB} = z_{AB} - \alpha \quad (3)$$
$$n_A = z_A + \alpha \quad (4)$$
$$n_B = \alpha \quad (5)$$

where n_{AB}, n_A, n_B – a number of substance molesof AB, A, B in the equilibrium state; z_{AB}, z_A – a number of substance moles of AB and A in initial state; α - adissociation degree.

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

$$\Sigma n = z_{AB} - \alpha + z_A + \alpha + \alpha = 1 + \alpha \quad (6)$$

The mole fraction of each mixture component will be as:

$$x_{AB}=\frac{z_{AB}-\alpha}{1+\alpha};\ x_A=\frac{z_A+\alpha}{1+\alpha};\ x_B=\frac{\alpha}{1+\alpha}. \quad (7)$$

In order to determine the dissociation degree of a congruently melting compound, it is necessary to know a value of equilibrium constant (K_p) of the dissociation reaction as a temperature function:

$$\ln K_p=-\frac{\Delta G_p(T)}{RT} \quad (8)$$

$$K_P=\frac{x_A x_B}{x_{AB}}=\exp\left(-\frac{\Delta G_p(T)}{RT}\right), \quad (9)$$

where DG_p- Gibbs energy of reaction.

The equilibrium constant in dissociation reaction should be shown through the mole fractions of the mixture components:

$$K_P=\frac{z_A\alpha-\alpha^2}{z_{AB}+z_{AB}\alpha-\alpha-\alpha^2}. \quad (10)$$

From this equation the dissociation degree of a congruently melting compound should becalculated:

$$\alpha_{1,2}=\frac{K_p Z_{AB}-Z_A-K_p\pm\sqrt{K_p^2(1+Z_{AB})^2}}{2+2K_p}+ \quad (11)$$
$$+\frac{\sqrt{2K_p(Z_A-Z_AZ_{AB}+2Z_{AB})+Z_A^2}}{2+2K_p}.$$

Thus, equation permits to calculate the dissociation degree of a congruently melting compound and the mole composition is equal to AB.

WAYS OF STUDY

A new approach was recommended to calculate the dissociation degree of a congruently melting compound (example: Fe – Si phase diagram for FeSi compound) through the mathematical formula of the liquidus line. This formula is represented as modified Le Chatelier-Shreder equation [5,6].

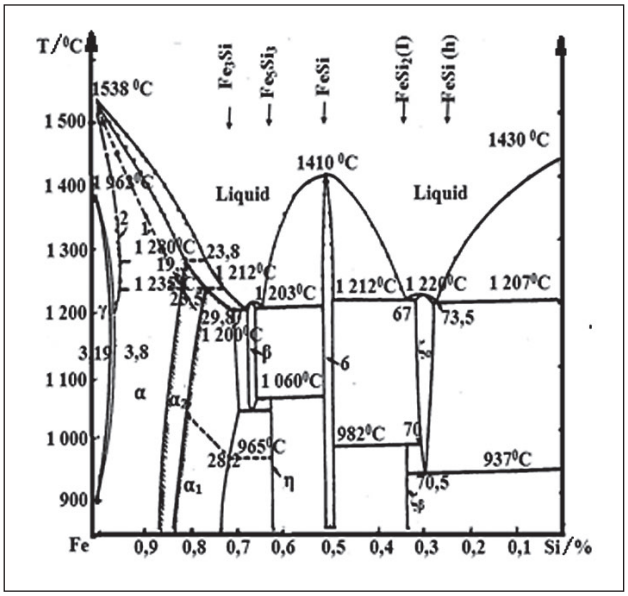

Figure 1 The phase diagram Fe-Si [5]

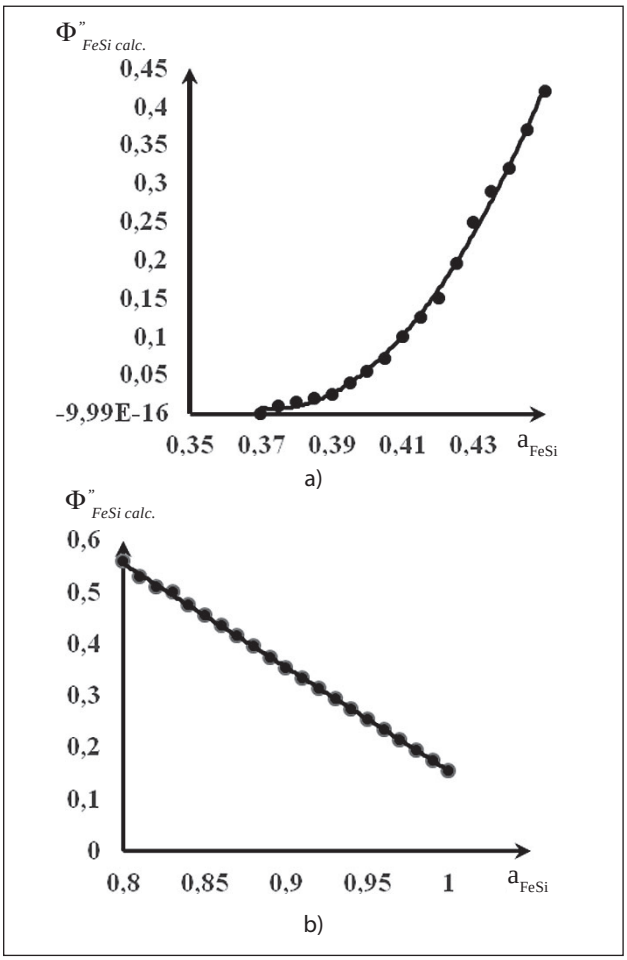

Figure 2 Dependence of the osmotic coefficient of Bjerrum-Guggenheim for FeSi -Fe quasi-system, where a) – $\Phi_{FeSi\ calc.}=f(a_{FeSi})$; b) - $\Phi_{FeSi\ new}=f(x_{FeSi})$.

The phase diagram of composition – temperature of the two-component Fe – Si system is shown in Figure 1.

In crystallization are FeSi the thermodynamic stability or cluster strength [Fe_xSi_y] 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 (Φ_i) on activity (a_i) 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 diagramsof the osmotic coefficient of Bjerrum-Guggenheim are shown in Figure 3 a, 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

Table1 The **crystallization area FeSion FeSi-Fesegment**

T, K	The crystallization are a FeSi on FeSi-Fe segment					The crystallization are a FeSi on FeSi-Si segment				
	ΔG^0	x^L_{FeSi}	α	$x^L_{(new)FeSi}$	$\Phi''_{(new)FeSi}$	ΔG^0	x^L_{FeSi}	α	$x^L_{(new)FeSi}$	$\Phi''_{(new)FeSi}$
1 683	18 401	0,269	0,46	0,36981	0	18 401	0,268	0,46	0,36982	0
1 682	18 480	0,267	0,45	0,37091	0,00140	18 480	0,267	0,43	0,37045	0,0014
1 677	18 878	0,259	0,44	0,37640	0,00857	18 878	0,258	0,39	0,37485	0,0085
1 672	19 275	0,249	0,39	0,38089	0,01593	19 275	0,250	0,37	0,37935	0,0159
1 667	19 672	0,242	0,36	0,38447	0,02347	19 672	0,242	0,36	0,38382	0,0234
1 660	20 221	0,231	0,33	0,38909	0,03430	20 221	0,231	0,33	0,38909	0,0343
1 650	21 002	0,216	0,29	0,39532	0,05036	21 002	0,216	0,29	0,39491	0,0503
1 640	21 780	0,202	0,26	0,40145	0,06714	21 780	0,202	0,26	0,39993	0,0669
1 630	22 555	0,189	0,24	0,40762	0,08467	22 555	0,189	0,23	0,40465	0,0840
1 620	23 327	0,177	0,22	0,41358	0,10293	23 327	0,177	0,21	0,40885	0,1016
1 610	24 096	0,165	0,19	0,41655	0,12099	24 096	0,165	0,18	0,40873	0,1184
1 600	24 861	0,154	0,18	0,42315	0,14096	24 861	0,154	0,16	0,41030	0,1361
1 590	25 623	0,144	0,16	0,42531	0,15988	25 623	0,144	0,15	0,41166	0,154
1 580	26 382	0,134	0,15	0,42923	0,18013	26 382	0,134	0,13	0,41092	0,1713
1 570	27 138	0,125	0,13	0,43091	0,19979	27 138	0,125	0,12	0,40784	0,1875
1 560	27 891	0,116	0,12	0,43387	0,22067	27 891	0,116	0,11	0,40709	0,2050
1 550	28 640	0,108	0,11	0,43614	0,24166	28 639	0,108	0,09	0,40797	0,2237
1 540	29 359	0,101	0,10	0,43752	0,26250	29 359	0,101	0,09	0,40803	0,2421
1 530	30 129	0,093	0,09	0,43863	0,28357	30 128	0,094	0,08	0,40920	0,2615
1 520	30 868	0,087	0,08	0,43883	0,30426	30 868	0,087	0,07	0,40826	0,2797
1 510	31 604	0,081	0,07	0,44261	0,32849	31 604	0,081	0,07	0,41106	0,3012
1 500	32 337	0,075	0,07	0,44163	0,34885	32 337	0,075	0,06	0,41353	0,3229
1 490	33 067	0,069	0,06	0,44151	0,37025	33 067	0,069	0,05	0,41565	0,3448
1 480	33 793	0,063	0,05	0,44084	0,39134	33 431	0,067	0,05	0,41504	0,3543
1 473	34 516	0,060	0,05	0,43771	0,40324	-	-	-	-	-

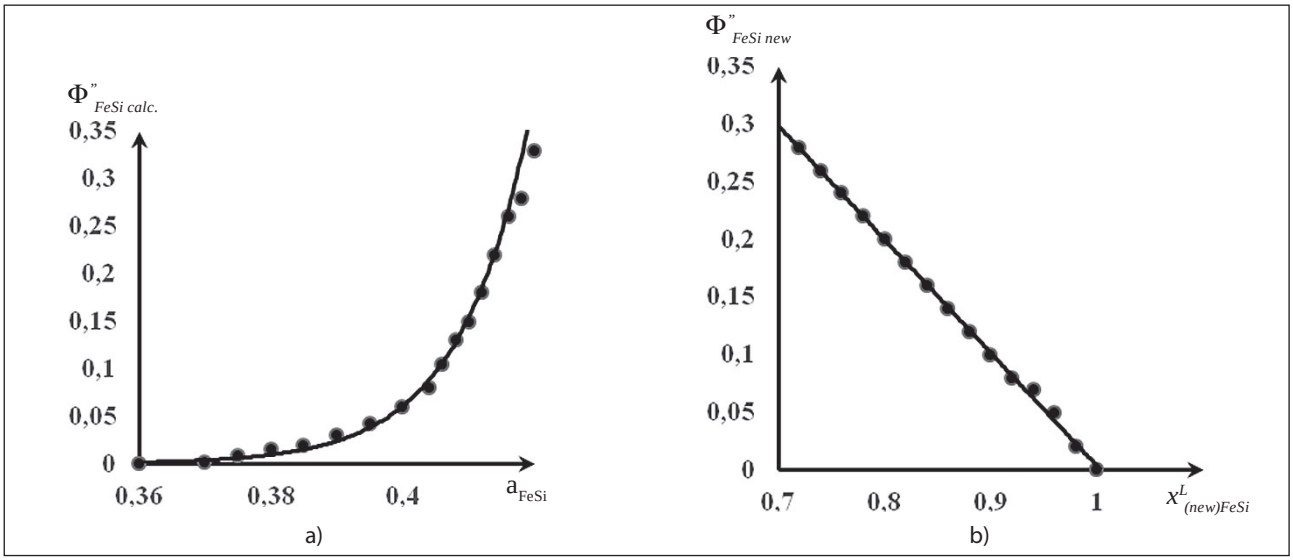

Figure 3 Dependence of osmotic coefficient of the Bjerrum-Guggenheim for the FeSi-Si quasi-system, where a) - $\Phi_{FeSi\ calc.} = f(a_{FeSi})$; b) - $\Phi_{FeSi\ new} = f(x^L_{(new)FeSi})$.

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 dissociationdegree of the congruently melting compound FeSiwere 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 compoundFeSiin compliance withthe conclusions of N.S. Kurnakov on dissociation of the congruent compound in the melting [2, 8].

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Note: The responsible translator for English language is Issakova Yelena Pavlovna, Karaganda, Kazakhstan.