

PHASE EQUILIBRIUM THERMODYNAMICS IN BINARY SYSTEMS

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ABSTRACT

The main regularities of the formation of the liquid-solid phase equilibria in binary systems are described in the article. The basic equations of the liquidus and solidus lines, as well as their behavior in the boundary conditions are adduced.

"Solid-liquid" and "solid-solid" phase equilibria in metallurgical systems (state diagrams) are of exclusive importance for a number of chemical and metallurgical processes. At that the solution of thermodynamic problems of phase equilibrium allows to predict the structure of a system and to obtain information on a state of components in equilibrium phases.

This article contains all the manifold relations of the thermodynamic properties of the components and the formation of crystallization phase lines in the state diagrams of the binary systems published in various deposited manuscripts, theses and reports, articles and monographs, in each of which a specific metal or oxide system and peculiarities found in them inherent only to these systems are considered. A generalization of these data was begun in doctoral dissertations and monographs, and even was not in full measure. The following are the methodology, mathematical apparatus and basic thermodynamic and concentration interconnects on the lines of the phase equilibrium "solid-liquid", which can be used to construction state diagrams and generalization of the results.

In the analysis of multitudinous state diagrams of both metallic and oxide systems, from the perspective of the Bjerrum-Guggenheim concept general regularity, which allows obtaining the mathematical expressions for the liquidus (L) and solidus (S) lines was discovered. This regularity is based on the deflection of the energy parameters of a real system's components from ideal. This deflection, by analogy to the activity coefficient, which may be called the coefficient of "energy non ideality", is observed along the "solid-liquid" and "solid-solid" equilibrium curves. It is represented as the ratio of the Gibbs energy of melting or the component's phase transition ($\Delta G_{m,i}^{S \rightarrow L}$ or $\Delta G_{t,i}^{\alpha \rightarrow \beta}$) to its ideal constituent ($\Delta G_{m,i,id}^{S \rightarrow L}$ or $\Delta G_{t,i,id}^{\alpha \rightarrow \beta}$). This coefficient is in correlation connection with the ratio of this component's activity in the liquid and solid phases (respectively in α and β phases). At the difference of ideal constituents $RT \ln X_i^L - RT \ln X_i^S = \Delta G_{m,i}^{id}$ of the components' partial chemical potentials in the solid and liquid phases along the liquidus and solidus curves in "solid-liquid" equilibria, respectively, in the α and β phases for $\alpha \rightleftharpoons \beta$ equilibria is understood that by the ideal constituent of the Gibbs energy of melting component.

As a measure of the deflection used the Bjerrum-Guggenheim coefficient known in the literature (Φ_i)

$$\ln a_i = \Phi_i \cdot \ln X_i$$

In this record the coefficient in contrast to the activity coefficient γ_i characterizes the measure of deflection of the Gibbs partial energy (chemical potential) of i-component in the solution (melt)

from its ideal constituent, i.e. $\mu_i = RT \ln a_i = RT \ln X_i [\mu_{i,id}] + RT \ln \gamma_i$ (where X_i - mole fraction, γ_i - activity coefficient,). From here

$$\Phi_i = \frac{\mu_i}{\mu_{i,id}} = \frac{RT \ln a_i}{RT \ln X_i} = \ln a_i / \ln X_i$$

This coefficient, as a rule, is used conformably to the partial thermodynamic properties of the components and is its energy characteristic, while γ_i serves as concentration parameter. In fact Φ is used fairly rarely because of the complexity of differential equations of the thermodynamics solutions' laws. They are often used to study the appearance of "osmosis" in electrolytes.

For "solid-liquid" equilibrium, where there is $S \rightarrow L$ reaction, i.e. chemical process, the coefficient Φ is written in the following form of a:

$$\Phi_i = \frac{\Delta G_{m,i}^{S \rightarrow L}}{\Delta G_{m,i,id}^{S \rightarrow L}} = \frac{\mu_i^L - \mu_i^S}{\mu_{i,id}^L - \mu_{i,id}^S} = \frac{RT \ln(a_i^L/a_i^S)}{RT \ln(x_i^L/x_i^S)} = 1 + \frac{\ln \gamma_i^L / \ln \gamma_i^S}{\ln x_i^L / \ln x_i^S} \quad (1)$$

Then the change in the of the components' distribution coefficients between the solid and liquid phases along the liquidus and solidus lines on the state diagrams in generalized form are represented as:

$$\ln X_1^L/X_1^S = (\ln a_1^L/a_1^S)/\Phi_1 \text{ и } \ln X_2^L/X_2^S = (\ln a_2^L/a_2^S)/\Phi_2' \quad (2)$$

where $\Phi_{1,2}'$ - Bjerrum-Guggenheim coefficients of 1st and 2nd components.

At that the ratio of the components' activities in the melt, in the solid solution along the line of phase equilibrium at a given temperature for a real system is calculated according to the equation Schroeder-Le Chatelier (3 - 4):

$$\ln \frac{a_1^L}{a_1^S} = \ln \frac{X_{1,id}^L}{X_{1,id}^S} = \frac{\Delta H_{m,i,1}}{R} \left(\frac{1}{T_{m,i,1}} - \frac{1}{T} \right) + \int_T^{T_{m,i,1}} \left[\frac{1}{RT^2} \int_T^{T_{m,i,1}} \Delta C_{p,1} dT \right] dT \quad (3)$$

$$\ln \frac{a_2^L}{a_2^S} = \ln \frac{X_{2,id}^L}{X_{2,id}^S} = \frac{\Delta H_{m,i,2}}{R} \left(\frac{1}{T_{m,i,2}} - \frac{1}{T} \right) + \int_T^{T_{m,i,2}} \left[\frac{1}{RT^2} \int_T^{T_{m,i,2}} \Delta C_{p,2} dT \right] dT \quad (4)$$

where $\Delta H_{m,1(2)}$ - the melting enthalpy of the 1st and 2nd components at a melting temperature, J / (mol·K); R - universal gas constant, J / mol·K, $T_{m,1(2)}$ and T - melting temperature of 1st and 2nd components and melt crystallization, K; $\Delta C_{p,1(2)}$ - change in heat capacity at the melting of components.

The heat capacity constituent in these equations for metallic systems can be neglected, and in polyatomic compounds its effect is essential, it should be considered.

At that from (3) and (4) equations must not be a view on equalities $a_i^L = x_{i,id}^L$ and $a_i^S = x_{i,id}^S$. They are not equal in all systems, and there is only the equality of their ratios $a_i^L/a_i^S = x_{i,id}^L/x_{i,id}^S$ for both components along the liquidus and solidus lines in the isomorphous system and with the solubility of the components in each other in the solid state (figure 1- 4).

This equation in its time (1890) was found by Schroeder when studying of changes of the saturation concentration of salts in water in the form of an empirical subject to $\log x_{i,sat} = a + b/t^{\circ}C$, which has found its rigorous thermodynamic confirmation of three independent methods for the melting process after more than 30 years:

1) through the integration of the Vant Hoff differential equation

$$\ln \frac{dK_{p,i}^{S \rightarrow L}}{dT} = -(\Delta H_{m,i} + \int_{T_{m,i}}^T \Delta c_{p,i}^{S \rightarrow L} dT) / RT^2$$

2) through the melting's Gibbs energy

$$\Delta G_{m,i,T}^0 = -RT \ln K_{p,i}^{S \rightarrow L} = \Delta H_{m,i,T_m} + \int_{T_m}^T \Delta c_{p,i}^{S \rightarrow L} dT - T \left[\frac{\Delta H_{m,i}}{T_{m,i}} + \int_{T_{m,i}}^T \frac{\Delta c_{p,i}^{S \rightarrow L}}{t} dT \right]$$

3) through the equality of the chemical potentials in the liquid and solid phases

$$\mu_i^L = \mu_i^S + \Delta H_{m,i} + \int_{T_{m,i}}^T \Delta c_{p,i}^{S \rightarrow L} dT - T(\Delta S_{m,i} + \int_{T_{m,i}}^T \frac{\Delta c_{p,i}^{S \rightarrow L}}{T} dT)$$

3 and 4 equations in real systems can be calculated only change of constant $k_p = a_i^L / a_i^S$ of components' distribution between the solid solution and melt, depending on the temperature. If this binary system is the ideal and isomorphous, then the liquidus L and solidus S lines can be calculated from these equations (V. Glazov). Application of these dependences to calculate the L and S in the various systems is very limited. To a great extent this is determined by the type of state diagrams. In nature the state diagrams of the binary systems (T-X diagram) mainly are divided into four types (figure 1-4).

3 and 4 equations for eutectic system with negligible solubility of the second component in a solid first (figure 1) of are used quite often. This type of system typical as a rule, of congruent multicomponent compounds (salts, oxides, etc.). $x_1^S = 1$ and $a_1^S = 1$ in them. At that the melting enthalpy of complex compounds can be determined by the liquidus lines built experimentally with a certain error (often too large). This is evident clearly from the various options of eutectic systems' SD (figure 1) with different levels of interpartial interactions in the melt. If the components behave "ideally", L lines for both components are calculated at the known $\Delta H_{m,i}$ and $T_{m,i}$ (figure 1).

In the presence of interactions in the melt even four options can be implemented:

- two components in the melt experience strong positive deviation from the ideal, which will bring to increase of the eutectic temperature relative to that of the ideal system (figure 1, option 2);
- the first component experiences strong negative, and the second - a positive deflection from the ideal, that causes mixture of the eutectic composition leftwards relative to the eutectic ideal system (figure 1, option 3);
- if on the contrary - the second component experiences a negative deflection, then the real eutectic shifts to the right (figure 1, option 4);
- when strong negative deflection is watched for both components due to strong interparticle interaction in the melt, the eutectic temperature will be much lower than the eutectic temperature in the ideal system (figure 1, option 5).

All this points to the virtual impossibility of SD theoretical calculation even for the simplest eutectic system due to the unavoidable presence very weak van der Waals interactions are in them.

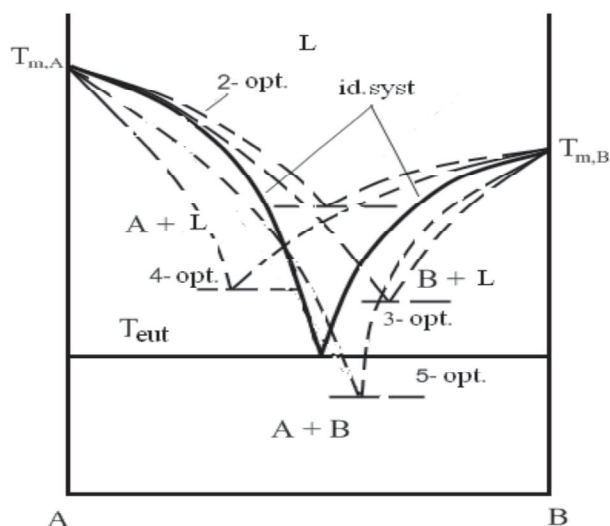


Figure 1: The eutectic system without solubility of the components in each other in the solid state

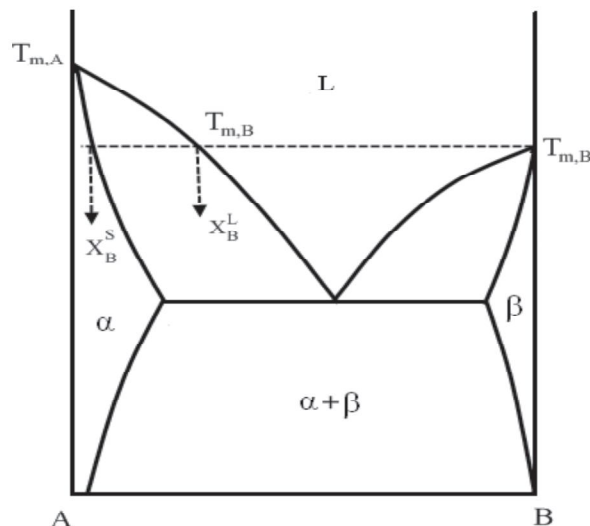


Figure 2: The eutectic system limited by solubility of components in the solid state

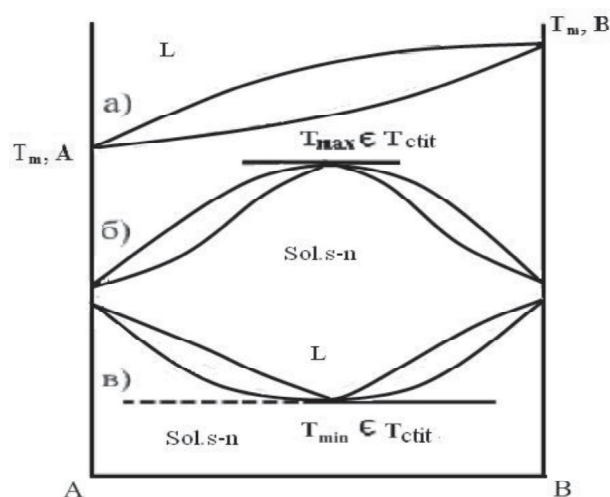


Figure 3: The isomorphous systems: a) close to the ideal, b) with the maximum on the liquidus, c) with minimum on the liquidus

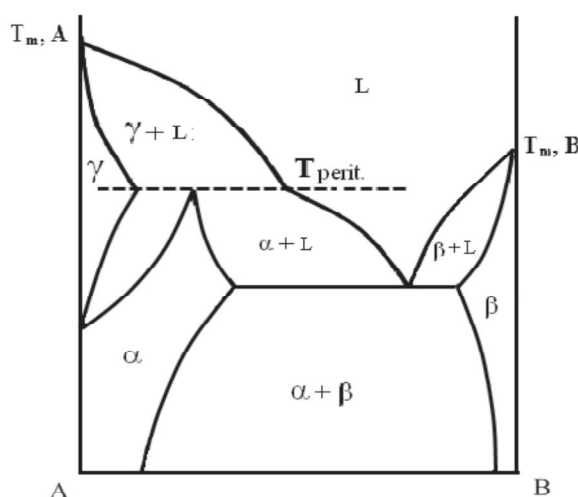


Figure 4: The systems with peritectic melting

Other types of SD with limited solubility of components in the solid state (figure 2), with isomorphous to each other to form an extremum on L and without it (figure 3) and with peritectic melting (figure 4) further complicate the L and S theoretical calculation in them, inasmuch as difference opposed x_i^S from 1, as well as the impossibility of separating and a_1^L and a_2^S and another a_2^L and a_2^S , (3) and (4) equations make virtually unusable to obtain thermodynamic information from such a SD. All of these types of SD in different combinations (combined) to form congruent and incongruent compounds are implemented in almost all of the binary systems, whatever they may have been difficult.

Since the (Φ) coefficient characterizes the degree of deflection from the ideal energy state of this component in equilibrium conditions, this deflection is greater, the stronger interparticle

interaction of the component to other components. Such interaction can be divided into two constituent: the van der Waals (interatomic or intermolecular interaction, which presents inevitably in any melt of the system) and directed interaction (related to the occurrence of directed hetero- and homeopolar bonds between the components in the melt, i.e. formation of clusters). Moreover, and in both cases the interaction force of considered component with the second as in the melt and in the solid solution, and hence the degree of deflection of the properties of ideal will be depended on the number of this component in the volume and other states. From the theory of statistical thermodynamics the first is defined as $\exp\left(-\frac{\Delta G_{m,i}^0}{RT}\right)$ and the second - as the difference between the numbers of particles which are there fully associated and freely states. Thus, Φ_i change along the phase equilibrium can be written as:

$$\Phi_i = A_i + B_i \cdot \exp\left(-\frac{\Delta G_{m,i}^0}{RT}\right) \quad (5)$$

or

$$\Phi_i = A_i + B_i \cdot \exp\left(-\frac{\Delta G_{m,i}^0}{RT}\right) + \frac{C_i}{\exp\left(-\frac{\Delta G_{as,i}}{RT}\right) - \exp\left(-\frac{\Delta G_{m,i}^0}{RT}\right)} \quad (6)$$

where $\Delta G_{as,i}$ - Gibbs energy of melting on reaching which a transition of this component completely in the associated state is possible, A_i , B_i , C_i - empirical coefficients.

Consequently, (5, 6) equations allow to explain the physical meaning Φ_i depending on the ratio of activities of the crystallizing component in equilibrium conditions with position of statistical thermodynamics.

It should be noted that, a different kind of change Φ_i will be observed along the liquidus and solidus lines depending on the nature of interparticle interaction in melts for different systems. As will be shown below, if only by van der Waals forces between elementary structural units of the considered component 1 with the second dominate in the melt along the liquidus line, the linear dependence (here the elementary structural units are the atoms or molecule compounds) will be observed. In the formation of the associates of the original elements or dissociation of the studied compounds in the melt, the true number of atoms or molecules of this phase will depend strongly (and in a very complex dependencies, including the degree of dissociation of compounds) on the temperature and composition of the melt, which must inevitably lead to a curvilinear relationship (6).

(2, 5, 6) expressions allow us to deduce semiempirical dependences as generalized Schroeder-Le Chatelier equations to calculate the liquidus and solidus lines for any of the real system in the crystallization area of the corresponding phase in the following relationships:

$$\frac{x_1^L}{x_1^S} = \exp \left[\frac{\frac{\Delta H_{m,1}}{R} \left(\frac{1}{T_{m,1}} - \frac{1}{T} \right) + \int_T^{T_{m,1}} \left[\frac{1}{RT^2} \int_T^{T_{m,1}} \Delta C_{p,1} dT \right] dT}{\Phi_1'} \right] = M_r$$

$$\frac{x_2^L}{x_2^S} = \exp \left[\frac{\frac{\Delta H_{m,2}}{R} \left(\frac{1}{T_{m,2}} - \frac{1}{T} \right) + \int_T^{T_{m,2}} \left[\frac{1}{RT^2} \int_T^{T_{m,2}} \Delta C_{p,2} dT \right] dT}{\Phi_2'} \right] = N_r \quad (7)$$

Solution of (7) equation systems gives the mathematical expressions for the solidus and liquidus lines for real systems:

$$x_{1,r}^L = M_r \cdot \frac{N_r - 1}{N_r - M_r}; \quad x_{1,r}^S = \frac{N_r - 1}{N_r - M_r} \quad (8)$$

This is the L and S equations for all types of SD. That these equations may to operate, first we have to find the empirical (5) and (6) expressions for each phase crystallizing (plus up to it and the second component) in all parts of the SD studied binary system. That is, in the crystallization of any phase (say the first) the Φ_1' equation must be found and simultaneously the same equation follows in the same field - for the second component. Two pairs of such dependences have to look for eutectic with solubility in solid states SD (figure 2): for areas on the left and right of the eutectic. There is the same for SD with isomorphous extremum on the liquidus line (figure 3), and for a simple isomorphous SD - only one pair. Finally, 5 pairs of such equations need take for a more complex system (figure 4).

Methodology of experimental data processing were built by (5-8) equations. The experimental data in binary phase diagrams by means of equations (1-4) are presented in other coordinates, i.e. Φ_1' and Φ_2' as a function of the ratio of the activities of the components in the liquid and solid phases, to assess the state of the melt along the lines of equilibrium.

Processing of the obtained results by least squares allows to find the values of the A, B, C constants, and the correlation coefficients for the different systems (5, 6) and to bring analytical expressions of fields' surfaces of phase crystallization in any quasi-system, detectable with the construction of the structure of the phase diagrams of multicomponent systems by thermodynamic-diagram analysis (7-8).

At that, the simple analysis of crystallization fields in the various systems on the relative position of the liquidus lines almost do not get about the features of the melts and the reliability of the experimental data, except for a weak or a strong decrease of melting temperature of the studying phase under the influence of the second component.

The picture changes dramatically, if the impact to consider from the perspective of the Bjerrum-Guggenheim osmotic coefficient. It was discovered from the conduct of larnite in different systems. At that in the C_2S - F_2S , C_2S - Mg_2S , C_2S - C_2AS and C_2S - CT (where C - CaO , S - SiO_2 , F - FeO , Mg - MgO , A - Al_2O_3 and T - TiO_2) systems the graphs show an evident dicalcium silicate instability in the molten state, which follows from the convex nature of the graphics. In the liquid phase larnite dissociates in the presence of the second components. It turned out that fayalite and forsterite, which are identical in structure to larnite, influence the most weakly on the degree of its dissociation.

- the study of the state diagrams of systems based on the iron from position of Bjerrum-Guggenheim concept implemented according to common known of their classification. The purpose of this research was an analytical representation of the lines of «solid-liquid» phase equilibria and identification of the behavior of components in their melt to the compositions of the melts concerning to silicon-manganese and ferro-silicon-aluminum.

- at that all the considered systems, on the basis of extensive literature data on their state diagrams, were divided into two groups:

- the eutectic systems with extensive solubility of the second component in the solid iron or without it and form different chemical compounds (congruent and incongruent): Fe-Al; Fe-Si; Fe-P; Fe-Ti; Fe-Ge-Fe-B; Fe-C; Fe-S, etc.;- systems with unlimited solubility in solid and liquid states with diagrams of the "cigar" type or with extreme point (maximum and minimum): Fe-Co; Fe-Mn; Fe-Cr; Fe-Ni; Fe-Au; Fe-Cu; Fe-Zn, etc.

The data on the changes in osmotic coefficients of both the first and second components in the target system and the compounds (figure 5, 6) were processed using the method of least squares according to the (5, 6) equations. Next, the lines of phase equilibriums were approximated using equations (7-8). The estimation of the correlation coefficients and variance of calculated results for the liquidus and solidus lines was carried out. At that for areas of systems where the linear dependence for the osmotic coefficients (Φ_i) are found, the correlation coefficients are characterized by values of at least 0.96, and in other parts of the same system, where there is a convex (due to dissociation of the compounds) and concave (caused by components in the association melts) the nature of the Φ_i curves (figure 5), the variance of the predicted values of the compositions of the liquid and solid phases does not exceed $\pm 0,008$ (abs.at.part). There is associating between the components in the most systems with decaying peritectic compounds as well as in systems with silicon, in melts, which indicates inclination of their melts to amorphization.

There is strong and a positive deviation from the ideal for the system Fe-Al in the area until the eutectic composition, whereas in the same areas at the Fe-Si from the first additives Si in melt begins negative deflection from the trend of a further sharp increase (figure 5). This indicates poor miscibility Al with liquid Fe than with Si. This explains the difficulty of obtaining Fe-Al-alloys in comparison with Fe-Si-alloys. A joint analysis of the Φ_{Si} osmotic coefficients for different temperatures (figure 7) when the beam crystallization of alloys from the system Si-Fe to Si-Al shows that only around the system Si-Fe melts experience associating components and huge deviation from the ideal (Φ_{Si} values much more unit). Reinforcement of negative deflection of Si properties from the ideal (figure 7, C) takes place with increasing of temperature, and hence there is the best of its miscibility with Fe and Al in the relationship Fe: Al = 0,7 ÷ 0,3% (at.). This corresponds to the composition of the alloy Fe-Si-Al with 12-37% Fe and 20-25% Al, based on the weight concentration. Reducing the temperature moves the discussed area on to the binary system Fe-Si. So at low temperatures Al dissolves better in rich Fe-Si alloys, and with increasing of temperature the process of alloy formation with a high content of aluminum is facilitated.

Thus, the obtained results of the behavior of crystallizing phases in two groups of iron-based systems allow to conclude that they are fully revealed the presence of natural connections between the degree of non-ideal on behavior of the crystallizing phase Φ_i to its activity in the melt along the line of phase equilibrium in two forms:

- as a linear dependence, caused mainly dominated by the melt of the van der Waals interactions between monomers of the crystallizing element (or molecules of a chemical compound melts congruently) with the second component of the system;

- in the form of a curvilinear dependence with concave or convex: in the first case there is a formation of associates of varying complexity in accordance with the present compounds in the diagram, and the second - there is mostly dissociation of compounds or the formation of dimers, trimers, etc.

Mathematical study of graphs of the function Φ_i of crystallizing phases near their melting temperature ($T_{mel.}$) showed that all types of liquidus lines found in various state diagrams can be divided mainly into five groups (types A-E, figure 8).

The first group (type A, figure 8) was characteristic of metallic systems in which the impurity component does not contribute to the formation of a melt of dimers and polymers from the

crystallizing component, and vice versa, the system components are prone to the formation of associates of varying difficulty, with or without such. For these systems the graphics of Bjerrum-Guggenheim osmotic coefficient of the crystallizing component are rarely rectilinear and often twisted, and always with a concavity. Especially such course of Φ_i graphic becomes more pronounced after the passage of peritectic points (if available in the system).

The liquidus line of this group of systems intersects the temperature axis at the point T_m at different angles depending on the degree of interaction between the first additions of the 2nd component with the solvent. In the diluted state (at the approach of a $T_{m,i}$) in such systems is the main component tends to the ideal state, without the formation of dimers, etc. Φ_i and graphics in them originate from a single point, where $\Phi_i = 1$ if $a_i = 1$.

The second group (type B, figure 8) is most characteristic for the crystallization lines of congruently melting chemicals. At that, Φ_i for them tends to zero with temperature approaches $T_{m,1}$.

The formula (2) for the eutectic system is uncertain. Therefore, by applying the L'Hospital's rule with the equations Φ_i (5, 6) we can find the limit to a value at $T=T_{m,1}$ for a curvilinear relation Φ_i :

$$\lim[\ln X_i^L]_{\text{при } T \rightarrow T_{m,1}} = \frac{(\ln a_i)'}{(\Phi_i)'} = \frac{1}{B + C/(a_{\text{кр}} - 1)} = \text{const} < 1$$

and for rectilinear (when $C = 0$) dependence Φ_i :

$$\lim[X_i^L]_{\text{при } T \rightarrow T_{\text{огн}}} = \exp(1/B) = \text{const} < 1$$

i.e. X_i^L differs from unity at $T=T_{m,1}$. That points to the dissociation of the connection. The degree of dissociation of the congruently melting compound is:

$$\alpha = 1 - \text{const}$$

The third group (type C, figure 8), by contrast, occurs in non dissociate at the melting compounds, but with a tendency to phase separation with decreasing temperature, due to the very strong positive deflections. Φ_i value to them is reduced sharply near $a_i = 1$, and further (for $a_i < 1$) is less than one, sometimes even closer to zero.

The fourth group (type D, figure 8) is similar to the first. It differs only in that the outside of the real coordinate system, i.e. for $X_i > 1$, Φ_i tends to infinity in the vicinity of a critical value X_{cr} . An imaginary noose, which is possibility by pointing of N. Kurnakov, has to formation according to (2, 5-8) equations on the liquidus line. Here as well as in the case of D (figure 8), melts of systems are subject to a strong association. Therefore, such systems may be important to find specific compositions excessively prone to amorphization of alloys to produce metallic glasses.

The fifth group (type E, figure 8) is especially, because the critical value occurs in a real range of compositions and temperatures (between $T_{m,i}$ and absolute zero). At that retrograde move liquidus curves will be observed or lines, which similar to ferritic-austenitic loop in systems based on iron, are detected. The first characteristics for the semiconductor systems based on silicon. Feature of these systems is the possible existence of a liquid phase to absolute zero, if there is current course of the liquidus in a figure 8 (type E) and applicable conditions for ultrafast cooling will be created.

This group also includes a class of isomorphic systems with an extremum (minimum or maximum) on the lines of the phase equilibriums. For them, the (7-8) equations should provide the aspiration of angle tangents of tangents to the liquidus and solidus lines ($\text{tg} \alpha^{L,S}$) to zero as $T \rightarrow T_{\text{ex}}$.

Only in this case the left and right branches of the phase equilibrium lines (figure 8, E) are conjugate lines with a common horizontal tangent. Then and only then (8) equation will meet the requirement of thermodynamics about second derivative continuity of the Gibbs energy of the melt, as well as a solid solution in the whole composition range at any temperature. This is ensured by aspiration values of Φ_i for both components to infinity at T_{ex} , i.e. at $a_i \rightarrow a_{cr}$ (figure 3).

It should be noted that the most distinctive feature of the (7-8) equations with regard to these systems is that at $T \rightarrow T_{max}$ values of M_r and N_r tend to unity and $X_i^{L,S}$ are not defined. However, taking into account the L'Hospital's rule, it is easy to find the limits $X_i^{L,S}$ by differentiating the numerator and the denominator of the equation for X_i^S at a_i :

$$\lim_{a_i \rightarrow a_{cr}} X_i^S = \frac{N_r'}{N_r' - M_r'} = \frac{1}{1 - M_r'/N_r'} \quad (9)$$

Taking into account the exponential of the form M_r and N_r dependences in (9) and give the expression $\Phi_{1,2}$ (5, 6) to a common denominator of $(a_{cr} - a_i)$, as well as to indicate the limiting values of a_i for the first and second components in points T_{max} and T_{min} of diagram (figure 8, the form E) through $a_{cr,1}$ and $a_{cr,2}$, it is easy to see that the limit X_i^S value at T_{max} and T_{min} will be equal:

$$X_i^S = X_i^L = \frac{1}{1 - K_0} \quad (10)$$

where $K_0 = \frac{\ln a_{kp,1} \cdot C_2}{\ln a_{kp,2} \cdot C_1}$; $a_{cr,1}$ - the value of the activities ratio of the first component at $T = T_{max}$, calculated according to the Schroeder-Le Chatelier equation; $a_{cr,2}$ - the same for the second component; $C_{1,2}$ - value of the third coefficient in the $\Phi_{1,2}'$ expressions, respectively in equation (6).

Some important conclusions about the mathematical description of the state diagram implies from this and from the graphics of Φ for the second component of the example of a number of systems (figure 6):

- in the isomorphic systems the expression of osmotic coefficients of 1st and 2nd components with presence of unlimited solubility of the components in the solid state, are interrelated, i.e. according of Φ_1 data the value of C_2 coefficient for Φ_2 is calculated or in other words we can say that the situation of Φ_2 graphics in the main is determined strictly;

- osmotic coefficient Graphics of 2nd component (Φ_2') necessarily have to pass through zero at the point $a_2^L/a_2^S = 1$ (figure 6) in accordance with the definition of this value (1);

- the C_1 and C_2 values for the three-item expressions of Φ_1' and Φ_2' must have opposite signs, that the quantity of K_0 in (10) was always less than zero (only in this case the $X_{\text{экр}}^{L,S} < 1$ condition is provided).

It should also be noted that at $T = T_{m,2}$ in the crystallization area of the 1st component (figure 2 and 3), where $T_{m,1} > T_{m,2} > T_{evt}$, another uncertainty is faced, i.e.

$$\left| \ln X_2^L / X_2^S \right|_{T=T_{m,2}} = \left[\ln a_2^L / a_2^S \right] / \Phi_2' = 0 / 0$$

although the X_B^L / X_B^S values are the end (figure 3). Differentiation of the numerator and denominator by a_2^L / a_2^S for this event give another important relationship:

$$\lim_{T \rightarrow T_{m,2}} [\ln X_2^L / X_2^S]^{npu} = 1 / [B_2 - C_2 / (a_{kp,2} - 1)^2]$$

There are Φ_2' graphics in the area of crystallization solvent, however they were curvilinear, they have two coefficients (B and C) known in advance: C_2 to C_1 , B_2 by the X_2^L and X_2^S values at $T=T_{m,2}$.

Study of the ratios gives the following relationship:

$$\lim_{T \rightarrow T_{m,1}} \frac{\ln X_1^L}{\ln X_1^S} \bigg|_{at} = N_r = \frac{X_2^L}{X_2^S}$$

The same analysis for $\ln X_2^L / \ln X$ in systems in which the values of Φ_2' at $T \rightarrow T_{m,1}$ are different from zero, gives the following result:

$$\lim_{T \rightarrow T_{m,1}} \frac{\ln X_2^L}{\ln X_2^S} \bigg|_{at} = 1$$

However, figure 6 shows that, for some systems, such as Fe-Al, Fe-Ga and Cr-Mn, Φ_2' graphics (for the second component) detects abnormal change at $T \rightarrow T_{m,1}$, i.e., unlike other systems, there is a clear presence of a "spike" in the quantity Φ_2' (figure 6). At that the values of Φ_2' for Al, Ga, and Mn, entering the role of dissolved components relative to Fe and Cr, tend to zero as $T \rightarrow T_{m,1}$ (on their schedule in parentheses are a_2^L/a_2^S values at $T_{m,1}$, 1, when $\Phi_2' = 0$). These graphs are, of course, cannot be approximated by a three-term expression type (6).

Therefore, for an adequate analytical description of such anomalous graphs Φ_2' in these and other mentioned (as they are discovered) systems four-term expression with the inclusion of quadratic component in the form $\Delta \cdot (a_2^L/a_2^S)^2$ to account for the presence of a "spike" in very dilute solutions may be used.

In this regard, we note only that this anomaly allows to find the following relations:

$$\lim_{T \rightarrow T_{m,2}} (\ln X_2^L / X_2^S = \frac{\ln a_2^L / a_2^S}{\Phi_2'}) \bigg|_{\text{при } T \rightarrow T_{m,2}} = \frac{\text{const}}{0} = +\infty$$

$$\text{i.e. } \lim_{T \rightarrow T_{m,2}} (X_2^L / X_2^S = \exp (\ln X_2^L / X_2^S)) \bigg|_{T \rightarrow T_{m,2}} \rightarrow +\infty$$

i.e. X value is converged several orders rapidly to zero, rather than X, at infinite temperature tends to the melting temperature of the solvent (in this case, Fe and Cr). This is very important for the cleaning process, for example iron, from Al and Ga, and chromium manganese, for example, by zone melting. Along with that the following relations for the lines of "solid-liquid" phase equilibriums in a state diagram result from the definition of the osmotic coefficient value:

$$\begin{aligned} 1) \ln a_1^L &= \Phi_1^L \cdot \ln X_1^L & 2) \ln a_1^L &= \Phi_1^{LS} \cdot \ln X_1^S \\ \ln a_1^S &= \Phi_1^S \cdot \ln X_1^S & \ln a_1^S &= \Phi_1^{SL} \cdot \ln X_1^L \end{aligned}$$

$$3) \quad \Phi_1^{LS} = \Phi_1^L \cdot \frac{\ln X_1^L}{\ln X_1^S} \quad 4) \quad \Phi_1^{LS} \cdot \Phi_1^{SL} = \Phi_1^L \cdot \Phi_1^S \quad \Phi_1^{SL} = \Phi_1^S \cdot \frac{\ln X_1^S}{\ln X_1^L}$$

$$5) \quad \Phi_1' = \frac{\ln a_1^L/a_1^S}{\ln X_1^L/X_1^S} = \frac{1}{1/\Phi_1^L - 1/\Phi_1^{LS}} - \frac{1}{1/\Phi_1^{SL} - 1/\Phi_1^S}$$

where Φ_1^{LS} - osmotic coefficients of 1st component in the liquid (L) and solid (S) phases; Φ_1^{LS} - the same coefficient, defined as the ratio of the chemical potential of first component in the real liquid phase to the ideal part of the chemical potential of this component in an ideal solid solution, equilibrium with the considered liquid; Φ^{SL} - the similar coefficient, but it is defined on the contrary; Φ_1' - reduced Bjerrum-Guggenheim coefficient.

The same relationship according to determining the value of Φ_2' (2) can be written similarly, for the second component. At that, the above expression (5) it can be seen that the adduced Φ_1' coefficient bit like a general formula of the common electrical resistivity in parallel electrical circuits.

In addition, the feature of a smooth transition from one kind of system (isomorphic) to the other (simple eutectic) one can derive the generalized equations of activity of the first component in the two equilibrium phases along the liquidus and solidus lines:

In (11-12) equations degree of non isomorphic (Δ_i) is determined by the known values of the measured activity of the first component to the liquidus and solidus lines for a given temperature. A study of this magnitude for a number of systems shows that it is close to zero for systems with very low solubility of the second component in a solid first component and vice versa.

$$\ln a_1^L = \ln(a_1^L/a_1^S) / \left[1 - \frac{1}{\left(\frac{\ln(a_1^L/a_1^S)}{\ln X_1^S} + 1 \right) (1 + \Delta_i)} \right] \quad (11)$$

$$\ln a_1^S = \ln(a_1^L/a_1^S) / \left[\left(\frac{\ln(a_1^L/a_1^S)}{\ln X_1^S} + 1 \right) (1 + \Delta_i) - 1 \right] \quad (12)$$

Thus, in the considered approach to identify the characteristics of the phase equilibriums in the different systems Φ_i value fully conform to the boundary conditions of almost all types of SD found in nature and predicted by N. Kurnakov. The equations of phase equilibriums' lines (8), derived from the same quantity Φ_i describe all the main types of state diagrams and fits with the principle of continuity of the second derivative of the Gibbs energy within the homogeneous state of any system.

In addition, the (11) and (12) equations by measure determining the nature of degree nonisomorphic (Δ_i) allow us to find the mathematical expression of the activity of one of the binary system components in its crystallization, and then on the Gibbs-Dyugem integration to derive analytical activity dependence of the second component, depending on the temperature along the liquidus and solidus lines in the same area.

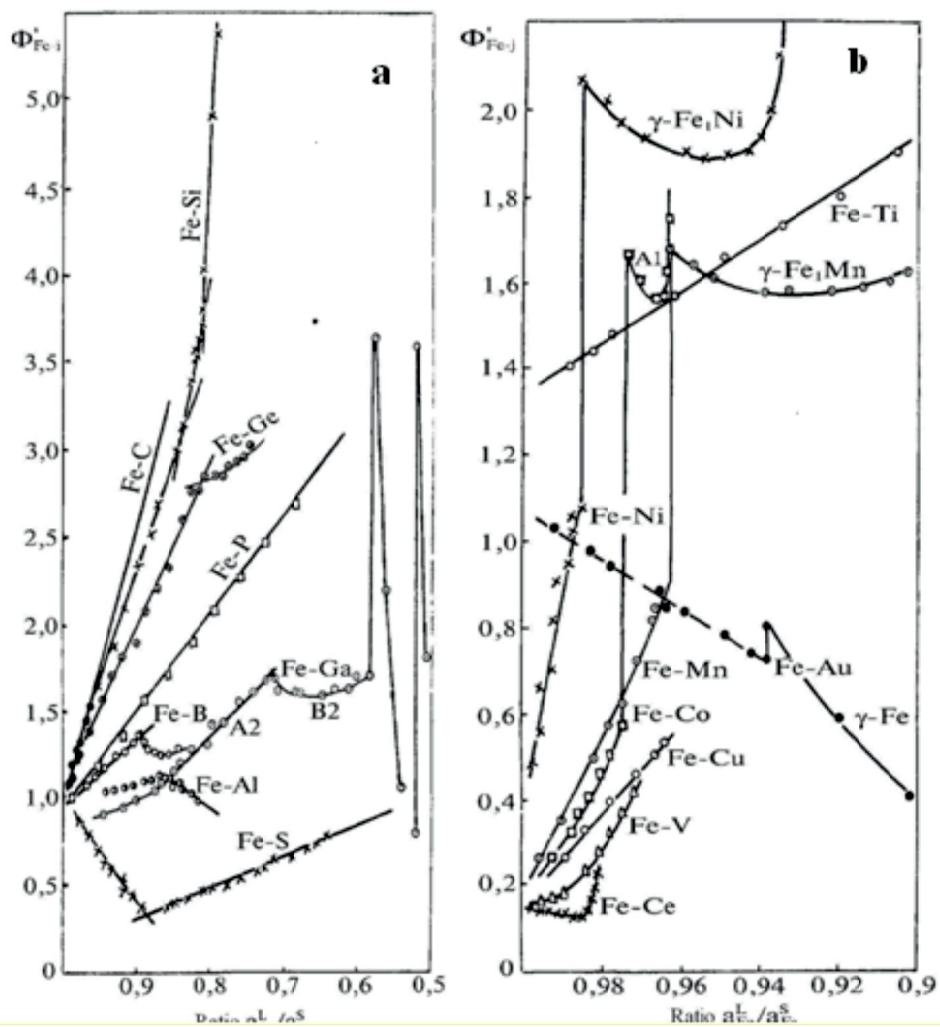


Figure 5: Combined graphics Φ'_1 for p- and d-elements

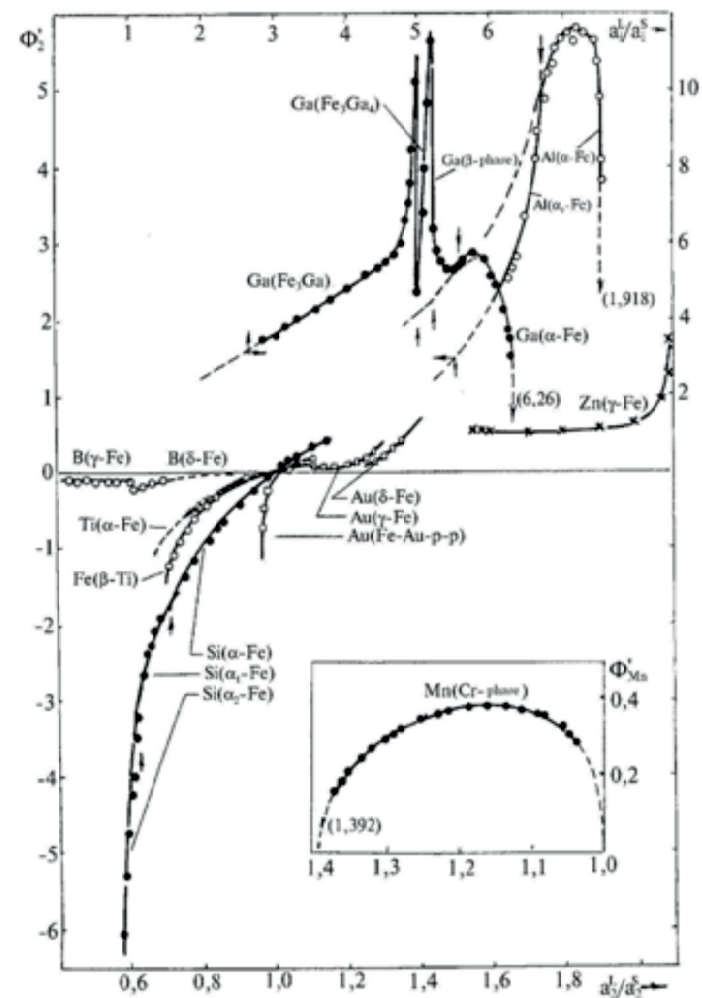


Figure 6: Graphics Φ'_2 for different systems

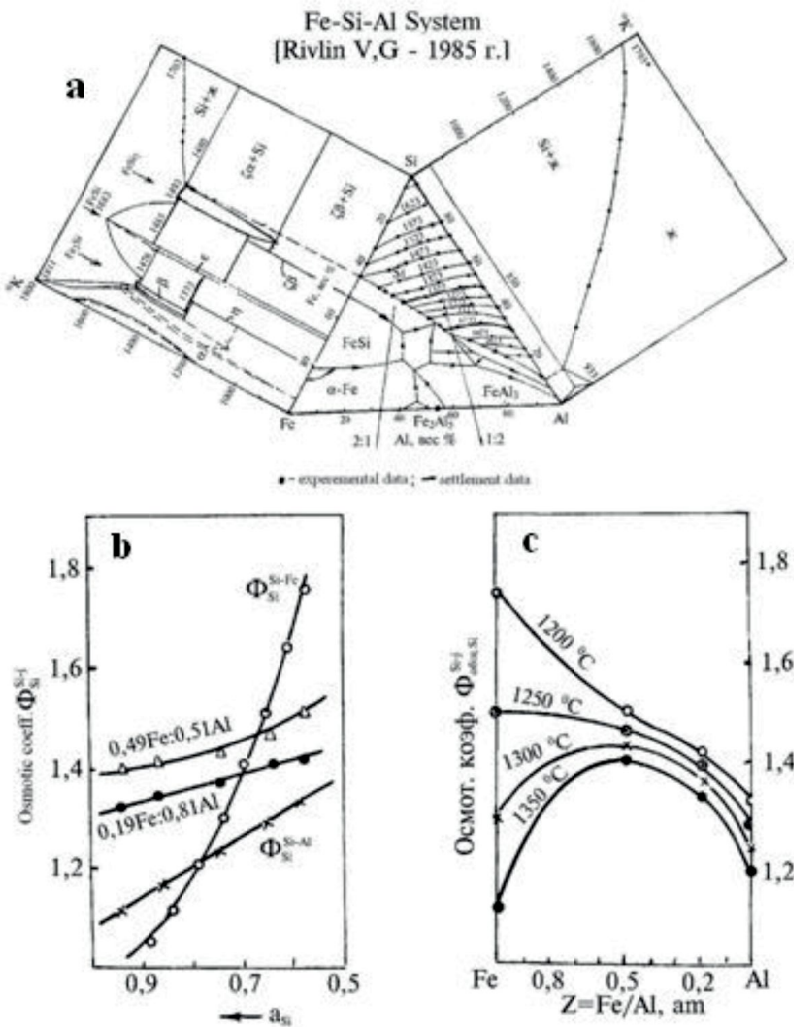


Figure 7: Graphics Φ_{Si} in Fe-Si-Al system

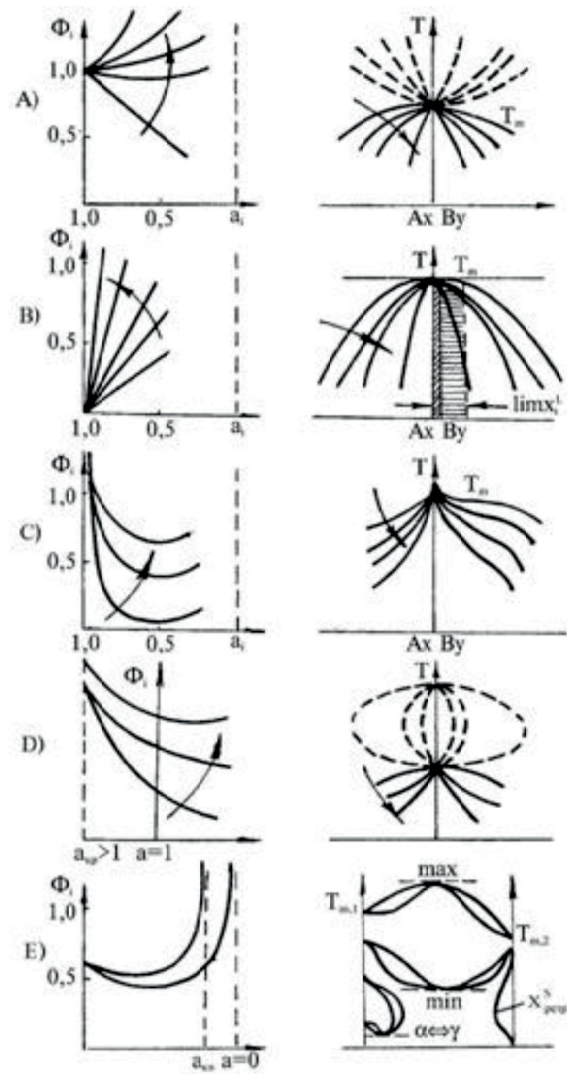


Figure 8: Analysis of the equations (5-10) in different system

On the basis of the detected well-formed changes of deviation value from the ideality distribution coefficients of elements between the equilibrium phases of the composition and temperature of both the oxide and metallic systems, the following are considered the wording and the ability to meet the challenges of creating a mathematical model of phase equilibrium in the various metal-slag systems, which are applied to the basic processes of steel, cast iron and ferroalloys obtaining.

To be specific, as an example, we consider the reaction of silicon reduction from slag in carbon-rich metal, which is largely carried out at the interface of the two phases:



The equilibrium constant K_p is defined by the relation:

$$K_p = \frac{a_{[\text{Si}]} \cdot p_{\text{CO}}^2}{a_{(\text{SiO}_2)} \cdot a_{[\text{C}]}^2} = \exp\left(-\frac{\Delta G_T^0}{RT}\right) \quad (14)$$

where a_i , p_{CO} - the activities of components in metal and slag and the partial pressure of carbon oxide at the equilibrium temperature (T); ΔG_T^0 - Gibbs energy change of the reaction of silicon reduction of molten slag in the metal dissolved carbon.

By analogy with the "solid-liquid" equilibriums the equilibrium transition of silicon at the metal-slag border can be viewed from the perspective of non-ideality coefficient, now the reduction reaction of the element that links the thermodynamic equilibrium constant K_p with the composition of the equilibrium phases (i.e., the apparent reaction constant K_c) as follows:

$$\Phi_{\text{Si}} \cdot \ln \frac{X_{[\text{Si}]} \cdot p_{\text{CO}}^2}{X_{(\text{SiO}_2)} \cdot X_{[\text{C}]}^2} = \Phi_{\text{Si}} \cdot \ln K_c = \ln K_p \quad (15)$$

where Φ_{Si} - coefficient of non ideality for the reaction of silicon reduction, $x_{[i]}$, $x_{(j)}$ - the concentration of the respective components in the equilibrium phases in mol units.

Hence, after the transformation (15) we obtain the expression:

$$\ln \frac{X_{[\text{Si}]}}{X_{(\text{SiO}_2)}} = \frac{1}{\Phi_{[\text{Si}]}} \cdot \ln K_p - \ln \frac{p_{\text{CO}}^2}{X_{[\text{C}]}^2} \quad (16)$$

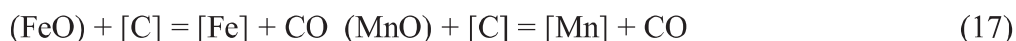
is the equation of the distribution coefficient of silicon between metal and slag, depending on the temperature and composition of the initial phases.

The main feature of the expression (16) is that it describes the nested multiple equilibriums: it is the equilibrium of the metal-slag and equilibrium of liquid metal-solid graphite. If and slag is heterogeneous, then it must be taken into account the "liquid slag-solid oxide phase (oxide compounds)" equilibrium. In this case the value of $X_{(\text{SiO}_2)}$ in (16) must be presented as a complex dependence, which includes an analytical expression surface crystallization of this compound in the slag melt. This can easily be found from the data on the SD in oxide systems, again with Φ_i . The last of these three equilibriums is expected at iron smelting under highly basic dicalcium itself scatter (possibly gellenit) slag, and the smelting of silico-manganese rich in silica under acidic slag. Such equilibriums are of particular interest for practice. Such structured analysis of the equilibrium of metal-slag in the scientific literature has not been studied. From the methodological point of view, this issue is discussed in more detail in my thesis and monographs.

The data obtained about Φ_{Si} on the reduction reaction of silicon allow obtaining the calculated curves of the change $[Si]$, depending on the content (SiO_2) in the slag by special program "Equilibrium» for IBM/PC with the help of (16). At that the results discover a satisfactory agreement, which allows concluding the perspectives of the intervention in the study of complex, embedded in one another phase equilibriums, using Bjerrum-Guggenheim osmotic coefficients, as in the description of "solid-liquid» phase equilibrium on the state diagrams.

However, the limited number of experimental data does not allow revealing the diversity in the behavior of this value in the interfacial reactions of transition elements in these complex systems as "metal-slag". Works in this area requires, above all, the accumulation of objective and reliable experimental data obtained (specially), with accounting features of the elements' transfer from one phase to another in accordance with the phase diagrams.

In conclusion, it should be noted that in the future you can remove the restrictions on iron. You can also include in the system manganese and its oxide, which increases the degree of freedom of the metal-slag-gas phase to 9. And so, apart from the initial content of Mn in the metal or slag it is need 2 more equations of connect. These are the equations of the equilibrium constants of reactions:



which can also be presented in an analytical form in the form of equation (16).

As a result, we have three equations with three unknowns (turning degrees $\alpha_{[Si]}$, $\alpha_{[Mn]}$, $\alpha_{[Fe]}$ of reduction or oxidation of all three elements of their original concentration), the solution of which on computer allows to estimate and calculate the state system («melt (Fe-Mn-Si-C) - slag (FeO-MnO-CaO-Al₂O₃-SiO₂) »).

In conclusion it can be shown by analogy Φ_i in SD the expansion Φ_{Si} of Si reduction reaction by carbon from SiO_2 .

In this case, we have from the Φ_{Si} definition:

$$\Phi_{Si} = \frac{\ln K_p}{\ln K_c} = \frac{\ln \frac{a_{[Si]} \cdot p_{CO}^2}{a_{(SiO_2)} \cdot a_{[C]}^2}}{\ln \frac{x_{[Si]}}{x_{(SiO_2)} \cdot x_{[C]}^2}}, [(where p_{CO}=1) = \frac{\ln a_{[Si]}}{\ln \frac{x_{[Si]}}{x_{(SiO_2)} \cdot x_{[C]}^2}} - \frac{\ln a_{(SiO_2)}}{\ln \frac{x_{[Si]}}{x_{(SiO_2)} \cdot x_{[C]}^2}} - \frac{2 \ln a_{[C]}}{\ln \frac{x_{[Si]}}{x_{(SiO_2)} \cdot x_{[C]}^2}}.]$$

Denoted the first term by A, we have:

$$A = \frac{1}{\frac{\ln x_{[Si]}}{\ln a_{[Si]}} - \frac{\ln x_{(SiO_2)}}{\ln a_{[Si]}} - \frac{2 \ln x_{[C]}}{\ln a_{[Si]}}} = \frac{1}{\frac{1}{\Phi_{[Si]}} - \frac{1}{\Phi_{[Si]-(SiO_2)}} - \frac{2}{\Phi_{[Si]-[C]}}}$$

similarly, identify the second item in B, we also get:

$$B = \frac{1}{\frac{1}{\Phi_{(SiO_2)-[Si]}} - \frac{1}{\Phi_{(SiO_2)}} - \frac{2}{\Phi_{(SiO_2)-[C]}}}$$

for the third item (denoted by C) can be obtained:

$$C = \frac{2}{\frac{1}{\Phi_{[C]-[Si]}} - \frac{1}{\Phi_{[C]-(SiO_2)}} - \frac{2}{\Phi_{[C]}}}$$

hence the common detailed expression for Φ_{Si} is recorded as follows:

$$\Phi_{Si} = \frac{1}{\frac{1}{\Phi_{[Si]}} - \frac{1}{\Phi_{[Si]-(SiO_2)}} - \frac{2}{\Phi_{[Si]-[C]}}} - \frac{1}{\frac{1}{\Phi_{(SiO_2)-[Si]}} - \frac{1}{\Phi_{(SiO_2)}} - \frac{2}{\Phi_{(SiO_2)-[C]}}} - \frac{2}{\frac{1}{\Phi_{[C]-[Si]}} - \frac{1}{\Phi_{[C]-(SiO_2)}} - \frac{2}{\Phi_{[C]}}}$$

where $\Phi_{[Si]}$ - Si osmotic coefficient in the liquid metal, i.e. ratio of the Si vapor pressure over the real liquid Me to the Si vapor pressure of an ideal liquid metal; $\Phi_{[Si]-(SiO_2)}$ - the ratio of the Si vapor pressure on a real liquid Me to the SiO₂ vapor pressure on an ideal liquid slag; $\Phi_{[Si]-[C]}$ - the same for the real and the ideal liquid metal; $\Phi_{(SiO_2)-[Si]}$ - the ratio of the SiO₂ vapor pressure on a real liquid slag to the Si vapor pressure on an ideal liquid Me; $\Phi_{(SiO_2)}$ - osmotic coefficient of SiO₂ in real liquid slag; $\Phi_{(SiO_2)-[C]}$ - the ratio of the SiO₂ vapor pressure on a real liquid slag to the vapor pressure of carbon on an ideal molten melt; $\Phi_{[C]-[Si]}$ - the ratio of the carbon vapor on an real liquid Me to the Si vapor pressure an ideal liquid metal; $\Phi_{[C]-(SiO_2)}$ - the same ratio, divided by the vapor pressure of SiO₂ on an ideal liquid slag; $\Phi_{[C]}$ - osmotic coefficient of carbon in liquid metal.

At detailed analysis presence of connection between $\Phi_{(SiO_2)-[Si]}$ and $\Phi_{[Si]-(SiO_2)}$, etc., for glassy $\Phi_{i-j}-\Phi_{j-i}$ by concentration as in the SD for Φ_i^L , Φ_i^S , Φ_i^{LS} and Φ_i^{SL} is not eliminate.

It should be noted that the resulting at that the expression of different osmotic coefficients for joint consideration of their literature data about thermodynamic properties of melts as metallic and slag melts and with the empirical expression of generalized Bjerrum-Guggenheim coefficient for the reaction to reduction of the corresponding element (16) according to the reactions (17), allows to determine the partial thermodynamic properties of the other components in the equilibrium phases from the experimental data on the equilibrium in the metal-slag system.

In conclusion, I can note that in this article a number of the behavior of the components in the equilibrium of the "solid-liquid", "solid-solid", "liquid metal - molten slag", revealed by the osmotic coefficient, an unused supra to study phase equilibriums have been collected. The presence of a very large reserve in using it and for the equilibrium of the "liquid-vapor", "water and salt" types, the chemical reactions in the homogeneous environment, etc. are not excluded.