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A CALCULATION OF PARAMETERS FOR LIQUID-PHASE EQUILIBRIUM IN SYSTEM Fe-O

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Thermodynamics of equilibrium Fe-O system has been studied from the point of view of modern condensed phase statistical model. Model parameters have been evaluated using four different methods. Results of calculations of phase composition and gas partial pressures are presented for the Fe-O system in the area of nonvariant equilibrium.
Keywords: thermodynamics, equilibrium, Fe-O system, liquid phase, Gibbs energy.

System *Fe-O* is fundamental basis at consideration of variety of the phenomena in the theory of metallurgical processes. Thermodynamics of metallic and slag so-lutions is based on co-operating of oxygen with a liquid metal the main component of which serves iron. Development of new adequate thermodynamics model of the condensed phase on the basis of quantum mechanical presentations and distribution of Gibbs [1-3] considerably extended possibilities of intellectual control system by fusible and out-of-furnace treatment of steel. However the exact tuning of her para-meters is one of unsolved to the end tasks. Among the parameters of thermodynamics model most essential parameters are serve, describing the action of elements in the double system *Fe-O* and triple systems of *Fe-Me-O*, where Me is a metal or me-talloid. Exactness of parameters of all triple systems of *Fe-Me-O* depends on exact-ness of determination of parameters for the basic system *Fe-O*, which is the article of this research.

The tast to define the parameters of thermodynamics model for the system *Fe-O* of different ways and to confront them and also on results the calculation of nonvariant equilibrium in the system to draw conclusion about reliability of model parameters and accordance of calculation and looked sizes.

According to data there are Fontana and Chirman [4] solubility of oxygen in liquid iron in a temperature interval 1801-2000 K described by equation:

$$\lg\left[\%O\right]=-\frac{6320}{T}+2{,}734 \ , \tag{1}$$

where T is an absolute temperature, K.

Energy of Gibbs is known also formations of hypothetical 1 % solution of oxygen in liquid iron, Jou/mole,

$$\Delta G_{1\%}=-117150-2{,}889T \ , \tag{2}$$

that in a count on the scale of Raul at a temperature 1873 K gives the size of activity coefficient of oxygen in liquid iron [5] at endless dilution:

$$\ln \gamma_O^\infty = \frac{\Delta G_{1\%}}{R \cdot T} + \ln \left[\frac{100 M_O}{M_{Fe}} \right] = -4,5144 \text{ or } \gamma_O^\infty = 0,01096, \qquad (3)$$

where M_O, M_{Fe} are accordingly atomic mass of oxygen and iron; R is universal gas constant.

There are accept, that a metallic phase is described by a thermodynamics model

$$\ln a_{[Fe]} = \ln x_{[Fe]} \cdot \psi_{[Fe]} + 1 - x_{[Fe]} \cdot \psi_{[Fe]} - x_{[O]} \cdot \psi_{[O]} \cdot \beta_{[Fe/O]} ; \qquad (4)$$

$$\ln a_{[O]} = \ln x_{[O]} \cdot \psi_{[O]} + 1 - x_{[O]} \cdot \psi_{[O]} - x_{[Fe]} \cdot \psi_{[Fe]} \cdot \beta_{[Fe/O]} , \qquad (5)$$

where $\psi_{[Fe]} = 1/\left(x_{[Fe]} + x_{[O]} \cdot \beta_{[Fe/O]} \right)$; $\psi_{[O]} = 1/\left(x_{[O]} + x_{[Fe]} \cdot \beta_{[Fe/O]} \right)$; $x_{[Fe]}$, $x_{[O]}$ are accordingly molefraction of iron and oxygen in a metal; $\beta_{[Fe/O]}$ is a model parameter, $\beta_{[Fe/O]} = \exp\left(-\varepsilon_{[Fe/O]} / R \cdot T \right)$, where $\varepsilon_{[Fe/O]}$ is energy of interatomic co-operation, determine by found value $\gamma_{[O]}^\infty = 0,01096$.

At the use of the traditional standard state «clean liquid metal» energy of Gibbs systems «metal - slag - gas» is expressed as follows:

$$G = \sum_{i=1}^{k} n_i \cdot \mu_{\{i\}}^\circ + R \cdot T \cdot \sum_{i=1}^{k} \left[n_{[i]} \cdot \left(\ln a_{[i]} + \ln K_{(i)} \right) + n_{(i)} \cdot \left(\ln a_{(i)} + \ln K_i \right) + n_{\{i\}} \cdot \ln a_{\{i\}} \right], \qquad (6)$$

where k is a number of elements in the system; n_i, $n_{[i]}$ $n_{(i)}$ $n_{\{i\}}$ are numbers of moles of clothes for element i accordingly in the system on the whole, metal, slag and gas; $\mu_{[i]}^0$, $\mu_{\{i\}}^0$ are chemical potential for element i in the standard state, in a gas phase accordingly; $a_{[i]}$ $a_{(i)}$ $a_{\{i\}}$ are activity of element i accordingly in a metal, slag and gas; $K_{[i)}$, $K_{(i]}$ are constants of equilibrium accordingly systems «metal - gas» and «slag - gas».

Size $\lg K_{[Fe)} = A/T + B$ determined by four different ways. Processing of calculation data allows to get molar energy of Gibbs for atomization of liquid iron and dissociation of oxygen as equations, Jou/mole:

$$\Delta G^0 = -119,4T + 370246 \quad (R^2 > 0.99), \qquad (7)$$

$$\Delta G^\circ = -133,55T + 510324 \quad (R^2 > 0.99), \qquad (8)$$

that corresponds to the sizes of logarithm for constant of equilibrium of $K_{[Fe\}}$ and $K_{(O]}$:

$$\ln K_{(Fe]} = -\frac{\Delta G^\circ}{R \cdot T} = \frac{\mu_{[Fe]}^\circ - \mu_{\{Fe\}}^\circ}{R \cdot T} = -\frac{44584}{T} + 14,386 \quad (R^2 > 0.99). \qquad (9)$$

$$\ln K_{(O]} = -\frac{\Delta G^\circ}{2R \cdot T} = \frac{\mu_{[O]}^\circ - \mu_{\{O\}}^\circ}{R \cdot T} = -\frac{30679}{T} + 8,026 \quad (R^2 > 0.99) \qquad (10)$$

Having all basic data for calculations, will write down the nonlinear system of three equations with three unknown μ_e, Y, Z:

$$\begin{cases} F_1 = \sum_{i=1}^{k} \dfrac{n_i \cdot \nu_i}{1+\exp\left(-A_i - Y + \mu_e \cdot \nu_i\right) \cdot \left[1+\exp\left(B_i + Z\right)\right]} = 0; \\[4mm] F_2 = \sum_{i=1}^{k} \dfrac{n_i}{1+\exp\left(-A_i - Y + \mu_e \cdot \nu_i\right) \cdot \left[1+\exp\left(B_i + Z\right)\right]} - \dfrac{N}{1+\exp\left(-Y\right) \cdot \left[1+\exp\left(Z\right)\right]} = 0; \quad (11) \\[4mm] F_3 = \sum_{i=1}^{k} \dfrac{n_i}{1+\left[1+\exp\left(A_i + Y - \mu_e \cdot \nu_i\right)\right] \cdot \exp\left(-Z - B_i\right)} - \dfrac{N}{1+\exp\left(-Z\right) \cdot \left[1+\exp\left(Y\right)\right]} = 0. \end{cases}$$

where A_i, B_i are accordingly natural logarithms of the consolidated constant of equilibrium of the systems «metal - slag» and «metal - gas»; $A_i = \ln(K_{[i]} \cdot \gamma_{[i]}/\gamma_{(i)})$; $B_i = \ln(K_{[i]} \gamma_{[i]}/\gamma_{\{i\}})$; Y, Z are natural logarithm of molar multipleness accordingly slag and gas.

The result of decision of the system (19) is a set of sizes μ_e, Y, Z, on which aquilibrium maintenances of elements are determined in all phases.

Conclusions. Results of calculations for the system *Fe-O* well comport with experimental data. At the same time, obviously, that parameterization of model for so-lution in a slag does not allow substantially to improve exactness of calculations of thermodynamics sizes as compared to the model of ideal ionic solution. Although in the system *Fe-O* this defect and a «metal - slag» is compensated by the temperature-dependent constants of equilibrium, for more difficult systems there is a requirement in further development of effective parameterization of slag constituent of general thermodynamics model «metal-slag-gas». There can one of variants may be approach with the use of individual pair energies of co-operation, analogical to the method of Wagner for a metallic phase.

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