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Abstract

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Thermodynamic Analysis of Equilibrium in the Dissociation of Ferrites

In our work ([1]) we proposed a scheme for calculating activities in the case of dissociation of simple ferrites, when the dissociation product—magnetite—forms a continuous series of solid solutions with the initial ferrite, and the second solid dissociation product is a phase of constant composition. In the present work a generalization of this scheme is given for the case when the second solid product is itself a phase of variable composition.

Let the equilibrium oxygen pressure over solid solutions of spinel and wüstite phases of a given composition be known to us, as well as the dependence of the composition of the wüstite phase on the composition of the spinel phase. We shall show that in this case it is possible to obtain an explicit form of the concentration dependence of the activities for the corresponding components, both in the wüstite and in the spinel phases.

The dissociation reaction of ferrites may be written in the general form

$$\mathrm{A}_c\mathrm{Fe}^{2+}_{1-c}\mathrm{Fe}^{3+}_2\mathrm{O}_4 = 3x(\mathrm{A}_y\mathrm{Fe}_{1-y})\mathrm{O}+$$

$$+(1-x)\mathrm{A}_{(c-3xy)/(1-x)}\mathrm{Fe}^{2+}_{[1-c-x(1-3y)]/(1-x)}\mathrm{Fe}^{3+}_2\mathrm{O}_4 + \tfrac{1}{2}x\mathrm{O}_2, \qquad (1)$$

where by A we mean a divalent metal (Mn, Mg, etc.); y is the parameter determining the composition of the solid phase; x is the degree of reduction. After simplifying (1) it is easy to obtain

$$\mathrm{A}_{3y}\mathrm{Fe}^{2+}_{1-3y}\mathrm{Fe}^{3+}_2\mathrm{O}_4 \rightleftharpoons 3(\mathrm{A}_y\mathrm{Fe}_{1-y})\mathrm{O} + \tfrac{1}{2}\mathrm{O}_2. \qquad (2)$$

Choosing magnetite and the corresponding ferrite as the components of the spinel solid solution (I), and the simple oxides FeO and AO as the components of the wüstite phase (II), equation (2) may be written in the form

$$3y\mathrm{AFe}_2\mathrm{O}_4 + (1-3y)\mathrm{Fe}_3\mathrm{O}_4 = 3y\mathrm{AO} + 3(1-y)\mathrm{FeO} + \tfrac{1}{2}\mathrm{O}_2. \qquad (3)$$

This equation describes the mechanism of ferrite dissociation under equilibrium conditions. Here the parameter y, which determines the composition of the solid phases, depends on the nature of the solid solutions and can be determined experimentally.

Since the equilibrium does not depend on the amount of substance, the partial reactions describing the equilibrium must contain constant coefficients. To determine such partial reactions it is necessary to write out all possible reactions between the components in the system and determine which of them are independent. This procedure is in the general case rather tedious, and we shall not dwell on it; instead, we shall describe a formal method that makes it possible to solve this problem considerably more simply.

If, in equation (3), the components are successively eliminated by setting equal to zero the coefficients standing before them and containing y, then three equations are obtained, by combining which one can obtain any reaction possible in this system:

$$\text{at } y = 0 \qquad [\mathrm{Fe_3O_4}]_\mathrm{I} \rightleftharpoons 3[\mathrm{FeO}]_\mathrm{II} + \tfrac{1}{2}(\mathrm{O_2})_2,$$

$$\begin{aligned} \text{for } y = \tfrac{1}{3} \quad & [\mathrm{AFe_2O_4}]_I \rightleftarrows [\mathrm{AO}]_\mathrm{II} + 2[\mathrm{FeO}]_\mathrm{II} + \tfrac{1}{2}(\mathrm{O_2})_2, \\ \text{for } y = 1 \quad & 3[\mathrm{AFe_2O_4}]_I \rightleftarrows 2[\mathrm{Fe_3O_4}]_I + 3[\mathrm{AO}]_I + \tfrac{1}{2}(\mathrm{O_2})_2. \end{aligned} \tag{4}$$

Let us consider system (4) as a system of linear homogeneous equations and determine the number of independent equations among them. To this end, we compose a matrix of coefficients, moving all terms to the left-hand side:

FeO	AO	AFe_2O_4	Fe_3O_4	O_2
−3	0	0	1	$-\frac{1}{2}$
−2	−1	1	0	$-\frac{1}{2}$
0	−3	3	−2	$-\frac{1}{2}$

(5)

If one chooses a nonzero determinant of the second order (the elements of this determinant in matrix (5) are enclosed in a frame), it is easy to show that all third-order determinants vanish, i.e., the rank of matrix (5) is 2. It follows that system (4) contains only 2 independent equations, for which we choose the first 2 (of the unknown components, 4).

Applying the law of mass action to the first two reactions (4), we obtain, respectively,

$$\ln a_4 - 3\ln a_1 = \ln p_{O_2}^{1/2} - \ln K_1,$$

$$\ln a_3 - 2\ln a_1 - \ln a_2 = \ln p_{O_2}^{1/2} - \ln K_2, \tag{6}$$

where, for the activities of the components a_i, the following notation has been adopted:

$$a_1 \equiv a_{\mathrm{FeO}}, \qquad a_2 \equiv a_{\mathrm{AO}}, \qquad a_3 \equiv a_{\mathrm{AFe_2O_4}}, \qquad a_4 \equiv a_{\mathrm{Fe_3O_4}}. \tag{7}$$

To determine the explicit form of the concentration dependence of the corresponding activities, we use the Gibbs–Duhem equations for oxide and ferrite solid solutions, expressed in terms of the ferrite concentration c,

$$cx_3 + (1-c)x_4 = 0, \tag{8}$$

$$N_1 x_1 + N_2 x_2 = 0,$$

where N_i are the concentrations of the corresponding components of the oxide phase,

$$x_1 = \frac{d}{dc}\ln a_1, \qquad x_2 = \frac{d}{dc}\ln a_2, \qquad x_3 = \frac{d}{dc}\ln a_3, \qquad x_4 = \frac{d}{dc}a_4. \tag{9}$$

If we now differentiate system (6) with respect to c and use the notation (9), then together with (8) we obtain a system of 4 equations from which it is easy to find x_i:

$$x_1 = -\frac{bN_2}{3N_2 - c} \equiv -\frac{b}{3 - c - cN_1/N_2}, \qquad x_2 = \frac{bN_1}{3N_2 - c} \equiv \frac{bN_1/N_2}{3 - c - cN_1/N_2}, \tag{10}$$

$$x_3 = \frac{b(1-c)}{3N_2 - c} \equiv \frac{b(1-c)(1+N_1/N_2)}{3 - c - cN_1/N_2}, \qquad x_4 = -\frac{bc}{3N_2 - c} \equiv \frac{bc(1+N_1/N_2)}{3 - c - cN_1/N_2},$$

where

$$b = \frac{d}{dc}\ln p_{O_2}^{1/2}. \tag{11}$$

In the simplest case, when

$$b = \alpha c + \alpha_0, \qquad \frac{N_1}{N_2} = \frac{1}{c}\beta + \beta_0, \tag{12}$$

it is easy to carry out the integration of (10) and obtain the analytical form for a_i. The expressions obtained for the activities can be used for

study of the solid-phase reaction, which can be obtained as the difference of any two reactions of system (4).

$$AFe_3O_4 + FeO \rightleftharpoons Fe_3O_4 + AO. \tag{13}$$

The equilibrium constant for this reaction has the form

$$K_4 = a_4 a_2 / a_1 a_3. \tag{14}$$

The proposed calculation scheme can be used for the thermodynamic analysis of equilibrium in the dissociation of manganese ferrites [2] and magnesium ferrites [3], for which the dissociation reaction can be written in the form (1).

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CITED LITERATURE

[1] A. N. Men' , N. M. Stafeeva, V. N. Bogoslovskii, M. G. Zhuravleva, G. I. Chufarov, DAN, **156**, No. 4, 912 (1964).
[2] G. I. Chufarov, M. G. Zhuravleva, A. N. Men' , B. D. Averbugh, G. P. Popov, N. M. Stafeeva, *Problems of Radioelectronics*, **3**, issue 16 (1962).
[3] A. A. Sheshin, L. G. Khromykh, V. N. Bogoslovskii, M. G. Zhuravleva, G. I. Chufarov, DAN, **152**, No. 1, 124 (1963).

Note: Figure translations are in progress. See original paper for figures.