



Soviet-era science, translated into English

Physical Chemistry

V. N. Bogoslovskii, A. N. Men,

1965

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196501.06070>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Physical Chemistry

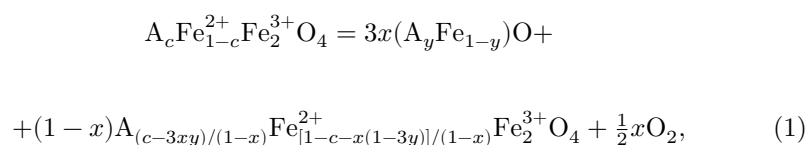
V. N. Bogoslovskii, A. N. Men,
Corresponding Member of the Academy of Sciences of the USSR G.
I. Chufarov

Thermodynamic Analysis of Equilibrium in the Dissociation of Ferrites

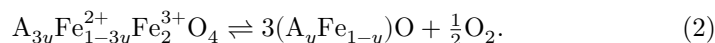
In our work ⁽¹⁾ we proposed a scheme for calculating activities in the case of dissociation of simple ferrites, when the dissociation product—magnetite—forms a continuous series of solid solutions with the initial ferrite, and the second solid dissociation product is a phase of constant composition.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



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



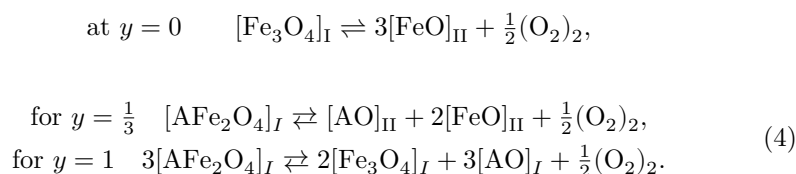
Choosing magnetite and the corresponding ferrite as the components of the spinel solid solution (I), and the simple oxides FeO and AO as the components of the wüstite phase (II), equation (2) may be written in the form



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:



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 ₂ O ₄	Fe ₃ O 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,

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

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

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

$$a_1 \equiv a_{FeO}, \quad a_2 \equiv a_{AO}, \quad a_3 \equiv a_{AFe_2O_4}, \quad a_4 \equiv a_{Fe_3O_4}. \quad (7)$$

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 ,

$$cx_3 + (1 - c)x_4 = 0, \quad (8)$$

$$N_1x_1 + N_2x_2 = 0,$$

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

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

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 :

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

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

where

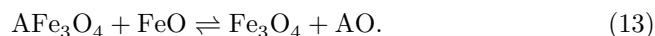
$$b = \frac{d}{dc} \ln p_{O_2}^{1/2}. \quad (11)$$

In the simplest case, when

$$b = \alpha c + \alpha_0, \quad \frac{N_1}{N_2} = \frac{1}{c} \beta + \beta_0, \quad (12)$$

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).



The equilibrium constant for this reaction has the form

$$K_4 = a_4 a_2 / a_1 a_3. \quad (14)$$

The proposed calculation scheme can be used for the thermodynamic analysis of equilibrium in the dissociation of manganese ferrites² and magnesium ferrites³, for which the dissociation reaction can be written in the form (1).

Institute of Metallurgy
Sverdlovsk

Received
13 II 1965

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.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.