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PHYSICAL CHEMISTRY

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Abstract

Full Text

PHYSICAL CHEMISTRY

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STATISTICAL-THERMODYNAMIC CONSIDERATION OF SOLID SOLUTIONS OF THE SPINEL TYPE

To determine the concentration dependence of the thermodynamic functions of mixing for solid solutions, one usually uses an explicit form of the dependence of the activities of the components on composition and temperature.

In the case of equilibrium of a spinel solid solution of variable concentration with a phase of constant composition, such a dependence for a_i was obtained by the method described in work ([1]), from data on the equilibrium oxygen elasticity and the composition of the solid phases. In work ([2]) a statistical method was proposed for calculating the activities of solid solutions of the MeO type, which gave satisfactory agreement with experiment.

In the present work this method is generalized to the case of solid solutions of the spinel type that are in equilibrium with a phase of variable composition.

Let us consider a solid solution of composition $\mathrm{Me}^{\mathrm{I}}_{c_1}\mathrm{Me}^{\mathrm{II}}_{c_2}\mathrm{Me}^{\mathrm{III}}_{2}\mathrm{O}_4$ $(c_1 + c_2 = 1)$, when the distribution of cations in the solution and in the pure components $\mathrm{Me}^{\mathrm{I(II)}}\mathrm{Me}^{\mathrm{III}}_{2}\mathrm{O}_4$ is specified, respectively, by matrices of the form

$$\begin{pmatrix} \lambda_1 & \lambda_2 & 1-\lambda_1-\lambda_2 \\ c_1-\lambda_1 & c_2-\lambda_2 & 1+\lambda_1+\lambda_2 \end{pmatrix}, \quad \begin{pmatrix} \lambda_1^0 & 0 & 1-\lambda_1^0 \\ 1-\lambda_1^0 & 0 & 1+\lambda_1^0 \end{pmatrix}, \quad \begin{pmatrix} 0 & \lambda_2^0 & 1-\lambda_2^0 \\ 0 & 1-\lambda_2^0 & 1+\lambda_2^0 \end{pmatrix}, \tag{1}$$

where the first row refers to the tetrahedral sites (A), the second to the octahedral sites (B) of the spinel; λ_i is the degree of inversion in the solution, and λ_i^0 is the degree of inversion in the pure components.

For the configurational entropy of mixing and the internal energy of mixing it is easy to obtain the expression

$$\begin{aligned} \Delta S = -R\{&\lambda_1 \ln \lambda_1 + \lambda_2 \ln \lambda_2 + (1-\lambda_1-\lambda_2)\ln(1-\lambda_1-\lambda_2) + \\ &+(c_1-\lambda_1)\ln(c_1-\lambda_1) + (c_2-\lambda_2)\ln(c_2-\lambda_2) + (1+\lambda_1+\lambda_2)\ln(1+ \\ &+\lambda_1+\lambda_2) - c_1[\lambda_1^0 \ln \lambda_1^0 + 2(1-\lambda_1^0)\ln(1-\lambda_1^0) + (1+\lambda_1^0)\ln(1+ \end{aligned}$$

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$$+\lambda_1^0)] - c_2(\lambda_2^0 \ln \lambda_2^0 + 2(1-\lambda_2^0)\ln(1-\lambda_2^0) + (1+\lambda_2^0)\ln(1+\lambda_2^0))\}; \qquad (2)$$

$$\Delta U = N c_1 c_2 \alpha, \qquad (3)$$

where $\alpha = v/kT$; N is Avogadro' s number; v is the algebraic sum of the energies of pair interactions of cations located at distances not exceeding the distance between tetrahedra.

Using (2) and (3) under the condition

$$\lambda_1 = c_1 \lambda_1^0, \qquad \lambda_2 = c_2 \lambda_2^0, \qquad (4)$$

we obtain an expression for the activities of the components in the solid solution

$$a_i = c_i \left[\frac{1 - c_1\lambda_1^0 - c_2\lambda_2^0}{1-\lambda_i^0}\right]^{1-\lambda_i^0} \left[\frac{1 + c_1\lambda_1^0 + c_2\lambda_2^0}{1+\lambda_i^0}\right]^{1+\lambda_i^0} e^{\alpha(1-c_i)^2}. \qquad (5)$$

Here, in contrast to formula (3) of paper [2],

$$a_j = c_j e^{\alpha'(1-c_j)^2}, \qquad (6)$$

the presence of factors in square brackets is due to taking into account the change in the degree of inversion with composition.

Let us consider, as an example, a solid solution of manganese ferrite with magnetite, for which $\lambda_1^0 = 0.8$ [3], $\lambda_2^0 = 0$. For the equilibrium

$$MnFe_2O_4 \rightleftarrows MnO + 2FeO + {}^{1/2}O_2$$

the constant is written as

$$K = \frac{a_{FeO}^2 a_{MnO} p_{O_2}^{1/2}}{a_{MnFe_2O_4}}. \qquad (7)$$

Substituting into (7) the explicit form of the activities (5) and (6), we obtain an expression for $\lg p_{O_2}^{1/2}$

$$\begin{aligned} \lg p_{O_2}^{1/2} = {} & \lg K + \lg c_\phi + (1-\lambda_1^0)\,[\lg(1 - c_\phi\lambda_1^0) - \lg(1-\lambda_1^0)] \\ & + (1+\lambda_1^0)\,[\lg(1 + c_\phi\lambda_1^0) - \lg(1+\lambda_1^0)] \\ & + 0.43\,[\alpha(1-c_\phi)^2 - 2\alpha' c_{MnO}^2 - \alpha' c_{FeO}^2] - 2\lg c_{FeO} - \lg c_{MnO}, \end{aligned} \qquad (8)$$

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

where $c_\phi = c_{MnFe_2O_4}$.

Using the experimental dependence $\lg p_{O_2}(c_i)$ at $c_\phi = 0.3$ and 0.8 [4], from formula (8) we obtain the value $\alpha = 1.9$ and $\lg K = -7.9$. Here α' was taken equal to 0 according to [2,5]. However, let us note that from expression (8) one can obtain the parameter α' by using not 2 but 3 experimental points. In this case α' is indeed small (0.07). From the values found for α and $\lg K$, the dependence $\lg p_{O_2}$ on c_ϕ was calculated, which agrees satisfactorily with experiment (see Fig. 1).

Fig. 1. Dependence of $\lg p_{O_2}$ on the concentration of ferrite in the solid solution manganese ferrite–magnetite, $T = 900°$. The curve is calculated; the points are experimental.

Fig. 2. Dependence of the activities a_ϕ and a_m on the composition c_ϕ and c_m for solid solutions manganese ferrite–magnetite, $T = 900°$. 1–a_ϕ; 2–a_m; 3–a_ϕ, calculated at a constant degree of inversion.

Fig. 3. Concentration dependence of the configurational entropy, internal energy, and free energy of mixing for solid solutions. 1–ΔS^{conf}_{mix}; 2–ΔU_{mix}; 3–ΔF_{mix}.

Substituting the corresponding values of α and λ_1^0 into (5), we obtain the activities of manganese ferrite and magnetite in the solution (Fig. 2). Figure 2 also gives the values of a_ϕ, calculated without taking into account the degree of inversion (curve 3), which indicates a significant contribution of the terms that take into account the distribution of cations over the sublattices.

Figure 3 gives the concentration dependences of ΔS^{conf}_{mix}, calculated by formula (2), ΔU_{mix} by formula (3) (curve 2), and $\Delta F = \Delta U - T\Delta S$. It should be noted that the value of ΔF agrees satisfactorily with the data available in the literature for the solid solution Mn_3O_4—Fe_3O_4 ([6]), if these data are recalculated, choosing $MnFe_2O_4$ and Fe_3O_4 as the components of the solid solution.

The calculation scheme presented can be applied to any solid solutions, provided experimental data are available on the dependence of $\lg p_{O2}$ on the composition of solid phases in equilibrium.

Fig. 3

Figure 3: Fig. 3

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It should be borne in mind that formulas (5) and (6) were obtained under the assumption that in the expression for the internal energy of mixing the concentrations c_i enter to the first power. However, the possibility is not excluded that ΔU_{mix} may be represented in a more complex form

$$\Delta U = N c_1^{n_1} c_2^{n_2} \alpha. \tag{9}$$

One of the criteria for the applicability of expression (3) may be the value of the activity obtained from formula (5), less than unity. If the nature of the temperature dependence of α is not specified (see formula (4) of work (2)), then the expression for ΔH_{mix} will also have the form (3), i.e., curve 2 in Fig. 3 will characterize the concentration dependence of the enthalpy of mixing.

The theoretical calculation of the parameters α for solid solutions of the spinel type will be considered separately.

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