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Abstract

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THERMODYNAMIC ANALYSIS OF EQUILIBRIUM IN THE DISSOCIATION OF FERRITES

Experimental data on the dependence of the equilibrium oxygen pressure during the dissociation of complex oxides on composition often make it possible to carry out a complete thermodynamic analysis of such systems. In this case oxides of variable composition are considered as solid solutions whose components are oxides of definite composition. For the present we shall restrict ourselves to considering binary solutions.

The literature gives thermodynamic analyses for the simplest cases: 1. Only one of the components of the solid solution dissociates, and the dissociation product is not soluble in the initial phase. For example, the dissociation of FeO dissolved in MgO (1,2), or in MnO (3). 2. The dissociation product of the oxide dissolves in another oxide; for example, magnetite, formed during the dissociation of Fe_2O_3, dissolves in magnesium ferrite (2).

There may also be a case in which one of the dissociation products dissolves in the initial oxide. An example is the dissociation of simple ferrites, when the dissociation product—magnetite—forms a continuous series of solid solutions with the initial ferrite. In this case the second solid product of dissociation may be either a) a phase of constant composition (4), or b) a phase of variable composition (5).

In the present work case a) is considered. Case b) will be considered separately.

The dissociation reaction of a ferrite is written in the form (6)

$$A_{3y}Fe^{2+}_{1-3y}Fe^{3+}_2O_4 \rightleftarrows 3\left(A_yFe_{1-y}\right)O + \frac{1}{2}O_2. \qquad (1)$$

Taking into account that y is a constant quantity and is determined only by the chemical reaction, and that for case a) the activity of the phase of constant composition is equal to unity, the reaction constant may be written as

$$K = \frac{p_{\mathrm{O2}}^{1/2} a_{\mathrm{m}}^{n}}{a_{\mathrm{f}}^{m}}, \tag{2}$$

where a_{m} and a_{f} are the activities of magnetite and ferrite, respectively, and $m = 3y$, while $n = 3y - 1$.

Using expression (2) and the Gibbs-Duhem equation, we obtain a system for determining the logarithms of the activities of the components of the spinel phase

$$-md\ln a_{\mathrm{f}} + nd\ln a_{\mathrm{m}} = -d\ln p_{\mathrm{O2}}^{1/2},$$

$$c_{\mathrm{f}} d\ln a_{\mathrm{f}} + c_{\mathrm{m}} d\ln a_{\mathrm{m}} = 0, \tag{3}$$

where c is the concentration of the corresponding component. Solving system (3),

we obtain

$$\ln a_{\phi} = \int_{1}^{c_{\phi}} \frac{1 - c_{\phi}}{[m + (n - m)c_{\phi}]}\, d\ln p_{O_2}^{\prime\,1/2}, \tag{4'}$$

$$\ln a_{\mathrm{m}} = -\int_{1}^{c_{\mathrm{m}}} \frac{1 - c_{\mathrm{m}}}{[n + (m - n)c_{\mathrm{m}}]}\, d\ln p_{O_2}^{1/2}, \tag{4''}$$

with the normalization $a_{\phi} = 1$ at $c_{\phi} = 1$ and $a_{\mathrm{m}} = 1$ at $c_{\mathrm{m}} = 1$. It should be noted that the same result will be obtained if c_{m} is chosen as the independent variable in equation ($4'$), and c_{ϕ} in ($4''$), but the limits of integration will then be different. A more substantial role is played by the choice of normalization, since if normalization to dilute solutions is used, then the values of p_{O_2} must be taken as equal to zero and infinity in order to ensure constancy of K in (2), and this, in turn, is associated with the difficulty of using experimental data for $p_{O_2}(c)$.

The formulas (4) have the simplest form if $\ln p_{O_2}^{\prime\,1/2}$ is a linear function of composition

$$\ln p_{O_2}^{\prime\,1/2} = b + kc. \tag{5}$$

Substituting (5) into ($4'$) and ($4''$), we obtain

Figure 1

Figure 1: Figure 1

$$\ln a_\phi = \frac{k}{n-m}\left[1 - c_\phi + \frac{n}{n-m}\ln\frac{m+(n-m)c_\phi}{n}\right],$$

$$\ln a_\mathrm{m} = \frac{k}{m-n}\left[1 - c_\mathrm{m} + \frac{m}{m-n}\ln\frac{+n(m-n)c_\mathrm{m}}{m}\right]. \tag{6}$$

As an example, let us consider the dissociation reaction of copper ferrite. According to (4), this reaction is written as

$$1.5\,\mathrm{CuFe_2O_4} = 1.5\,\mathrm{CuFeO_2} + 0.5\,\mathrm{Fe_3O_4} + \frac{1}{2}\mathrm{O_2}, \tag{7}$$

which corresponds to equation (1) at $y = \frac{1}{2}$, i.e. $m = \frac{3}{2}$, $n = \frac{1}{2}$. The dissociation product–magnetite–forms solid solutions with copper ferrite.* Experimental data for the dependence of $\ln p'^{1/2}_{O_2}$ on the ferrite content in the solid solution (c) are given in Fig. 1. This dependence can most simply be described by an equation of two straight lines. Thus, for example, for 1100°C

$$\ln p'^{1/2}_{O_2} = 11.0c - 10.5 \qquad (0 \le c \le 0.7),$$

$$\ln p'^{1/2}_{O_2} = 9.1c - 9.1 \qquad (0.7 \le c \le 1). \tag{8}$$

Fig. 1. Dependence of $\lg p^{1/2}_{O_2}$ on the composition of solid solutions $\mathrm{CuFe_2O_4}$—$\mathrm{Fe_3O_4}$

Using the first of equations (6) for each of the straight lines (8), we obtain the values of a_ϕ. The values of a_m were calculated directly from the second equation of the system (3). The data obtained at 900° were treated in an analogous manner. The results are given in Table 1. Also given there are

data on the concentration dependences of partial and integral quantities: the free energy ΔZ, enthalpy ΔH, and entropy ΔS of mixing for solid solutions of copper ferrite with magnetite. As is seen from the data in Table 1, the activities differ little from the concentrations at high contents of the corresponding components.

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* In solid solutions of copper ferrite with magnetite, the copper ion is assumed to be divalent ([7,8]).

Of the thermodynamic functions obtained, the integral entropy of mixing is the simplest to estimate theoretically.

Table 1

Activities of the components of solid solutions $CuFe_2O_4$—Fe_3O_4, partial and integral free energies, enthalpies, and entropies of mixing

c_ϕ and c_M	900° a_ϕ	900° a_M	1100° a_ϕ	1100° a_M	$\Delta\overline{Z}_\phi$	$\Delta\overline{Z}_M$	ΔZ_p	$\Delta\overline{H}_\phi$	$\Delta\overline{H}_M$	ΔH_p	$\Delta\overline{S}_\phi$	$\Delta\overline{S}_M$	ΔS_{int}	ΔS_{mix}^{conf*}
0.1	0.004	0.003	0.014	0.011	−10.46	−11.15	−1.12	−6.88	−7.84	−0.88	3.33	3.00	0.22	1.74
0.2	0.01	0.006	0.032	0.032	−8.57	−8.69	−1.98	−5.50	−5.70	−1.29	2.80	2.78	0.62	1.13
0.3	0.02	0.02	0.06	0.056	−6.82	−6.86	−2.60	−4.28	−3.78	−1.55	2.37	2.87	0.97	1.38
0.4	0.005	0.085	0.10	0.16	−5.65	−4.37	−3.17	−3.40	−2.22	−1.94	2.09	2.00	1.15	1.50
0.5	0.12	0.22	0.19	0.33	−4.17	−2.65	−3.41	−3.04	−1.30	−2.17	1.05	1.25	1.15	1.52
0.6	0.25	0.42	0.37	0.54	−2.84	−1.52	−3.45	−2.42	−0.96	−2.34	0.38	0.52	1.03	1.45
0.7	0.47	0.64	0.58	0.72	−1.52	−0.79	−3.14	−1.67	−0.38	−2.16	−0.13	0.37	0.95	1.30
0.8	0.76	0.83	0.74	0.87	−0.84	−0.33	−2.41	−1.03	−0.24	−1.96	−0.18	0.08	0.41	1.06
0.9	0.90	0.95	0.93	0.97	−0.20	−0.08	−1.23	−0.20	−0.21	−0.96	−0.003	−0.12	0.30	0.67

* Calculated from equation (9).

It is usually assumed that the entropy of mixing for solid solutions is determined mainly by its configurational part. It is easy to obtain the configurational entropy of mixing for solid solutions $\Delta S_{mix}^{conf} = S_{r.p.}^{conf} - cS_\phi^{conf} - (1-c)S_M^{conf}$, assuming that the distribution of ions over tetrahedral and octahedral sites for the solid solution $Cu_cFe_{1-c}^{2+}Fe_2^{3+}O_4$ is described by $(Cu_{1-\lambda}^{2+}Fe_\lambda^{3+})[Cu_{c+\lambda-1}^{2+}Fe_{1-c}^{2+}Fe_{2-\lambda}^{3+}]O_4$, and for magnetite and copper ferrite, respectively, by $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$ and $(Cu_{1-\lambda}^{2+}Fe_\lambda^{3+})[Cu_\lambda^{2+}Fe_{2-\lambda}^{3+}]O_4$, where the cations located in tetrahedral sites are written in parentheses, and λ is the degree of inversion.

$$\Delta S_{mix}^{conf} = R\{-(c+\lambda-1)\ln|c+\lambda-1| - (1-c)\ln(1-c)$$
$$-(1-c)(2-\lambda)\ln(2-\lambda) - (1-2c)\lambda\ln\lambda - (1-c)(1-\lambda)\ln(1-\lambda)\}. \qquad (9)$$

If magnetite dissolves in a completely inverse ferrite ($\lambda = 1$), then formula (9) has a maximum at $c = 0.5$. If, however, the degree of inversion for the ferrite differs little from unity, then one may put $\lambda = 1 - c\alpha$ in equation (9). In this case the maximum of the configurational entropy will be shifted toward higher concentrations by an amount $\alpha/8$.

Since for copper ferrite at a temperature of 900° and above λ is of the order of 0.66 (^{8}), α may be taken as 0.34, and the maximum will occur at $c = 0.54$.

Then, for the solid solution $CuFe_2O_4$—Fe_3O_4 at $c = 0.5$, $\lambda = 0.83$, whereas according to magnetic measurements (^{9}) λ should be equal to 0.75. This indicates that the linear dependence of λ on c is a first approximation.

In view of the fact that, for these solid solutions, the maximum of the entropy of mixing is strongly broadened, the shift could not be detected. The effect will probably be stronger for the case of solid solutions of normal spinel with inverse spinel.

Comparing the values of $\Delta S_{\text{mix}}^{\text{conf}}$, calculated from equation (9), with the values of ΔS^{int} (see Table 1), one can see that for all compositions the difference $\Delta S_{\text{mix}}^{\text{conf}} - \Delta S^{\text{int}}$ is approximately 0.4 kcal/mol. This difference may be due to the fact that, in the theoretical calculation of the entropy of mixing, the influence of short-range order and thermal vibrations of the ions was not taken into account.

Despite the assumptions adopted, the theoretical values of the entropy of mixing agree satisfactorily with the experimental ones.

The proposed scheme for calculating activities can in principle also be applied in the case when the solid dissociation product is not a phase of constant composition, provided that the activities of the components in this phase are known.

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