THERMODYNAMIC PROPERTIES OF THE SOLID SOLUTION MnO –FeO

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Abstract

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THERMODYNAMIC PROPERTIES OF THE SOLID SOLUTION MnO–FeO

The information available in the literature (^{1}-^{3}) on the thermodynamics of the MnO–FeO solid solution is contradictory. On the basis of the concentration dependence of the equilibrium oxygen pressure, it is asserted (^{1}, ^{2}) that the solution is ideal, whereas according to measurements of the e.m.f. of a galvanic cell (^{3}) the activity of wüstite shows a positive deviation from ideality.

The authors' investigations of phase equilibria during the reduction of manganese ferrochromites and ferroaluminates (^{4}) made it possible to establish the following analytical dependences of the equilibrium composition of the gas phase (P_{H_2O}/P_{H_2}) on the concentration of wüstite in the oxide solution MnO–FeO for 900, 1000, and 1100° C, respectively:

$$\lg(P_{H_2O}/P_{H_2}) = -0.6594 + 0.4590\, C_{FeO_{1.018}},$$

$$\lg(P_{H_2O}/P_{H_2}) = -0.5847 + 0.4394\, C_{FeO_{1.018}},$$

$$\lg(P_{H_2O}/P_{H_2}) = -0.4910 + 0.3804\, C_{FeO_{1.018}}, \qquad (1)$$

where $C_{FeO_{1.018}}$ is the mole fraction of wüstite in the solid solution. The composition of the hypothetical wüstite $FeO_{1.018}$ was found from the value of the parameter of its crystal lattice (4.321 ± 0.003 Å) (^{4}) from data (^{5}) extrapolated toward stoichiometric FeO.

It is assumed that the indicated defectiveness of wüstite changes insignificantly with a change in the composition of the solid solution.

Reduction of the MnO–FeO solution is reduced to the reaction

$$(FeO_{1.018})_{soln} + 1.018H_2 \rightleftarrows Fe + 1.018H_2O, \qquad (2)$$

the equilibrium constant of which is

$$K = \frac{(P_{\mathrm{H_2O}}/P_{\mathrm{H_2}})^{1.018}}{a_{\mathrm{FeO}_{1.018}}}. \tag{3}$$

In the general case, upon reduction of an oxide solid solution, a metallic alloy is formed. But for the solution under consideration the concentration of manganese at the indicated temperatures is negligible. Therefore the activity of iron in equation (3) has been taken as equal to unity.

The data given were used to calculate the concentration dependence of the activities of the components of the MnO—FeO solid solution from the statistical equation

$$a_i = C_i e^{\alpha'(1-C_i)^2}, \tag{4}$$

where a_i and C_i are the activity and concentration of the i-th component (MnO or FeO), and α' is an energy parameter. Combining (3) and (4), we obtain

$$\lg K = 1.018 \lg\left(\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}}\right) - \lg C_{\mathrm{FeO}_{1.018}} - 0.4343\,\alpha'(1 - C_{\mathrm{FeO}_{1.018}})^2. \tag{5}$$

Substituting (1) into (5), the solution of the system of two equations (for mole fractions of wüstite equal to 0.3 and 0.5) gives the values of the equilibrium constant K and of the energy parameter α' at 900, 1000, and 1100°: $K_{900^\circ} = 0.537$, $\alpha a'_{900^\circ} = 1.234$, $K_{1000^\circ} = 0.619$, $\alpha a'_{1000^\circ} = 1.272$, $K_{1100^\circ} = 0.700$, $\alpha a'_{1100^\circ} = 1.387$.

The equilibrium constants found in this way correspond to their values for the reduction reaction of pure wüstite (7): $K_{900^\circ} = 0.590$, $K_{1000^\circ} = 0.638$, $K_{1100^\circ} = 0.751$.

The activities of the components of the solid solution were obtained from the expressions:

$$a_i^{900^\circ} = C_i e^{1.234(1-C_i)^2}, \qquad a_i^{1000^\circ} = C_i e^{1.272(1-C_i)^2}, \qquad a_i^{1100^\circ} = C_i e^{1.387(1-C_i)^2}. \tag{6}$$

The concentration dependence of the activities of MnO and FeO, presented in the form of an "activity—composition of the solid solution" plot, indicates the presence in the solution under study of a significant positive deviation from ideality and agrees with the data of the investigation (^{3}).

In order to check the reliability of the results obtained, the activities of wüstite and manganous oxide were calculated by an essentially different method, described in detail in work (^{7}). In this case the activity of MnO was calculated from the Gibbs—Duhem equation, using graphical integration for its solution.

Comparison of the activity values of the components of the solid solution (Table 1), obtained by two independent methods, gives sufficiently satisfactory agreement.

The maximum possible error in determining the activities of the solution components was estimated in accordance with (4) from the equation

$$\Delta a/a = e^{\pm\Delta\alpha'(1-C\mathrm{FeO}_{1.018})^2} - 1. \tag{7}$$

The value of $\Delta\alpha'$ required for this was calculated, on the basis of (5), from the equation

$$\frac{\Delta\alpha'}{\alpha'} = \frac{\Delta\lg\varphi}{\lg\varphi} + 2\frac{\Delta C}{1-C\mathrm{FeO}_{1.018}}, \tag{8}$$

where

$$\varphi = \frac{(P_{\mathrm{H_2O}}/P_{\mathrm{H_2}})^{1.018}}{KC_{\mathrm{FeO}_{1.018}}}.$$

The error in the value $P_{\mathrm{H_2O}}/P_{\mathrm{H_2}}$ is, in total, 9.5%. The value of K has the same error. Hence the maximum relative error in determining the activities of wüstite and manganous oxide in the solid solution does not exceed 20%.

Since the change in the activity coefficient γ in the temperature interval 900-1100° investigated lies within the error of determining γ ($\Delta\gamma/\gamma \approx 20\%$), according to the equation

$$\lg\gamma_i = \Delta\bar{H}_i/4.574T + J_i, \tag{9}$$

obtained by integration

$$\partial\ln\gamma_i/\partial T = -\Delta\bar{H}_i/RT^2, \tag{10}$$

the partial molar enthalpy of mixing $\Delta\bar{H}_i$ of the components of the binary solution was taken to be zero. By graphical solution of equation (9) using the limiting values of γ, the region in which the values of the integral enthalpy of mixing ΔH_{m} lie was estimated to be (+0.1) ÷ (−0.7) kcal/mole. The partial molar free energy

Table 1

Thermodynamic characteristics of the solid solution MnO–FeO

C_{FeO}	a_{FeO} 900°	a_{FeO} 1000°	a_{FeO} 1100°	a_{MnO} 900°	a_{MnO} 1000°	a_{MnO} 1100°	ΔF_p, cal/mole 900°	ΔF_p, cal/mole 1000°	ΔF_p, cal/mole 1100°	ΔS_p, cal/deg·mole 900°	ΔS_p, cal/deg·mole 1000°	ΔS_p, cal/deg·mole 1100°	ΔS_p^{ex}, cal/deg·mole 900°	ΔS_p^{ex}, cal/deg·mole 1000°	ΔS_p^{ex}, cal/deg·mole 1100°
0	$\frac{0}{0}$	$\frac{0}{0}$	$\frac{0}{0}$	$\frac{1{,}0}{1{,}0}$	$\frac{1{,}0}{1{,}0}$	$\frac{1{,}0}{1{,}0}$	0	0	0	0	0	0	0	0	0
0 05	$\frac{0{,}1522}{0{,}1175}$	$\frac{0{,}1575}{0{,}1403}$	$\frac{0{,}1747}{0{,}1625}$	$\frac{0{,}9528}{0{,}9504}$	$\frac{0{,}9530}{0{,}9592}$	$\frac{0{,}9532}{0{,}9610}$	−326,4	−349,5	−362,2	0,2783	0,2744	0,2636	−0,1162	−0,1200	−0,1309
0,1	$\frac{0{,}2715}{0{,}2116}$	$\frac{0{,}2800}{0{,}2486}$	$\frac{0{,}3073}{0{,}2820}$	$\frac{0{,}9111}{0{,}9081}$	$\frac{0{,}9114}{0{,}9204}$	$\frac{0{,}9124}{0{,}9252}$	−498,9	−533,0	−546,3	0,4253	0,4188	0,3978	−0,2206	−0,2272	−0,2481
0,2	$\frac{0{,}4403}{0{,}3616}$	$\frac{0{,}4512}{0{,}4106}$	$\frac{0{,}4859}{0{,}4538}$	$\frac{0{,}8407}{0{,}8408}$	$\frac{0{,}8418}{0{,}8600}$	$\frac{0{,}8464}{0{,}8680}$	−705,8	−750,9	−756,9	0,6018	0,5899	0,5514	−0,3921	−0,4042	−0,4427
0,3	$\frac{0{,}5491}{0{,}4719}$	$\frac{0{,}5594}{0{,}5202}$	$\frac{0{,}5930}{0{,}5616}$	$\frac{0{,}7821}{0{,}7805}$	$\frac{0{,}7848}{0{,}8071}$	$\frac{0{,}7930}{0{,}8253}$	−820,0	−869,6	−870,2	0,6989	0,6830	0,6337	−0,5148	−0,5304	−0,5797
0,4	$\frac{0{,}6138}{0{,}5580}$	$\frac{0{,}6322}{0{,}5984}$	$\frac{0{,}6589}{0{,}6344}$	$\frac{0{,}7308}{0{,}7302}$	$\frac{0{,}7353}{0{,}7640}$	$\frac{0{,}7489}{0{,}7890}$	−893,3	−922,6	−928,4	0,7617	0,7308	0,6762	−0,5750	−0,6059	−0,6605
0,5	$\frac{0{,}6808}{0{,}6500}$	$\frac{0{,}6871}{0{,}6630}$	$\frac{0{,}7071}{0{,}6920}$	$\frac{0{,}6808}{0{,}6885}$	$\frac{0{,}6871}{0{,}7095}$	$\frac{0{,}7071}{0{,}7515}$	−896,1	−949,1	−945,2	0,7640	0,7456	0,6884	−0,6130	−0,6312	−0,6884
0,6	$\frac{0{,}7308}{0{,}7284}$	$\frac{0{,}7353}{0{,}7348}$	$\frac{0{,}7489}{0{,}7469}$	$\frac{0{,}6138}{0{,}6240}$	$\frac{0{,}6322}{0{,}6430}$	$\frac{0{,}6589}{0{,}6808}$	−893,3	−922,6	−928,4	0,7617	0,7308	0,6762	−0,5750	−0,6059	−0,6605
0,7	$\frac{0{,}7821}{0{,}7607}$	$\frac{0{,}7848}{0{,}7759}$	$\frac{0{,}7930}{0{,}7891}$	$\frac{0{,}5491}{0{,}5433}$	$\frac{0{,}5594}{0{,}5603}$	$\frac{0{,}5930}{0{,}5934}$	−820,0	−869,6	−870,2	0,6989	0,6830	0,6337	−0,5148	−0,5304	−0,5797
0,8	$\frac{0{,}8407}{0{,}8303}$	$\frac{0{,}8418}{0{,}8370}$	$\frac{0{,}8467}{0{,}8433}$	$\frac{0{,}4403}{0{,}4356}$	$\frac{0{,}4512}{0{,}4412}$	$\frac{0{,}4859}{0{,}4756}$	−705,8	−750,9	−756,9	0,6018	0,5899	0,5514	−0,3921	−0,4042	−0,4427
0,9	$\frac{0{,}9111}{0{,}9082}$	$\frac{0{,}9114}{0{,}9101}$	$\frac{0{,}9124}{0{,}9120}$	$\frac{0{,}2715}{0{,}2606}$	$\frac{0{,}2800}{0{,}2880}$	$\frac{0{,}3073}{0{,}3049}$	−498,9	−533,0	−546,3	0,4253	0,4188	0,3978	−0,2206	−0,2272	−0,2481
0,95	$\frac{0{,}9528}{0{,}9517}$	$\frac{0{,}9530}{0{,}9521}$	$\frac{0{,}9532}{0{,}9528}$	$\frac{0{,}1522}{0{,}1486}$	$\frac{0{,}1575}{0{,}1640}$	$\frac{0{,}1747}{0{,}1739}$	−326,4	−349,5	−362,2	0,2783	0,2744	0,2636	−0,1162	−0,1200	−0,1309
1,0	$\frac{1{,}0}{1{,}0}$	$\frac{1{,}0}{1{,}0}$	$\frac{1{,}0}{1{,}0}$	$\frac{0}{0}$	$\frac{0}{0}$	$\frac{0}{0}$	0	0	0	0	0	0	0	0	0

Note. Above the line are activity values calculated according to the statistical formula; below the line are activity values calculated by the method set forth in work (7).

of mixing $\Delta \overline{F}_i$ was calculated from the relation

$$\Delta \overline{F}_i = RT \ln a_i, \tag{11}$$

and the integral free energy of mixing ΔF_p (Table 1) is equal to

$$\Delta F_p = C_{FeO} \Delta \overline{F}_{FeO} + (1 - C_{FeO}) \Delta \overline{F}_{MnO}, \tag{12}$$

with the relative error averaging 30%.

The partial molar entropy of mixing $\Delta \overline{S}_i$ of the components was found from the equation

$$\Delta \overline{S}_i = \frac{\Delta \overline{H}_i - \Delta \overline{F}_i}{T} = -\frac{\Delta \overline{F}_i}{T} = -R \ln a_i \quad (\text{for } \Delta \overline{H}_i = 0), \tag{13}$$

and the integral entropy of mixing ΔS_p (Table 1), analogously to (12),

$$\Delta S_{\text{p}} = \sum C_i \Delta \overline{S}_i. \tag{14}$$

Using the limiting values of the range of existence of ΔH_{p}, the interval of values of ΔS_{p} was calculated for various concentrations of the solid solution; in particular, at $C_{\text{FeO}} = 0.5$ and $t = 1000°$ it is $0.2 \div 0.8$ cal/deg • mol.

The excess integral entropy of mixing $\Delta S_{\text{p}}^{\text{ex}}$ of the solution components (Table 1) is the difference

$$\Delta S_{\text{p}}^{\text{ex}} = \Delta S_{\text{p}} - \Delta S_{\text{p}}^{\text{id}}, \tag{15}$$

where $\Delta S_{\text{p}}^{\text{id}}$ is the integral entropy of mixing of an ideal solution.

In accordance with the interval of values of ΔS_{p}, the quantity $\Delta S_{\text{p}}^{\text{ex}}$ at $C_{\text{FeO}} = 0.5$ and $t = 1000°$ lies within the limits $(-0.6) \div (-1.2)$ cal/mol • deg. The negative sign of the excess integral entropy of mixing gives grounds to suppose that in MnO–FeO solid solutions there is some ordering. Apparently, this is due to elements of short-range order or to submicroinhomogeneities with ions of one kind, which have been found in a number of oxides ([8],[9]).

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