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The Standard Free Energy of Formation of $YbFe_2O_4$, $Yb_2Fe_3O_7$, $YbFeO_3$, and $Yb_3Fe_5O_{12}$ at 1200°C

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The standard free energy of formation of $YbFe_2O_4$, $Yb_2Fe_3O_7$, $YbFeO_3$, and $Yb_3Fe_5O_{12}$ from metallic iron, Yb_2O_3, and oxygen was determined to be −100.38, −158.38, −58.17, and −283.40 kcal/mole, respectively, at 1200°C on the basis of the phase equilibria in the $Fe–Fe_2O_3–Yb_2O_3$ system. The $Fe–Fe_2O_3$–Lanthanoid sesquioxide systems were classified into four types with respect to the assemblage of the ternary compounds in stable existence at 1200°C, and the standard free energy of formation of $YbFeO_3$ was compared with those of the other lanthanoid-iron perovskites.

Introduction

Recently, Kimizuka and Katsura (*1*, *2*) and Sugihara et al. (*3*) determined the standard free energy of formation of $LaFeO_3$, $YFeO_3$, $Y_3Fe_5O_{12}$, YFe_2O_4, $EuFeO_3$, and $Eu_3Fe_5O_{12}$ from metallic iron, respective lanthanoid sesquioxide, and oxygen after establishing the phase equilibria in the $Fe–Fe_2O_3–La_2O_3$, $Fe–Fe_2O_3–Y_2O_3$, and $Fe–Fe_2O_3–Eu_2O_3$ systems at 1200°C. Katsura et al. (*4*) have also revealed the thermochemical properties of lanthanoid-iron-perovskite (La, Nd, Sm, Eu, Gd, Tb, and Dy) at high temperatures. Kimizuka et al. (*5*) have synthesized a series of new compounds of AFe_2O_4 (A = Ho, Er, Tm, Yb, and Lu) and $B_2Fe_3O_7$ (B = Yb and Lu) at fixed conditions of temperature and oxygen partial pressure. These new compounds have been found independently by Tannieres et al. (*6*) and Evrard et al. (*7*). On the basis of these studies, Kato et al. (*8*) have determined the crystal structure of AFe_2O_4 belonging to the trigonal crystal system in the space group $R\bar{3}m$.

In the present study, we have established the phase equilibria in the $Fe–Fe_2O_3–Yb_2O_3$ system at 1200°C, in which two nonstoichiometric compounds, $YbFe_2O_4$ and $Yb_2Fe_3O_7$, are stable. Based on the phase equilibria, the standard free energy of formation of $YbFe_2O_4$, $Yb_2Fe_3O_7$, $YbFeO_3$, and $Yb_3Fe_5O_{12}$ have been determined by the method of controlling oxygen partial pressure described by Kimizuka and Katsura (*2*).

Experimental

Yb_2O_3 (99.9% purity) and a guaranteed reagent grade Fe_2O_3 were employed for every

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starting material. The oxygen partial pressure was controlled by mixing CO_2 and H_2. Methods for preparing the samples, the apparatus adopted, the general procedures, and the method of identification of solid phases in equilibrated samples are the same as those described in the previous papers (*1–4*). Thus, the accuracy of the present data for the standard free energy values is the same as that of the previous studies.

Results and Discussion

(*1*) *Phase Equilibria*

Figure 1 shows the phase equilibria in the $Fe–Fe_2O_3–Yb_2O_3$ system at 1200°C under varying oxygen partial pressures from 1–$10^{-15.80}$ atm. The following phases were stable under the present conditons; ytterbium sesquioxide (Yb_2O_3), hematite (Fe_2O_3), magnetite (Fe_3O_4), ytterbium–iron–perovskite ($YbFeO_3$), ytterbium–iron–garnet ($Yb_3Fe_5O_{12}$), $YbFe_2O_4$, $Yb_2Fe_3O_7$, and wustite (FeO).

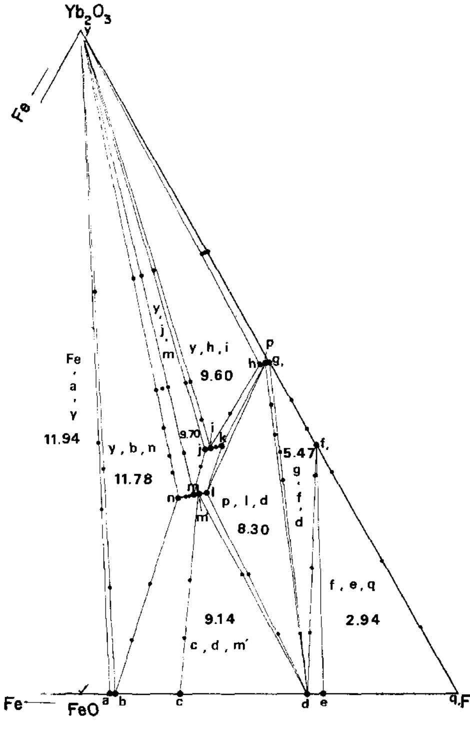

FIG. 1. The phase diagram of the $Fe–Fe_2O_3–Yb_2O_3$ at 1200°C. Numbers in three solid phases mean the values of $-\log P_{O_2}$. The composition at each letter is: (a) $Fe_{0.953}O$, (b) $Fe_{0.947}O$, (c) $Fe_{0.858}O$, (d) $Fe_{3.000}O_4$, (e) $Fe_{2.957}O_4$, (f) $Yb_3Fe_5O_{7.000}$, (g) $YbFeO_{3.000}$, (h) $YbFeO_{2.973}$, (i) $Yb_2Fe_3O_{6.885}$, (j) $Yb_2Fe_3O_{6.884}$, (k) $Yb_2Fe_3O_{7.000}$, (l) $YbFe_2O_{4.052}$, (m) $YbFe_2O_{4.002}$, (n) $YbFe_2O_{3.929}$, (p) $YbFeO_{2.989}$. Solid circles show the experimental results.

Ytterbium sesquioxide was stable in the oxygen partial pressures ranging from 1–$10^{-15.80}$ atm. This oxide showed a very slight deficiency, but we could not determine its maximum value. Yb_2O_3 was more volatile than La_2O_3 and Y_2O_3, and we corrected the weight change as it resulted from the volatility of Yb_2O_3. YbO could not be observed in the present range of oxygen partial pressure.

The deviation from the stoichiometric composition of ytterbium–iron–perovskite was observed based on the weight change, and we determined its composition range to be from $YbFeO_{2.973}$ to $YbFeO_{3.000}$. The lattice constants as an orthorhombic crystal system are given in Table I. As seen in Table I, no significant effects due to the nonstoichiometry were observed on lattice constants; this is the same result as that obtained in $EuFeO_3$.

It was hard to find the existence of the nonstoichiometry in the ytterbium–iron–garnet phase. The lattice constants of $Yb_3Fe_5O_{12}$ prepared under various conditions are also summarized in Table I.

$YbFe_2O_4$ and $Yb_2Fe_3O_7$ were stable with variable compositions. As seen in Figs. 1 and 2, the compositional variation in $YbFe_2O_4$ ranged from $YbFe_2O_{3.929}$ to $YbFe_2O_{4.052}$, and that of $Yb_2Fe_3O_7$ from $Yb_2Fe_3O_{6.884}$ to $Yb_2Fe_3O_{7.000}$. Both phases are black and not attacted by a hand magnet at room temperature. The crystal structure of $YbFe_2O_4$ has been analyzed by Kato et al. (*8*), and an analysis of that of $Yb_2Fe_3O_7$ is still in progress.

The compositional variation of the wustite phase ranged from $Fe_{0.858}O$ to $Fe_{0.953}O$; this is substantially identical to that obtained by Darken and Gurry (*9*). The composition of magnetite in equilibrium with hematite was taken to be the value cited by Smiltens (*10*). In the present study, we concluded on the basis of the X-ray powder method that the

TABLE I

CRYSTALLOGRAPHIC DATA OF $YbFeO_3$, $Yb_3Fe_5O_{12}$, $YbFe_2O_4$, AND $Yb_2Fe_3O_7$

Compound	$-\log P_{O_2}$	a(Å)	b(Å)	c(Å)	V(Å^3)
$YbFeO_3$	0.68[a]	5.232 ± 0.001	5.560 ± 0.001	7.569 ± 0.001	220.1 ± 0.1
	0.68[b]	5.230 ± 0.001	5.559 ± 0.001	7.569 ± 0.001	220.1 ± 0.1
	0.68	5.231 ± 0.001	5.562 ± 0.001	7.569 ± 0.001	220.2 ± 0.1
	9.55	5.230 ± 0.001	5.564 ± 0.001	7.569 ± 0.001	220.2 ± 0.1
$Yb_3Fe_5O_{12}$	0.68[c]	12.300 ± 0.001			1860.6 ± 0.1
	0.68[d]	12.300 ± 0.001			1860.9 ± 0.1
	0.68	12.300 ± 0.001			1861.2 ± 0.1
$YbFe_2O_4$	9.55	5.993 ± 0.002		25.128 ± 0.003	781.7 ± 0.1
	10.65	5.985 ± 0.001		25.109 ± 0.002	779.0 ± 0.1
$Yb_2Fe_3O_7$	9.20	3.473 ± 0.001		28.351 ± 0.001	296.2 ± 0.1
	9.70	3.472 ± 0.001		28.730 ± 0.001	295.8 ± 0.1

[a] Equilibrated with Yb_2O_3.
[b] Equilibrated with $Yb_3Fe_5O_{12}$.
[c] Equilibrated with Fe_2O_3.
[d] Equilibrated with $YbFeO_3$.

wustite and magnetite phases may contain no significant amount of Yb_2O_3. This may also be supported by the conjugation lines represented by oxygen isobars in Fig. 1.

Figures 2(a), 2(b), 2(c), and 2(d) show the relationship between the weight loss of starting materials and the equilibrium oxygen partial pressures to determine the boundary of each phase assembly. The essential features, except for the existence of the $Yb_2Fe_3O_7$ phase, are similar to those of the Fe–Fe_2O_3–Y_2O_3 system obtained in the previous study (*2*).

(*2*) *Calculation of the Standard Free Energy of Formation of $YbFe_2O_4$, $Yb_2Fe_3O_7$, $YbFeO_3$, and $Yb_3Fe_5O_{12}$*

On the basis of the present phase equilibria in the Fe–Fe_2O_3–Yb_2O_3 system, we will determine the standard free energy of formation of $YbFe_2O_4$, $Yb_2Fe_3O_7$, $YbFeO_3$, and $Yb_3Fe_5O_{12}$ from metallic iron, Yb_2O_3, and oxygen referred to the following equations,

$$2Fe + \tfrac{1}{2}Yb_2O_3 + \tfrac{5}{4}O_2 = YbFe_2O_4 \quad (1)$$

$$3Fe + Yb_2O_3 + 2O_2 = Yb_2Fe_3O_7 \quad (2)$$

$$Fe + \tfrac{1}{2}Yb_2O_3 + \tfrac{3}{4}O_2 = YbFeO_3 \quad (3)$$

$$5Fe + \tfrac{3}{2}Yb_2O_3 + \tfrac{15}{4}O_2 = Yb_3Fe_5O_{12}. \quad (4)$$

Before proceeding to calculations of the standard free energy, we will summarize the activity-composition relations found in the four nonstoichiometric compounds in the present Fe–Fe_2O_3–Yb_2O_3 system, FeO, $YbFe_2O_4$, $Yb_2Fe_3O_7$, and $YbFeO_3$. The present method for determining the activity is based on the Gibbs–Duhem equation. Thus, the activity of each component changes when each oxygen molecule is mixed in each stoichiometric composition. For example, the activity of $Yb_2Fe_3O_7$ ($a_{Yb_2Fe_3O_7}$) in the $Yb_2Fe_3O_7$ solid solution is expressed by the following equation,

$$\log a_{Yb_2Fe_3O_7} = -1/2 \int_{\log P_{O_2}(1)}^{\log P_{O_2}(2)} (N_o/N_{Yb_2Fe_3O_7})\, d\log P_{O_2}$$

where $\log P_{O_2}(1)$ means the value of oxygen partial pressure at which the activity of $Yb_2Fe_3O_7$ is set equal to one at a specified composition, and $N_o/N_{Yb_2Fe_3O_7}$ gives the deviation of oxygen atoms from the stoichiometric composition, because the present four compounds changed their compositions only in the reaction with oxygen. In addition, it was found in the present experiments that the values of N_o/N_{FeO}, $N_o/N_{YbFe_2O_4}$, $N_o/N_{Yb_2Fe_3O_7}$,

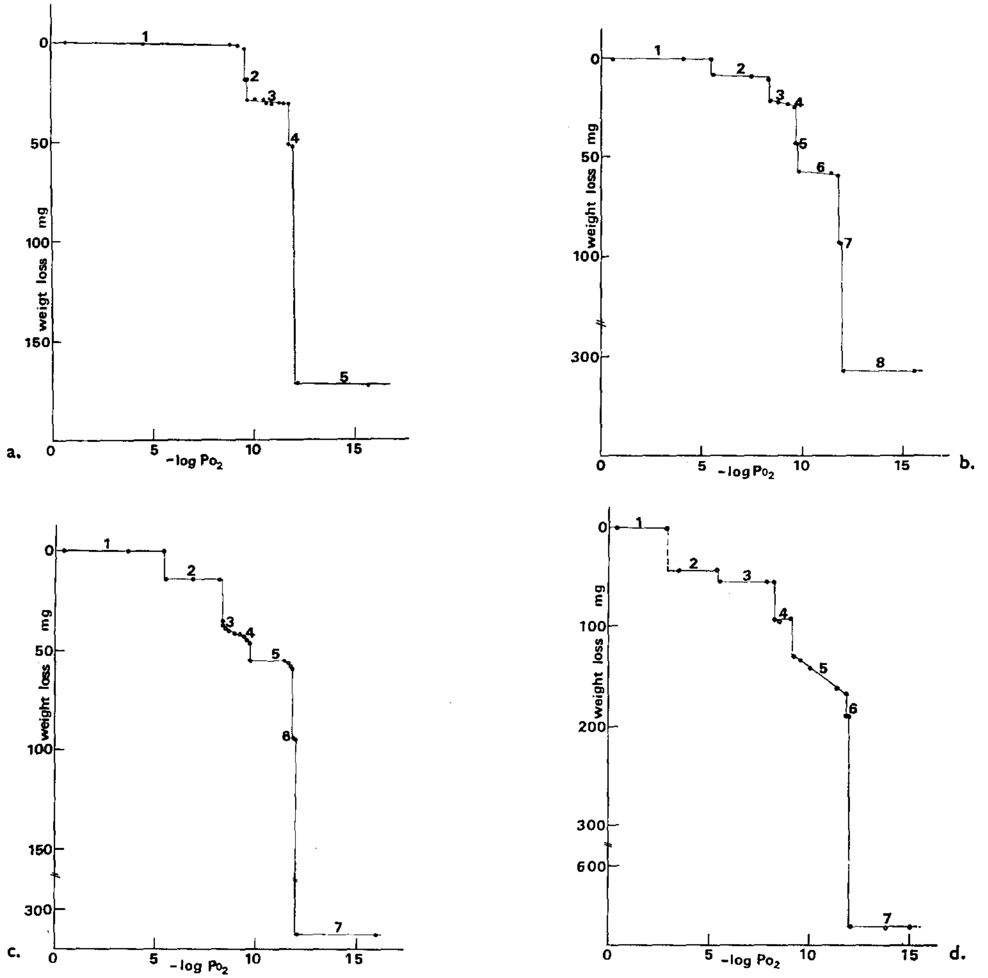

FIG. 2. Relationship between weight loss and –log Po_2 for various compositions in starting materials. (a) $Yb_2O_3/Fe_2O_3 = 2$, starting weight, 3.3778 g. Numbers in figure mean the assembly of co-existing phases. 1$Yb_2O_3 + YbFeO_3$, 2$Yb_2O_3 + Y_2Fe_3O_7$, 3$Yb_2O_3 + YbFe_2O_4$, 4$Yb_2O_3 + FeO$, 5$Yb_2O_3 + Fe$. (b) $Yb_2/Fe_2O_3 = \frac{4}{5}$, 3.0242 g; 1 $YbFeO_3 + Yb_3Fe_5O_{12}$, 2 $YbFeO_3 + Fe_3O_4$, 3 $YbFeO_3 + YbFe_2O_4$, 4$YbFeO_3 + Yb_2Fe_3O_{12}$, 5 $Yb_2O_3 + Yb_2Fe_3O_7$, 6 $Yb_2O_3 + YbFe_2O_4$, 7 $Yb_2O_3 + FeO$, 8 $Yb_2O_3 + Fe$. (c) $Yb_2O_3/Fe_2O_3 = 3/5$, 2.5750 g; 1 $Yb_3Fe_5O_{12}$, 2 $YbFeO_3 + Fe_3O_4$, 3 $YbFeO_3 + YbFe_2O_4$, 4 $Yb_2Fe_3O_7 + YbFe_2O_4$, 5 $Yb_2O_3 + YbFe_2O_4$ 6 $Yb_2O_3 + FeO$, 7 $Yb_2O_3 + Fe$. (d) $Yb_2O_3/Fe_2O_3 = \frac{1}{4}$, 3.5585 g; 1 $Fe_2O_3 + Yb_3Fe_5O_{12}$, 2 $Fe_3O_4 + Yb_3Fe_5O_{12}$, 3 $Fe_3O_4 + YbFeO_3$, 4 $Fe_3O_4 + YbFe_2O_4$, 5 $FeO + YbFe_2O_4$, 6 $FeO + Yb_2O_3$, 7 $Yb_2O_3 + Fe$.

and N_o/N_{YbFeO_3} in the respective compounds were substantially proportional to related oxygen partial pressures in terms of log Po_2 within the experimental errors, and thus, it is convenient to express respective activity as a simple function of logPo_2 as

$$\log a_i = -1/2 \int_{\log Po_2(1)}^{\log Po_2(2)} (A + B \log Po_2)\, d \log Po_2 \qquad (5)$$

where a_i is the activity of the i component, and A and B are constants for each solid solution. The values of log$Po_2(1)$, A, and B determined in the present study are given in Table II. The present values of loga_{FeO} at 1200°C calculated by Eq. (5) were identical to those obtained by Darken and Gurry (*9*) to three significant digits. The free energy data necessary for converting the CO/CO_2 ratios obtained by them to logPo_2 were cited

TABLE II

NUMERICAL VALUES FOR CALCULATING ACTIVITIES IN FOUR SOLID SOLUTIONS IN THE $Fe–Fe_2O_3–Yb_2O_3$ SYSTEM

	$\log P_{O_2}(1)$	Limit of $\log P_{O_2}(2)$	*A*	*B*	Composition range
FeO	−11.94	−9.14	0.5388[a]	0.0410[a]	$FeO_{1.0495}$ to $FeO_{1.166}$
$YbFe_2O_4$	−11.78	−8.30	0.3437[a]	0.0352[a]	$YbFe_2O_{3.929}$ to $YbFe_2O_{4.052}$
$Yb_2Fe_3O_7$	−9.70	−8.2[b]	0.0190	0.0100	$Yb_2Fe_3O_{6.884}$ to $Yb_2Fe_3O_{7.000}$
$YbFeO_3$	−9.60	−7.40[c]	0.0911	0.0123	$YbFeO_{2.973}$ to $YbFeO_{3.000}$

[a] These values were calculated by the least squares method.

[b] An exact limit of $\log P_{O_2}$ could not be determined.

[c] Nearly stoichiometric composition was maintained at $\log P_{O_2}$ ranging from −7.40 to 0.00.

from the JANAF-Thermochemical Tables (*11*).

Based on the present experiments, we determined the standard free energy of formation of FeO, $\Delta G°(6)$, at 1200°C referred to Eq. (6) to be −40 240 cal/mole of FeO:

$$Fe + \tfrac{1}{2}O_2 = FeO. \qquad (6)$$

The Standard Free Energy of Formation of $YbFe_2O_4$

Based on the present phase equilibria, we may calculate the standard free energy change using

$$\tfrac{1}{2}Yb_2O_3 + 2FeO + \tfrac{1}{4}O_2 = YbFe_2O_4. \qquad (7)$$

The equilibrated $\log P_{O_2}$value connected with Eq. (7) was −11.78, and thus, the $\log a_{FeO}$ is calculated to be −0.0042 by adopting Eq. (5). Here, the activity of $YbFe_2O_4$ is set equal to one where the composition of $YbFe_2O_4$ was $YbFe_2O_{3.929}$. Since the activity of Yb_2O_3 is one, we may calculate the standard free energy change, $\Delta G°(7)$, referred to Eq. (7) to be −19 900 cal/mole of $YbFe_2O_4$. Adding $2\Delta G°(6)$ and $\Delta G°(7)$, we obtain the standard free energy of formation of $YbFe_2O_4$, $\Delta G°(1)$, referred to Eq. (1) to be −100 380 cal/mole of $YbFe_2O_4$.

The Standard Free Energy of Formation of $Yb_2Fe_3O_7$

Based on the phase equilibria, we may calculate the standard free energy change as

$$\tfrac{3}{2}YbFe_2O_4 + \tfrac{1}{4}Yb_2O_3 + \tfrac{1}{8}O_2 = Yb_2Fe_3O_7. \qquad (8)$$

The value of $\log P_{O_2}$ in Eq. (8) was −9.70, and the activity of $YbFe_2O_4$ in Eq. (8) is calculated as +0.0358. The activity of $Yb_2Fe_3O_7$ in Eq. (8) is set equal to one. Thus, the standard free energy for Eq. (8), $\Delta G°(8)$, is −7810 cal/mole of $Yb_2Fe_3O_7$. Adding $\tfrac{3}{2}\Delta G°(1)$ and $\Delta G°(8)$, we obtain the standard free energy of formation of $Yb_2Fe_3O_7$, $\Delta G°(2)$, referred to Eq. (2), as −158 380 cal/mole of $Yb_2Fe_3O_7$.

The Standard Free Energy of Formation of $YbFeO_3$

From the phase equilibria, we may calculate the standard free energy change using

$$\tfrac{1}{6}Yb_2O_3 + \tfrac{1}{3}Yb_2Fe_3O_7 + \tfrac{1}{12}O_2 = YbFeO_3. \qquad (9)$$

The value of $\log P_{O_2}$ related to Eq. (9) was −9.60, and the activity of $YbFeO_3$ is set equal to one at this oxygen partial pressure. The activity of $Yb_2Fe_3O_7$ referred to Eq. (9) is calculated as 0.0039 on the basis of Eq. (5). Thus, the standard free energy change of Eq. (9), $\Delta G°(9)$, is calculated to be −5380 cal/mole of $YbFeO_3$. Adding $\tfrac{1}{3}\Delta G°(2)$ and $\Delta G°(9)$, we obtain the standard free energy of formation of $YbFeO_3$, $\Delta G°(3)$, referred to Eq. (3) to be −58170 cal/mole of $YbFeO_3$.

It is worthwhile to compare the present value of $\Delta G°(3)$ with that calculated by a different process. Consider the following

TABLE III

SUMMARY OF THE STANDARD FREE ENERGY VALUES

Reaction	ΔG°(kcal)/mole
(1) $2\,Fe + \frac{1}{2}\,Yb_2O_3 + \frac{5}{4}\,O_2 = YbFe_2O_4$	−100.38
(2) $3\,Fe + Yb_2O_3 + 2\,O_2 = Yb_2Fe_3O_7$	−158.38
(3) $Fe + \frac{1}{2}\,Yb_2O_3 + \frac{3}{4}\,O_2 = YbFeO_3$	−58.17
(4) $5\,Fe + \frac{3}{2}\,Yb_2O_3 + 15/4\,O_2 = Yb_3Fe_5O_{12}$	−283.40
(6) $Fe + \frac{1}{2}\,O_2 = FeO$	−40.24
(7) $\frac{1}{2}\,Yb_2O_3 + 2\,FeO + \frac{1}{4}\,O_2 = YbFe_2O_4$	−19.90
(8) $\frac{3}{2}\,YbFe_2O_4 + \frac{1}{4}\,Yb_2O_3 + \frac{1}{8}\,O_2 = Yb_2Fe_3O_7$	−7.81
(9) $\frac{1}{6}\,Yb_2O_3 + \frac{1}{3}\,Yb_2Fe_3O_7 + \frac{1}{12}\,O_2 = YbFeO_3$	−5.38
(10) $YbFe_2O_4 + \frac{1}{6}\,O_2 = YbFeO_3 + \frac{1}{3}\,Fe_3O_4$	−9.29
(11) $3\,Fe + 2\,O_2 = Fe_3O_4$	−154.50
(12) $3\,YbFeO_3 + \frac{2}{3}\,Fe_3O_4 + \frac{1}{6}\,O_2 = Yb_3Fe_5O_{12}$	−5.90

equilibrium based on the present phase equilibria,

$$YbFe_2O_4 + \tfrac{1}{6}O_2 = YbFeO_3 + \tfrac{1}{3}Fe_3O_4. \quad (10)$$

The values of $\log a_{Fe_3O_4}$ and $\log Po_2$ related to Eq. (10) are 0 and −8.30, respectively, and the other activity values are calculated by Eq. (5) as: $\log a_{YbFe_2O_4} = +0.0169$, $\log a_{YbFeO_3} = +0.0124$. Thus, we may calculate the standard free energy change, ΔG°(10), referred to Eq. (10), as −9290 cal/mole of $YbFeO_3$. The standard free energy of formation of Fe_3O_4,ΔG° (11), referred to

$$3Fe + 2O_2 = Fe_3O_4, \quad (11)$$

is calculated as −154 500 cal/mole of Fe_3O_4 on the basis of the present study by adopting Eqs. (5) and (6). This value at 1200°C is identical with that calculated by Darken and Gurry (*9*). Adding ΔG°(10), $-\frac{1}{3}\Delta G$°(11), and ΔG°(1), we obtain the standard free energy of formation of $YbFeO_3$, ΔG°(3′), referred to Eq. (3), as −58 170 cal/mole of $YbFeO_3$, which is identical to the ΔG°(3) value obtained before.

The Standard Free Energy of Formation of $Yb_3Fe_5O_{12}$

Based on the phase equilibria, we may calculate the standard free energy change ΔG°(12) referred to

$$3YbFeO_3 + \tfrac{2}{3}Fe_3O_4 + \tfrac{1}{6}O_2 = Yb_3Fe_5O_{12}. \quad (12)$$

The following activity data referred to Eq. (12) are obtained: $a_{Fe_3O_4} = 1$, $a_{Yb_3Fe_5O_{12}} = 1$, $\log a_{YbFeO_3} = +0.0124$, and $\log Po_2 = -5.47$. Thus, the standard free energy change ΔG°(12) is calculated to be −5900 cal/mole of $Yb_3Fe_5O_{12}$. Adding $\frac{2}{3}\Delta G$°(11), ΔG°(12), and ΔG°(3) we obtain the standard free energy of formation of $Yb_3Fe_5O_{12}$, ΔG°(4), referred to Eq. (4) to be −283 400 cal/mole of $Yb_3Fe_5O_{12}$. Table III summarizes the standard free energy data obtained for Eq. (1) to Eq. (12).

Other Remarks

In concluding the present study, we will point out the two remarkable trends found in the $Fe–Fe_2O_3–Ln_2O_3$ systems (*Ln* = La, Nd,

TABLE IV

THE CLASSIFICATION OF THE $Fe–Fe_2O_3–Ln_2O_3$ SYSTEM

Type	Stable ternary compounds	Lanthanoid sesquioxide
A	$LnFeO_3$	La_2O_3, Nd_2O_3
B	$LnFeO_3$ and $Ln_3Fe_5O_{12}$	Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, and Dy_2O_3
C	$LnFeO_3$, $Ln_3Fe_5O_{12}$, and $LnFe_2O_4$	Ho_2O_3, Er_2O_3, Tm_2O_3, and (Y_2O_3)
D	$LnFeO_3$, $Ln_3Fe_5O_{12}$, $LnFe_2O_4$, and $Ln_2Fe_3O_7$	Yb_2O_3 and Lu_2O_3

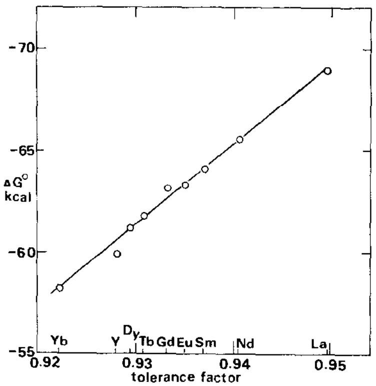

FIG. 3. Relationship between the standard free energy of formation and the tolerance factor.

Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y). The first remark is deduced by our previous studies together with some unpublished data.

The Fe–Fe_2O_3–Ln_2O_3 systems (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) can be classified into four kinds of representatives with respect to the assemblage of the ternary compounds in stable existence at 1200°C. The proposed classification is given in Table IV. It may be clearly pointed out in Table IV that the trivalent ionic radius of rare earth elements plays an essential role in the phase relation in these ternary systems at 1200°C at one total pressure.

The second remark is related to the standard free energy of formation of lanthanoid–iron–perovskite from metallic iron, Ln_2O_3 and oxygen. In the previous study, we determined the standard free energy of formation of $YFeO_3$ to be −59 800 cal/mole and now, we have obtained the standard free energy of formation of $YbFeO_3$. Katsura et al. (*4*) have revealed that the standard free energy of formation of lanthanoid–iron–perovskite (La, Nd, Sm, Eu, Gd, Tb, and Dy) is proportional to the tolerance factor defined by Goldschmidt (*12*). This experimental relation is also applied to $YFeO_3$ and $YbFeO_3$, as illustrated in Fig. 3. As seen in Fig. 3, the proportionality is excellent in the lanthanoid–iron–perovskite series, though we could distinguish the Gd-anomaly. However, in case of $YFeO_3$, we can recognize some significant deviation from the normal proportionality found in lanthanoid series.

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