

Phase Equilibrium in the Er-Fe-O System at 1100°C

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Phase equilibrium was established in the Er-Fe-O system at 1100°C by altering the oxygen partial pressure from $-\log(P_{O_2}/\text{atm}) = 15.00$ to 0, allowing construction of a phase diagram at 1100°C for the system $\text{Er}_2\text{O}_3\text{-Fe-Fe}_2\text{O}_3$. In the system, two ternary compounds, ErFeO_3 and $\text{Er}_3\text{Fe}_5\text{O}_{12}$, were deemed stable and had nonstoichiometric composition, whereas ErFe_2O_4 was not found to be stable. The present result was different from that of previous studies at 1200 °C, in which ErFe_2O_4 was stable along with the above two ternary compounds.

Lattice constants of ErFeO_3 and $\text{Er}_3\text{Fe}_5\text{O}_{12}$, prepared in air by a quenching method, were determined and compared with previous values, and showed slight differences.

The Gibbs energy changes of the reactions in the Fe-O system, $\text{Fe} + 1/2 \text{O}_2 = \text{FeO}$, $3 \text{FeO} + 1/2 \text{O}_2 = \text{Fe}_3\text{O}_4$, and $2/3 \text{Fe}_3\text{O}_4 + 1/6 \text{O}_2 = \text{Fe}_2\text{O}_3$, were determined, and the obtained values were compared with the previous values. The Gibbs energy changes of the reactions, $\text{Fe} + 1/2 \text{Er}_2\text{O}_3 + 3/4 \text{O}_2 = \text{ErFeO}_3$, and $3 \text{ErFeO}_3 + 2/3 \text{Fe}_3\text{O}_4 + 1/6 \text{O}_2 = \text{Er}_3\text{Fe}_5\text{O}_{12}$, were calculated from the oxygen partial pressures in equilibrium.

Key words: Phase equilibrium, Thermogravimetry, Erbium-iron oxide, Gibbs energy.

1. INTRODUCTION

Phase relations in the Fe-O system have been reported on the standpoint of Steelmaking (1,2,3). The Fe-O system includes three oxides, "FeO" (wustite), Fe_3O_4 (magnetite), and Fe_2O_3 (hematite). "FeO" has a cubic structure and forms a metal defect solid solution, considering the solid solution with iron and oxygen of two-components system. It is known that Fe_3O_4 has an inverse spinel structure and a low solid solution range in its oxygen-rich state from ~900°C, and the solid solution range changes with the temperature. Fe_2O_3 has a stoichiometric composition and a rhombohedral crystal system. In the Fe-O it was noted that the oxygen pressures of the gas phase in equilibrium with condensed phases vary over a very wide range as

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temperatures fluctuate between 0 and 1600°C.

The oxygen partial pressure in equilibrium with Fe and FeO, with FeO and Fe₃O₄, and with Fe₃O₄ and Fe₂O₃ were obtained from JANAF data (4) to be 13.33, 11.75, and 3.74 in $-\log(P_{O_2}/\text{atm})$ at 1100°C, respectively.

The phase equilibrium in the Er-Fe-O system at 1200°C has been reported and ErFeO₃, ErFe₂O₄, and Er₃Fe₅O₁₂ are stable as ternary compounds (5). As for LnFe₂O₄ (Ln = lanthanoids), the phase equilibria in the Fe-Fe₂O₃-Y₂O₃ system have been established at 1200°C and a new phase, YFe₂O₄, has been found by Kimizuka and Katsura (6), and Piekarczyk et al.(7) have also reported the YFe₂O₄ phase to be stable above 1010°C. According to Kato et al.(8), the crystal structure of this compound is a new type for AB₂X₄, where A and B are cations and X is an anion, and belongs to the trigonal system with the space group R3m. The structure consists of alternate layers of Ln₂O₃ and Fe₄O₅, and thus the anisotropies both in magnetic exchange interaction and electrical conductivity are expected.

The crystal structure and magnetic properties of ErFe₂O₄, together with YFe₂O₄, have also been studied by Matsumoto et al. (9), and the pressure dependence of the magnetic phase transitions of YFe₂O₄ was found to be different in both oxides, even though their structures were similar.

The objectives of the present study are to: (1) establish a detailed phase diagram of Er-Fe-O system at 1100°C as a function of oxygen partial pressure; (2) ascertain whether or not the phase diagram at 1100°C is different from that at 1200°C; (3) determine thermochemical properties based on the phase diagram at 1100°C.

2. EXPERIMENTAL

Analytical grade Er₂O₃ (99.9%) and Fe₂O₃ (99.9%) were used as starting materials.

Both of the oxides were calcined at 1100°C. Mixtures having desired mole ratios of Er₂O₃/Fe₂O₃ were prepared by mixing thoroughly in an agate mortar and by performing repeated calcination during the intermediate mixing. This was followed by the same procedures described previously (10). The thermogravimetric method was used in the present experiment; oxygen partial pressure was varied passing a gas or mixed gases through the furnace.

The desired oxygen partial pressures were obtained by use of mixed gases of CO₂

with H₂ and of CO₂ with O₂, and single-component gases of O₂ and CO₂. The actual oxygen partial pressures of the gas phase was measured by means of a solid electrolytic cell composed of (ZrO₂)_{0.85}(CaO)_{0.15}.(11) The apparatus and procedures for controlling the oxygen partial pressure and maintaining a constant temperature, the method of thermogravimetry, and the criterion for the establishment of equilibrium were the same as described in the previous paper (10). The method of establishing equilibrium can be briefly described as follows. To ensure equilibrium, the equilibrium weight of each sample at a particular oxygen partial pressure was determined from both sides of the reaction; that is, as the oxygen partial pressure increased from a low value and as it decreased from a high value. The balance, furnace, and gas mixer were schematically shown in Kitayama (12). The furnace was installed vertically, and a mullite tube wound with Pt 60%-Rh 40% alloy wire served as its heating element. Mixed gases, which ensure the desired oxygen partial pressures, passed from the bottom of the furnace to the top.

The identification of phases and the determination of lattice constants were performed by use of a Rint 2500 Rigaku X-ray diffractometer, employing Ni-filtered CuK α radiation. Instrumental errors were calibrated by measuring the diffraction angles of a standard specimen of silicon.

3. RESULTS AND DISCUSSIONS

3-1. Phase Equilibrium

3-1-1. Fe-O system.

As described above, the Fe-O system contains three oxides, FeO, Fe₃O₄, and Fe₂O₃. In the present experiment, the Fe-O system was reinvestigated by use of the present apparatus and techniques. The results have been reported in the previous report(13). These results can be summarized as follows. Fig. 1 shows the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$, versus the O/Fe mol ratio of the Fe-O system. As is evident from Fig. 1, weight breaks are found at 13.25, 10.86, and 3.20 in $-\log(P_{O_2}/\text{atm})$. These values correspond to the equilibrium oxygen partial pressure of the three reactions, 1) $\text{Fe} + 1/2 \text{O}_2 = \text{FeO}$, 2) $3 \text{FeO} + 1/2 \text{O}_2 = \text{Fe}_3\text{O}_4$, and 3) $2/3 \text{Fe}_3\text{O}_4 + 1/6 \text{O}_2 = \text{Fe}_2\text{O}_3$.

As is well known, the phase FeO has nonstoichiometric composition. As is shown in Fig. 1, the so-called wustite, "FeO", solid solution is stable from $-\log$

$(P_{O_2}/\text{atm}) = 13.25$ to 10.86 (from A to B in Fig. 1), and the $-\log(P_{O_2}/\text{atm})$ vs the O/Fe mole ratio of the FeO solid solution in the range of A and B is represented by a linear equation: $N_{O}/N_{Fe} = 4.077 \times 10^{-2} \log P_{O_2} + 1.577$. Here, N_{O} and N_{Fe} represent the

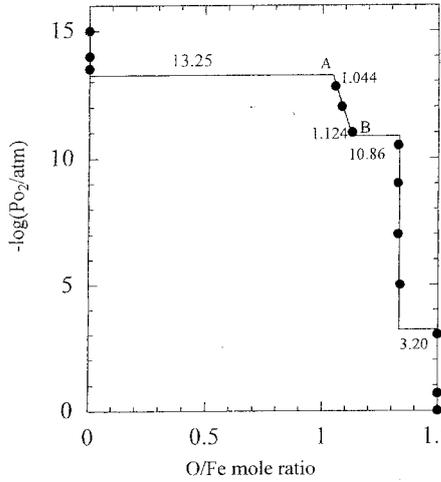


Fig. 1. Relationship between the oxygen partial pressure, $\log(P_{O_2}/\text{atm})$, and the O/Fe molar ratio in the Fe-O system.

mole fraction of oxygen and Fe in the FeO solid solution. This equation will be used to obtain the activity of Fe and FeO components in the solid solution by the Gibbs-Duerm equation and can be solved to show that the FeO phase would have an O/Fe mole ratio = 1.044 (A in Fig. 1) at -13.25 and an O/Fe mole ratio = 1.124 (B in Fig. 1) at -10.86 in $\log(P_{O_2}/\text{atm})$. As is shown in Fig. 1, the stoichiometric FeO is not stable, and at the end composition of wustite, the O/Fe mole ratio of 1.044 is in equilibrium with Fe metal at $\log P_{O_2} = -13.25$ and the O/Fe mole ratio of 1.124 is in equilibrium with Fe_3O_4 at $\log(P_{O_2}/\text{atm}) = -10.86$.

In Fe_3O_4 , a slight weight increase has been observed from $\log(P_{O_2}/\text{atm}) = -10.86$ to 3.20 as is well known, although it is not evident in Fig. 1, because of the scale of abscissa and the small changes in the composition.

3-1-2 Er_2O_3 -Fe- Fe_2O_3 system.

Five samples having Er_2O_3/Fe_2O_3 mole ratios of 0.6/0.4, 0.45/0.55, 0.4/0.6, 0.3/0.7, and 0.2/0.8 were prepared for thermogravimetry. Fig. 2 shows the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$, versus the weight changes, W_{O_2}/W_T , for four representative

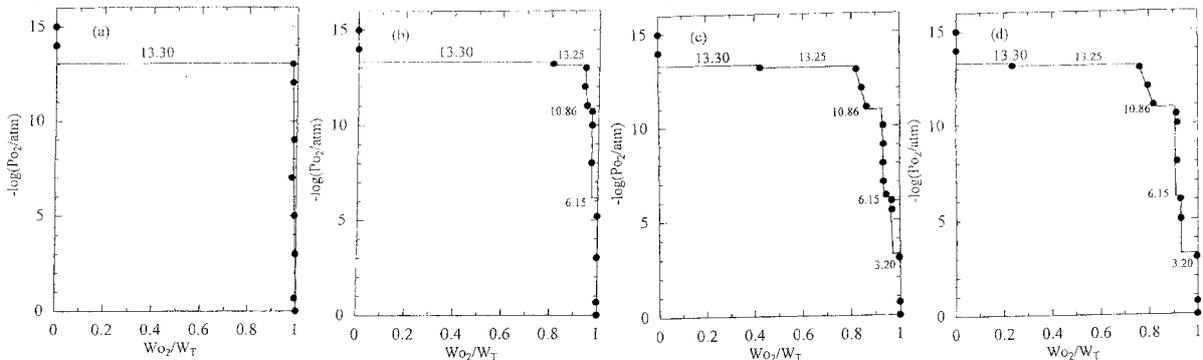


Fig. 2. Relationship between the oxygen partial pressure, $\log(P_{O_2}/\text{atm})$, and the weight change of the samples, W_{O_2}/W_T . (a) $Er_2O_3/Fe_2O_3 = 0.6/0.4$, (b) $Er_2O_3/Fe_2O_3 = 0.45/0.55$, (c) $Er_2O_3/Fe_2O_3 = 0.4/0.6$, and (d) $Er_2O_3/Fe_2O_3 = 0.3/0.8$.

samples: $\text{Er}_2\text{O}_3/\text{Fe}_2\text{O}_3 = 0.6/0.4$ (Fig. 2a), $0.45/0.55$ (Fig. 2b), $0.3/0.7$ (Fig. 2c), and $0.2/0.8$ (Fig. 2d). Here, also, W_{O_2} represents the weight increase of a sample from the reference weight at $\log(\text{Po}_2/\text{atm}) = -15.00$, at which Er_2O_3 and Fe are stable, and W_T is the total weight-gained from the reference state to the state at 1 atm O_2 . At this point Er_2O_3 and ErFeO_3 , ErFeO_3 and $\text{Er}_3\text{Fe}_5\text{O}_{12}$, $\text{Er}_3\text{Fe}_5\text{O}_{12}$ and Fe_2O_3 were stable depending upon the total compositions of samples, as is shown in Fig. 3. These phases were identified by a powder X-ray analysis. As is evident from Fig. 2, weight breaks were found at 13.30, 13.25, 10.86, 6.15, and 3.20 in $-\log(\text{Po}_2/\text{atm})$. These values correspond to the oxygen partial pressure in equilibrium with the three solid phases, $\text{Er}_2\text{O}_3 + \text{ErFeO}_3$ (P_1) + Fe, ErFeO_3 (P_2) + FeO (W_1) + Fe, ErFeO_3 (P_3) + FeO (W_2) + Fe_3O_4 (M_1), ErFeO_3 (P_4) + Fe_3O_4 (M_2) + $\text{Er}_3\text{Fe}_5\text{O}_{12}$ (G_1), and $\text{Er}_3\text{Fe}_5\text{O}_{12}$ (G_2) + Fe_3O_4 (M_3) + Fe_2O_3 , respectively.

Table 1 shows the identified phases in the Er-Fe-O system, along with the experi-

Er_2O_3	Fe_2O_3	$-\log \text{Po}_2$	Time	Phases
Mol ratio		atm	hr	
0.2	0.8	14.00	7	Fe + Er_2O_3
		13.25	25	Fe + ErFeO_3
		13.00	7	FeO + ErFeO_3
		11.00	16	FeO + ErFeO_3
		10.00	22	Fe_3O_4 + ErFeO_3
		9.00	22	Fe_3O_4 + ErFeO_3
		5.50	23	Fe_3O_4 + $\text{Er}_3\text{Fe}_5\text{O}_{12}$
		0.68	64	Fe_2O_3 + $\text{Er}_3\text{Fe}_5\text{O}_{12}$
0.3	0.7	14.00	7	Fe + Er_2O_3
		13.25	25	Fe + ErFeO_3
		13.00	7	FeO + ErFeO_3
		11.00	16	FeO + ErFeO_3
		10.00	22	Fe_3O_4 + ErFeO_3
		6.00	19	Fe_3O_4 + ErFeO_3
		0.68	64	Fe_2O_3 + $\text{Er}_3\text{Fe}_5\text{O}_{12}$
0.4	0.6	5.50	23	ErFeO_3 + $\text{Er}_3\text{Fe}_5\text{O}_{12}$
0.6	0.4	14.00	7	Fe + Er_2O_3
		13.25	25	ErFeO_3 + Er_2O_3
		10.00	22	ErFeO_3 + Er_2O_3
		0.68	64	ErFeO_3 + Er_2O_3

mental conditions. Samples of about 500mg were prepared for the identification of phases by means of the quenching method. Seven phases, Er_2O_3 , Fe, FeO, Fe_3O_4 , Fe_2O_3 , $\text{Er}_3\text{Fe}_5\text{O}_{12}$, and ErFeO_3 were evaluated by the powdered X-ray analysis. The mixed hydroxide $3 \text{Er}(\text{OH})_3 + 5 \text{Fe}(\text{OH})_3$ was thermally treated upto 1300°C by Ristic' et al.(14). The samples obtained up to 650°C were found to be amorphous, as observed by X-ray diffraction, and the first appearance of $\text{Er}_3\text{Fe}_5\text{O}_{12}$ was observed in the sample

obtained at 750°C (14). The present result, $\text{Er}_3\text{Fe}_5\text{O}_{12}$ being stable at 1100°C , is not inconsistent with the above result. ErFe_2O_4 was not found to be stable under the experimental conditions. From the above results of thermogravimetry and the identification of the phase, a phase diagram was constructed for the Er_2O_3 -Fe- Fe_2O_3 system, as shown in Fig.3. The numerical values in the three solid fields in Fig. 3 are the values of $-\log \text{Po}_2$ in equilibrium with the three solid phases, as described above. The nonstoichiometries of ErFeO_3 and $\text{Er}_3\text{Fe}_5\text{O}_{12}$ were found to have,

although both composition ranges were very short, nonstoichiometric composition in the range of $\log(P_{O_2}/\text{atm}) = -13.30$ to 0 and the range of $\log(P_{O_2}/\text{atm}) = -6.15$ to 0, respectively. The relationship between the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$

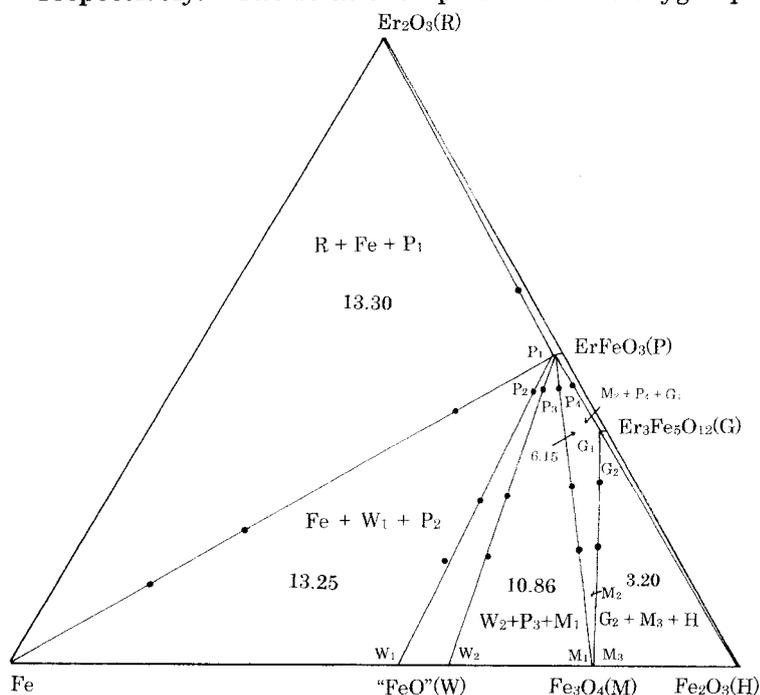


Fig. 3. Phase equilibrium in the $\text{Er}_2\text{O}_3\text{-Fe-Fe}_2\text{O}_3$ system at 1100°C .

Numerical values indicated in the three phase regions display the oxygen partial pressures in $-\log(P_{O_2}/\text{atm})$ in equilibrium with solid phases shown in each region.

Abbreviations are the same as those in Table 2.

stability ranges in oxygen partial pressures of compounds and activities of components in the solid solutions

are tabulated in Table 2. In the next section, the activities will be used in calculations of Gibbs energy change of reactions.

The lattice constants and the unit cell volume of ErFeO_3

perovskite and $\text{Er}_3\text{Fe}_5\text{O}_{12}$ which were prepared in air were determined. The results are tabulated in Table 3, together with the previously reported values. Slight differences were found in the lattice constants.

3-2. Standard Gibbs Energy Change of Reaction

On the basis of the established phase diagram, the standard Gibbs energy changes

and the composition, $N_{\text{O}}/N_{\text{ErFeO}_3}$, of the ErFeO_3 was represented by the equation $N_{\text{O}}/N_{\text{ErFeO}_3} = 2.256 \times 10^{-3} \log P_{O_2}$, which was obtained by the least square method. Here, N_{O} and N_{ErFeO_3} represent the mole fraction of oxygen and ErFeO_3 in the solid solution. This equation can be solved to show that erbium-iron perovskite would be stoichiometric at $-\log(P_{O_2}/\text{atm}) = 0$ and $\text{ErFeO}_{2.970}$ at $\log(P_{O_2}/\text{atm}) = -13.30$, respectively.

Compositions, symbols,

Table 2. Compositions, Symbols, Stability Ranges of Oxygen Partial Pressures, and Activities of Components in Solid Solutions.

Component	Compositions	Symbols	$-\log(P_{O_2}/\text{atm})$	$\log a_i$
FeO	$\text{FeO}_{1.044}$	W_1	13.25	0
	$\text{FeO}_{1.124}$	W_2	10.86	-0.102
ErFeO_3	$\text{ErFeO}_{2.970}$	P_1	13.30	0
	$\text{ErFeO}_{2.972}$	P_2	13.25	7.50×10^{-4}
	$\text{ErFeO}_{2.986}$	P_3	10.86	0.0333
	$\text{ErFeO}_{2.990}$	P_4	6.15	0.0784
$\text{Er}_3\text{Fe}_5\text{O}_{12}$	$\text{Er}_3\text{Fe}_5\text{O}_{11.98}$	G_1	6.15	0
	$\text{Er}_3\text{Fe}_5\text{O}_{11.98}$	G_2	3.20	~ 0

of reactions were determined by the equation, $\Delta G^\circ = -RT \ln K$. Here, R is the gas constant, T the absolute temperature, and K the equilibrium constant of the reaction.

Table 3. Lattice constants of $\text{Er}_3\text{Fe}_5\text{O}_{12}$ and ErFeO_3

As is represented in Table 4, five chemical reactions are found in the established phase diagram. In calculation of the Gibbs	Sample	$-\log P_{\text{O}_2}/\text{atm}$	Time/h	Coexisting Phase	a/A	b/A	c/A	V/A ³
Er ₃ Fe ₅ O ₁₂	Er ₂ O ₃	0.3	64	Fe ₂ O ₃	12.339(2)			1878.5(3)
	Fe ₂ O ₃	0.7	64		12.347			
Ref. 15	ErFeO ₃	0.68	64	Er ₂ O ₃	5.265(3)	5.580(2)	7.591(5)	223.0(2)
	Er ₂ O ₃	0.4	64		5.2628	5.5824	7.5942	
Ref. 16								

energies of these reactions the activity of each component in the solid solution has to be used. For example, as is apparent from the phase diagram, the activity of FeO in the reaction 1) is different from that of reaction 2). The activity of the FeO component in composition A in Fig. 1 that is in equilibrium with Fe should be different from that of the FeO component in composition B that is in equilibrium with Fe₃O₄. The Gibbs-Duhem

Table 4. Standard Gibbs Energy Changes of Reactions

Reaction	$-\log P_{\text{O}_2}$ (atm)	$-\Delta G^\circ$ (kJ/mol)
1) $\text{Fe} + 1/2 \text{O}_2 = \text{FeO}$	13.25	174.2
	13.33 ^b	175.3 ^d
	13.36 ^b	175.6 ¹⁸⁾
	13.30 ¹⁾	
2) $3 \text{FeO} + 1/2 \text{O}_2 = \text{Fe}_3\text{O}_4$	10.86	150.8
	10.86	142.8 ^a
	11.75 ^b	154.6 ^d
	11.46 ^b	150.6 ¹⁸⁾
3) $2/3 \text{Fe}_3\text{O}_4 + 1/6 \text{O}_2 = \text{Fe}_2\text{O}_3$	10.83 ¹⁾	
	3.20	14.0
	3.74 ^b	16.4 ^d
4) $\text{Fe} + 1/2 \text{Er}_2\text{O}_3 + 3/4 \text{O}_2 = \text{ErFeO}_3$	3.87 ^b	17.0 ¹⁸⁾
	13.30	262.3
5) $3 \text{ErFeO}_3 + 2/3 \text{Fe}_3\text{O}_4 + 1/6 \text{O}_2 = \text{Er}_3\text{Fe}_5\text{O}_{12}$	6.15	20.8
	6.15	26.9 ^e

equation was used to calculate the activities of Fe and FeO components in the FeO solid solution from the obtained No/N_{Fe} relation, and the details of the calculation can be found in the report of Darken and Gurry(1) and in the book of Wagner(17). The ΔG° value

- a Value calculated under the assumption that activity of FeO is unity.
- b Values calculated from ΔG° values.
- c Activity of the ErFeO₃ component in the ErFeO₃ solid solution is assumed to be unity.

of -174.2 kJmol⁻¹ for reaction 1) determined in the present investigation agrees well with the values -175.3 and -175.6 kJmol⁻¹ calculated from JANAF Table(4) and Robie et al.(18). For reactions 1) and 2), the present values of the oxygen partial pressure in equilibrium agree with those of Darken and Gurry (1) that was published in 1945. Assuming that the activity of the ErFeO₃ component is unity, the calculated ΔG° value for reaction 5) is about 6 kJ/mol smaller than the value 20.8 kJ/mol.

4. Conclusion

- (1) Phase equilibrium in the system Er-Fe-O at 1100°C was established under an oxygen partial pressure from 0 to -15.00 in $\log(P_{O_2}/\text{atm})$.
- (2) Under the present experimental conditions, Er_2O_3 , Fe, FeO, Fe_3O_4 , Fe_2O_3 , ErFeO_3 , and $\text{Er}_3\text{Fe}_5\text{O}_{12}$ phases are stable, whereas ErFe_2O_4 is not stable. This is the major difference from the previous result at 1200°C.
- (3) Fe_3O_4 , ErFeO_3 , and $\text{Er}_3\text{Fe}_5\text{O}_{12}$ have nonstoichiometric composition, but the range of the nonstoichiometry of Fe_3O_4 was too small to show in Fig. 1 and Fig. 3.
- (4) Lattice constants of ErFeO_3 and $\text{Er}_3\text{Fe}_5\text{O}_{12}$ were determined and were in fairly good agreement with previous values.
- (5) Standard Gibbs energies of reactions found in the phase diagram were calculated with the oxygen partial pressures in equilibrium with three solid phases.

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