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The Standard Free Energy of the Formation of $LaFeO_3$ at 1204°C

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Synopsis. The standard free energy of the formation of $LaFeO_3$ was detemined to be -68700 ± 200 cal·mol^{-1} at 1204 °C by the following reaction: $1/2\ La_2O_3(s) + Fe(s) + 3/4\ O_2(g) = LaFeO_3(s)$, based on precise phase equilibria in the $Fe–Fe_2O_3–La_2O_3$ system.

Moruzzi and Shafer[1] have investigated phase equilibria in the La_2O_3–iron oxide system at high temperatures up to 1900 °C in air. They found two compounds in this system; one is the orthorhombic perovskite-type $LaFeO_3$, while the other is a compound, $LaFe_{12}O_{19}$, with a magnetoplumbite structure. The latter is stable at temperatures between 1380 and 1421 °C. Cassedanne and Forestier[2] have also studied the Fe_2O_3–La_2O_3 system at temperatures from 900 to 1300 °C in air, and determined the cell constants of $LaFeO_3$.

One objective of the present study is to determine the standard free energy of the formation of $LaFeO_3$ on the basis of precise phase equilibria in the $Fe–Fe_2O_3–La_2O_3$ system at 1204 °C by changing the oxygen partial pressure from one to $10^{-15.75}$ atm under one atmospheric total pressure.

Experimental

Since the experimental methods and apparatus used in this study are the same as those described elsewhere,[3,4] a brief description will suffice for the general procedure.

A vertical quench furnace was used for every equilibrium run under a controlled oxygen partial pressure at 1204 °C. The atmospheres of the desired oxygen partial pressures were obtained by using CO_2–H_2 mixtures. Every value of P_{O_2} was measured by means of a solid electrolyte cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$.[5] The calculated values of P_{O_2} based on the thermochemical data[6] and the measured ones showed a very good consistence within ± 0.01 in terms of $\log P_{O_2}$. The funance temperature was measured by means of a Pt-87%Pt13%Rh thermocouple calibrated against the gold point; it was kept constant within ±1 °C.

A guaranteed reagent, Fe_2O_3, metallic iron powder (99.98%), and optical-grade La_2O_3 were used as the starting materials. The mixture of Fe_2O_3/La_2O_3 or Fe/La_2O_3 was primarily calcined at 1300 °C, then it was ground finely in an agate mortar and heated again at 1300 °C for 20 hr in air. The sintered material thus obtained was put into an alumina crucible, and the weight change was followed thermogravimetrically with an automatic balance at every controlled P_{O_2} value at 1204 °C. The equilibrated specimens were quenched rapidly, as has been described before,[3,4] and the phases present were identified by an X-ray powder method.

Results and Discussion

The phase equilibria obtained in the present study are illustrated in Fig. 1. No solubility of the lanthanum ion in the hematite, wüstite, and metallic iron phases was observed within present limits of experimental error. The La_2O_3 phase was stable in reducing atmospheres below $10^{-15.75}$ atm P_{O_2} without any deviation from the stoichiometry.

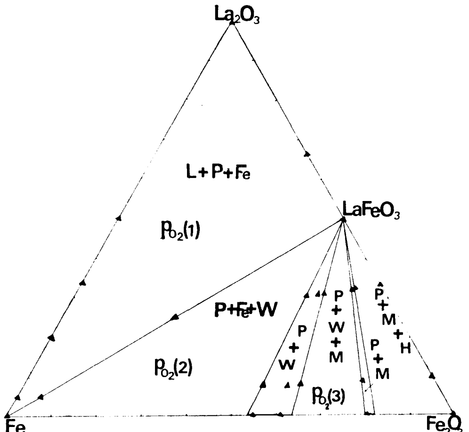

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Fig. 1. Phase diagram of the $Fe–Fe_2O_3–La_2O_3$ system at 1204 °C.
L: La_2O_3, P: $LaFeO_3$, Fe: γ-iron, W: wüstite, M: magnetite, H: hematite.
$-\log P_{O_2}(1) = 13.57$, $-\log P_{O_2}(2) = 11.92$,
$-\log P_{O_2}(3) = 9.12$
where $P_{O_2}(1)$, $P_{O_2}(2)$, and $P_{O_2}(3)$ mean the equilibrium oxygen partial pressures over the three phases L+P+Fe, P+Fe+W, and P+W+M, respectively.

A perovskite-type compound, $LaFeO_3$, was stable in the range of oxygen partial pressures from one to $10^{-13.57}$ atm P_{O_2}, at which point $LaFeO_3$ was decomposed to form metallic iron and La_2O_3. The equilibrium state may be written as follows at an oxygen partial pressure of $10^{-13.57}$ atm:

$$1/2La_2O_3(s) + Fe(s) + 3/4O_2(g) = LaFeO_3(s) \qquad (1)$$

The existence of ferric iron in the $LaFeO_3$ structure under such an extremely low oxygen partial pressure may be attributed to the stable lattice energy of the perovskite-type structure, and also to the fact that the association of the oxygen ion with the La^{3+} ion in the structure has a profound influence upon the bonding between Fe^{3+} and oxygen ions.

The lattice constants of $LaFeO_3$ equilibrated with Fe_2O_3 and with La_2O_3 are almost identical within the limits of experimental errors (see Table 1). On the basis of these X-ray data, together with the thermogravimetric results, it may be safely said that the $LaFeO_3$ phase exists only as a stoichiometric compound under the present experimental conditions.

Since the La_2O_3, metallic iron, and $LaFeO_3$ phases

Table 1. Lattice constants of $LaFeO_3$
(Space group: D_{2h}^{16}–Pbnm, distorted Perovskite structure)

Lattice constant (A)	$LaFeO_3$ equilibrated with		$LaFeO_3$ pure phase	$LaFeO_3$[a)]
	La_2O_3	Fe_2O_3		
a	5.566	5.558	5.553	5.556
b	5.557	5.557	5.560	5.565
c	7.846	7.856	7.865	7.862
$V(A^3)$	242.7	242.7	242.8	243.1

a) After Ref. 9.

are all stoichiometric at 1204 °C, the standard free energy of the formation of $LaFeO_3$ from La_2O_3, Fe, and oxygen may be directly calculated on the bais of Eq. (1) as follows:

$$\Delta G^\circ(1) = -3/4RT \ln P_{O_2}(1)$$
$$= -68700 \pm 200 \text{ cal}\cdot\text{mol}^{-1}$$

where R means the gas constant and T is the absolute temperature. The experimental error was estimated on the basis of the fluctuations of both temperature and oxygen partial pressure during the present study. In addition, as is shown in Fig. 1, the equilibrium oxygen partial pressures, $P_{O_2}(2)$ for metallic iron and wüstite, and $P_{O_2}(3)$ for wüstite and magnetite, were identical with those obtained by Darken and Gurry.[7,8)]

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