Activity of Iron Oxide in Magnesio-wüstite in Equilibrium with Solid Metallic Iron

Masakatsu Hasegawa, Tatsuro Tsukamoto* and Masanori Iwase

Department of Energy Science and Technology, Kyoto University, Kyoto 606-8501, Japan

By employing an electrochemical technique incorporating magnesia-stabilized zirconia electrolyte, the activities of iron oxide, Fe_xO , were measured in magnesio-wüstite, Fe_xO – MgO solid solution, in equilibrium with solid metallic iron at temperatures between 1373 and 1573 K. The sub-regular solution model was applied to the Fe_xO activities, and the calculated Fe_xO activities were in good agreement with the experimental values in this study and the literatures at temperatures between 1073 and 1573 K with an accuracy of ± 0.02 .

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1. Introduction

Magnesium oxide, MgO , is one of the important components of blast furnace slag. For better understanding the activity of iron oxide, Fe_xO , in blast furnace slag, it is essential to estimate the interaction between Fe_xO and MgO . Magnesio-wüstite, Fe_xO – MgO solid solution, is known to be continuous between the end members at temperatures below the melting point of Fe_xO , *i.e.*, 1644 K, shown in Fig. 1.^{1–3)} A number of studies have been done on the system of Fe_xO – MgO in equilibrium with solid metallic iron. The Fe_xO activities reported for Fe_xO – MgO solid solutions at 1573, 1473, 1373, 1273, 1173, 1123 and 1073 K are summarized in Fig. 2.

Schmahl *et al.*⁴⁾ measured the Fe_xO activities in Fe_xO – MgO solid solutions equilibrated with pure iron in the gas mixture of $\text{CO} + \text{CO}_2$ at 1073, 1173 and 1273 K. Their data are expressed by open squares in Fig. 2.

Hahn and Muan⁵⁾ determined the chemical potentials of Fe_xO at 1373 and 1573 K by using gas equilibrium technique involving $\text{CO}_2 + \text{H}_2$. Open circles in Fig. 2 express their values.

Half-filled triangles in Fig. 2 show the Fe_xO activities in Fe_xO – MgO solid solutions in equilibrium with pure solid iron, investigated under a stream of $\text{H}_2 + \text{H}_2\text{O}$ at 1123 K by Berthet and Perrot.⁶⁾

Electrochemical measurements involving CaO -stabilized zirconia as a solid electrolyte and a two-phase mixture of $\text{Fe} + \text{pure Fe}_x\text{O}$ as a reference electrode were conducted in order to determine the Fe_xO activities in magnesio-wüstite in contact with solid iron at temperatures between 1073 and 1373 K by Abbattista *et al.*⁷⁾ (solid squares in Fig. 2).

By employing both an electrochemical technique (solid triangles in Fig. 2) and a gas equilibrium method (open triangles), the activities of Fe_xO in Fe_xO – MgO solid solutions in equilibrium with metallic iron were measured in the temperature interval from 1050 to 1400 and at 1573 K by Srecec *et al.*⁸⁾

The literature data for Fe_xO activities were in good agreement with each others at temperatures between 1073

Fig. 1 Phase diagram of the system MgO – Fe_xO in equilibrium with metallic iron.

and 1273 K. Agreements, however, were not satisfactory among the values of Fe_xO potentials reported at 1373 and 1573 K, respectively. Therefore, in this study, the activities of Fe_xO in magnesio-wüstite were measured at temperatures between 1373 and 1573 K, in order to estimate the dependence of the Fe_xO potential on temperature. Fe_xO – MgO solid solutions were brought into equilibrium with pure solid iron, and the equilibrium oxygen partial pressures were measured by means of a solid-oxide galvanic cell:

2. Experimental Aspects

Fe_xO – MgO solid solutions were prepared by mixing iron oxide and magnesia. The mixtures were pressed in a steel die to form pellets of 20 mm diameter and fired in a magnesia crucible at 1573 K for 200 h under a stream of purified argon.

*Graduate Student, Kyoto University

Fig. 2 Activity-composition relationship in Fe_xO - MgO solid solution in equilibrium with metallic iron.

The compositions of the Fe_xO - MgO solid solutions were determined by wet chemical analysis. The mole fractions of Fe_xO , $X_{\text{Fe}_x\text{O}}$, were calculated by using a manner described elsewhere.⁹⁾

The experimental apparatus and procedures have also been described elsewhere.⁹⁾ An iron crucible was charged with 2 to 4 g of the Fe_xO - MgO solid solution and 35 g of pure silver, and heated to the experimental temperature under a stream of purified argon inside a SiC resistance furnace. The gas purification train consisted of silica-gel, phosphorus pentoxide and magnesium chips held at 823 K.

The electrochemical oxygen probe, $\text{Mo}/\text{Mo} + \text{MoO}_2/\text{ZrO}_2(\text{MgO})$, consisted of a zirconia tube and a two-phase mixture of $\text{Mo} + \text{MoO}_2$. A molybdenum rod of 3 mm diameter was used as an electrical lead to the reference electrode, which consisted of four parts Mo and one part MoO_2 by weight. The electrical contact to the outer electrode of the zirconia probe was made by the liquid silver and a steel rod soldered to the iron crucible. The use of dissimilar electrical connectors required a correction for the thermo-electromotive force of the steel-molybdenum couple.¹⁰⁾ The

Fig. 3 Measured electromotive force as function of temperature.

zirconia tube used in this study had satisfactory resistance to even Fe_xO -containing liquid slags, as already reported elsewhere.⁹⁾ In this study, the oxide phase occurred at solid state, hence, reaction was negligible.

The open-circuit emfs of the oxygen probes were monitored on a strip-chart recorder of $2\text{ M}\Omega$ internal impedance with an accuracy of $\pm 0.1\text{ mV}$. The emf values could also be read with a digital voltmeter of $100\text{ M}\Omega$ input resistance with an accuracy of $\pm 0.01\text{ mV}$. Emf readings were continued until the values became stable, and the reproducibilities of cell potentials were confirmed by temperature cycling.

Temperatures were measured with a Pt-PtRh13 thermocouple and controlled to $\pm 1\text{ K}$ by using a control thermocouple and PID-type temperature regulator.

3. Experimental Results

The experimental results are summarized in Table 1, and Fig. 3 shows the measured values of emfs as functions of temperature.

The oxygen partial pressures of the Fe_xO - MgO solid solution in equilibrium with solid iron, P_{O_2} , can be calculated by¹¹⁾

$$E = (RT/F) \ln \left[\frac{P_{\text{O}_2}(\text{ref.})^{1/4}}{P_e^{1/4}} \right] + E_t, \quad (2)$$

where E is cell voltage, R is the gas constant, T is temperature, F is the Faraday constant, E_t is thermo-emf between Mo (positive) and Fe (negative), and P_e is the oxygen partial pressure at which the ionic and the n -type electronic conductivities are equal. Values for this parameter for the magnesia-stabilized zirconia tubes used in this study have been reported elsewhere.¹²⁾

$$\log(P_e/\text{Pa}) = 2.54 \times 10 - 6.45 \times 10^4/(T/\text{K}) \quad (3)$$

The oxygen partial pressure at the reference electrode, $P_{\text{O}_2}(\text{ref.})$, was calculated by using the authors' previous results.¹³⁾

$$\log(P_{\text{O}_2}(\text{ref.})/\text{Pa}) = 1.39 \times 10 - 3.01 \times 10^4/(T/\text{K}) \quad (4)$$

Table 1 The experimental results.

Sample No.	Mole fraction of Fe_xO , $X_{\text{Fe}_x\text{O}}$	x	Electromotive force, Emf/mV	Temperature, T/K	Oxygen partial pressure, $\log(P_{\text{O}_2}/\text{Pa})$
1	0.117	0.987	105.5	1375	-9.35
			111.3	1426	-8.59
			108.2	1403	-8.92
			112.4	1449	-8.24
			127.2	1497	-7.72
			122.5	1475	-7.98
			132.2	1523	-7.41
			126.0	1486	-7.86
			125.0	1511	-7.48
			101.1	1384	-9.13
			116.4	1433	-8.55
			108.4	1409	-8.82
			118.2	1459	-8.17
2	0.198	0.992	71.2	1373	-8.88
			90.2	1474	-7.55
			79.4	1399	-8.57
			86.4	1448	-7.89
			85.6	1424	-8.26
			98.0	1525	-6.93
			93.7	1498	-7.25
			89.2	1486	-7.36
			86.5	1461	-7.70
3	0.291	0.994	84.2	1437	-8.03
			62.5	1373	-8.75
			82.3	1472	-7.47
			68.1	1398	-8.42
			75.9	1451	-7.70
			71.9	1424	-8.06
			88.2	1525	-6.80
			85.4	1497	-7.15
			82.3	1484	-7.30
			84.6	1513	-6.92
			70.0	1411	-8.24
			78.5	1461	-7.59
4	0.395	0.985	74.1	1440	-7.84
			68.1	1385	-8.64
			54.0	1373	-8.63
			68.9	1474	-7.26
			56.7	1394	-8.32
			64.5	1448	-7.59
			58.2	1423	-7.88
			75.2	1525	-6.62
			70.2	1498	-6.93
			69.9	1487	-7.09
			71.7	1512	-6.76
			62.1	1435	-7.75
			64.6	1460	-7.41
			57.5	1409	-8.09
			55.0	1384	-8.46

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Table 1 (Continued)

Sample No.	Mole fraction of Fe_xO , $X_{\text{Fe}_x\text{O}}$	x	Electromotive force, Emf/mV	Temperature, T/K	Oxygen partial pressure, $\log(P_{\text{O}_2}/\text{Pa})$
5	0.495	0.994	46.1	1373	-8.51
			61.0	1472	-7.18
			50.4	1397	-8.18
			57.8	1448	-7.49
			53.0	1422	-7.82
			67.9	1523	-6.55
			65.6	1498	-6.87
			63.5	1487	-7.00
			55.1	1435	-7.65
			59.4	1462	-7.31
			53.9	1413	-7.98
			49.1	1388	-8.31
6	0.584	0.995	42.9	1374	-8.45
			59.9	1475	-7.12
			48.5	1398	-8.14
			57.1	1451	-7.44
			50.0	1425	-7.74
			64.7	1525	-6.49
			62.9	1498	-6.84
			63.5	1510	-6.68
			54.9	1460	-7.27
			58.9	1485	-6.97
			53.2	1435	-7.63
			46.1	1384	-8.33
7	0.703	0.999	38.3	1372	-8.41
			51.5	1472	-7.05
			43.4	1421	-7.70
			48.5	1449	-7.35
			43.2	1398	-8.06
			61.0	1527	-6.41
			55.6	1497	-6.75
			58.5	1509	-6.62
			54.9	1485	-6.91
			51.2	1438	-7.55
8	0.806	0.993	49.5	1456	-7.26
			64.3	1571	-5.87
			57.3	1524	-6.40
			61.4	1548	-6.13
			50.1	1473	-7.02
			53.3	1498	-6.71
			47.3	1448	-7.35
			41.9	1396	-8.08
			44.0	1421	-7.71
			36.3	1375	-8.34
			63.3	1558	-6.03
			56.3	1506	-6.63
			59.9	1535	-6.29
			49.6	1457	-7.25
			40.3	1384	-8.25
			46.2	1435	-7.53
			43.1	1408	-7.90
			52.3	1486	-6.86

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Table 1 (Continued)

Sample No.	Mole fraction of Fe _x O, $X_{\text{Fe}_x\text{O}}$	x	Electromotive force, Emf/mV	Temperature, T/K	Oxygen partial pressure, $\log(P_{\text{O}_2}/\text{Pa})$
9	0.900	0.986	29.4	1373	-8.27
			59.6	1573	-5.79
			52.9	1523	-6.36
			56.2	1549	-6.05
			46.9	1474	-6.96
			48.0	1497	-6.65
			39.8	1423	-7.62
			42.3	1447	-7.29
			46.1	1484	-6.81
			43.4	1459	-7.13
			54.5	1557	-5.93
			48.6	1509	-6.49
			51.0	1534	-6.18
			39.9	1435	-7.44
			32.1	1374	-8.29
			35.4	1398	-7.95

The standard state for Fe_xO was taken as pure non-stoichiometric solid Fe_xO in equilibrium with pure solid iron. The activities of Fe_xO were calculated by

$$a_{\text{Fe}_x\text{O}} = (P_{\text{O}_2}/P_{\text{O}_2}^\circ(\text{Fe}_x\text{O}))^{1/2}, \quad (5)$$

where $P_{\text{O}_2}^\circ(\text{Fe}_x\text{O})$ is the equilibrium oxygen partial pressure of the mixture of pure solid iron and pure solid Fe_xO, as given by the formula¹⁰⁾

$$\log(P_{\text{O}_2}^\circ(\text{Fe}_x\text{O})/\text{Pa}) = 1.17 \times 10 - 2.74 \times 10^4/(T/\text{K}) \quad (6)$$

4. Discussion

The mole ratios of Fe³⁺/Fe²⁺ in Fe_xO–MgO solid solutions in equilibrium with solid metallic iron and values of x in Table 1 were considered to change slightly, depending upon temperature. In this study, however, the compositions of Fe_xO–MgO solid solutions were determined only after preparations at 1573 K, and are superimposed on the isothermal section of the ternary system of stoichiometric FeO, Fe₂O₃ and MgO at 1573 K,¹⁴⁾ shown in Fig. 4.

The present values of Fe_xO activities are plotted against Fe_xO mole fractions in Fig. 2, in comparison with the literature data. The Fe_xO activities determined in this study show positive deviations from Raoult's law, and are in good agreement with those reported by Hahn and Muan with a gas equilibrium method at 1373 and 1573 K.

In order to estimate the dependence of the Fe_xO potential on temperature, the sub-regular solution model was applied to the activity coefficient of Fe_xO in Fe_xO–MgO solid solutions in equilibrium with solid metallic iron:

$$\begin{aligned} \ln \gamma_{\text{Fe}_x\text{O}} &\equiv \ln(a_{\text{Fe}_x\text{O}}/X_{\text{Fe}_x\text{O}}) \\ &= \alpha(1 - X_{\text{Fe}_x\text{O}})^3 + \beta(1 - X_{\text{Fe}_x\text{O}})^2, \end{aligned} \quad (7)$$

where parameters α and β depend on temperature only. By using the least squared method to all the data for Fe_xO activities determined in this study and the literatures,

parameters α and β could be derived as follows:

$$\alpha = -1.72 \times 10^{-1} - 3.34 \times 10^2/(T/\text{K}) \quad (1073\text{--}1573 \text{ K}) \quad (8)$$

$$\beta = 1.78 - 4.84 \times 10^2/(T/\text{K}) \quad (1073\text{--}1573 \text{ K}) \quad (9)$$

Thus, we have

$$\begin{aligned} \ln \gamma_{\text{Fe}_x\text{O}} &= \{-1.72 \times 10^{-1} - 3.34 \\ &\quad \times 10^2/(T/\text{K})\}(1 - X_{\text{Fe}_x\text{O}})^3 \\ &\quad + \{1.78 - 4.84 \times 10^2/(T/\text{K})\}(1 - X_{\text{Fe}_x\text{O}})^2 \end{aligned} \quad (10)$$

The Fe_xO activity-composition relationships at 1573, 1473, 1373, 1273, 1173, 1123 and 1073 K were calculated by using eq. (10), and are expressed by the solid curves in Fig. 2. At 1373 and 1573 K, the Fe_xO activity values reported by the present authors and Hahn and Muan are in good agreement with those derived from eq. (10), while values of Srecec *et al.* (gas) and Abbattista *et al.* (emf) show negative deviation from the calculated ones. The smooth curves calculated by eq. (10), however, could represent the Fe_xO activities at temperatures between 1073 and 1573 K with an accuracy of ± 0.02 , which was attributed to the average difference of the calculated values from the experimental data. The deviation of Fe_xO activities from Raoult's law increases slightly with an increase in temperature in this temperature range.

By applying the sub-regular solution model to Fe_xO–MgO solid solution, the activity coefficient of MgO was also given as:

$$\begin{aligned} \ln \gamma_{\text{MgO}} &\equiv \ln(a_{\text{MgO}}/(1 - X_{\text{Fe}_x\text{O}})) \\ &= -\alpha X_{\text{Fe}_x\text{O}}^3 + \{(3\alpha + 2\beta)/2\}X_{\text{Fe}_x\text{O}}^2 \end{aligned} \quad (11)$$

$$\begin{aligned} &= \{1.72 \times 10^{-1} + 3.34 \times 10^2/(T/\text{K})\}X_{\text{Fe}_x\text{O}}^3 \\ &\quad + \{1.52 - 9.85 \times 10^2/(T/\text{K})\}X_{\text{Fe}_x\text{O}}^2 \end{aligned} \quad (12)$$

Fig. 4 Iso-thermal section of the system FeO-Fe₂O₃-MgO at 1573 K.

Equations (7) and (11) satisfy the Gibbs–Duhem equation (13) at constant temperature.

$$X_{\text{Fe}_x\text{O}}d(\ln \gamma_{\text{Fe}_x\text{O}}) + (1 - X_{\text{Fe}_x\text{O}})d(\ln \gamma_{\text{MgO}}) = 0 \quad (13)$$

The MgO activities were calculated by eq. (12), and are represented by the broken curves in Fig. 2.

The relative partial molar Gibbs free energy of Fe_xO, $\Delta\bar{G}_{\text{Fe}_x\text{O}}$, referred to pure nonstoichiometric solid Fe_xO in equilibrium with pure solid metallic iron was calculated from eq. (10).

$$\Delta\bar{G}_{\text{Fe}_x\text{O}} \equiv RT \ln \gamma_{\text{Fe}_x\text{O}} + RT \ln X_{\text{Fe}_x\text{O}} \quad (14)$$

$$\begin{aligned} \Delta\bar{G}_{\text{Fe}_x\text{O}}/\text{J}\cdot\text{mol}^{-1} = & \{-1.43(T/\text{K}) - 2.78 \times 10^3\} \\ & \times (1 - X_{\text{Fe}_x\text{O}})^3 + \{1.48 \times 10(T/\text{K}) \\ & - 4.02 \times 10^3\}(1 - X_{\text{Fe}_x\text{O}})^2 \\ & + RT \ln X_{\text{Fe}_x\text{O}} \end{aligned} \quad (15)$$

The relative partial molar enthalpy, $\Delta\bar{H}_{\text{Fe}_x\text{O}}$, and entropy, $\Delta\bar{S}_{\text{Fe}_x\text{O}}$, could be given by using eq. (15) and the Gibbs–Helmholtz equations. (16) and (18), respectively.

$$\Delta\bar{H}_{\text{Fe}_x\text{O}} \equiv -T^2[\partial(\Delta\bar{G}_{\text{Fe}_x\text{O}}/T)/\partial T]_P \quad (16)$$

$$\begin{aligned} \Delta\bar{H}_{\text{Fe}_x\text{O}}/\text{J}\cdot\text{mol}^{-1} = & -2.78 \times 10^3(1 - X_{\text{Fe}_x\text{O}})^3 \\ & - 4.02 \times 10^3(1 - X_{\text{Fe}_x\text{O}})^2 \end{aligned} \quad (17)$$

$$\Delta\bar{S}_{\text{Fe}_x\text{O}} \equiv -[\partial\Delta\bar{G}_{\text{Fe}_x\text{O}}/\partial T]_P \quad (18)$$

$$\begin{aligned} \Delta\bar{S}_{\text{Fe}_x\text{O}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = & 1.43(1 - X_{\text{Fe}_x\text{O}})^3 - 1.48 \\ & \times 10(1 - X_{\text{Fe}_x\text{O}})^2 - R \ln X_{\text{Fe}_x\text{O}} \end{aligned} \quad (19)$$

The relative partial molar quantities for MgO referred to pure solid MgO were also calculated from eq. (12).

$$\begin{aligned} \Delta\bar{G}_{\text{MgO}}/\text{J}\cdot\text{mol}^{-1} = & \{1.43(T/\text{K}) + 2.78 \times 10^3\}X_{\text{Fe}_x\text{O}}^3 \\ & + \{1.26 \times 10(T/\text{K}) - 8.19 \\ & \times 10^3\}X_{\text{Fe}_x\text{O}}^2 + RT \ln(1 - X_{\text{Fe}_x\text{O}}) \end{aligned} \quad (20)$$

Fig. 5 Enthalpy and entropy of mixing, and relative partial molar quantities in Fe_xO-MgO solid solution in equilibrium with metallic iron.

$$\begin{aligned} \Delta\bar{H}_{\text{MgO}}/\text{J}\cdot\text{mol}^{-1} = & 2.78 \times 10^3 X_{\text{Fe}_x\text{O}}^3 - 8.19 \\ & \times 10^3 X_{\text{Fe}_x\text{O}}^2 \end{aligned} \quad (21)$$

$$\begin{aligned} \Delta\bar{S}_{\text{MgO}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = & -1.43 X_{\text{Fe}_x\text{O}}^3 - 1.26 \\ & \times 10 X_{\text{Fe}_x\text{O}}^2 - R \ln(1 - X_{\text{Fe}_x\text{O}}) \end{aligned} \quad (22)$$

Then, the enthalpy and entropy of mixing, ΔH^M , ΔS^M could be given as follows, respectively.

$$\Delta H^M = X_{\text{Fe}_x\text{O}}\Delta\bar{H}_{\text{Fe}_x\text{O}} + (1 - X_{\text{Fe}_x\text{O}})\Delta\bar{H}_{\text{MgO}} \quad (23)$$

$$\Delta S^M = X_{\text{Fe}_x\text{O}}\Delta\bar{S}_{\text{Fe}_x\text{O}} + (1 - X_{\text{Fe}_x\text{O}})\Delta\bar{S}_{\text{MgO}} \quad (24)$$

The relative partial molar quantities for Fe_xO and MgO and the enthalpy and entropy of mixing are summarized in Fig. 5. In this model, the relative partial molar enthalpy and entropy are independent of temperature.

On the other hand, the relative partial molar enthalpy and entropy of Fe_xO can be determined by using the Gibbs–Helmholtz equations. (16) and (18) and the linear relationships between the electromotive forces and temperature, shown in Fig. 3.

$$\Delta \bar{G}_{\text{Fe}_x\text{O}} \equiv -2F(E - E^\circ) \quad (25)$$

$$= \Delta \bar{H}_{\text{Fe}_x\text{O}} - T \Delta \bar{S}_{\text{Fe}_x\text{O}}, \quad (26)$$

where E and E° denote the voltages of the galvanic cells:

$\Delta \bar{H}_{\text{Fe}_x\text{O}}$ and $\Delta \bar{S}_{\text{Fe}_x\text{O}}$ determined from the experimental data in this study are plotted in Fig. 5. As shown in this figure, the scatters, which are illustrated by the error bars, are large, because $\Delta \bar{H}_{\text{Fe}_x\text{O}}$ and $\Delta \bar{S}_{\text{Fe}_x\text{O}}$ correspond to the intercept and the slope of eq. (25) extrapolated at 0 K, respectively.

For $\text{Fe}_x\text{O-MgO}$ solid solutions, the Fe_xO activities have been reported by Tamura *et al.* between 1823 and 1923 K.¹⁵⁾ These authors reported nearly ideal behavior. In general, with an increase in temperature, activities would approach ideal solutions. Hence, the difference is not surprising.

5. Conclusions

- (1) By employing an electrochemical technique, the activities of iron oxide, Fe_xO , were measured in magnesio-wüstite, $\text{Fe}_x\text{O-MgO}$ solid solution, in equilibrium with solid metallic iron at temperatures between 1373 and 1573 K.
- (2) The Fe_xO activities in $\text{Fe}_x\text{O-MgO}$ solid solutions showed positive deviations from Raoult's law.
- (3) Equation (10) could represent the Fe_xO activity-composition relationship in the temperature range 1073 to 1573 K with an accuracy of ± 0.02 .

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