

# Equilibria in the System $\text{FeO-Fe}_2\text{O}_3\text{-MgO}$ at $1160^\circ\text{C}$

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The system  $\text{FeO-Fe}_2\text{O}_3\text{-MgO}$  is one of the most important systems not only for ceramics, but also for metallurgy and geochemistry. The subsolidus study of this system may establish the fundamental thermodynamic properties of both magnesioferrite and magnesiowüstite solid solutions. This knowledge will in turn furnish chemical data for the investigation of the system  $\text{FeO-Fe}_2\text{O}_3\text{-MgO-SiO}_2$ , which is very important since it includes the stability relationship between the pyroxene solid solution,  $\text{FeSiO}_3\text{-MgSiO}_3$ , and the olivine solid solution,  $\text{Fe}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$ , which usually coexist in igneous rocks. However, no investigation of a complete isothermal phase diagram of the system  $\text{Fe-Mg-O}$  at a subsolidus temperature under various oxygen partial pressures has yet been published.

Darken and Gurry<sup>1)</sup> studied the system  $\text{Fe-O}$  and precisely re-determined the thermodynamic properties of metallic iron, wüstite, and magnetite in their equilibrated states. Richards and White<sup>2)</sup> and Woodhouse and White<sup>3)</sup> studied the system  $\text{Fe-Mg-O}$  at high temperatures, up to  $1650^\circ\text{C}$ , in air and constructed a modified phase diagram showing the extensive solid solubility of iron(II) oxide and iron(III) oxide in periclase. Phillips, Sōmiya, and Muan<sup>4)</sup> also studied the system and determined the phase relations in air at temperatures up to  $1800^\circ\text{C}$  by means of the quenching technique. Moreover, Brynstad and Flood<sup>5)</sup> studied this system at  $1400^\circ\text{C}$  and at various oxygen partial pressures in order to clarify the equilibrium between ferrous and ferric iron in wüstite containing various amounts of magnesium oxide; these data were then used for a discussion of the applicability of the mass-action law on the redox equilibrium. Roberts and Merwin<sup>6)</sup> investigated the system  $\text{FeO-Fe}_2\text{O}_3\text{-MgO}$  at temperatures above  $1000^\circ\text{C}$  in an isobar  $1/5$  atmosphere of  $\text{O}_2$ . As for the

binary system  $\text{MgO-Fe}_2\text{O}_3$ , they found no compound other than  $\text{MgO-Fe}_2\text{O}_3$  which dissociates slightly on heating, and established that the solid solution extends from this compound for a short distance toward  $\text{MgO}$ . On the basis of studies by Schenck and Dingmann<sup>7)</sup> and of those by Roberts and Merwin<sup>6)</sup> and Bowen and Schairer<sup>8)</sup> on the system  $\text{FeO-MgO}$ , White<sup>9)</sup> constructed approximate phase relations for the system  $\text{Fe-Mg-O}$ .

The purpose of the present study is to determine the detailed phase equilibria in the system  $\text{FeO-Fe}_2\text{O}_3\text{-MgO}$  at  $1160^\circ\text{C}$  by varying partial oxygen pressures from  $0.21$  atm. to  $10^{-13.5}$  atm. The temperature of  $1160^\circ\text{C}$  was adopted for convenience in studying the subsolidus equilibria in the system  $\text{FeO-Fe}_2\text{O}_3\text{-MgO-SiO}_2$ .

## Experimental Methods

**General Procedures.**—The different experimental methods were used in the present investigation—quenching and thermogravimetric methods as previously described by Katsura and Muan.<sup>10)</sup>

In the thermogravimetric method, pellets of oxide mixtures of iron(III) oxide and magnesium oxide were suspended by a thin platinum wire from one beam of an analytical balance, and the weight changes were recorded as a function of the oxygen pressure at  $1160^\circ\text{C}$ . The data thus obtained were used to locate oxygen isobars. According to Richards and White,<sup>2)</sup> no change was observed in the weight of mixtures of iron(III) oxide and magnesium oxide in any ratio when the mixtures (starting materials) were heated at  $700^\circ\text{C}$  and in air. In the present study, we checked the fact mentioned above. The weight in air at  $700^\circ\text{C}$  was taken as the reference state for calculation of the amount of  $\text{Fe}^{2+}$  produced in drawing the isobaric line, and subsequently in determining the phase boundary.

In the quenching method, oxide samples were heated at  $1160^\circ\text{C}$  and at a chosen oxygen pressure until equilibrium was attained among gas and condensed phases. The samples were then quenched rapidly to the temperature of ice by burning away the thin platinum wire with an electric current. The sample thus obtained were used for determining:

1) L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.*, **67**, 1398 (1945); *ibid.*, **68**, 798 (1946).

2) R. G. Richards and J. White, *Trans. Brit. Ceram. Soc.*, **53**, 422 (1954).

3) D. Woodhouse and J. White, *ibid.*, **54**, 333 (1955).

4) B. Phillips, S. Sōmiya and A. Muan, *J. Am. Ceram. Soc.*, **44**, 167 (1961).

5) J. Brynstad and H. Flood, *Z. Elektrochem.*, **62**, 953 (1958).

6) H. S. Roberts and H. E. Merwin, *Am. J. Sci.*, **21**, 145 (1931).

7) R. Schenck and H. Dingmann, *Z. anorg. u. allgem. Chem.*, **166**, 133 (1927).

8) N. L. Bowen and J. F. Schairer, *Am. J. Sci.*, [5th Series], **29**, 151 (1935).

9) J. White, *J. Iron and Steel Inst.*, **148**, 579 (1943).

10) T. Katsura and A. Muan, *Trans. AIME*, **230**, 77 (1964).

the phases present by X-ray and the microscopic examinations and for the determination of the compositions by chemical analysis. The amounts of ferrous iron determined by thermogravimetric and by chemical analysis were in good agreement.

**Materials.**—Guaranteed reagents of iron(III) oxide and magnesium oxide were used as the starting materials. Each oxide was heated separately in air at  $1000^\circ\text{C}$  for several hours. Mixtures of the desired ratios of the two oxides were then prepared. Each mixture was finely ground by an agate mortar, mixed, and heated at  $1250$  to  $1300^\circ\text{C}$  in air for 3 to 12 hr., depending on the composition. The sintered mixture was again finely ground and repeatedly heated in air at  $1300^\circ\text{C}$ . A suitable starting material for thermogravimetry was obtained by this treatment. Some of the mixed samples thus prepared were heated for several hours at  $1160^\circ\text{C}$  and at the low oxygen pressures necessary to produce the magnesiowüstite. Reduced samples with the same iron/magnesium ratios were obtained by this treatment, and equilibrium could be approached in opposite directions by using these reduced samples in subsequent equilibration runs, as will be described later.

**The Control of the Atmosphere.**—Atmospheres of the desired oxygen pressures were obtained by using pure oxygen, air, carbon dioxide, and  $\text{CO}_2\text{-H}_2$  mixtures. The  $\text{CO}_2\text{-H}_2$  mixtures were prepared by proportioning the two gas components in the desired ratios in a gas mixer principally similar to that described by Darken and Gurry.<sup>11</sup> Oxygen pressures in the  $\text{CO}_2\text{-H}_2$  mixtures were calculated from the thermodynamic data summarized by Elliot and Gleiser.<sup>11</sup> The fluctuation of the  $\text{CO}_2/\text{H}_2$  ratio was within  $\pm 1\%$  throughout the present study, the fluctuation of the value of  $\log P_{\text{O}_2}$  due to the maximum variation in the  $\text{CO}_2/\text{H}_2$  ratio is thus about 0.01. The oxygen partial pressures at  $1160^\circ\text{C}$  were checked by means of the relationship between the chemical composition of wüstite and the oxygen pressure at which the composition is equilibrated as has previously been established by Darken and Gurry,<sup>11</sup> Katsura and Muan,<sup>10</sup> and Taylor.<sup>12</sup> The purities of the carbon dioxide and hydrogen used in the present study were sufficient for the present purposes.

**Furnaces and Temperature Control.**—A vertical tube quench furnace with an 80%Pt20%Rh winding was used for the equilibration runs. A brass-made attachment for quenching was connected with the lower end of a mullite furnace tube with a 30 mm. diameter. The gases used for controlling the oxygen partial pressure were passed through the furnace from bottom to top.

The furnace temperatures were kept constant to approximately  $\pm 2^\circ$  by means of electric controllers activated by a Pt-87%Pt13%Rh thermocouple inserted close to the hot spot of the furnace. The actual temperatures within the furnace were measured with another Pt-90%Pt10%Rh thermocouple which was calibrated against the melting points of

diopside ( $\text{CaMgSi}_2\text{O}_6$ ),  $1391.5^\circ\text{C}$ , and Gold (Au),  $1063^\circ\text{C}$ . (This thermocouple was provided by the courtesy of Dr. E. F. Osborn and Dr. A. Muan, of the Pennsylvania State University).

**The Identification of Phases and the Determination of the Lattice Parameter.**—The phases present in the quenched samples were identified by an X-ray diffractometer. Silicon powder was used as the standard in determining the lattice parameters of the phase present.

An indirect and useful check on the phases present is afforded by the location and shape of the oxygen isobars, as determined in the thermogravimetric study. These relations have been explained in detail in recent papers by Taylor<sup>12</sup> and Katsura and Muan.<sup>10</sup>

The presence of metallic iron in the phase assemblages was evidenced by the liberation of hydrogen gas when samples were dipped in hydrochloric acid. This test is sensitive enough to detect iron in amounts as small as 0.2%.

**Chemical Analysis.**—The ferrous iron content of the quenched samples was determined volumetrically by the method described in detail by Iwasaki et al.,<sup>13</sup> while the total iron content was determined by the zinc-amalgam method described by Katsura.<sup>14</sup> In cases of small amounts of iron, the colorimetric method was adopted to determine the total iron by using  $\alpha, \alpha'$ -dipyridyl.

**Checking Equilibration and Quenching Procedures.**—First, the most suitable linear rate of flow of a homogeneous mixture of gases through the mixing apparatus to the furnace was checked for the equilibration within the gas phase at  $1160^\circ\text{C}$ . When the linear rates of flow was kept at 5 mm./sec., and 4 mm./sec. respectively, the equilibrium state in the condensed phases was never attained. That is to say, the chemical composition was not constant in each run of the same starting material under identical conditions; even in a quenched pellet with about a 1 cm. cube, an appreciable difference was observed in appearance. When we adopt 2.5 mm./sec., the equilibrium was approached within a reasonable period of time and the relationships between the oxygen partial pressures and the chemical compositions of both magnetite and wüstite were just the same as those obtained by Darken and Gurry<sup>11</sup> although they used a mixture of  $\text{CO}_2\text{-CO}$  instead of  $\text{CO}_2\text{-H}_2$  to obtain constant oxygen partial pressure. In the present study, the linear rate of flow, therefore, was kept close to 2.5 mm./sec.

The rate of approach to equilibrium was studied thermogravimetrically. Mixtures with identical iron/magnesium ratios but of different initial degrees of oxidation were used in these experiments to ensure that the equilibrium measured was independent of the time and could be established from both sides. The procedures were as follows: A pellet with a fixed ratio of iron/magnesium which has been heated preliminarily at  $700^\circ\text{C}$  was heated at  $1160^\circ\text{C}$  in air for 3 hr. After ensuring no

11) J. F. Elliot and M. Gleiser, "Thermochemistry for Steelmaking," Addison-Wesley Publishing Co., Inc., Reading, Mass. (1960).

12) R. W. Taylor, *Am. Mineralogist*, **49**, 1016 (1964).

13) I. Iwasaki, T. Katsura, M. Yoshida and T. Tarutani, *Japan Analyst*, **6**, 211 (1957).

14) T. Katsura, "Zikken Kagaku Koza," Vol. 15, Maruzen Shuppan, Tokyo (1959), pp. 272-275.

change in the weight by the thermobalance, the degree of weight-loss was followed by the thermobalance at a desired oxygen partial pressure. When there was no recognizable change in weight over, at least, one hour, the weight thus obtained was regarded as the nearest point to the equilibrated state during the course from the oxidized state to the reduced state. Then the oxygen pressure was very greatly decreased to form magnesiowüstite with a large amount of ferrous iron. After fixing the desired oxygen partial pressure as the same as that in the course from the oxidized state to the reduced state, the degree of weight-gain was measured. The results obtained from both sides were identical within the limits of experimental error.

The thermogravimetric determination of ferrous iron was also ascertained by chemical analysis after rapid quenching. In addition, the composition of both the inside and the outside of a pellet equilibrated after a reasonable period of time was determined to check whether or not there was a uniform compositional distribution, as has been pointed out by Katsura<sup>15)</sup> in the case of magnetite solid solution. These careful checks showed that the equilibrium point with regard to composition was experimentally determined by the thermogravimetric method.

Whereas the total compositions of condensed phases remained constant during the quenching, the phase assemblages present after the quenching were not always the same as they were at the end of the equilibration. For instance, the magnesiowüstite of the composition in the vicinity of the magnesiowüstite-spinel boundary curve could not be quenched. In such cases, the phase evidence given by the thermogravimetric data (the shape and location of oxygen isobars) is more reliable than that obtained by the quenching technique.

## Results and Discussion

The equilibrium data obtained at 1160°C are summarized in Table I, while they are illustrated graphically in Fig. 1.

Three oxide phases are stable under the present experimental conditions: hematite,  $\text{Fe}_2\text{O}_3$ , with a rhombohedral structure; an oxide solid solution with a spinel structure (it is simply called spinel in this paper), and an oxide solid solution with sodium chloride structure (simply called magnesiowüstite). The detailed phase relations were studied mainly in those areas with both spinel and magnesiowüstite phases.

Figure 2 shows the relationship between the oxygen partial pressure (as  $-\log P_{\text{O}_2}$ ) and the mole fraction of iron(II) oxide produced in a starting material of iron(III) oxide. We can see the discontinuous points in Fig. 2 as marked by letters from a to e. These may reasonably be responsible for the points where the starting material is in characteristic states at specified,

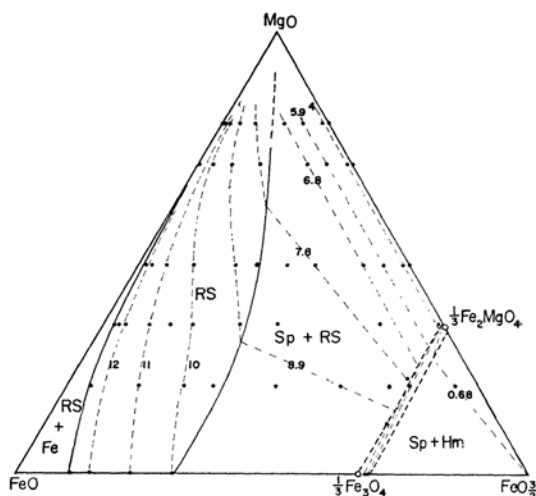


Fig. 1. Diagram illustrating phase relationship in the system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{MgO}$ . For convenience, the three components are taken as  $\text{FeO}$ ,  $\text{FeO}_{3/2}$ , and  $\text{MgO}$ . Heavy lines are boundary curves. Heavy dashed lines are for the approximate spinel phase, and light dashed lines are isobaric lines with numbers meaning  $-\log P_{\text{O}_2}$ . Solid circles represent compositions, as shown in Table I. Abbreviations used have the following meaning: Hm = hematite, Sp = oxide with spinel structure, RS = oxide with NaCl structure, and Fe = metallic iron.

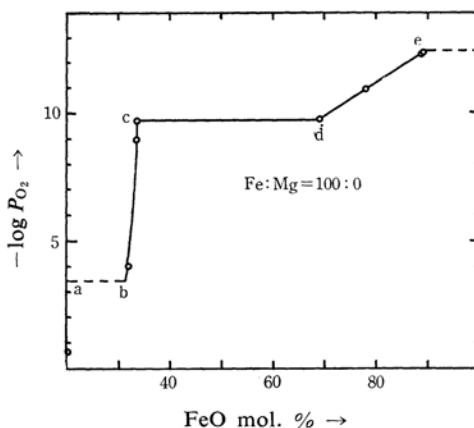


Fig. 2. The relationship between the oxygen partial pressure and the mole fraction of  $\text{FeO}$  produced in a starting material of  $\text{Fe}_2\text{O}_3$ .

respective oxygen pressures, and they represent the points where the equilibrium relationship among condensed phases greatly changes. In view of the experimental results, the line a-b shows the stable coexistence of hematite and magnetite, b-c is for one phase region of magnetite, c-d is for the stable coexistence of magnetite and wüstite, d-e is for one phase region of wüstite, and the right side of e shows the

15) T. Katsura, *Bull. Phys. Soc. Japan*, 19, 21 (1964).

TABLE I.

Starting material Fe <sub>2</sub> O <sub>3</sub> : MgO mol. %	P <sub>O<sub>2</sub></sub>	FeO mol. %* in product	Phases present**	Starting material Fe <sub>2</sub> O <sub>3</sub> : MgO mol. %	P <sub>O<sub>2</sub></sub>	FeO mol. %* in product	Phases present**
100 : 0	10 <sup>-0.68</sup>	0.1	Hm	25.8 : 47.2	10 <sup>-7.80</sup>	18.4	
	10 <sup>-4.04</sup>	31.9	Sp		10 <sup>-8.10</sup>	23.9	Sp+RS
	10 <sup>-9.00</sup>	33.4	Sp		10 <sup>-8.34</sup>	29.8	Sp+RS
	10 <sup>-9.73</sup>	33.4	Sp		10 <sup>-8.89</sup>	33.7	
	10 <sup>-9.78</sup>	69.0	RS		10 <sup>-10.0</sup>	42.0	
	10 <sup>-10.98</sup>	77.9			10 <sup>-11.0</sup>	47.6	RS
	10 <sup>-12.38</sup>	89.2	RS		10 <sup>-12.0</sup>	50.6	RS
	10 <sup>-12.40</sup>		Fe		10 <sup>-12.8</sup>	51.1	RS
80.2 : 19.8	10 <sup>-0.68</sup>	4.6	Hm+Sp	30.0 : 70.0	10 <sup>-12.9</sup>		RS+Fe
	10 <sup>-4.04</sup>	13.4	Sp		10 <sup>-0.68</sup>	0.2	Sp+RS
	10 <sup>-7.81</sup>	14.5	Sp		10 <sup>-4.04</sup>	1.6	Sp+RS
	10 <sup>-8.34</sup>	17.4	Sp+RS		10 <sup>-5.89</sup>	4.7	
	10 <sup>-8.88</sup>	27.0			10 <sup>-6.82</sup>	8.8	Sp+RS
	10 <sup>-9.10</sup>	39.7			10 <sup>-7.80</sup>	17.8	Sp+RS***
	10 <sup>-9.42</sup>	51.8	Sp+RS***		10 <sup>-8.89</sup>	23.5	
	10 <sup>-10.0</sup>	57.7	Sp+RS***		10 <sup>-10.0</sup>	27.5	RS
	10 <sup>-11.0</sup>	66.8	RS		10 <sup>-12.0</sup>	29.7	
	10 <sup>-12.5</sup>	75.1	RS		10 <sup>-12.5</sup>	29.3	
	10 <sup>-12.6</sup>		RS+Fe		10 <sup>-12.7</sup>	29.3	
					10 <sup>-12.9</sup>	29.7	
66.3 : 33.7	10 <sup>-0.68</sup>	0.4	Sp	20.7 : 79.3	10 <sup>-13.0</sup>	29.7	RS
	10 <sup>-4.04</sup>	1.5			10 <sup>-13.1</sup>		RS+Fe
	10 <sup>-7.65</sup>	12.6	Sp+RS		10 <sup>-0.68</sup>	0.2	Sp+RS
	10 <sup>-8.75</sup>	32.7	Sp+RS		10 <sup>-4.04</sup>	1.3	Sp+RS
	10 <sup>-8.90</sup>	39.9	Sp+RS		10 <sup>-5.89</sup>	5.2	
	10 <sup>-9.00</sup>	41.4			10 <sup>-6.82</sup>	8.7	Sp+RS
	10 <sup>-9.95</sup>	49.2			10 <sup>-7.81</sup>	14.1	
	10 <sup>-10.45</sup>	53.5			10 <sup>-8.87</sup>	17.3	
	10 <sup>-10.97</sup>	57.5	RS		10 <sup>-10.0</sup>	19.4	
	10 <sup>-11.98</sup>	62.4	RS		10 <sup>-11.0</sup>	20.1	RS
	10 <sup>-12.47</sup>	63.8	RS		10 <sup>-12.0</sup>	20.4	
	10 <sup>-12.62</sup>		RS+Fe		10 <sup>-13.0</sup>	20.6	
52.8 : 47.2	10 <sup>-0.68</sup>	0.3	Sp+RS		10 <sup>-13.2</sup>	20.6	
	10 <sup>-4.04</sup>	1.6			10 <sup>-13.5</sup>		RS+Fe
	10 <sup>-5.89</sup>	5.4	Sp+RS				
	10 <sup>-6.82</sup>	9.2					

\* FeO mol. % was calculated on the basis of FeO+FeO<sub>3/2</sub>+MgO=100.

\*\* Abbreviations used have the following meaning: Hm=hematite, Sp=oxide with spinel structure, RS=oxide with NaCl structure, and Fe=metallic iron.

\*\*\* The phases at 1160°C could not be quenched.

stable coexistence of wüstite and metallic iron. These assignments are generally consistent with the Gibbs' Phase Rule. Figure 3 (a-e) was constructed on the basis of the treatment described above, but with different ratios of iron/magnesium in the starting materials. Figure 1 shows the phase boundaries over the whole system of FeO-Fe<sub>2</sub>O<sub>3</sub>-MgO based on the results obtained from Fig. 2 and Fig. 3. The isobaric lines are also given by the broken lines Fig. 1. Each isobaric line is uniquely bent on the phase boundary curve.

The compositions of the spinel solid solution are generally represented by the formula (Fe, Mg)<sub>3</sub>O<sub>4</sub>. However, the solid solubility of the

iron(III) oxide component into spinel extends pretty widely, as is approximately shown by the heavy broken line in Fig. 1. In addition, this solid solution seems to be stable, with a small deviation in the oxygen-to-cation ratio below the stoichiometric 4:3 value and with, at least, a 1 mole per cent of excess FeO. Table II shows the chemical composition of spinel with excess FeO at various oxygen partial pressures and at 1160°C. The lattice parameters of these metal-rich spinels were almost identical;  $a_0 = 8.398 \pm 0.003$  Å. The lattice parameter of the stoichiometric spinel solid solution was also measured, but the difference was very small, ranging from 8.396 Å

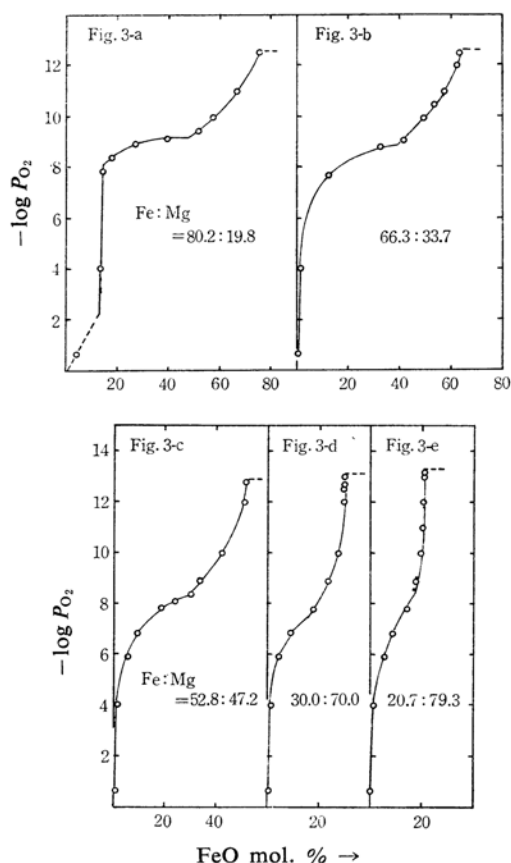


Fig. 3. The relationship between the oxygen partial pressure and the mole fraction of FeO produced in starting materials with different ratios of Fe/Mg.

TABLE II. CHEMICAL COMPOSITION OF METAL-RICH OXIDES WITH SPINEL STRUCTURE

Mg Mg+Fe	FeO, mol. %*	Metal Oxygen	P <sub>O<sub>2</sub></sub> (atm)
0.307	3.7	3.012 : 4	10 <sup>-4.04</sup>
0.202	13.7	3.006 : 4	10 <sup>-7.58</sup>
0.120	22.6	3.014 : 4	10 <sup>-8.90</sup>

\* FeO has the same meaning as in Table I.

of Fe<sub>3</sub>O<sub>4</sub> to 8.399 Å of MgFe<sub>2</sub>O<sub>4</sub>.

The wüstite phase is characterized by wide variations in the iron/oxygen ratios; a continuous areal solid solution (magnesiowüstite) with sodium chloride structure is seen in Fig. 1. The present results sustain the observations of Brynstad and Flood<sup>5)</sup> that the magnesiowüstite field in the FeO-Fe<sub>2</sub>O<sub>3</sub>-MgO ternary system has an extensive range of stable existence at 1400°C and at various oxygen pressures ranging from 10<sup>-3.1</sup> atm. to 10<sup>-7.46</sup> atm. Figure 4 shows the relationship between the mole fraction of MgO and the ratio of Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) within the field of magnesiowüstite. It may be seen

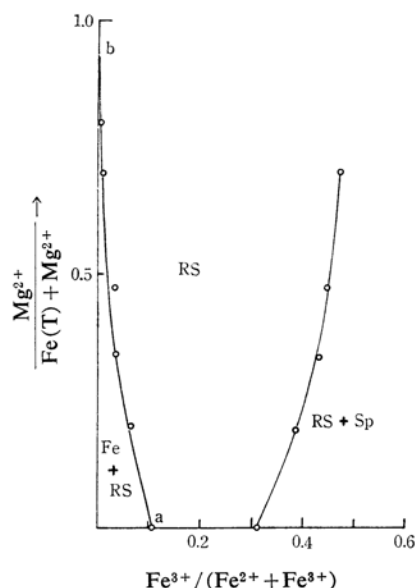


Fig. 4. The relationship between mole fraction of Mg<sup>2+</sup> and the ratio of Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) within the field of magnesiowüstite. The curve a—b is the equilibrium boundary between magnesiowüstite and metallic iron + magnesiowüstite.

from Fig. 4 that the amount of Fe<sup>2+</sup> increases with an increase in the amount of magnesium on the equilibrium boundary between magnesiowüstite and metallic iron + magnesiowüstite (a—b in Fig. 4); the ratio of Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) becomes nearly zero when the Mg<sup>2+</sup>/(Fe<sub>total</sub> + Mg<sup>2+</sup>) ratio exceeds 0.7, while, as has been established by Darken and Gurry,<sup>1)</sup> wüstite is unstable when the Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio becomes smaller than 0.10 (0.106 in the present study) at 1160°C.

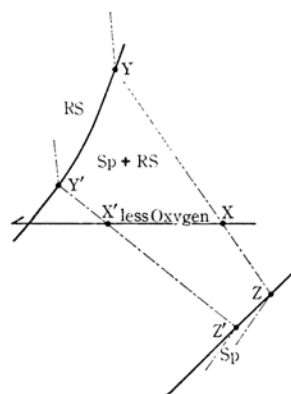
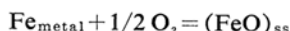


Fig. 5. A distorted diagram illustrating the equilibrated compositions within the field of spinel + magnesiowüstite. Heavy lines are the boundary curves. Light dash-hot lines are isobaric lines.

The area between the field of the magnesio-wüstite solid solution and that of the magnetite-magnesioferrite solid solution is for the two phases. A mixed oxide with composition within this area, say X, consists of an extremely reduced spinel, lettered Z and an extremely oxidized magnesio-wüstite, lettered Y as in Fig. 5.

The left side of the area of magnesio-wüstite is for the two phases comprising metallic iron and magnesio-wüstite. The metallic iron in equilibrium with magnesio-wüstite within the range of oxygen pressures used in the present investigation is assumed to be pure because of the great stability of MgO. Therefore, consider the reaction:



where  $(\text{FeO})_{\text{ss}}$  means the molality in the solid solution considered. The equilibrium constant  $K$  is, therefore, expressed by:

$$K = a_{\text{FeO}}/a_{\text{Fe}} \cdot (P_{\text{O}_2})^{1/2} = a_{\text{FeO}}/(P_{\text{O}_2})^{1/2}$$

where  $a$  means activity. When we assume that Raoult's law is applicable in the vicinity of  $N_{\text{FeO}} \cong 1$ , we have

$$K = N_{\text{FeO}}/P_{\text{O}_2}^{1/2}$$

where  $N$  indicates the mole fraction.

According to the present study the maximum value of  $N_{\text{FeO}}$  in pure wüstite was 0.894 at 1160°C (see Fig. 2) and  $\log P_{\text{O}_2}$  was -12.40, while the interpolated values based on the results of Darken and Gurry<sup>17</sup> were 0.903 and -12.48 respectively. From the present values, we get:

$$\log K = 6.15$$

and

$$\log N_{\text{FeO}} = 1/2 \log P_{\text{O}_2} + 6.15$$

The calculated values of  $N_{\text{FeO}}$  in magnesio-wüstite in equilibrium with metallic iron are plotted against  $-\log P_{\text{O}_2}$  in Fig. 6 on the basis of the present study. The dotted line shows the experimental values in order to facilitate comparison with the calculated values. It is clear from Fig. 6 that a solid solution with more than 30 mole per cent of magnesium oxide deviates significantly from ideality. On the other hand, the calculated values agree rather well with the experimental values in the oxide solid solution with less than 30 mole per cent of magnesium oxide. This means that the assumption of Raoult's law may be correct near the composition  $N_{\text{FeO}} \cong 1$ . On the basis of this assumption, we can calculate the standard free energy of the formation of the stoichiometric ferrous iron oxide,  $\text{FeO}_{1.000}$ , which has never been synthesized in the standard state:

$$\Delta F^\circ_{1160^\circ\text{C}} = -RT \ln K = -40.3 \text{ kcal./mol.}$$

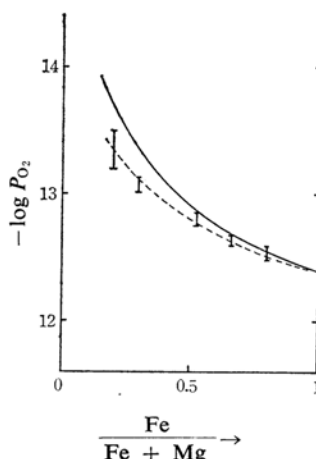
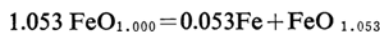


Fig. 6. The deviation from the Raoult's law in magnesio-wüstite solid solution in equilibrium with metallic iron. Solid line is for calculated values, and dashed line is for observed with the width of experimental error.

When we compare this with the standard free energy of the formation of the most reduced and the actual wüstite,  $\text{FeO}_{1.053}$  ( $N_{\text{FeO}} = 0.894$ ), we recognize that the stoichiometric compound,  $\text{FeO}_{1.000}$ , is unstable by +0.4 kcal. based on the following calculations: we calculate the free energy change on the reaction,



to be

$$\Delta F^\circ = 1.053 \times (-40.7) - 1.053 \times (-40.3), \text{ (cal.)}$$

Here, the standard free energy of the formation of  $\text{FeO}_{1.053}$  is equal to  $1.053 RT \ln P_{\text{O}_2}$  where  $P_{\text{O}_2}$  is  $10^{-12.40}$  atm.

Hahn and Muan<sup>16)</sup> studied the activity of wüstite "FeO" in "FeO"-MgO solid solution in the temperature interval from 1100 to 1300°C by equilibrating oxide samples with pure metallic iron in atmospheres of known oxygen partial pressures. In their study, the component iron(III) oxide in the solid solution was neglected; they pointed out that the system shows a considerable positive deviation from Raoult's law. However, when we discuss the deviation from ideality, we must not neglect the actual component iron(III) oxide in magnesio-wüstite; that is to say, we have to plot the values of  $a_{\text{FeO}}$  against the actual values of  $N_{\text{FeO}}$  instead of  $(1 - N_{\text{MgO}})$ , which is equal to the marked "FeO." The results derived from the Gibbs-Duhem equation will, therefore, inform us only about the approximate thermodynamic properties of systems involving an iron(II) oxide component.

16) W. C. Hahn, Jr., and A. Muan, *Trans. AIME*, **224**, 416 (1962).

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