Statistico-Thermodynamical Studies on the Fundamental Reactions concerning Steel-Making. V : The Oxidation and Reduction Equilibrium of Mn-wustite (Fe, Mn) O with Gas Phase

Statistico-Thermodynamical Studies on the Fundamental Reactions concerning Steel-Making. V

The Oxidation and Reduction Equilibrium of Mn-wüstite (Fe, Mn) O with Gas Phase*

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Synopsis

It is known that Mn-wüstite (Fe, Mn) O takes a from of solid solution over all compositions of Fe- and Mn-atoms, and its oxygen content varies with oxygen pressure in the thermal equilibrium and with temperature. So we examined the quantitative relation between the solid and gas phases in the above-mentioned system. Taking into consideration the previous papers in which wüstite and magnetite solid solutions were discussed, a configurational model for the Mn-wüstite was assumed as follows: (1) O^{--} and metal ions are arranged on the lattice of NaCl type, (2) in the negative ion lattice-sites O^{--} ions are perfectly packed, (3) in the positive ion sites Fe^{++}, Mn^{++} and vacancies are randomly distributed, and (4) on some of Fe^{++} ions the electron-defects are trapped, producing Fe^{+++} so that the total electrical charge of crystal is neutralized. Considering such a model, the partition function of Mn-wüstite was formulated on the base of statistical thermodynamics, and the equilibrium relation between the solid composition and oxygen pressure in the gas phase was calculated. The calculated result was in agreement with the experimental values by Matoba and Gunji (1954) and our data obtained by repeated measurements of weight change using a spring balance.

I. Introduction

Previously we reported the theoretical studies of the oxidation and reduction equilibrium of solid solution phases of wüstite[1] and magnetite[2] with gas phases as the fundamentals in the study of Fe-O slag. In these studies it was found that they were composed of definite ionic crystal structure having one vacancy and two electron defects per one O^{--} added by oxidation. On an assumption that these arrangements are special forms not contrary to various physical properties, they were treated statistico-thermodynamically, and the experimental values of equilibrium oxygen pressure could be explained well.

(1) S. Takeuchi and K. Igaki, Sci. Rep. RITU, **A4** (1952), 164.
(2) S. Takeuchi and K. Furukawa, Sci. Rep. RITU, **A12** (1960), 120.

Furthermore, as the extension of the above treatments, we studied the Fe–O molten slag on the basis of quasi-crystal structure model of liquid, assuming that the Fe ions were arranged at the interstices of tetrahedral and octahedral lattices composed of O^{--} ions under some rigorous restriction looser than that for the solid solution. Consequently, it was shown that the oxidation and reduction equilibrium of this system in the range of O atom number/Fe atom number = 1.02~1.38 and oxygen partial pressure 10^{-10}~1 atm can be sufficiently explained[3].

In this report and that follows, studies are made of the systems by adding the tertial elements to Fe–O system. As a first step, the theoretical consideration was applied to the experimental results on the oxidation and reduction equilibrium of solid phase Fe–Mn–O system with CO–CO_2 mixed gas phase, which had been performed by Matoba and Gunji[4]. The experiment included the range of the magnetic (spinel) phase, but in this paper the theoretical treatment was limited to the range of Mn–wüstite solid solution. In the cases of the actual iron-making and steel-making reactions, the vicinity of the region in which the molten phase of this solid solution was in equilibrium with the metallic phase was most important.

II. The structure of Mn-wüstite

First, we wish to consider the structure of the phase containing only divalent Fe and Mn ions. Both wüstite (FeO) and (MnO) are NaCl–type ionic crystals having O^{--} ions and divalent metallic cations. Furthermore, the ionic radii of both cations are $Fe^{++} = 0.75$Å and $Mn^{++} = 0.80$Å respectively so that these compounds are completely solid-soluble with one another. According to a report[5] of a X-ray investigation with the specimen prepared by quenching the equilibrium oxide phase with metallic iron at 1000°C, FeO and MnO form an all-proportion solid-solution of which the lattice constants change linearly by Vegard's rule from 4.295Å (FeO) to 4.438Å (MnO).

Next we must consider the change in an oxide solid solution made by oxidation. Perhaps O^{--} ion which increases by oxidation may not enter the lattice interstice, and on the contrary, the metallic ion lattice point may become vacant. The direct proof of this hypothesis is not found yet, but as mentioned in the second report[1], this hypothesis is confirmed in Fe–wüstite. Therefore, it may be correct also in Mn–wüstite.

Another point in this investigation is whether both Fe and Mn ions are oxidized together or not. Of course, Fe^{+++} ion is produced. In the case of pure Mn oxide it is deduced from the theoretical data that CO_2 content in CO–CO_2 equilibrium gas mixture is required to be about 100 per cent in order to make Mn_3O_4, Mn_2O_3 and MnO_2 from MnO. The ionization potential values of gaseous atoms are Fe^{++}

(3) S. Takeuchi and K. Furukawa, "Internat. Sympo. on the Phys. Chem. of Process Metal-lurgy" April 1959, Pittsburgh. Sci. Rep, RITU **A12** (1960), 137.

(4) S. Matoba and K. Gunji, Bull. Res. Inst. Min. Dress. and Metallur. Tohoku Univ., **10** (1954), 133 (in Japanese).

(5) Vincenzo Montoro, Gazz. Chim. Italiana, **70** (1940), 150 ; see also P.K. Foster and A.J.E. Welch, Trans. Far. Soc., **52** (1956), 1626.

$\rightarrow Fe^{+++}$: 31.69 eV, $Mn^{++} \rightarrow Mn^{+++}$: 33.97 eV respectively : the differance between Fe^{++} and Mn^{++} is about 50K cal/mole. Therefore, Mn^{++} may be rather difficult to ionize than Fe^{++} even in the solid phase. It was reported previously[4] that the presence of Mn^{+++} could not be observed by current analytico-chemical technique, but that whether Mn^{+++} ion was present in Mn-wüstite or not must be examined directly by means of optical or magneto-chemical measurements, etc. However, the following hypothesis is tentatively established : "The concentration of Mn^{+++} can be neglected in Mn-wüstite solid solution". This hypothesis may be supported for correctness by a comparatively good agreement between the calculated results in this paper and the experimental values.

The ionic radius of oxidized Fe^{+++} ion is 0.60Å, so it would be placed in the positive-ion lattice point mentioned above.

Furthermore, in the range of oxygen content discussed in this paper, non-existence of magnetite phase was recognized by means of X-ray diffraction analysis.

As the result of the above consideration, a configurational model of Mn-wüstite solid solution was postulated as follows :

(i)   It has a sodium-chloride-type ionic crystal structure.

(ii)   All negative-ion lattice points are occupied by O^{--} ions.

(iii)   In the positive-ion lattice points Fe^{++}, Mn^{++} ions and lattice vacancies are distributed at random statistically.

(iv)   Electron defects are distributed at random on the Fe^{++} ions, and then the cations become Fe^{+++} ions so that the electrical neutrality is maintained over all compositions of solid solution.

III. Statistico-thermodynamical calculation of the equilibrium oxygen pressure

The calculation will be discussed according to the consideration in Section II. First the stoichiometric compound $Fe^{++}_1 Mn_y^{++} O^{--}_{(1+y)}$ in solid state must be investigated, in which N_o ions of oxygen are arranged on the face-centered cubic sites and N_f ions of Fe and N_m ions of Mn occupy the octahedral lattice interstices of the oxygen lattice at random, and therefore their partition functions can be written as follows :

$$K^0(T, f) = \frac{N_o!}{N_f! \, N_m!} \cdot \{K_f(T)\}^{N_f} \cdot \{K_m(T)\}^{N_m} \cdot \{K_o(T)\}^{N_0} \cdot$$

$$\times \exp\{-W(f)/kT\} \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

$$f = N_f/(N_f + N_m) \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

where $W(f)$ is the lattice energy, K_f, K_m and K_o are partition functions per Fe^{++}, Mn^{++} and O^{--} ions respectively and the functions of temperature T. And K^0 is the function of T and the composition f.

Next, when the standard compound is oxidized, holes are produced in the positive-ion lattice as the number of oxygen atoms increases by oxidation. If this number is N_h, $2N_h$ electron defects are produced for holding electrical neutrarity, which play a role in changing Fe^{++} ions to Fe^{+++} ions. As they are distributed randomly, the distinguishable number of configuration regarding the lattice vacancies is

$$\frac{(N_f + N_m + N_h)!}{(N_f + N_m)! \, N_h!} \quad \cdots\cdots (3)$$

and for the distribution of electron defects

$$\frac{N_f!}{(2N_h)! \, (N_f - 2N_h)!} \quad \cdots\cdots (4)$$

The energy change $\Delta W(f)$ in this reaction can be written as follows:

$$\Delta W(f) = N_h \cdot E(f) = N_h \cdot [\varsigma(f) - \xi(f)], \quad \cdots\cdots (5)$$

where $\varsigma(f)$ is the energy which take off a neutral Fe atom out of crystal leaving one lattice vacancy and two electron defects in the inner Fe lattice points, and $\xi(f)$ is the energy which adds one FeO molecule to the lattice surface by allowing a Fe atom to react with a gaseous oxygen molecule.

From the above equations the partition function of this solid solution is written as follows:

$$\Gamma_s = K^0\,(T, f) \cdot \left(\frac{\kappa_{\#}}{\kappa_f}\right)^{2N_h} \cdot \left(\kappa_o\right)^{N_h} \cdot \frac{(N_f + N_m + N_h)!}{(N_f + N_h)! \, N_h!} \cdot$$

$$\times \frac{N_f!}{(2N_h)! \, (N_f - 2N_h)!} \times \exp\{-N_h \cdot E(f)/kT\}, \quad \cdots\cdots (6)$$

where $\kappa_{\#}$ is the partition function per Fe^{+++} ion. Therefore, the free energy is

$$F_s = -kT \cdot \ln \Gamma_s\,(T, f). \quad \cdots\cdots (6)'$$

If the free energy of gaseous oxygen is F_g, the equilibrium condition between gas and solid phases is

$$\delta F_g + \delta F_s = 0, \quad \cdots\cdots (7)$$

in which as variable parameters the number of gaseous oxygen molecules n_{O_2} and N_h should be taken so that (7) may be

$$\frac{\partial F_g}{\partial n_{O_2}} \cdot \delta n_{O_2} + \frac{\partial F_s}{\partial N_h} \cdot \delta N_h = 0. \quad \cdots\cdots (7)'$$

Since the numbers of total atoms of oxygen, Fe and Mn in the total system are constant,

$$\begin{cases} 2n_{O_2} + N_h + N_f + N_m = \text{const.} \\ N_f = \text{const.} \\ N_m = \text{const.} \end{cases}$$

$$\therefore \quad 2\delta n_{O_2} + \delta N_h = 0. \quad \cdots\cdots (8)$$

Therefore (7) is

$$\frac{\partial F_s}{\partial N_h} - \frac{1}{2} \frac{\partial F_g}{\partial n_{O_2}} = 0. \tag{9}$$

Substituting (1), (6) and (6)' in this equation and solving it by means of Stirling's formula, the value of absolute activity of oxygen λ_{O_2} is

$$[\lambda_{O_2}]^{1/2} = \exp\left(\frac{1}{2} \frac{1}{kT} \cdot \frac{\partial F_g}{\partial n_{O_2}}\right) = \left(\frac{\kappa_f{}^2}{\kappa_o \cdot \kappa^2_{\#}}\right) \cdot$$

$$\times \frac{4(N_h)^3}{(N_f + N_m + N_h) \cdot (N_f - 2N_h)^2} \cdot \exp\left(\frac{E(f)}{kT}\right) + [\lambda_{O_2}(T, f)]_0{}^{1/2}. \tag{10}$$

where the term $[\lambda_{O_2}(T,f)]_0$ is the absolute activity of oxygen to the standard state $[Fe_f{}^{++} Mn^{++}{}_{1-f}O^{--}]$ and is introduced as the correction term since our treatment is concerned only with the deviations from the standard state.

As the experimental value for comparison is that of CO–CO_2 mixed gas phase, λ_{O_2} is obtained from the equilibrium condition $CO_2 \rightleftarrows CO + 1/2O_2$ as follows;

$$[\lambda_{O_2}]^{1/2} = \frac{[\lambda_{CO_2}]}{[\lambda_{CO}]} = \frac{n_{CO_2}}{n_{CO}} \cdot \frac{f_{CO}}{f_{CO_2}} \cdot \frac{\exp(-\chi_{CO}/kT)}{\exp(-\chi_{CO_2}/kT)}, \tag{11}$$

where n_{CO_2} and n_{CO} are molecular numbers of CO_2 and CO respectively, and f_{CO_2} and f_{CO} are partition functions per molecule which can be calculated as follows:

$$\frac{f_{CO_2}}{f_{OC}} = \left(\frac{m_{CO_2}}{m_{CO}}\right)^{3/2} \cdot \frac{I_{CO_2}}{I_{CO}} \cdot \frac{\{1 - \exp(-\theta/T)\}_{CO}}{\prod_i \{1 - \exp(-\theta_i/T)\}_{CO_2}} \cdot \frac{\varepsilon_{CO_2}}{\varepsilon_{CO}} \cdot \frac{\rho_o}{2} \tag{12}$$

where m_{CO_2}, m_{CO}; I_{CO_2}, I_{CO} and ε_{CO_2}, ε_{CO} are the mass, the moment of inertia of rotation and the partition function concerning the electronic states of CO_2 and CO molecules respectively. ε is the weight value at the lowest electronic state, since it does not excite in the range of temperarures considered. θ is the characteristic temperature of oscillation of each molecule and ρ_0 is the weight value of nuclear spin of oxygen atom.

To the right side of equation (11), the following substitution is applied:

$$\frac{N_h}{N_f + N_m + N_h} = \frac{N_h}{N_o} = x, \qquad \frac{N_f}{N_f + N_m} = f. \tag{13}$$

Then the equation (11) is simplified as follows:

$$\frac{n_{CO_2}}{n_{CO}} = \frac{x^3}{\{f(1-x) - 2x\}^2} \cdot \alpha(T,f) + \beta(T,f), \tag{14}$$

$$\alpha(T,f) = 4 \frac{f_{CO_2}}{f_{CO}} \cdot \frac{\kappa_f{}^2}{\kappa_{\#}{}^2 \cdot \kappa_o} \cdot \exp\left[\frac{\{E(f) + (\chi_{CO} - \chi_{CO_2})\}}{kT}\right] \tag{15}$$

$$\beta(T,f) = \frac{f_{CO_2}}{f_{CO}} \cdot \exp[(\chi_{CO} - \chi_{CO_2})/kT] \cdot [\lambda_{O_2}(T,f)]_0{}^{1/2} \tag{16}$$

As $\frac{n_{CO_2}}{n_{CO}} = \frac{P_{CO_2}}{P_{CO}}$, and the coefficient of α is the function of concentration alone, the relationship among the equilibrium pressure, the concentration and the temperature can be calculated from this equation (14).

IV. Comparipon with experimental values

As mentioned in the introduction, the experimental values obtained by Matoba and one of the authors (Gunji)[4] were used, together with Sanbongi's values[6] for the pure Fe–O system as limited values.

In comparing the (14) with the experimental values, the value of $\beta(T, f)$ should be determined first. Now in comparing with the equation (11), $[\lambda_{O_2}]_0$ is expressed as follows:

$$[\lambda_{O_2}]_0^{1/2} = \left[\frac{n_{CO_2}}{n_{CO}}\right]_0 \cdot \frac{f_{CO}}{f_{CO_2}} \cdot \frac{\exp(-\chi_{CO}/kT)}{\exp(-\chi_{CO_2}/kT)},$$

and combining it with (16), we have

$$\beta(T, f) = \left[\frac{n_{CO_2}}{n_{CO}}\right]_0 = \left[\frac{P_{CO_2}}{P_{CO}}\right]_0.$$

Therefore, β is approximated by the value P_{CO_2}/P_{CO} of gas which is in equilibrium with the two solid phases of Mn–wüstite and metal. However, the experimental values contain serious errors so that the most probable values can be obtained as follows: Only Fe ions are connected with the oxidation and reduction equilibrium, of which the chemical equation is

$$FeO + CO \rightleftarrows Fe + CO_2. \tag{17}$$

And the equilibrium constant of this reaction K is

$$K = \frac{P_{CO_2}}{P_{CO}} \cdot \frac{a_{Fe}}{a_{FeO}}$$

where a_{Fe}, the activity of Fe, should be 1, since no Mn exists in the metallic phase; and a_{FeO}, the activity of FeO, can be substituted by f, because in the system of standard state FeO and MnO constitute the ideal solid solution, as shown in equation (1) . Therefore, considering $F = -RT\ln K$, the equation of the following type is obtained:

$$-\ln\left\{\frac{P_{CO_2}}{P_{CO}} \Big/ f\right\} = \Delta F/RT = -\frac{A}{RT} + B. \tag{18}$$

By using the experimental values of P_{CO_2}/P_{CO} which are obtained by the extrapolation of the number of Fe^{+++} ion to zero conposition, the experimental formula of the equation (18) will be as follows:

$$\log_{10}\beta = \log_{10}f + \frac{965}{T} - 1.143 \tag{18)'}$$

or

$$-\ln(\beta/f) = (-4450 + 5.27T)/RT \tag{18)''}$$

The comparison with the experimental values is shown in Fig. 1. The free energy change ΔF with regard to the equation (17) has been found[7] to be

(6) K. Sanbongi, Sci. Rep. RITU, A1 (1949), 213.

(7) See : F.D. Richardson and J.H.E. Jeffes, J. Iron and Steel Inst., 160(1948), 261.

$(-5500 \; +5.80T)$, and this value shows a good agreement with $(18)''$.

Equation (14) can be deformed to

$$\log\left(\frac{P_{CO_2}}{P_{CO}} - \beta\right) = \log\frac{x^3}{\{f(1-x)-2x\}^2} + \log\alpha \tag{19}$$

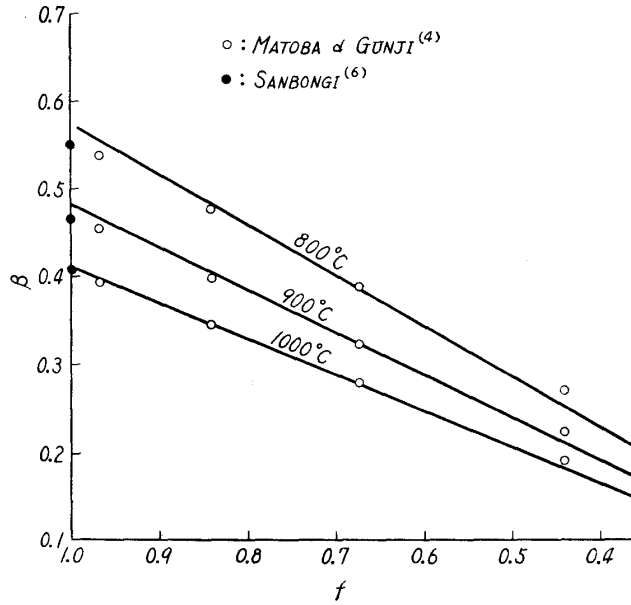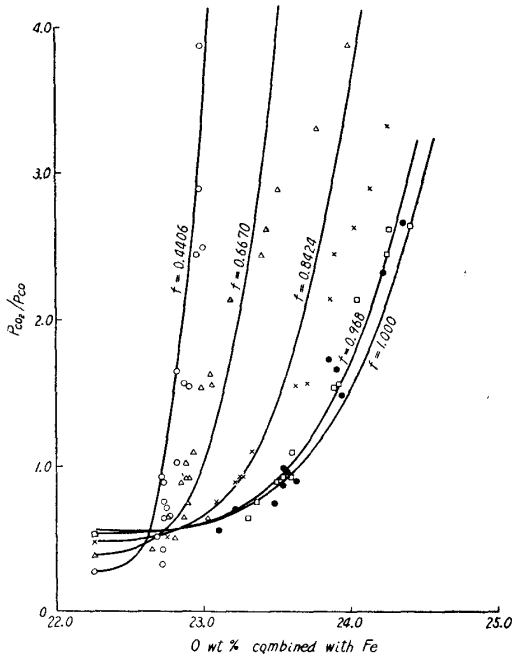Fig. 1. The relations between β and $f = \dfrac{N_f}{N_f + N_m}$

Fig. 2. Relations between P_{CO_2}/P_{CO} and oxygen % combined with iron in the solid solution at 800°C.

Fe–Mn–O $f=1.000$ ● Sanbongi[6]
           $=0.968$ □⎫
           $=0.8424$ × ⎪Matoba
           $=0.6670$ △⎪ and Gunji[4]
           $=0.4406$ ○⎭
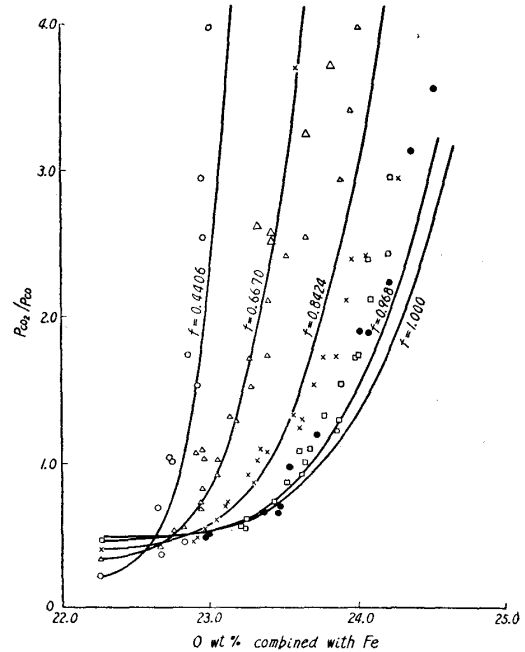   —— calculated values

Fig. 3. Relations between $/P_{CO_2}$ P_{CO} and oxygen % combined with iron in the solid solution at 900°C.

Fe–Mn–O

     large △ $(f = 0.6670)$
     Reexamined values

So by using the above β values and comparing with the experimental values directly, $\log \alpha$ can be obtained. As shown in the equation (15), however, the factors known numerical values like f_{CO_2}/f_{CO} and $(\chi_{CO} - \chi_{CO_2})$ are included in α, so these terms are subtracted from α. Then

$$\left(\frac{\kappa_f}{\kappa_{\#}}\right)^2 \cdot \frac{1}{\kappa_o} \cdot \exp\left(\frac{E(f)}{kT}\right) = \exp\left\{\frac{1}{RT}(-102830 - 18640 f)\right\}, \qquad (20)$$

and α can be determined.

The calculated curves of the equation (14) or (19) obtained by using the above estimated values are illustrated by the curves in Fig. 2 (800°C), Fig. 3 (900°C) and Fig. 4 (1000°C). The experimental values fluctuate, but seem to coincide with one another fairly well. This problem will be discussed in the next section.

V. Discussion

As shown in Figs. 2 to 4, the fluctuation of experimental values is so marked that six points of re-experiment were performed at 1000°C and five at 900°C. The results obtained show comparatively good agreements with the calculated curve. However, a simple curve tends not to show itself in the medium range of f values. In order to re-examine with the conventional experimental procedure, an experiment

Fig. 4. Relations between P_{CO_2}/P_{CO} and oxygen % combined with iron in the solid solution at 1000°C

Fe-Mn-O

large $\begin{cases} \square\, f = 0.968 \\ \triangle\, f = 0.6670 \\ \bigcirc\, f = 0.4406 \end{cases}$ Reexamined values

was carried out on the system of $f = 0.6670$ at 900°C. The results obtained are shown in Fig. 3. These values approach the calculated curve, which supports the correctness of our hypothesis. Therefore, it may be considered that there were some unsatisfactory conditions in the conventional experimental procedure during rapid cooling operation.

After the above work had been presented at the meeting of the Japan Institute of Metals (October 1955), the study on MnO–FeO solid solution which was in equilibrium with the Fe–Mn alloy phase and CO–CO$_2$ gas mixture was reported[8]. Acording to this study, the activity coefficients of MnO and FeO are both 1.00 ±0.07. Therefore, this solid solution cad be cosidered as an ideal solution, which fact accords with the characteristic of standard state in our calculation [see the equation (1)]. If the values of β used in our calculation are compared with their
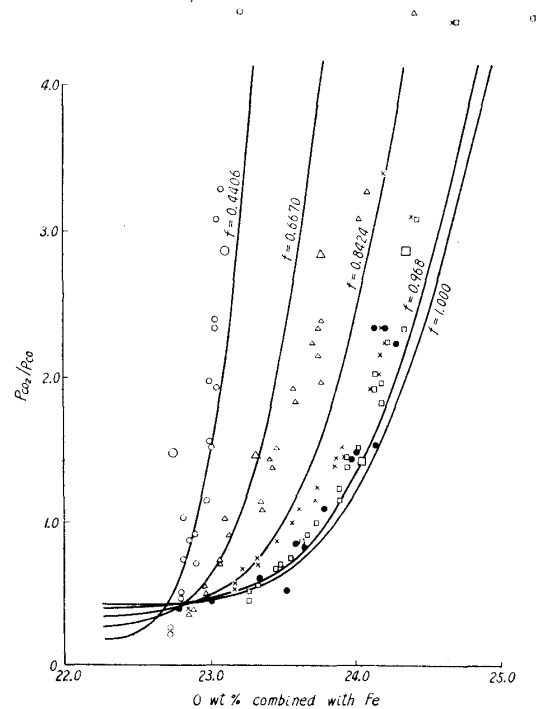
(8) P.K. Foster and A.J.E. Welch, Trans. Faraday Soc., 52 (1956), 1626, 1636.

experimental values, a very good agreement can be obtained, as shown in Table 1.

Table 1.   The values of P_{CO_2}/P_{CO} in equilibrium with Mn-wüstite
and metallic phase at 1000°C.

f	P_{CO_2}/P_{CO} (Matoba, Gunji)[4]	P_{CO_2}/P_{CO} (Foster, Welch)[8]	β (This paper)
0.968	0.394	0.389	0.399
0.8424	0.349	0.347	0.345
0.6670	0.278	0.276	0.278
0.4406	0.190	0.195	0.181

Summary

It is known that MnO and FeO form all proportional solid solution, and according to the partial oxygen pressure of equilibrium gas phase, they have some solubility of oxygen at high temperature. In order to explain this fact, the following mechanism was considered. Fe atoms move out to the surface, leaving vacancies at the positive ion lattice sites of FeO-MnO solid solution which forms NaCl-type ionic crystal structure and makes new lattice by combining oxygen gas phase, and two electron defects produced by this process change other Fe^{++} ions to three valency Fe^{+++}. It is considered that these defects are distributed statistically on the positive ion lattice-sites. The relationship among composition of the solid solution, temperature and equilibrium pressure in gas phase can be deduced by treating this mechanism statistico-thermodynamically. A comparatively good agreement is shown in the experimental values of $N_f/(N_f+N_m)$ in the range of 1.0 and 0.44 at 800°, 900° and 1000°C, including reexperimented values reported in this paper.

In the case of Mn-wüstite system, the mechanism is simple since it is sufficient to treat the case where two valency Mn ions alone are to be considered. Further investigation on the more general systems must be made, which will be given in the reports to follow.

Acknowledgment