Mathematical Expression of Phosphorus Distribution in Steelmaking Process by Quadratic Formalism

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Phosphorus distribution between slag and liquid iron has been studied at the temperature range from 1 573 to 1 953 K. The slag system of FeO·P2O5·CaO·MgO·SiO2 ternary, and of FeO·P2O5·CaO·MgO·SiO2 quaternary was studied to clarify the effect of oxides on the phosphorus distribution equilibrium at steelmaking process.

In view of ionic theory, the approximate validity of regular solution model was examined to formulate the equilibrium reaction of phosphorus distribution between slag and metal. As the result, it was confirmed that the regular solution model was satisfied for all the experimental results including the present work and the previous studies by other investigators, except for extremely high iron oxide region. The phosphorus and oxygen contents in liquid iron in equilibrium with slag can be estimated within the accuracy of ±10 % by the quadratic formalism derived from an assumption of the regular solution of slag.

KEY WORDS: thermochemistry; steelmaking reaction; oxygen distribution; phosphorus distribution; quadratic formalism; steelmaking slag; activity; regular solution model; mathematical modeling.

1. Introduction

Numerous laboratory studies1-10) have been made concerning the equilibrium of phosphorus distribution between slag and metal at steelmaking process, but the physico-chemical treatment of their results was very different by the investigators. Many attempts1,2,5-11) were made in the past to predict the phosphorus content in iron in slag-melt equilibrium by means of theoretical or empirical slag model. Some of the models were successful to evaluate the phosphorus distribution ratio over a restricted range of slag composition, but the same model was inadequate for the data from other sources when the composition range of slag was changed. This is probably due to the fact that the slag model proposed is not enough to evaluate the interaction between the oxides in slag and the activities of slag constituents.

In the present work, the approximate validity of the regular solution model for slag was studied to formulate the equilibrium relation of phosphorus distribution for all the experimental results including the present work and the previous studies by other investigators, in succession to the successful application of the model for the oxygen distribution in steelmaking process.

For this purpose, the phosphorus distribution between slag and liquid iron has been studied at the temperatures from 1 573 to 1 953 K. The slag system studied at present work were of FeO·P2O5·CaO saturated with CaO, FeO·P2O5·MgO saturated with (Mg,Fe)O, FeO·P2O5·SiO2 saturated with SiO2, FeO·P2O5·SiO2·CaO saturated with 2CaO·SiO2 and FeO·P2O5·CaO·MgO saturated with (Mg,Fe)O to know the effect of oxides on the phosphorus distribution.

The previous data used to check the applicability of the model were the experimental results of the slag saturated with CaO by Fischer and Ende,12) Peter et al.,13) Knüppel et al.,14) and Trömel and Fritze,15) those saturated with (Mg,Fe)O by Winkler and Chipman,16) Trömel and Schwerdtfeger17) and Suito et al.,18) those saturated with SiO2 by Trömel and Schwerdtfeger,19) those saturated with 2(Ca,Mg)O·SiO2 by Balajiva et al.,20) and those by the levitation melting of Shirota et al.21)}
from a reaction chamber, and then was quenched into water bath to solidify the liquid iron as quickly as possible. After that, the crucible was immediately moved to a chamber of He atmosphere to be cooled to room temperature. The slag and metal in the quenched crucible were separated by crushing. The contents of ferrous iron, total iron and the other kinds of oxides were determined by chemical analysis. The time to approach to equilibrium is influenced by the rate of solution of crucible material into liquid slag, and the equilibrium time was about 9×10^4 s in case of CaO crucible, 3.6×10^4 s in case of SiO_2 crucible, and 1.44×10^4 s in case of MgO crucible.

The MgO crucible was bought from market, and the SiO_2 crucible was made from pure silica glass tube. The CaO crucible was fabricated from the calcined powder of 10% FeO·CaO mixture, by stamping with the binder of linseed oil-kerosene (1: 1) solution, and by firing with CaH_2·O_2 flame at 1973 K. According to the recent phase diagram of CaO·FeO system, the solid CaO makes a solid solution containing about 10% FeO at steelmaking temperature. Therefore, pure wustite powder was added in calcining process to stabilize the solid CaO. The CaO-FeO crucible made by this technique was durable for about 3.6×10^4 s in present work, but was unable to be used in the measurement of very low oxygen potential.

3. Phosphorus Reaction

Since the phosphorus dissolved in liquid iron, [P^0], is oxidized to (P^2+) in the oxidizing process of steelmaking, it has been considered that the reaction product in the dephosphorizing of iron with liquid slag may be phosphorus pentoxide (P_2O_5), tricalcium phosphate (3CaO·P_2O_5) or tetracalcium phosphate (4CaO·P_2O_5) in the molecular theory of slag. On the other hand, it is well-known that the liquid slag is one of the ionic melts, and that the phosphorus in liquid slag exists as the species of phosphate anion (PO_4^3-) containing one atom of phosphorus. Even in the ionic theory of slag, however, an equilibrium constant can not be derived without making some assumption, because of the lack of the enough knowledge concerning the ionic nature of the liquid slag. Moreover, it is theoretically difficult to determine the activities or activity coefficients of ions in the fused salts. Therefore, in the present work, the hypothetical species (PO_4^3-) containing one atom of phosphorus was assumed as the reaction product to represent the dephosphorizing reaction of liquid iron in view of ionic theory. The same idea is also valid in the regular solution model of slag described in the later. The equilibrium relation of phosphorus reaction in the steelmaking process can be written as follows:

\[ P + 2.5\Omega = (PO_4^3-)_{\text{in slag}} \]  

\[ K_{P1} = a_{PO_4}/(a_P·a_0^{2.5}) \]  

In the equilibrium state of the system, the oxygen distribution between slag and liquid iron should also be in equilibrium. The following equilibria are established at the same time.

\[ Fe(l) + \Omega = (Fe\Omega)_{\text{in slag}} \]  

\[ AG^\circ = -123900 + 57990T^{13/2} \]  

\[ P + 2.5(Fe\Omega)_{\text{in slag}} = (PO_4^3-)_{\text{in slag}} + 2.5Fe(l) \]  

\[ K_{P2} = a_{PO_4}/(a_P·a_0^{2.5}) \]  

Therefore, the distribution ratio of phosphorus between slag and liquid iron can be defined as follows;

\[ E_P = (\%)o/[\%P] = 0.44(\%)PO_4/[\%P] = 0.44(\%)P_2O_5/[\%P] \]

Many models have been proposed to express the ionic nature of liquid slag. The regular solution model of slag has proposed by Lumsden in 1961. In present work, an attempt has been made to quantitatively represent the equilibrium relation of phosphorus distribution in steelmaking process as a function of temperature and slag composition by the model, in continuation of our previous studies on the oxygen distribution in steelmaking process. The activity coefficient of a component i in a multicomponent regular solution is expressed by the following equation.

\[ G^i = \Delta H_i = RT \ln \gamma_i = \gamma_i = 1 \]  

When the relation of Eq. (8) is valid to express the activity coefficient of component i in the experiments, the quadratic formalism of Eq. (8) can be applied as an approximate expression of activity coefficient of component i in slag, even if the liquid slag is not real regular solution (\(S_i^f \neq 0\)). This is the similar idea to the quadratic formalism of metallic solution proposed by Darken.

4. Distribution Ratio of Phosphorus

Many of the experiments in the present work were carried out over a wide range of FeO content and at 3 temperatures of 1823, 1873 and 1923 K. The phosphorus distribution ratio is a function of the temperature, oxygen potential of the system and the composition of slag, as seen in Eqs. (1) and (5). The values of the distribution ratio (\(\%P/\%_{O}P\)) obtained at 1873 K were shown as a function of FeO content in Figs. 1 to 3. Fig. 1 shows the results of FeO·P_2O_5·MgO slag system (MgO_s = CaO, MgO, SiO_2) ternary systems saturated with oxide MgO_s, which is the crucible material. The distribution ratio in FeO·P_2O_5·CaO slag were the highest among 3 ternary systems studied, and the maximum value of the distribution ratio was observed at the range of (mass\%FeO) = 10~20. The maximum phosphorus distribution ra-
tios in each slag system were \( L_f \approx 1000 \) in Fe\(_2\)O\(_3\)-P\(_2\)O\(_5\)-CaO slag, \( L_f \approx 10 \) in Fe\(_2\)O\(_3\)-P\(_2\)O\(_5\)-MgO slag, and \( L_f \approx 1 \) in Fe\(_2\)O\(_3\)-P\(_2\)O\(_5\)-SiO\(_2\) slag, respectively. The approximate value of \( L_f \) in Fe\(_2\)O\(_3\)-P\(_2\)O\(_5\) binary slag will be given by extrapolation of \( L_f \)-values in 3 each slag system to 100 mass\% Fe\(_2\)O in Fig. 1. The distribution ratio in Fe\(_2\)O\(_3\)-P\(_2\)O\(_5\) binary slag was estimated to be \( L_f \approx 1 \). The distribution ratio in Fe\(_2\)O\(_3\)-P\(_2\)O\(_5\)-SiO\(_2\)-CaO system saturated with 2CaO-SiO\(_2\) is shown in Fig. 2. This series of the measurement was conducted using solid CaO crucible, but the interface between the solid CaO and the liquid was always covered with 2CaO-SiO\(_2\), as was expected from the phase diagram of CaO-Fe\(_2\)O-SiO\(_2\) system. The distribution ratio in this slag increased with increasing basicity defined with (mass\% CaO)/(mass\% SiO\(_2\)), and an optimum Fe\(_2\)O content, at which the value of \( L_f \) is maximum, was observed at the composition of (mass\% Fe\(_2\)O)\( \approx 20 \). As shown in Fig. 3, the distribution ratio in Fe\(_2\)O-P\(_2\)O\(_5\)-CaO-MgO saturated with (Mg,Fe)O increased from \( L_f \approx 10 \) to \( L_f \approx 1000 \) with increasing CaO content, and it was clear that CaO and MgO were not equivalent for the dephosphorizing of iron in steelmaking process.

From the above experimental results, it will be seen that the ability of oxides increasing the phosphorus distribution ratio increases with the order of SiO\(_2\) \(<\) Fe\(_2\)O \(<\) MgO \(<\) CaO. However, the same property of desulfurizing of iron is the order of CaO \( \approx \) Fe\(_2\)O \( \approx \) MgO \( \approx \) SiO\(_2\).

It was confirmed that the phosphorus distribution ratio decreased with increasing temperature, but the results obtained were omitted from the limited page of the paper.

5. Equilibrium of Oxygen Distribution

In our previous papers,\(^{16,20}\) it was confirmed that the regular solution model of slag was satisfactory for predicting the oxygen content in metal in the equilibrium state of steelmaking process over the wide range of silicate slag composition. To establish the same relation for the dephosphorization in steelmaking process, the validity of the model for phosphate slag should be confirmed, and the interaction energies between cations and phosphorus ion such as \( \alpha(Ca^{2+} - P^{5+}) \), \( \alpha(Mg^{2+} - P^{6+}) \) and \( \alpha(Si^{4+} - P^{5+}) \) should be determined if the model was valid for the data obtained. The experimental results of oxygen distribution equilibrium was applied for this purpose.

The equilibrium relation of FeO-Fe\(_2\)O\(_3\)-P\(_2\)O\(_5\)-CaO
(1-2-4-5 system) slag with oxygen in metal can be written as follows by the model:

$$\text{Fe}(l) + Q = (\text{FeO})_{\text{in slag}}, \quad \text{.........................(3)}$$

$$R T \ln K_a = R T \ln (\text{FeO})_{\text{in slag}} = \frac{R T \ln (\text{FeO})_{\text{in slag}}}{Q}$$

$$R T \ln \gamma_{\text{FeO}} = -18660X_{\text{FeO}} - 31380X_{\text{FeO}_3}$$

$$-31380X_{\text{FeO}_3} + 64680X_{\text{FeO}_5} - X_{\text{FeO}_3}$$

$$+ 45770X_{\text{FeO}_3} - X_{\text{FeO}}$$

$$-62760X_{\text{FeO}_3} - X_{\text{FeO}} = -a_{\text{FeO}}X_{\text{FeO}} - \phi_{\text{FeO}}$$

$$\text{.........................(9)}$$

In the above equation, $a_{\text{FeO}}(\text{Ca}^{2+}-\text{P}^{5+})$ is only an unknown term to be determined at present work, and other terms of interaction energy between cations have been already known$^{20,22-27}$ as listed in Table 1. By the combination of Eqs. (4), (9) and (10), the unknown term is moved to left hand side and the known terms are written to the right hand side, and the following equation can be given.

$$a_{\text{FeO}}(\text{Ca}^{2+}-\text{P}^{5+}) = (1/X_{\text{FeO}_3}) \{ R T \ln (\text{FeO})_{\text{in slag}} - 18660X_{\text{FeO}_3} \}$$

$$- 31380X_{\text{FeO}_3} + 64680X_{\text{FeO}_5} - 45770X_{\text{FeO}_3} - 62760X_{\text{FeO}_3} - X_{\text{FeO}} - 128090 + 57990T$$

$$\text{.................................}(11)$$

If the regular solution model is valid for the data in this slag, the values of $Y_4$ in Eq. (11) should be a linear function of the term of $(X_{\text{FeO}_3}/X_{\text{FeO}_3})$, passing through the origin.

The oxygen distribution ratio, $L_0 = X_{\text{FeO}_3}/[\text{mass} \text{O}]$, obtained in FeO-P2O5-CaO system was shown in Fig. 4, in which the previous data by other investigators$^{21,23}$ were also illustrated. The present results were in good agreement with the data by Peter et al.$^{21}$ Knüppel et al.$^{23}$ and Trömel and Fritre.$^{24}$ and the oxygen distribution ratios obtained by Fischer and Endle$^{25}$ were a little lower than those of others. On the other hand, the phosphorus distribution ratio in the same system obtained at present work agreed well with those by Fischer and Endle$^{25}$ Knüppel et al.$^{23}$ and Trömel and Fritre.$^{24}$ except for those by Peter et al.$^{21}$ as shown in Fig. 1. Therefore, all of the present work, our previous work$^{21,23}$ Knüppel et al.$^{23}$ and Trömel et al.$^{24}$ were applied to check the validity of Eq. (11). The results obtained were shown in Fig. 5. Four sets of data fit to one straight line passing through the origin. The slope of a line is the interaction energy between Ca$^{2+}$ and P$^{5+}$. The following interaction energies between cations were given by the same procedure.

$$a(\text{Ca}^{2+}-\text{P}^{5+}) = -251040$$

$$a(\text{Mg}^{2+}-\text{P}^{5+}) = -37660$$

$$a(\text{Si}^{4+}-\text{P}^{5+}) = +83680$$

From the above results, the activity coefficient of FeO in the FeO-FeO$_2$-P$_2$O$_5$-SiO$_2$-CaO-MgO slag, which are major components in steelmaking, can be written as follows:

$$\text{Fe}(l) + Q = (\text{FeO})_{\text{in slag}} \quad \text{.........................(3)}$$

$$R T \ln K_a = R T \ln (\text{FeO})_{\text{in slag}} = \frac{R T \ln (\text{FeO})_{\text{in slag}}}{Q}$$

$$R T \ln \gamma_{\text{FeO}} = -18660X_{\text{FeO}} - 31380X_{\text{FeO}_3}$$

$$-31380X_{\text{FeO}_3} + 64680X_{\text{FeO}_5} - 45770X_{\text{FeO}_3} - 62760X_{\text{FeO}_3} - X_{\text{FeO}}$$

$$-128090 + 57990T$$

$$\text{.................................}(13)$$

### Table 1. Interaction energies between cations.

<table>
<thead>
<tr>
<th>ion-ion</th>
<th>$a_{ij}(J)$</th>
<th>Ref.</th>
<th>Other investigators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$-Fe$^{3+}$</td>
<td>$-18660$</td>
<td>Lamudden</td>
<td>0 Fujita et al.</td>
</tr>
<tr>
<td>Fe$^{2+}$-Na$^+$</td>
<td>$+19230$</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$-Mg$^{2+}$</td>
<td>$+33470$</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$-Ca$^{2+}$</td>
<td>$-31380$</td>
<td>20</td>
<td>$-48120$ Sommerville et al.</td>
</tr>
<tr>
<td>Fe$^{2+}$-Mn$^{2+}$</td>
<td>$+7110$</td>
<td>26</td>
<td>0 Fujita et al., Bell et al.</td>
</tr>
<tr>
<td>Fe$^{2+}$-Al$^{3+}$</td>
<td>$-37660$</td>
<td>23</td>
<td>$-3350$ Martin et al.</td>
</tr>
<tr>
<td>Fe$^{2+}$-Ti$^{4+}$</td>
<td>$-18480$</td>
<td>23</td>
<td>Sommerville et al.</td>
</tr>
<tr>
<td>Fe$^{2+}$-Si$^{4+}$</td>
<td>$-41840$</td>
<td>23</td>
<td>$-28030$ Fujita et al.</td>
</tr>
<tr>
<td>Fe$^{3+}$-P$^{5+}$</td>
<td>$-31380$</td>
<td>22</td>
<td>$-2760$ Fujita et al.</td>
</tr>
<tr>
<td>Na$^{+}$-Si$^{4+}$</td>
<td>$-74890$</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Na$^{+}$-P$^{5+}$</td>
<td>$-50210$</td>
<td>25</td>
<td></td>
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<tr>
<td>Mg$^{2+}$-Ca$^{2+}$</td>
<td>$-100420$</td>
<td>20</td>
<td></td>
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<tr>
<td>Mg$^{2+}$-Mn$^{2+}$</td>
<td>$+61920$</td>
<td>27</td>
<td>$-23850$ Suito et al.</td>
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<tr>
<td>Mg$^{2+}$-Si$^{4+}$</td>
<td>$-66940$</td>
<td>20</td>
<td>$+38910$ Suito et al.</td>
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<tr>
<td>Mg$^{2+}$-P$^{5+}$</td>
<td>$-37660$</td>
<td>Present work</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$-Mn$^{2+}$</td>
<td>$-92050$</td>
<td>27</td>
<td>$-16740$ Sommerville et al.</td>
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<td>Ca$^{2+}$-Ti$^{4+}$</td>
<td>$-167360$</td>
<td>Sommerville et al.</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$-Si$^{4+}$</td>
<td>$-133890$</td>
<td>20</td>
<td>$-138490$ Fujita et al.</td>
</tr>
<tr>
<td>Ca$^{2+}$-P$^{5+}$</td>
<td>$-251040$</td>
<td>Present work</td>
<td></td>
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<td>Mn$^{2+}$-Al$^{3+}$</td>
<td>$-20920$</td>
<td>Sommerville et al.</td>
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<td>Mn$^{2+}$-Ti$^{4+}$</td>
<td>$-66940$</td>
<td>Sommerville et al.</td>
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<td>Mn$^{2+}$-Si$^{4+}$</td>
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<td>Fujita et al.</td>
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<td>Mn$^{2+}$-P$^{5+}$</td>
<td>$-76780$</td>
<td>Sommerville et al.</td>
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<td>Si$^{4+}$-Al$^{3+}$</td>
<td>$-52300$</td>
<td>Sommerville et al.</td>
<td></td>
</tr>
<tr>
<td>Si$^{4+}$-Ti$^{4+}$</td>
<td>$+104600$</td>
<td>Martin et al.</td>
<td></td>
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</table>
Fig. 4. Relation between oxygen distribution ratio and $N_{p2o}$ in CaO saturated FeO-P$_2$O$_5$-CaO slags in contact with liquid iron at 1873 K.

Since the above equation is quadratic formalism, the minor components which are less than 5 mass% can be neglected for the approximate calculation.

The reference state of FeO activity in the model is taken to the hypothetical stoichiometric FeO in which the regular nature of the solution is kept. However, the reference state of conventional iron oxide activity is the pure iron oxide in equilibrium with metallic iron. The conversion of the reference state for both activities is written as follows:

$$FeO(l) + (1 - l)Fe(s or l) = FeO(l, R.S.)$$

$$JG_{FeO} = -8540 + 7.142T (J) \quad (14)$$

$$RT \ln a_{FeO} = RT \ln a_{FeO} = 8540 + 7.142T (J) \quad (15)$$

The activity coefficient of iron oxide in phosphate slags obtained by present authors and other investigators was compared with the values calculated from Eqs. (13) and (16) in Fig. 6. The points of data lie on a line with the slope of unity, and the agreement of calculated values with the measured was excellent within the experimental error.

![Graph](graph1.png)

Fig. 5. Relation between $Y_F$ and $X_{CaO}/X_{P_{2O}_5}$ in FeO-Fe$_{2O}_3$-PO$_2$-CaO slags.

6. Equilibrium of Phosphorus Distribution

From the above results, the equilibrium relation of dephosphorization with FeO-Fe$_2$O$_3$-P$_2$O$_5$-CaO-MgO slag can be written as follows:

$$P + 2.5Q = (PO_2)_{in slag} \quad (1)$$

$$RT \ln K_{P1} = RT \ln \{X_{FeO}/(X_{FeO}^{th})\} + RT \ln \gamma_{PO_2} \quad (17)$$

$$RT \ln \gamma_{PO_2} = -31380X_{FeO}^{3} + 14640X_{FeO}^{3} + 251040X_{FeO}^{4}$$

$$- 37660X_{FeO}^{3} + 83680X_{FeO}^{3} + 1920X_{FeO}^{3}$$

$$- 251040X_{FeO}^{3} + 102510X_{FeO}^{3}$$

$$+ 94140X_{FeO}^{3} + 140590X_{FeO}^{3}$$

$$- 20900X_{FeO}^{3} + 65680X_{FeO}^{3} + 65680X_{FeO}^{3}$$

$$- 188280X_{FeO}^{3} + 33470X_{CaO}^{0}$$

$$+ 112960X_{MgO}^{0} - 5900X_{FeO}^{3} \quad (18)$$

According to the all of experimental results, the range of slag composition covered the wide range of $N_{P2O} < 0.5$ and $N_{FeO} < 0.2$ in which the relation of Eqs. (17) and (18) is valid to evaluate the equilibrium constant. The slag composition for basic steelmaking is within this range. In order to show the validity of the model, in Fig. 7, the values of equilibrium constant of Eq. (17), $K_{P1}$, calculated from the data obtained in FeO-P$_2$O$_5$-CaO slag were plotted as a function of $X_{po2}/X_{po2}^{th}$ at 1873 K. As seen in Fig. 7, the values of $K_{P1}$ evaluated by the model were truly a constant within experimental error over the wide range of slag composition. The similar results were given in the other slag systems studied at
The effect of temperature on the log $K_{P1}$ evaluated by the same procedure was shown in Fig. 8, in which the data reported by other 5 groups of Winkler and Chipman,$^{1}$ Knüppel et al.,$^{3}$ Trömel et al.,$^{4,5}$ Suito et al.,$^{6,8}$ and Kor$^{8}$ were also shown by the recalculations. The results obtained by different kinds of slags and by many different investigators were in fairly good agreement each other, and the following equations were given.

$$\log K_{P1} = 17.060/T - 8.510 (\sigma = 0.4) \quad (19)$$

$$\Delta G_{P1}^o = -326.520 + 162.883 T (\sigma = 13.810) \quad (J) \quad (20)$$

Where, the standard state for phosphorus oxide in slag is pure liquid hypothetical PO$_4$, under an assumption of regular solution, and those for oxygen and phosphorus being 1% by mass in iron.

The equilibrium relation of phosphorus in iron with iron oxide in slag can be derived as follows by the combination of Eqs. (4) and (20).

$$\log K_{P2} = 328/T - 0.936 (\sigma = 0.4) \quad (5)$$

$$\Delta G_{P2} = 6.280 + 17.908 T (\sigma = 13.810) \quad (J) \quad (22)$$

The data obtained by the extensive work of Balajiva et al.$^{21}$ were good example to check the validity of the model by Eq. (21), because the oxygen content in iron in the equilibrium was not determined in their measurement. As shown in Fig. 9, the points of data recalculated from the results by Balajiva et al. at 1 858 K lie on a horizontal line of log $K_{P2}$ (1 858 K) = -0.76 within experimental error. Therefore, the validity of the model and the accuracy of Eq. (21) were also verified from the data by Balajiva et al. The effect of temperature on the equilibrium constant of Eq. (5) were shown in Fig. 10, in which the results by present authors and other investigators of Winkler and Chipman,$^{1}$ Balajiva et al.,$^{21}$ Knüppel et al.,$^{3}$ Trömel et al.,$^{4,5}$ Suito et al.,$^{6,8}$ and Shirota et al.$^{9}$ were plotted for comparison. The results shown in Fig. 10 were a little scattered in comparison with those in Fig. 8, but it will be seen that they fairly agreed with each other within the experimental error. In Fig. 11, the phosphorus distribution ratio $L_2$ calculated from the model was plotted against the measured $L_2$ for the data by present authors and other investigators,$^{1,2,5,6,8-10}$ The agreement between both calculated and measured values was also good within the experimental error.

As similar to the case of the activities of FeO and FeO in slag, the conversion factor between the ac-

![Fig. 7. Relation between log $K_{P1}$ and $(X_{CaO} + X_{FeO}) / X_{P2}$ in FeO–FeO$_{1.5}$–PO$_ {2.5}$–SiO$_2$–CaO slags equilibrated with liquid iron and solid CaO at 1 873 K.](image)

![Fig. 8. Temperature dependence of log $K_{P1}$.](image)

![Fig. 9. Relation between log $K_{P2}$ and slag basicity in FeO–FeO$_{1.5}$–PO$_ {2.5}$–SiO$_2$–CaO–MgO slags equilibrated with liquid iron and solid 2(Ca, Mg)O–SiO$_2$ at 1 858 K from the data of Balajiva et al.](image)

![Fig. 10. Temperature dependence of log $K_{P2}$.](image)
tivities of conventional liquid P₄O₅ and hypothetical liquid P₂O₅ in slag is necessary. Turkdogan and Pearson[13] have derived the standard free energy of formation of liquid P₂O₅ from solutes in liquid iron as follows:

\[ 2P(1\%)+5O(1\%) = P_2O_5 \text{(Pure liquid)} \]  
\[ \Delta G_{298} = -705420 + 556472T \]  

The conversion factor can be derived by the combination of Eq. (19) with Eq. (24) as follows:

\[ P_2O_5(l) = 2PO_{2.5}(l, R.S.) \]  
\[ RT \ln a_{PO_{2.5}} = 2RT \ln a_{P_2O_5} = 52270 \]  
\[ -230706T \]  

In Fig. 12, the activity coefficients of P₂O₅ derived by applying Eq. (24) to the present data and previous data by other investigators[1-3,9,10] were compared with the values estimated from the model by using Eq. (25). As shown in Fig. 12, the most points of the data showed good agreement within the experimental error.

In the past, the slag models, proposed by Flood and Grjotheim,[13] and Turkdogan and Pearson,[13] were enough accurate to predict the phosphorus content in metal and the phosphorus distribution ratio between slag and metal for basic slag, but the models of the same idea were not successful to predict the oxygen content in metal and the oxygen distribution between slag and metal. However, in the approximate application of the regular solution model, the both oxygen and phosphorus contents in metal and the distribution ratios of oxygen and phosphorus can be estimated within the error of ±10% over the wide

range from basic slag to acid slag.

7. Conclusions

The phosphorus distribution between slag and liquid iron has been measured to study the approximate validity of the regular solution model of slag. It was confirmed that the model was satisfied over the wide range of slag composition from basic to acid slag. The phosphorus and oxygen contents in iron in equilibrium with the slag can be evaluated within the accuracy of ±10%.

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