A Model for Activity Coefficient of P_2O_5 in BOF Slag and Phosphorus Distribution between Liquid Steel and Slag

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Received on February 27, 2007; accepted on June 1, 2007

1. Introduction

Removal of phosphorus from hot metal is a challenge to the steelmaker, particularly in several steel plants where the chemical composition of the raw materials inevitable leads to high phosphorus content in the hot metal. The partition of phosphorus between liquid steel and slag, for any given input load of phosphorus, depends on the activity of P_2O_5 in the slag, which in turn is a function of chemical composition and temperature. The presence of basic oxides (e.g. CaO), and lowering of temperature, cause reduction in the activity coefficient of P_2O_5, and thus enhances the magnitude of phosphorus partition. Several researchers have worked towards estimation of γ(P_2O_5) in metallurgical slags of different chemical compositions. Experimental measurement of the equilibrium phosphorus partition ratio was recently carried out by the present authors for several metallurgical slags.1,2)

2. Activity coefficient of P_2O_5

Turkdogan and Pearson, in 1953, estimated the equilibrium constant for the reaction 2[P]+5[O]=(P_2O_5).3)

\[
\log K_p = 37160/T - 29.67 \quad \cdots (1)
\]

Where \( K_p \) is the activity coefficient of P_2O_5 in slag, and \( a_{(P_2O_5)} \) is activity of P_2O_5 in slag (considering pure liquid P_2O_5 as standard state), \( x_{(P_2O_5)} \) is molar fraction of P_2O_5 in slag, \( x_{(P_2O_5)} \) is activity coefficient of P_2O_5 in slag, \( h_p, h_0 \) are interaction parameters of P and O, respectively, in steel (considering 1 mass% solution in liquid Fe as standard state), \( f_p, f_0 \) are Henrian activity coefficient of P and O, respectively, in steel.

Therefore,

\[
\gamma_{P_2O_5} = K_p \times \frac{[\%P]^2 \times [\%O]}{x_{(PO2)}} \quad \cdots (3)
\]

Turkdogan and Pearson assumed ideal Henrian behaviour of phosphorus and oxygen in liquid iron, i.e. \( f_p=f_0=1 \). Equation (3) is therefore simplified to

\[
\gamma_{P_2O_5} = K_p \times \frac{[\%P]^2 \times [\%O]^2}{x_{(PO2)}} \quad \cdots (4)
\]

Combining the data of Balajiva et al.4,5) and Fisher and vom Ende,6) with the activity of FeO compiled in their earlier work,3) Turkdogan and Pearson3) calculated the activity coefficient of P_2O_5 from Eq. (4). They observed that \( \log(\gamma_{P_2O_5}) \) could be expressed as a linear function of slag composition expressed in molecular fraction of oxides.

\[
\log(\gamma_{P_2O_5}) = -1.12(22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO}) - 2N_{SiO} - 40,000/T + 23.58 \quad \cdots (5)
\]

In 1981, Suito et al.8) experimentally measured phosphorus distribution between liquid iron and MgO-saturated CaO–MgO–FeO–SiO2 slags, containing 30–40 mass% CaO, over the temperature range 1 823–1 923 K. Based on the experimental results, they derived the activity coefficient of P_2O_5 by using Eq. (4). They observed that the overall form of Eq. (5) holds good for their data but changes were required in the coefficients.8)

\[
\log(\gamma_{P_2O_5}) = -1.01\left(23N_{CaO} + 17N_{MgO} + 8N_{FeO}\right) - 26,300/T + 11.2 \quad \cdots (6)
\]

The correlation proposed by Suito et al. indicates significantly lower temperature dependence of \( \gamma_{P_2O_5} \) compared to that suggested by Turkdogan and Pearson.3) They further suggested that the variation of \( K_p \) vs. mass% CaO became non-linear for CaO concentrations exceeding approximately 35 mass%.

In 2000, Turkdogan published an exhaustive assessment of \( \gamma_{P_2O_5} \) for slags with a wide range of CaO, FeO and P_2O_5 concentrations.9) Combining the data of Suito et al.3) Selin,10) Wrampelmyer et al.11) and Knüppel and Oeters,12) and using Eq. (4), the following correlation for CaO-based slags containing 0.2–1.0 mass% P_2O_5 was proposed.

\[
\log(\gamma_{P_2O_5}) = -9.84 - 0.142(\%CaO + 0.3(\%MgO)) \quad \cdots (7)
\]

It is interesting to note that \( \gamma_{P_2O_5} \) is independent of temperature in this correlation. Unfortunately, the works of Suito et al.9) as well as Turkdogan3) persisted with the assumption of ideal Henrian behaviour of phosphorus and oxygen in liquid iron.

Equilibrium partition of phosphorus between slag and steel, at 1 873 K and 1 923 K, was recently measured by the present authors.2) The data was used to calculate \( \gamma_{P_2O_5} \) using Eq. (3). The activity coefficients of phosphorus and oxygen were calculated using the appropriate interaction parameters from standard sources.13)

\[
\log f_p = \sum e_i^p[\%i] \quad \cdots (8a)
\]

where \( e_i^p \) is interaction parameter of solute i on phosphorus dissolved in liquid Fe.

\[
\log f_o = \sum e_j^o[\%j] \quad \cdots (8b)
\]

where \( e_j^o \) is interaction parameter of solute j on oxygen dissolved in liquid Fe.

The values of \( f_p \) and \( f_o \) were calculated to be in the range of 1.01–1.05 and 0.912–0.996, respectively. Since Eq. (3) involves \( f_p \) and \( f_o \) raised to their second and fifth powers respectively, neglecting the activity coefficients of phosphorus and oxygen may lead to significant error in the estimation of \( \gamma_{P_2O_5} \).

Purely for the sake of comparison with the earlier correlations, \( \gamma_{P_2O_5} \) was calculated from the data of the present authors, following the assumption of \( f_p=f_0=1 \). The results
are shown in Fig. 1(a) along with \( \gamma_{P_2O_5} \) obtained through the use of Eq. (5)–(7). It was seen that \( \gamma_{P_2O_5} \) predicted by Turkdogan and Pearson\(^3\) deviate widely from the experimentally measured values. The calculations using the correlation of Suito et al.\(^8\) offer the best agreement while that of Turkdogan\(^9\) shows slightly more scatter. However, the results differ from the values calculated through Eq. (4) by as much as two orders of magnitude. Similar comparison is shown in Fig. 1(b), but with \( \gamma_{P_2O_5} \) calculated through the use of Eq. (3). No good agreement is observed in either case. It was therefore necessary to develop a correlation for prediction of \( \gamma_{P_2O_5} \), which would be valid over the entire range of composition and temperature studied.

In an attempt to have a better understanding of the dependency of \( \gamma_{P_2O_5} \) on chemical composition, correlations were attempted in terms of molar fraction, ionic fraction as well as optical basicity. The equation based on the molar fractions in the present work was

\[
\log \gamma_{P_2O_5} = -6.775N_{CaO} - 4.995N_{FeO} + 2.816N_{MgO} - 1.377N_{SiO_2} + 1007/T - 13.992 \quad (r^2=0.77) 
\tag{9}
\]

where the \( N \) terms represent the molecular fractions of the respective oxides in slag.

The equation based on the ionic fractions was

\[
\log \gamma_{P_2O_5} = -8.172X_{Ca^2+} - 7.169X_{Fe^2+} + 1.323X_{Mg^2+} - 1.377X_{SiO_4^{2-}} + 340/T - 11.66 \quad (r^2=0.86) 
\tag{10}
\]

where the \( X \) terms represent the ionic fractions of the respective species.

No definite correlation with optical basicity could be derived. The correlation coefficient is clearly better in case of Eq. (10) than Eq. (9). Also, the coefficients of \( N_{CaO} \) and \( N_{SiO_2} \) in Eq. (9) have the same sign. This contradicts the well-known fact that CaO and SiO\(_2\) concentrations influence \( \gamma_{P_2O_5} \) in opposite directions. On the other hand, the coefficients in Eq. (10) are physically more meaningful. It is seen from Eq. (10) that the activity coefficient of P\(_2\)O\(_5\) decreases with an increase in the concentrations of Ca\(^{2+}\), Fe\(^{2+}\) and Mg\(^{2+}\), and increases with SiO\(_4^{2-}\) concentration. Equation (10) further indicates that CaO is most effective in lowering the activity coefficient of P\(_2\)O\(_5\), followed by FeO, whereas MgO is least effective.

The coefficients of \( X \) in Eq. (10) are much smaller in magnitude than the corresponding coefficients of \( N \) in Eqs. (5) and (6). The cationic fractions \( X_{Ca^2+}, X_{Fe^2+} \) and \( X_{Mg^2+} \) are significantly larger in magnitude than the corresponding molar fractions \( N_{CaO}, N_{SiO_2} \) and \( N_{MgO} \). The magnitude of \( X_{SiO_4^{2-}} \) is similarly greater than that of \( N_{SiO_2} \). This is a major factor contributing to the lower numerical values of the coefficients in Eq. (10).

The range of chemical composition studied by the present authors was also wider than the data used for derivation of the correlations (5) and (6). The ranges of CaO concentrations in the data used by the authors,\(^1,2\) Suito et al.\(^8\) and Turkdogan and Pearson\(^3\) were \( N_{CaO}=0.19–0.6, 0.32–0.47 \) and 0.5–0.61 respectively. Thus, Eq. (10) covers a wider range of CaO content than either Eq. (5) or Eq. (6). Suito et al.\(^8\) and Turkdogan and Pearson\(^3\) considered slags with SiO\(_2\) concentrations in the range of \( N_{SiO_2}=0.13–0.3 \) and did not detect any appreciable effect of SiO\(_2\) content on \( \gamma_{P_2O_5} \). The correlation of Turkdogan and Pearson\(^3\) was also based on limited variation of SiO\(_2\) content and the coefficient of \( N_{SiO_2} \) in Eq. (5) is less than one-tenth of that of \( N_{CaO} \). On the other hand, the molar fraction of SiO\(_2\) in the work of the present authors, varied in the range 0.09–0.30. This wider range of SiO\(_2\) concentration may have helped in better detection of the effect of SiO\(_2\) and the coefficient of \( N_{SiO_2} \) is close to one-fourth of that of \( X_{SiO_4^{2-}} \).

Similarly, the ranges of FeO concentrations in the data used by Suito et al.\(^8\) and Turkdogan and Pearson\(^3\) varied as \( N_{FeO}=0.2–0.29 \) and 0.11–0.22, respectively. On the other hand, the range of FeO concentrations in the work of the present authors\(^1,2\) was \( N_{FeO}=0.05–0.36 \) (\( X_{Fe^2+}=0.07–0.42 \)). This may explain the relative stronger effect of FeO concentration on \( \gamma_{P_2O_5} \) seen in Eq. (10), in comparison with Eqs. (5) and (6).

The coefficient of 1/T in Eq. (10) is approximately two orders of magnitude smaller than the corresponding coefficients in Eqs. (5) and (6). The temperature range of the data used for deriving Eq. (10) was restricted to 1873–1923 K. Therefore, the coefficient of temperature is likely to contain some error. However, Turkdogan\(^9\) has recently observed that the activity coefficient of P\(_2\)O\(_5\) in CaO-based steelmaking slag is practically independent of temperature in the range 1823–1923 K. Thus the effect of temperature, within the range of interest in steelmaking, may not really be very strong.

\( \gamma_{P_2O_5} \) was calculated from the data reported by Wrampelmeyer et al.\(^11\) Suito et al.\(^8\) and Vajragupta\(^14\) using Eqs. (3), (6a) and (8b) and also by using Eq. (10). The results are presented in Fig. 2, along with the \( \gamma_{P_2O_5} \) determined from the data of the present authors. It is seen in Fig. 2 that the correlation derived in this work (Eq. (10)) exhibits reasonably good agreement with the measurements. The values of \( \gamma_{P_2O_5} \) determined from the data of Suito et al.\(^8\) are fairly close to those calculated using Eq. (10). However, the agreement with the data reported by Wrampelmeyer et al.\(^11\) and Vajragupta\(^14\) is only partial.

Wrampelmeyer and co-workers\(^11\) allowed equilibration time of only 60 min, or less, while performing the phosphorus partition experiments. This was probably not sufficient for attainment of equilibrium. \( \gamma_{P_2O_5} \) reported by these researchers is similarly greater than that of \( N_{SiO_2} \). This is a major factor contributing to the lower numerical values of the coefficients in Eq. (10).
workers, consequently, deviate from the equilibrium values. The data of Balajiva et al.2,4,11 as well as of Vajragupta12 also suffered from similar problems. Suito et al., on the other hand, used equilibration duration of at least 6 h and hence could obtain $\gamma_{(P,O_3)}$ values fairly close to equilibrium.9)

3. Healy’s Correlation

Healy’s equation of 1970, correlating equilibrium phosphorus partition ratio with slag composition and temperature, has become extremely popular with steelmakers, mainly due to its simplicity and ease of calculation using parameters that are regularly measured in any steel plant.15

$$\log \left( \frac{[P]}{[P]_{\text{measured}}} \right) = \frac{22,350}{T} + 0.08(\%\text{CaO})$$

$$+2.5\log(\text{Fe}_{\text{eq}})-16 \pm 0.4$$

Equation (11)

Figure 3 compares the experimentally measured equilibrium phosphorus partition ratio with that obtained through the use of Healy’s equation. The partition ratio estimated using this correlation contains an inherent uncertainty equivalent to a factor of $10^{0.4–2.5}$, i.e. 0.4–2.5 (shown by the dotted lines in Fig. 3). However, once the partition ratio reaches approximately $10^{2.3–10^{2.4}}$, the calculated partition ratio begins to show large deviations from the measured values, much in excess of the uncertainty permitted by Healy’s equation. Careful analysis revealed that these data correspond to high concentrations of CaO in slag. Suito et al.9 also showed limitations of Healy’s correlation in predicting the phosphorus partition for a range of slag compositions.

A correlation, similar in form to that proposed by Healy, was developed using the recent results of the authors1,2,4,11 and has been shown graphically in Fig. 4. The values calculated from the work of the present authors fall within a scatterband of ±0.2, shown by the two dotted lines. It has been seen in Fig. 2 that the activity coefficients of P$_2$O$_5$, calculated from the chemical composition and temperature reported by Suito et al.9,11 are closest to those measured by the present authors. Therefore, phosphorus partition ratio calculated from the data of Suito et al.9,11, using the correlation developed in the present work, has been plotted in Fig. 4. Similar to the case with $\gamma_{(P,O_3)}$, the correlation for equilibrium phosphorus partition ratio was attempted in terms of mass% molecular fractions as well as ionic fractions. All of these correlations have $r^2$ values in the range of 0.86–0.87. However, the use of the ionic fractions (Eq. (12)) yielded best match for the data of the present authors as well as of Suito et al.9

$$\log \left( \frac{[P]}{[P]_{\text{measured}}} \right) = 1.97X_{\text{CaO}} + 2.0X_{\text{Fe}}$$

4. Conclusions

(1) $\gamma_{(P,O_3)}$ was recalculated for a large number of slag compositions after incorporating appropriate interaction parameters for the solutes in liquid Fe.

(2) A correlation was developed for prediction of $\gamma_{(P,O_3)}$ from chemical composition and temperature of slag. The correlation was satisfactorily applicable to data of other workers as well.

(3) A Healy-type equation involving slag composition and temperature was developed, which made better prediction of phosphorus partition ratio than Healy’s original correlation.

(4) No correlation of $\gamma_{(P,O_3)}$ with optical basicity of slag was observed.

Acknowledgement

The authors are indebted to Tata Steel, Jamshedpur, India, for financially supporting the investigations. The support extended by the Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden, towards carrying out several experiments is also gratefully acknowledged.

The authors wish to extend special thanks to their numerous colleagues in Stockholm and in Jamshedpur whose support and cooperation made this work possible.

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