Note

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

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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 $\gamma(P_2O_5)$ 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⁾

$$\log K_p = 37\,160/T - 29.67 \dots\dots\dots(1)$$

K_p can be expressed in terms of the activities of the respective species as

$$K_p = \left(\frac{a_{(P_2O_5)}}{h_p^2 \times h_o^5} \right) = \left(\frac{x_{(P_2O_5)} \times \gamma_{(P_2O_5)}}{([P]f_p)^2 \times ([O]f_o)^5} \right) \dots\dots\dots(2)$$

Where $a_{(P_2O_5)}$ = activity of P_2O_5 in slag (considering pure liquid P_2O_5 as standard state)

$x_{(P_2O_5)}$ = molar fraction of P_2O_5 in slag

$\gamma_{(P_2O_5)}$ = activity coefficient of P_2O_5 in slag

h_p, h_o = Henrian activity of P and O, respectively, in steel (considering 1 mass% solution in liquid Fe as standard state)

f_p, f_o = Henrian activity coefficient of P and O, respectively, in steel

Therefore,

$$\gamma_{P_2O_5} = \frac{K_p \times [P]^2 \times f_p^2 \times [O]^5 \times f_o^5}{x_{(P_2O_5)}} \dots\dots\dots(3)$$

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

$$\gamma_{P_2O_5} = \frac{K_p \times [P]^2 \times [O]^5}{x_{(P_2O_5)}} \dots\dots\dots(4)$$

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,⁷⁾ 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.

$$\log(\gamma_{P_2O_5}) = -1.12(22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} - 2N_{SiO_2}) - 42\,000/T + 23.58 \dots\dots\dots(5)$$

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⁾

$$\log(\gamma_{P_2O_5}) = -1.01(23N_{CaO} + 17N_{MgO} + 8N_{FeO}) - 26\,300/T + 11.2 \dots\dots\dots(6)$$

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 $\log K_p$ 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.*,⁸⁾ Selin,¹⁰⁾ Wrampelmeyer *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.

$$\log(\gamma_{P_2O_5}) = -9.84 - 0.142(\%CaO + 0.3\%MgO) \dots\dots\dots(7)$$

It is interesting to note that $\gamma_{P_2O_5}$ is independent of temperature in this correlation. Unfortunately, the works of Suito *et al.*⁸⁾ as well as Turkdogan⁹⁾ 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.^{1,2)} 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⁾

$$\log f_p = \sum e_p^i [\%i] \dots\dots\dots(8a)$$

where e_p^i = interaction parameter of solute i on phosphorus dissolved in liquid Fe

$$\log f_o = \sum e_o^j [\%j] \dots\dots\dots(8b)$$

where e_o^j = 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 $f_p = f_o = 1$. The results

Fig. 1. Comparison of $\gamma_{(P_2O_5)}$ predicted by different correlations, (a) Assuming ideal Henrian behaviour. (b) Considering appropriate interaction parameters.

Fig. 2. Comparison of measured P_2O_5 activity coefficient with the correlation developed.

are shown in Fig. 1(a) along with $\gamma_{P_2O_5}$ obtained through the use of Eq. (5)–(7). The dotted lines indicate a scatter-band of ± 2 . It is seen that $\gamma_{P_2O_5}$ predicted by Turkdogan and Pearson³⁾ deviate widely from the experimentally measured values. The calculations using the correlation of Suito *et al.*⁸⁾ offers the best agreement while that of Turkdogan⁹⁾ 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

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

where the N_i terms represent the molecular fractions of the respective oxides in slag.

The equation based on the ionic fractions was

$$\log \gamma_{(P_2O_5)} = -8.172X_{Ca^{2+}} - 7.169X_{Fe^{2+}} + 1.323X_{Mg^{2+}} - 1.377X_{SiO_4^{4-}} + 340/T - 11.66 \quad (r^2 = 0.86) \dots (10)$$

where the X_i 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_2O_5 decreases with an increase in the concentrations of Ca^{2+} , Fe^{2+} and Mg^{2+} , and increases with SiO_4^{4-} concentration. Equation (10) further indicates that CaO is most effective in lowering the activity coefficient of P_2O_5 , followed by FeO, whereas MgO is least effective.

The coefficients of X_i in Eq. (10) are much smaller in magnitude than the corresponding coefficients of N_i 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_{FeO} and N_{MgO} . The magnitude of $X_{SiO_4^{4-}}$ is similarly greater than that of N_{SiO_2} . This is a major factor contributing to the lower numerical values of the co-

efficients 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 Pearson³⁾ 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⁾ 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 Pearson³⁾ 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 $X_{SiO_4^{4-}}$ is close to one-fourth of that of $X_{Ca^{2+}}$.

Similarly, the ranges of FeO concentrations in the data used by Suito *et al.*⁸⁾ and Turkdogan and Pearson³⁾ 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, Turkdogan⁹⁾ has recently observed that the activity coefficient of P_2O_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 Vajragupta¹⁴⁾ using Eqs. (3), (8a) 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 Vajragupta¹⁴⁾ is only partial.

Wrampelmeyer and co-workers¹¹⁾ 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

Fig. 3. Comparison of phosphorus partition ratio—Healy's correlation vs. experimental measurement.

workers, consequently, deviate from the equilibrium values. The data of Balajiva *et al.*^{4,5)} as well as of Vajragupta¹⁴⁾ also suffered from similar problems. Suito *et al.*, on the other hand, used equilibration duration of at least 6 h and hence could obtain $\gamma_{(P_2O_5)}$ values fairly close to equilibrium.⁸⁾

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⁾

$$\log \frac{(\%P)}{[\%P]} = \frac{22\,350}{T} + 0.08(\%CaO) + 2.5 \log(Fe_{total}) - 16 \pm 0.4 \dots \dots (11)$$

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 $10^{\pm 0.4}$, 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.*⁸⁾ 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 authors^{1,2)} and has been shown graphically in Fig. 4. The values calculated from the work of the present authors fall within a scatter-band of ± 0.2 , shown by the two dotted lines. It has been seen in Fig. 2 that the activity coefficients of P_2O_5 , calculated from the chemical composition and temperature reported by Suito *et al.*⁸⁾ are closest to those measured by the present authors. Therefore, phosphorus partition ratio calculated from the data of Suito *et al.*⁸⁾, using the correlation developed in the present work, has been plotted in Fig. 4. Similar to the case with $\gamma_{(P_2O_5)}$, 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.*⁸⁾

$$\log \frac{(\%P)}{[\%P]} = 1.97X_{Ca^{2+}} + 2.0X_{Fe^{2+}}$$

Fig. 4. Comparison of equilibrium phosphorus partition ratio—experimental measurement vs. correlation developed.

$$-2.04X_{SiO_4^{4-}} + 6\,713/T - 1.84 \dots \dots (12)$$

Figure 4 clearly shows that practically all the data of the present authors and more than 50% of the data of Suito *et al.*⁸⁾ have deviations of magnitude less than 0.2. Therefore Eq. (12) has been retained in the present work.

4. Conclusions

(1) $\gamma_{(P_2O_5)}$ 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 $\gamma_{(P_2O_5)}$ 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 $\gamma_{(P_2O_5)}$ with optical basicity of slag was observed.

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