Assessment of SiO\textsubscript{2} Activity Coefficients in Molten Slags Relative to the CaO–SiO\textsubscript{2} System

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1. Introduction

The thermodynamic oxide activities measured in binary and related ternary oxide melts, cannot be readily transposed to the multi-component slags used in the metal manufacturing and refining processes. With this problem in mind, recent studies made by the author\textsuperscript{1,2)} revealed that the activity coefficients of FeO, MnO\textsuperscript{1)} and P\textsubscript{2}O\textsubscript{5}\textsuperscript{2)} can be related in a simple manner to the composition of the multi-component slags, e.g. \(\gamma_{\text{FeO}}\) and \(\gamma_{\text{MnO}}\) decrease with an increasing slag basicity and \(\log(\gamma_{\text{P}_2\text{O}_5})\) decreases linearly with an increasing CaO content of the slag.

Many experimental studies have been made during the past five decades on the activities of silica in binary and ternary oxide melts. The \(a_{\text{SiO}_2}\) values were measured either directly or derived from the activities of other oxides through the Gibbs–Duhem equation. In the present study, the slag composition dependence of the silica activity coefficients \(\gamma_{\text{SiO}_2}\), is assessed relative to that in the binary CaO–SiO\textsubscript{2} melts. In all cases \(\gamma_{\text{SiO}_2}\) is relative to solid SiO\textsubscript{2}.

2. CaO–SiO\textsubscript{2} System

The silica activity coefficients plotted in Fig. 1 are based on the following experimental data which are in close agreement: Kay and Taylor\textsuperscript{3)} Eriksson et al.\textsuperscript{4)} and Morita et al.\textsuperscript{5)} for 1 600°C; Rein and Chipman\textsuperscript{6)} and Morita et al.\textsuperscript{5)} for 1 550°C; Carter and Macfarlane\textsuperscript{7)} and Sharma and Richardson\textsuperscript{8)} for 1 500°C. Since reference is made to the \(\gamma_{\text{SiO}_2}\) values for the CaO–SiO\textsubscript{2} system in all the subsequent diagrams, the dotted curves for these log(\(\gamma_{\text{SiO}_2}\)) values will be abbreviated as the ‘C–S curve’.

3. CaO–MgO–SiO\textsubscript{2} System

The experimental values of \(a_{\text{SiO}_2}\) in all previous publications have been summarised in graphical form. The points for \(\gamma_{\text{SiO}_2}=(a_{\text{SiO}_2}/x_{\text{SiO}_2})\) shown in the following diagrams, are read off the iso-\(a_{\text{SiO}_2}\) curves for oxide compositions in mol fraction \(x_{\text{OX}}\).

Comparison of the \(\gamma_{\text{SiO}_2}\) values for the CaO–SiO\textsubscript{2} system with those of the CaO–MgO–SiO\textsubscript{2} system, using the experimental data of Morita et al.\textsuperscript{5)} and Rein and Chipman\textsuperscript{6)} for 1 600°C, has indicated that the CaO molar equivalence is \(x_{\text{CaO}}=0.8x_{\text{MgO}}\) with respect to the \(\gamma_{\text{SiO}_2}\) values. It is on the basis of this assertion that in Fig. 2, \(\log(\gamma_{\text{SiO}_2})\) is plotted against \(x_{\text{CaO}}=(x_{\text{CaO}}+0.8x_{\text{MgO}})\) for \(x_{\text{MgO}}/x_{\text{CaO}}\) ratios of 3 and 0.5. The curve representing these data differs little from the ‘C–S curve’. Gradual departure from this curve at high values of \(\gamma_{\text{SiO}_2}\) is due to the decrease in SiO\textsubscript{2} solubility in the melt at higher MgO contents.

4. CaO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} System

Only the two previous publications\textsuperscript{5,6)} show the composition diagram with the alumina formulation as Al\textsubscript{1.5}O\textsubscript{1.5}, i.e. in mol fraction \(x_{\text{CaO}}+x_{\text{AlO}_{1.5}}+x_{\text{SiO}_2}=1\). The reason being that with this formulation, the mol percentages of the oxides are similar to their weight percentages. In all other publications on slags containing alumina, Al\textsubscript{2}O\textsubscript{3} has always been used for the alumina formulation.

The \(\gamma_{\text{SiO}_2}\) values for 1 550°C in Fig. 3, for the molar ratios of \(x_{\text{AlO}_{1.5}}/x_{\text{CaO}}=0, 0.5\) and 2, are from the experimental
data of Morita et al.,5) Rein and Chipman6) and Kay and Taylor.9) At compositions $x_{CaO} = 0.67x_{AlO1.5}$, the $g_{SiO2}$ values are scattered about the 'C–S values', suggesting that the CaO molar equivalence is $x_{CaO} = 0.67x_{AlO1.5}$. Departure from the 'C–S curve' is due to an increase in the SiO2 solubility in melts with an increasing $x_{AlO1.5}/x_{CaO}$ ratio.

5. CaO–MgO–Al2O3–SiO2 System

The $\gamma_{SiO2}$ values for 1600°C in Fig. 4, for the molar ratio of $x_{MgO}/x_{CaO} = 1$ in melts containing 10% and 20% MgO, are from the experimental work of Rein and Chipman.9) The curve representing the data is almost identical with the 'C–S curve' corresponding to the sum of the oxides $OX = x_{CaO} + 0.8x_{MgO} + 0.67x_{AlO1.5}$.

6. CaO–FeO–SiO2 System

Using the Gibbs–Duhem equation, Elliott et al.10) and Timucin and Morris11) derived the silica activities from the measured FeO activities in the iron-saturated CaO–FeO–SiO2 melts at 1600°C and 1550°C, respectively. In the case of the work of Elliott et al., the melts are pseudoternary with (CaO+MgO) as one of the components. The log$(\gamma_{SiO2})$ values from these data are plotted in Fig. 5 for the molar ratios $x_{FeO}/x_{CaO} = 0.5$ and 2, with the assumption of the CaO molar equivalence being $x_{CaO} = 0.6x_{FeO}$. The $\gamma_{SiO2}$ values are also included in this diagram for the binary FeO–SiO2 melts, using the data compiled by Ban-ya and Hino.12) Over a wide composition range, the 'C–S curve' does give a good representation of the $\gamma_{SiO2}$ values in these melts.

7. MnO–Al2O3–SiO2 System

The activities of oxides in the MnO–Al2O3–SiO2 melts at 1550 and 1650°C shown in Fig. 6 were computed by Fujisawa and Sakao13) from previous available thermodynamic data which were applied to a simple solution model. They also determined experimentally the activities of MnO and SiO2 by selected slag–metal equilibrium measurements and found close agreement with their computed data. The log$(\gamma_{SiO2})$ values read off the curves in Fig. 6 are plotted in Fig. 7 for the binary MnO–SiO2 system and the ternary system for the molar ratio of $x_{AlO3}/x_{AlO1.5} = 3$. For comparison with the CaO–SiO2 system, the 'C–S curve' for 1600°C is also included in this diagram. Upon close scrutiny of the data in this diagram, it is surmised that the CaO molar equivalence of MnO and Al2O3 is $x_{CaO} = 0.8x_{MnO} = 0.8x_{AlO3}$. This deduction of the CaO equivalence of MnO and Al2O3 with respect to the silica activity coefficients, is substantiated by the plot in Fig. 8 for both the binary and ternary systems.

8. Concluding Remarks

The composition dependence of the silica activity coeffi-
Cations in silicate and aluminosilicate melts do relate to \( SiO_2 \) in the \( CaO-SiO_2 \) melts, in terms of the apparent molar equivalence of the oxides with respect to \( CaO \), as summarised below:

For \( CaO-MgO-Al_2O_3-SiO_2 \) melts:
\[
OX = x_{CaO} + 0.8x_{MgO} + 0.67x_{AlO_3} \text{ for } OX > 0.45.
\]

For \( CaO-FeO-SiO_2 \) melts:
\[
OX = x_{CaO} + 0.6x_{FeO} \text{ at all compositions.}
\]

For \( MnO-Al_2O_3-SiO_2 \) melts:
\[
OX = 0.8(x_{MnO} + x_{AlO_3}) \text{ for } x_{AlO_3} < 0.3.
\]

As shown in a recent publication by the author,\(^2\) the activity coefficients of \( P_2O_5 \), with respect to liquid \( P_2O_5 \), are many orders of magnitude lower than the silica activity coefficients. For example, in the \( Ca, Fe \) silicophosphate melts, the log(\( \gamma_{P_2O_5} \)) at temperature of 1,550 to 1,650°C is about -15 at 30% \( CaO \), decreasing to about -18 at 55% \( CaO \). Yet in the \( CaO \) saturated \( Ca, Fe \) silicates, log(\( \gamma_{SiO_2} \)) is about -2.5 with respect to liquid \( SiO_2 \).

\[^1\] See Ref. 2) for this estimate.  \(^2\) From well established free energy data.

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