A Newly Developed Method for Determining SiO₂ Activity of the Silicate Slags Equilibrated with Molten Silicon Alloys

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In the determination of activities of components other than SiO₂ for the CaO–SiO₂–AlO₁.₅–MgO slags equilibrated with molten Si alloys, activities of SiO₂ in the slags are required and their accuracy will considerably affect the results. For the CaO–SiO₂, CaO–SiO₂–AlO₁.₅ and CaO–SiO₂–MgO slags, the activities of SiO₂ were obtained from the distribution of each element between slags and metals, and each thermodynamic property in molten Si alloys at 1 823 and 1 873 K using a newly developed method with the Gibbs–Duhem equation. The data obtained in the present research were compared with those reported by other investigators, and showed reasonable agreement in wide slag composition ranges. These activity data of SiO₂ will be employed in the subsequent determination of other component activities for the binary and ternary slag systems concerned.

KEY WORDS: thermodynamics; activity of SiO₂; CaO–SiO₂–AlO₁.₅–MgO slags; Si based alloy; Gibbs–Duhem equation.

1. Introduction

Thermodynamic properties of the CaO–SiO₂–AlO₁.₅–MgO slags are of great importance for the investigation of the refining reactions in iron- and steelmaking processes.

The SiO₂ activities of silicate systems have been measured by many researchers, but there are considerable discrepancies among them, which accordingly affect the derived activity values of other oxide components.

Rein and Chipman¹) determined the activity of SiO₂ in the ternary systems of CaO–SiO₂–AlO₁.₅ and CaO–SiO₂–MgO, and at the 10, 20, 30 mass% MgO of CaO–SiO₂–AlO₁.₅–MgO quaternary system mainly at 1 873 K by measuring the silicon distribution between slags and Fe–Si–C alloys saturated with either graphite or silicon carbide under a CO atmosphere.

Kay and Taylor²,³) determined the activity of SiO₂ in the entire liquid region in the CaO–SiO₂–AlO₁.₅ system and on the 11, 21 mass% AlO₁.₅ planes of the CaO–SiO₂–AlO₁.₅–MgO system mainly at 1 873 K by measuring the silicon distribution between slags and Fe–Si–C alloys saturated with either graphite or silicon carbide under a CO atmosphere.

On the other hand, by applying a slag–metal equilibration technique using Si based alloys, the activities of components other than SiO₂ can be obtained directly at each experimental point when SiO₂ activity and that of each component in such alloys are available. The activity coefficients of such components together with interaction effects in such alloys at concerned temperatures have been extensively studied by Miki et al.⁴,⁵)

In the present study, SiO₂ activities for the CaO–SiO₂, CaO–SiO₂–AlO₁.₅ and CaO–SiO₂–MgO systems have been derived over a wide range of liquid composition by a newly developed analytical method from the equilibrium compositions of slags and molten Si alloys in prior to determination of the activities of oxide components other than SiO₂ for these slag systems.

2. Experimental Procedure

An electric resistance furnace was used for equilibration of silicate slags and Si based alloys. The temperature was controlled at 1 823 and 1 873 K within the accuracy of ±2 K by a Pt–6%Rh/Pt–30%Rh thermocouple. The slags were prepared from reagent grade AlO₁.₅, SiO₂, MgO and CaO calcined from CaCO₃ in air, while Si based alloys were from semiconductor grade Si with a small amount of reagent grade Ca, Al and Mg.

Sixteen grams of CaO–SiO₂, CaO–SiO₂–AlO₁.₅ or CaO–SiO₂–MgO slags and 8 g of Si based alloys with various Ca, Al and Mg contents in a graphite crucible were held in a
graphite holder and equilibrated under a deoxidized argon atmosphere. A graphite lid was placed on the top of the crucible to prevent excess evaporation of Ca and Mg. Equilibration time was determined to be 18 h by preliminary experiments. After equilibration, the sample was quenched in a flaming argon gas and subjected to chemical analysis. The Ca, Al and Mg contents of the alloy were determined by inductively coupled plasma spectroscopy (ICP). Silica content of the slag was determined by gravimetry, and the other component contents of the slag by ICP.

3. Principle of the Activity Determination

3.1. Derivation of the Activity of SiO$_2$

The activities of SiO$_2$ in the binary and ternary silicate slags were obtained by using the Gibbs–Duhem equation and the exchange reaction equilibria for components in slags.

The Gibbs–Duhem equation for the 1–2 binary system is expressed as follows:

$$X_i d \ln \gamma_i + X_2 d \ln \gamma_2 = 0 \quad \text{(1)}$$

where $X_i$ and $\gamma_i$ denote the molar fraction and the activity coefficient of component $i$, respectively. Equation (1) can be rewritten as follows.

$$X_i d \ln \gamma_i + X_2 d \ln (B \cdot \gamma_2) = 0 \quad \text{(2)}$$

where $B = \frac{X_2}{\gamma_2}$. Therefore, if the relationship between $X_2$ and $\ln B$ is obtained, the activity coefficient of component 1 can be calculated by integration of Eq. (5).

In the case of the CaO–SiO$_2$ system, the reaction of Eq. (6) is considered to be in equilibrium, assuming component 1 is Si$_{1/2}$O and 2 is CaO in order that each activity coefficient in Eq. (7) may have the same order of magnitude.

$$\text{Si} _{1/2} \text{O(s)} + \text{CaO(s)} = \frac{1}{2} \text{Si} \text{O}_2\text{(s)} + \text{CaO(s)} \quad \text{(6)}$$

$$K_i = \frac{X_{\text{CaO}} \cdot X_{\text{Si} \text{O}_2} \cdot a_{\text{CaO}}}{X_{\text{Si} \text{O}_2} \cdot X_{\text{CaO}} \cdot a_{\text{SiO}_2}} \quad \text{(7)}$$

$$B = \frac{X_{\text{Si} \text{O}_2} \cdot X_{\text{CaO}}}{X_{\text{Si} \text{O}_2} \cdot X_{\text{CaO}} \cdot a_{\text{SiO}_2} \cdot a_{\text{CaO}}} \quad \text{(8)}$$

The values of $B$, defined as Eq. (8), can be derived from the composition of the slag and metal when the activity coefficients of Ca and Si in metal are available. In this system, the value of the silica-saturated composition was used as the lower limit of integration in Eq. (5). Then the derived activities of Si$_{1/2}$O were converted to those of SiO$_2$ by the relationship of $a_{\text{SiO}_2} = a_{\text{Si} \text{O}_2}$. The activity of SiO$_2$ in the ternary system can be analogously obtained. The Gibbs–Duhem equation for the ternary system is expressed by the activity coefficients as follows:

$$X_i d \ln \gamma_i + X_2 d \ln \gamma_2 + X_3 d \ln \gamma_3 = 0 \quad \text{(9)}$$

Equation (9) may be rewritten as follows.

$$d \ln \gamma_i + X_2 d \ln B + X_3 d \ln C = 0 \quad \text{(10)}$$

where $B = \frac{X_2}{\gamma_2}$ and $C = \gamma_3$. Therefore, $\ln \gamma_i$ with constant ratio of 2 and 3 components can be calculated by this integration.

In the case of the CaO–SiO$_2$–M$_O$ system, components 1, 2 and 3 are supposed to be Si$_{1/2}$O, CaO and M$_O$, respectively, for the same reason as the case of the binary system, where M denotes Al or Mg. The value of $B$ is calculated be Eq. (8) and $C$ is defined as Eq. (15) for the exchange reaction between Si$_{1/2}$O and M$_O$.

$$\text{Si}_{1/2} \text{O(s)} + kM(l) = M_\text{O(s)} + \frac{1}{2} \text{Si(l)} \quad \text{(13)}$$

$$K_i = \frac{X_{M_\text{O}} \cdot X_{\text{SiO}_2} \cdot a_{M_\text{O}}}{X_{\text{SiO}_2} \cdot X_{M_\text{O}} \cdot a_{\text{SiO}_2}} \quad \text{(14)}$$

$$C = \frac{X_{M_\text{O}} \cdot K_i}{X_{\text{SiO}_2} \cdot X_{M_\text{O}} \cdot a_{M_\text{O}} \cdot a_{\text{SiO}_2}} \quad \text{(15)}$$

When the value of $\ln (B \cdot C^k)$ is calculated at each slag composition in the ternary system, the activity of Si$_{1/2}$O, hence that of SiO$_2$ can be obtained by Eq. (12).

The standard Gibbs energy changes for exchange reactions$^{6,8}$ and activity coefficients of Ca, Al and Mg in Si based alloys$^{6,8}$ employed in the present study are summarized in Table 1.

### Table 1

| Expression | Value | Temperature (°C) |
|------------|-------|------------------|
| $\frac{1}{2}$ SiO(s) + CaO(s) = $\frac{1}{2}$ SiO$_2$ + Ca(l) | $\Delta G^\circ = 156,000 - 20.07T$ (kJ/mol) |  |
| $\frac{3}{4}$ SiO$_2$ + AlO$_3$(s) = $\frac{3}{4}$ SiO$_2$ + Al(l) | $\Delta G^\circ = 132,000 - 14.31T$ (kJ/mol) |  |
| $\frac{1}{2}$ SiO$_2$ + MgO(s) = $\frac{1}{2}$ SiO$_2$ + Mg(l) | $\Delta G^\circ = 134,700 - 16.85T$ (kJ/mol) |  |

3.2. Estimation of the Activity of Si

As the activity coefficients of Ca, Al and Mg in molten silicon alloys are known, the activities of Si in the alloys are obtained by using the Gibbs–Duhem equation.

Suppose the ternary alloy consists of components 1, 2 and 3, and component 1 is Si. Equation (9) can be rewritten as follows.

$$X_i d \ln \gamma_i + X_2 d \ln \gamma_2 + kX_3 d \ln \gamma_3 = 0 \quad \text{(16)}$$
where \( k = X_1 / X_2 \).

\[
d \ln \gamma_i = -d \ln (X_i) \quad \text{Eq. (17)}
\]

\[
\ln \gamma_i = \int_{X_i=0}^{X_i=X} -d \ln (X_i) \quad \text{Eq. (18)}
\]

Therefore, the activity of Si with a constant ratio of 2 and 3 components can be calculated by integration of Eq. (18).

For the binary alloy, the activity of Si can be obtained by an even simpler method.

In most of the experiments in the present study, the activity of Si was found to be equal to the molar fraction of Si since it was nearly unity, as described later.

4. Results and Discussion

4.1. The CaO–SiO\(_2\) System

The activities of components in this system have been investigated by various techniques such as electrochemical cells, Knudsen effusion, gas–slag equilibration (the gas containing sulfur or SO\(_2\)), gas pressure over slag–graphite–SiC system, and equilibration between slag and Fe–Si–C alloy, etc.

The experimental results for equilibrating molten Si alloy with the CaO–SiO\(_2\) slags and the activity of SiO\(_2\) at 1823 and 1873 K are listed in Table 2, where the value for SiO\(_2\) saturated composition at 1823 K reported by Miki et al. was employed.

In prior to the derivation of SiO\(_2\) activity, Si activity of molten Si alloy was obtained by the Gibbs–Duhem integration. As shown in Fig. 1, activity of Si in the molten Si–Ca binary system showed negative deviation from the Raoult’s law, when molar fraction of Si is lower than 0.98.

Relationship between SiO\(_2\) content of the slag and its activity is shown in Fig. 2 together with those of the other researchers. The activity of SiO\(_2\) obtained by the present method agrees well with others at 1773 and 1873 K, showing small temperature dependence. Hence, the way of calculation from the Gibbs–Duhem equation through Eqs. (1)–(5) was confirmed to be adequate.

4.2. The CaO–SiO\(_2\)–AlO\(_{1.5}\) System

The experimental results for the CaO–SiO\(_2\)–AlO\(_{1.5}\) slags at 1823 K are summarized in Table 3. When the alloys are equilibrated with the slags in the lower SiO\(_2\) liquid region, Ca and Al contents of the alloys are considerably high.

Equilibrium distribution ratios of Ca and Al between Si based alloy and this slag system at the composition of the liquidus were measured by some researchers. When the slag is saturated with SiO\(_2\), the present results agree well with those of Weiss and Schwerdtfeger at 1773 K in spite of temperature difference as shown in Fig. 3. Distribution ratios of Ca and Al between the alloy and the slag saturated with AlO\(_{1.5}\), CaO·12AlO\(_{1.5}\) and CaO·4AlO\(_{1.5}\) were reported by Fujiwara et al. at 1873 K. In Figs. 4 and 5, the present results for the slag composition adjacent to the liquidus saturated with such aluminate compounds are plotted together with their results. Although their temperature was 50 K higher, present results are in reasonable agreement for both Ca and Al.

Activity of Si in the alloy was calculated as described earlier, and the results are drawn in the Si–Ca–Al ternary diagram (Fig. 6). The activity of SiO\(_2\) was derived from the experimental results also in accordance with the procedure described in Experimental. The iso-value contours of ln(B·C\(^2\)) drawn in the CaO–Si\(_{1/2}\)O–Al\(_{2/3}\)O system are
Table 3. Slag and metal compositions after equilibrium and the activities of SiO$_2$ in the CaO–SiO$_2$–MgO system at 1823 K.

| Sample No. | Slag Composition | Metal Composition | Activity | $a_{SiO_2}$ |
|------------|------------------|-------------------|----------|--------------|
| 101        | X$_{SiO_2}$ | X$_{CaO}$ | X$_{MgO}$ | mass% Ca | mass% Al |
| 0.876      | 0.039            | 0.085            | 0.00657  | 0.192 | 1 |
| 102        | 0.818            | 0.091            | 0.0147   | 0.0689 | 1 |
| 103        | 0.761            | 0.014            | 0.0005   | 0.0220 | 0.0237 | 1 |
| 104        | 0.706            | 0.046            | 0.0142   | 0.00611 | 1 |
| 105        | 0.489            | 0.362            | 0.00731  | 0.253 | 0.428 |
| 106        | 0.542            | 0.312            | 0.00875  | 0.214 | 0.505 |
| 107        | 0.602            | 0.253            | 0.0308   | 0.152 | 0.606 |
| 108        | 0.660            | 0.198            | 0.0391   | 0.127 | 0.714 |
| 109        | 0.705            | 0.150            | 0.0162   | 0.0095 | 0.820 |
| 110        | 0.412            | 0.402            | 0.0134   | 0.431 | 0.315 |
| 111        | 0.462            | 0.341            | 0.0228   | 0.288 | 0.400 |
| 112        | 0.497            | 0.271            | 0.0385   | 0.192 | 0.480 |
| 113        | 0.538            | 0.205            | 0.0451   | 0.105 | 0.578 |
| 114        | 0.561            | 0.153            | 0.0288   | 0.0458 | 0.656 |
| 115        | 0.635            | 0.101            | 0.0535   | 0.0247 | 0.845 |
| 116        | 0.314            | 0.432            | 0.107    | 0.737 | 0.158 |
| 117        | 0.364            | 0.370            | 0.0702   | 0.362 | 0.234 |
| 118        | 0.389            | 0.351            | 0.0468   | 0.296 | 0.296 |
| 119        | 0.406            | 0.314            | 0.0732   | 0.241 | 0.313 |
| 120        | 0.415            | 0.271            | 0.0978   | 0.200 | 0.328 |
| 121        | 0.461            | 0.222            | 0.0805   | 0.119 | 0.432 |
| 122        | 0.478            | 0.172            | 0.0900   | 0.0625 | 0.487 |
| 123        | 0.536            | 0.062            | 0.0872   | 0.0344 | 0.646 |
| 124        | 0.263            | 0.405            | 0.226    | 1.08  | 0.0893 |
| 125        | 0.278            | 0.351            | 0.369    | 0.771 | 0.0955 |
| 126        | 0.297            | 0.389            | 0.284    | 0.703 | 0.120 |
| 127        | 0.315            | 0.339            | 0.302    | 0.451 | 0.131 |
| 128        | 0.340            | 0.284            | 0.337    | 0.344 | 0.152 |
| 129        | 0.361            | 0.235            | 0.434    | 0.299 | 0.162 |
| 130        | 0.398            | 0.187            | 0.364    | 0.223 | 0.225 |
| 131        | 0.389            | 0.135            | 0.478    | 0.173 | 0.133 |
| 132        | 0.405            | 0.112            | 0.205    | 0.105 | 0.332 |
| 133        | 0.453            | 0.064            | 0.286    | 0.0323 | 0.288 |
| 134        | 0.212            | 0.463            | 1.14     | 2.04  | 0.0345 |
| 135        | 0.242            | 0.409            | 1.16     | 1.49  | 0.0382 |
| 136        | 0.254            | 0.362            | 1.33     | 1.24  | 0.0292 |
| 137        | 0.265            | 0.313            | 1.74     | 1.18  | 0.0227 |
| 138        | 0.296            | 0.259            | 2.20     | 1.03  | 0.0350 |
| 139        | 0.322            | 0.208            | 2.12     | 0.741 | 0.0439 |
| 140        | 0.342            | 0.155            | 1.66     | 0.412 | 0.0500 |
| 141        | 0.368            | 0.111            | 1.80     | 0.347 | 0.0646 |
| 142        | 0.411            | 0.060            | 0.962    | 0.117 | 0.117 |
| 143        | 0.417            | 0.046            | 0.0159   | 0.322 | 0.321 |
| 144        | 0.356            | 0.436            | 0.0401   | 0.416 | 0.232 |
| 145        | 0.166            | 0.345            | 15.9     | 2.57  | 0.00186 |
| 146        | 0.094            | 0.474            | 14.9     | 4.46  | 0.00090 |
| 147        | 0.071            | 0.562            | 10.4     | 6.46  | 0.00085 |

Fig. 3. Relationship between Ca and Al contents of Si based alloys and CaO contents of the CaO–SiO$_2$–AlO$_3$ slags.

Fig. 4. Relationship between $X_{CaO}/(X_{SiO_2}+X_{CaO})$ and log[mass% Ca] in Si-based alloys in equilibrium with the CaO–SiO$_2$–AlO$_3$ slags saturated with AlO$_{1.5}$, CaO·12AlO$_{1.5}$ or CaO·4AlO$_{1.5}$.

Fig. 5. Relationship between $X_{CaO}/(X_{SiO_2}+X_{CaO})$ and log[mass% Al] in Si-based alloys in equilibrium with the CaO–SiO$_2$–AlO$_3$ slags saturated with AlO$_{1.5}$, CaO·12AlO$_{1.5}$ or CaO·4AlO$_{1.5}$.

Fig. 6. Iso-activity contours for Si in the Si–Ca–Al alloy at 1823 K.
shown in Fig. 7. Although the values scatter when \( \text{Si}_{1/2}O \) content is higher than the iso-ln(\( B \cdot C_k \)) line of 0.5, the error in the integration was estimated so small that its effect on activity coefficient of \( \text{Si}_{1/2}O \) was as low as 1% in the present system. An example of integration, \( k = 1.5 \), is demonstrated in Fig. 8. Iso-activity lines of \( \text{SiO}_2 \) for this system are drawn in Fig. 9(a). These contours are parallel to that of the \( \text{SiO}_2 \)-saturated liquidus down to lower-\( \text{SiO}_2 \) content. The present results may be compared with those of Rein and Chipman\(^1\) and those of Kay and Taylor\(^2\) because their experimental temperatures are the same and the activity of \( \text{SiO}_2 \) was measured in this slag over a wide range of liquid. As shown in Fig. 9(b), the present results were found to agree well with both data when \( \text{SiO}_2 \) content is less than 30 mol%.

4.3. The CaO–SiO\(_2\)–MgO System

The experimental results for the CaO–SiO\(_2\)–MgO slags and the activity of each component at 1873 K are listed in Table 4. Weiss and Schwerdtfeger\(^{19}\) also reported the Ca and Mg contents of the metals as a function of CaO content of \( \text{SiO}_2 \) saturated slags at 1773 K, which are compared with the present results and shown in Fig. 10. Present results for Ca and Mg contents were found two times higher probably due to the temperature difference of 100 K, but the tendencies are similar. In the same manner as the CaO–SiO\(_2\)–Al\(_2\)O\(_3\) system, the activity of Si in the alloy and the value of ln(\( B \cdot C_k \)) were calculated. Iso-activity contours of Si are drawn in Fig. 11, and iso-value contours of ln(\( B \cdot C_k \)) in the CaO–Si\(_{1/2}O\)–MgO system in Fig. 12. Iso-activity lines for \( \text{SiO}_2 \), which are parallel to the \( \text{SiO}_2 \)-saturated liquidus, are drawn in Fig. 13(a). The numerical values of the present re-
results are in good agreement with those of Rein and Chipman\(^1\) in the low-MgO area, while they are almost twice as large as those of Rein et al. in the high-MgO area (Fig. 13(b)).

5. Conclusions

A new method for determining an activity of an oxide component in the systems in equilibrium with reference metals was developed and applied to binary and ternary silicate systems in equilibrium with molten Si alloys. The activities of SiO\(_2\) in the CaO–SiO\(_2\)–MgO systems were determined at 1823 and 1873 K by integrating equilibrium distribution data between the alloys and the slags.

In most cases, the present results show reasonable agreement with those reported by other investigators. This newly developed method is considered to be applicable to other silicate systems.

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