(2) The Estimation of Slag Basicity from Sulfide Capacity

C. Wagner\(^5\) and many researchers\(^6–8\) have insisted that the sulfide capacity has been a measure of the slag basicity. But Ban-ya\(^9\) and Ban-ya et al.\(^11\) commented on the paper by C. Wagner,\(^5\) and it was emphasized that the sulfide capacity is unable to be applied as a measure of the basicity index of the slag.

The equilibrium constant of Eq. (1) is written as follows,

\[
K_i = \left( \frac{\text{mass}\% S}{f_i} \right) \cdot \left( \frac{P_{O_2}}{P_{S_2}} \right)^{1/2} \quad \text{(7)}
\]

\[
(a_{O_2}) = \left( \frac{f_i}{K_i} \right) \cdot C_i \quad \text{(8)}
\]

where, \((a_{O_2})\) is the basicity of slag, and it is theoretically unable to be obtained. If the value of \(\{f_i/K_i\}\) is constant or unity, the value of \((a_{O_2})\) will be proportional to the sulfide capacity, \(C_i\). However, the relation of the equilibrium constant and activity coefficient is not so simple in multi-components solution like molten slag, flux and salt. As the more simple case, Ban-ya et al.\(^11\) showed the treatment of Fe–Ni–H system as follows.

Since two unknown terms of \(a_{O_2}\) and \(a_{S_2}\) are involved in the thermodynamic treatment of sulfide capacity, the relationship of the equilibrium constant and the activity coefficients in Henrian standard of multi-component solutions becomes complicated. The molten slags are primary multi-component solutions containing the many kinds of oxides and halides. Therefore, as the simplest example involving one unknown term in Henrian standard of multi-component solutions, the solubilities of hydrogen in liquid iron and iron-nickel alloys are described in Table 1.

As already well known, the solubilities of hydrogen in liquid iron and iron-nickel alloys obey Sieverts’ law, and the hydrogen content dissolved in the liquid metals is proportional to the square root of hydrogen pressure in the gas phase at a given temperature. If the standard state of hydrogen activity in liquid alloys is taken to infinitely dilute solution of hydrogen in liquid alloys as a solvent, as shown in the case I in Table 1, the activity coefficients of hydrogen are always unity, but the apparent equilibrium constant, that is, the Sieverts’ constant varies with the composition of liquid alloys. In the case II, the standard state of hydrogen activity in liquid alloys is taken to infinitely dilute solution of hydrogen in liquid iron as a solvent. The equilibrium constant is truly a constant value independent of metal composition, but the activity coefficients of hydrogen in liquid iron alloys vary with the nickel content in the alloys. Namely, it is clear that the apparent or true equilibrium constant and activity coefficient in Henrian standard in multi-component solutions never take a constant value or unity at the same time, respectively. The treatments of Case I and Case II in gas-metal reaction are mathematically correct, but the example of Case II is commonly applied in the thermodynamics of solution. Therefore, it is concluded that the activity coefficient of component \(i\) is the function of composition of multi-component solutions except for the case of ideal solution, as seen in Case II of Table 1.

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**Note**

Comments on “Evaluation of Thermodynamic Activity of Metallic Oxide in a Ternary Slag from the Sulphide Capacity of the Slag”

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Many papers have been published on the sulfide capacity of the slag since the proposal after Richardson and Fincham.\(^1\) They are classified to following three categories.

1. The measurement of the sulfide capacity related to the sulfur distribution between slag and metal.
2. The estimation of slag basicity from the sulfide capacity.
3. The determination of the activity of the basic oxide in the slag from the sulfide capacity of the same slag.

(1) The Sulfur Distribution between Slag and Metal

The sulfide capacity of slag is defined as follows, Sulfur reaction. \((P_{O_2} \leq 10^{-7})\)

\[
\frac{1}{2} S_2(g) + (O^2-) = \frac{1}{2} O_2(g) + (S^2-) \quad \text{(1)}
\]

Sulfide capacity, \(C_i = \text{mass}\% S \cdot \left( \frac{P_{O_2}}{P_{S_2}} \right)^{1/2} \quad \text{(2)}
\]

\[
\log C_i = \log(\text{mass}\% S) + \frac{1}{2} \log P_{O_2} - \frac{1}{2} \log P_{S_2} \quad \text{(3)}
\]

Gas–metal reaction of sulfur

\[
[S] = \frac{1}{2} S_2(g) \quad \text{(4)}
\]

\[
\log \{P_{S_2}^{1/2}/a_{S([S])}\} = -6535/T + 0.964 \quad \text{(5)}
\]

Sulfur distribution between slag and metal

\[
\log(\text{mass}\% S)/a_{S([S])} = \log C_i - \frac{1}{2} \log P_{O_2} - 6535/T + 0.964 \quad \text{(6)}
\]

The oxygen potential of the system is necessary to estimate the sulfur distribution ratio from the sulfide capacity. Venketadri and Bell\(^9\) reported that the sulfur distribution between slag and metal in the blast furnace agreed well with the calculated values from the sulfide capacity by using the oxygen potential of \((FeO)/Fe(II)\) equilibrium. Shim and Ban-ya\(^9\) also showed the same results for steel-making slags of FeO-CaO-SiO\(_2\)-MgO\(_{sat}\) system. Therefore the sulfide capacity is the most useful thermodynamic value to determine the sulfur distribution in iron- and steel-making processes.
The Determination of the Activity of the Basic Oxide in the Slag from the Sulfide Capacity of the Same Slag

For the third category, two papers12,13) have already been published for CaO–SiO2 binary system as the simplest case since 1957. In the paper by Hayashi et al.,14) a similar idea was extended to the ternary and binary systems of BaO–MnO–SiO2(sat.) , BaO–MnO–SiO2, MnO–SiO2 and BaO–MnO.

It is the most important whether Eq. (9) in Hayashi et al.’s paper14) is reasonable or not.

\[ a_{MxO} = \gamma_{MxS} / \left( \frac{1}{K_i} \sum X_i M_i / 100M_S \right) \]

where, \( a_{MxO} \) and \( \gamma_{MxS} \) are activity of MxO and activity coefficient of MxS, \( K_i \) is the equilibrium constant of reaction (1), and \( X_i, M_i \) and \( M_S \) are mole fraction and atomic weight of component \( i \), and atomic weight of sulfur, respectively.

The questions are the following three items to solve the problems concerning Eq. (9).

i) Ionic and molecular models define the following of Eqs. (10) and (11) in Hayashi et al.’s paper.

Ionic model
\[ a_{MxO} = \left( \frac{\gamma_{MxS}}{K_i} \right) \left( \sum X_i M_i / 100M_S \right) C_S \]

Molecular model
\[ a_{MxO} = \left( \frac{\gamma_{MxS}}{K_i} \right) \left( \sum X_i M_i / 100M_S \right) C_S \]

The standard state of activity is its pure substance. Since the activity of ion in fused salt theoretically cannot be determined, next relation is assumed.

\[ a_{O^2-} = a_{MxO} \] (12)

It can agree that Eq. (12) might be permitted as the first order approximation of oxide activity in a simple slag system like CaO (highly basic oxide)–SiO2(highly acidic oxide)–CaS (very small amount). This first order approximation of Eq. (12) is unable to be permitted in complex systems like CaO–FeO–MnO–SiO2–P2O5. The theoretically reasonable equation is as follows,

\[ a_{MxO} = a_{Mx^{2+}} a_{O^2-} \] (13)

where, the standard state of activity is its pure substance, and the value of \( a_{O^2-} \) is unknown but it should be a function of the concentration of coexistent cations even at dilute solution of sulphur content in slag. The three slag systems of CaO–Al2O3–SiO2, MnO–SiO2–TiO2 and BaO–MnO–SiO2 in the paper14) are not simple case, in which Eq. (12) is applicable to estimate the \( a_{MxO} \) in slag. Because the attraction force between O2– and cations of many kinds must be considered.

ii) In Eq. (11) in the paper, it is clearly written that the standard state of the activity of MxS for the estimation of \( \gamma_{MxS} \) is taken to Henry’s law. On the other hand, the standard states of activities of components for the determination of \( K \) are not clear. If the standard states of the activity are pure CaO (solid or liquid) and CaS (solid or liquid), \( \gamma_{MxS} \) and \( K \) of different standard
state should not be used in one equation of Eq. (11).

iii) The paper by Ban-ya et al.\textsuperscript{11)} described the relation of $\gamma_i$ and $K_i$ in multi-components melt. The application of Henry’s law as the standard state of activity cannot be used without the definition of solvent and solute. If the sulphur concentration dissolved in multi-components slag obeys Henry’s law in the range of low sulphur content, the Henry’s constant, $\gamma_{MxS}$, is a function of solute composition. The detail of this relation is written in the paper by Ban-ya et al.\textsuperscript{11)}. The value of $\gamma_{MxS}$ is not a constant, and it is the function of slag composition.

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