Evaluation of Thermodynamic Activity of a Metallic Oxide in a Ternary Slag from the Sulphide Capacity of the Slag

M. HAYASHI, N. SANO¹⁾ and P. FREDRIKSSON

Royal Institute of Technology, Department of Materials Science and Engineering, SE-10044 Stockholm, Sweden.

1) Executive Advisor, Nippon Steel Corporation, Shintomi, Futtsu, Chiba 293-8511 Japan.

(Received on December 1, 2003; accepted in final form on August 31, 2004)

The correlation between the activity of a metallic oxide in a ternary slag system and the sulphide capacity of the slag was investigated. The solubility of sulphur in the binary systems CaO–SiO₂ and Al₂O₃–CaO along with its sulphide capacity of the Al₂O₃–CaO–SiO₂ system respectively have been used to estimate the activities of CaO at the compositions of some Al₂O₃–CaO–SiO₂ intermediate compounds. Estimation has been carried out assuming that the Gibbs free energy of fusion for the ternary composition is additive of those for pure substances. The estimated values of the activities are in good agreement with the measured values. This correlation is not only used to evaluate the activity but also, by comparing the estimated activities with the measured ones, it is possible to elucidate the applicability of Henry's law to the activity of a metallic sulphide and to determine the order in the affinity of a cation to sulphur between two metallic oxides in a slag.

KEY WORDS: activity; sulphide capacity; sulphur solubility; slag.

1. Introduction

In the refining of steel, activities of slag components and sulphide capacities of slag systems are both important thermodynamic concepts. In view of the great importance of these properties, considerable efforts have been made to obtain reliable experimental data regarding these properties as well as to extrapolate the data using suitable theoretical models. It is to be noted that the relative partial molar Gibbs energy of mixing, which is equal to $RT \ln a_{M_xO}$ (where R is the gas constant, T the temperature and a_{M_xO} the thermodynamic activity of the component oxide M_xO in the slag) as well as the sulphide capacity are partial molar properties of the system. In fact, the sulphide capacity of a binary silicate slag is related to the thermodynamic activity of the basic oxide in the system. Nilsson *et al.*¹⁾ have shown for a number of binary oxide systems that the sulphide capacities are linear functions of the activities of the basic oxides. Similar correlations are extremely desirable for higher order systems. Development of such correlations is difficult due to the non-adherence of the sulphide activities in the complex slags to Henry's law and the uncertainty regarding the relative effects of the various metal oxides with respect to their affinities to sulphur. A successful thermodynamic exercise in correlating the sulphide capacities with thermodynamic activities will yield a sounder theoretical basis for the use of thermodynamic principles in the desulphurization process in steelmaking. This is due to the fact that, the concept of sulphide capacity itself is built on the assumption that the activity coefficient of the sulphide ion in the slag as well as the oxide ion activity are independent of the

sulphur content.

However, the present attempt has a dissimilar aim. The thermophysical and thermochemical properties of slags are strongly dependent on the slag structure. Hence, it is natural to expect that these properties are interrelated. Based on this concept, considerable work has been carried out in the Division of Metallurgy, Royal Institute of Technology on relating viscosities with thermodynamic properties²⁾ and phase diagram information,³⁾ and enthalpies as well as densities.⁴⁾ Establishment of such mutual correlations would enable to estimate one property from another having reliable experimental data available. In the present study, a correlation between the activity and sulphide capacity respectively was developed for ternary systems in order to evaluate the activity of the metallic oxide of ternary systems from the sulphide capacity. It is expected that this approach will pave the way for developing models for the prediction of the thermodynamic activity of slag components from the vast amount of experimental data available for the sulphide capacities of multicomponent slag systems.

2. Basic Considerations

The equilibrium controlling the incorporation of sulphur in a slag from the gas phase at low chemical potential of oxygen can be represented by the equation,

The equilibrium constant for this reaction is given by,

$$K = \left(\frac{a_{S^{2-}}}{a_{O^{2-}}} \right) \cdot \left(\frac{p_{O_2}}{p_{S_2}} \right)^{1/2} = \frac{(x_{S^{2-}} \cdot \gamma_{S^{2-}})}{a_{O^{2-}}} \cdot \left(\frac{p_{O_2}}{p_{S_2}} \right)^{1/2} \dots (2)$$

The concentration of sulphur in weight percent is written as follows:

$$\text{wt\%S} = \frac{100x_{S^{2-}}M_S}{\sum_i x_i M_i} \dots (3)$$

where $x_{S^{2-}}$, M_S , x_i and M_i are the molecular fraction of sulphide (M_xS), the atomic weight of sulphur, and the molecular fraction and weight of component i , respectively. From Eqs. (2) and (3),

$$a_{O^{2-}} = \frac{\gamma_{S^{2-}}}{K} \cdot \frac{\sum_i x_i M_i}{100M_S} \cdot (\text{wt\%S}) \cdot \left(\frac{p_{O_2}}{p_{S_2}} \right)^{1/2} \dots (4)$$

The sulphide capacity is defined by Fincham and Richardson⁵⁾ as:

$$C_S = (\text{wt\%S}) \cdot \left(\frac{p_{O_2}}{p_{S_2}} \right)^{1/2} \dots (5)$$

By substituting Eq. (5) into Eq. (4),

$$a_{O^{2-}} = \frac{\gamma_{S^{2-}}}{K} \cdot \frac{\sum_i x_i M_i}{100M_S} C_S \dots (6)$$

Since activities of O^{2-} and S^{2-} ions cannot be directly measured, Eq. (1) can be rewritten in terms of neutral molecules dissolved in the slag:

$$\frac{1}{2} S_2(g) + (M_xO)_{\text{slag}} = \frac{1}{2} O_2(g) + (M_xS)_{\text{slag}} \dots (7)$$

The activity of M_xO can then be expressed as:

$$a_{M_xO} = \frac{\gamma_{M_xS}}{K} \cdot \frac{\sum_i x_i M_i}{100M_S} C_S \dots (8)$$

3. Evaluation of a_{CaO} from C_S in the $CaO-Al_2O_3-SiO_2$ System

In order to develop a method for evaluating the activity of the metallic oxide of ternary systems from the sulphide capacity, the $CaO-Al_2O_3-SiO_2$ system is considered as an example. Equations (7) and (8) can be rewritten as follows:

$$\frac{1}{2} S_2(g) + CaO = \frac{1}{2} O_2(g) + CaS \dots (9)$$

$$a_{CaO} = \frac{\gamma_{CaS}}{K_9} \cdot \frac{\sum_i x_i M_i}{100M_S} C_S \dots (10)$$

The standard Gibbs energy change for Eq. (9) is⁶⁾:

$$\Delta G_9^\circ = -RT \ln K_9 = 92\,048 - 4.73T \quad (\text{J/mol}) \dots (11)$$

To evaluate the value of a_{CaO} from the sulphide capacity by using Eq. (10), the value of γ_{CaS} at a ternary composition is

Table 1. Standard free-energy data for intermediate compounds.⁶⁾

Reaction	ΔH° (J/mole)	ΔS° (J/mole)
$<3CaO \cdot Al_2O_3> = 3<CaO> + <Al_2O_3>$	12 550	-24.7
$<CaO \cdot Al_2O_3> = <CaO> + <Al_2O_3>$	17 990	-18.8
$<CaO \cdot SiO_2> = <CaO> + <SiO_2>$	92 470	2.5
$<3CaO \cdot Al_2O_3 \cdot 3SiO_2> = 3<CaO> + <Al_2O_3> + 3<SiO_2>$	384 930	100.4
$<2CaO \cdot Al_2O_3 \cdot SiO_2> = 2<CaO> + <Al_2O_3> + <SiO_2>$	171 130	8.8
$<CaO \cdot Al_2O_3 \cdot SiO_2> = <CaO> + <Al_2O_3> + <SiO_2>$	105 860	14.2
$<CaO \cdot Al_2O_3 \cdot 2SiO_2> = <CaO> + <Al_2O_3> + 2<SiO_2>$	138 910	17.2

required.

When a ternary composition is containing substances 1 and 2 besides CaO and, the activity coefficients of CaS in CaO -1, and CaO -2 binary systems are known, the value of γ_{CaS} at the ternary composition can be calculated by using the activity coefficients in CaS for the two binary systems, i.e., $\gamma_{CaS,1}$ and $\gamma_{CaS,2}$ by employing the following equation,⁷⁾

$$\ln \gamma_{CaS} = x_1 \ln \gamma_{CaS,1} + x_2 \ln \gamma_{CaS,2} - \frac{\Delta G_1^E}{RT} \dots (12)$$

where ΔG_1^E is the excess Gibbs free energy of mixing for the liquid state, and x_1 and x_2 are the mole fractions of substances 1 and 2 respectively. The values of γ_{CaS} in the binary systems $CaO-SiO_2$ and $CaO-Al_2O_3$ were obtained by employing data on the CaS solubilities in the $CaO-SiO_2-CaS$ and $CaO-Al_2O_3-CaS$ systems⁸⁾ assuming that the activities of CaS in these systems obey Henry's law. This is, $\gamma_{CaS} = 1/x_{CaS}^\circ$ where x_{CaS}° is the CaS solubility. For Eq. (12), the value of ΔG_1^E is required. The excess Gibbs free energy of mixing for the liquid state, ΔG_1^E , required in Eq. (12) is:

$$\Delta G_1^E = \Delta G_1^M - RT(x_1 \ln x_1 + x_2 \ln x_2) \dots (13)$$

where ΔG_1^M is the Gibbs free energy of mixing for the liquid state. ΔG_1^M is correlated with the Gibbs free energy of mixing for the solid state ΔG_s^M as follows:

$$\Delta G_1^M = \Delta G_s^M + \Delta G_m - (x_1 \Delta G_{1m}^\circ + x_2 \Delta G_{2m}^\circ) \dots (14)$$

where ΔG_m , ΔG_{1m}° and ΔG_{2m}° are the Gibbs free energy of fusion for the ternary composition and the pure substances 1 and 2, respectively. If the following additivity rule is assumed,

$$\Delta G_m = x_1 \Delta G_{1m}^\circ + x_2 \Delta G_{2m}^\circ$$

then

$$\Delta G_1^M = \Delta G_s^M \dots (15)$$

The values of ΔG° for the formation of the intermediate compounds $CaO-Al_2O_3$, $CaO-SiO_2$, $3CaO-Al_2O_3$, $2CaO-Al_2O_3-SiO_2$, $CaO-Al_2O_3-2SiO_2$, $CaO-Al_2O_3-SiO_2$ and $3CaO-Al_2O_3-3SiO_2$ from CaO , Al_2O_3 and/or SiO_2 respectively presented in **Table 1** were taken from the compilation of Turkdogan.⁶⁾ These compounds correspond to the points a, b, c, I, II, III and IV respectively in **Fig. 1** and $(1/2)(CaO \cdot Al_2O_3)$, $(1/2)(CaO \cdot SiO_2)$, $(1/4)(3CaO \cdot Al_2O_3)$, $(1/4)(2CaO \cdot Al_2O_3-SiO_2)$, $(1/4)(CaO \cdot Al_2O_3 \cdot 2SiO_2)$, $(1/3) \times (CaO \cdot Al_2O_3 \cdot SiO_2)$, and $(1/7)(3CaO \cdot Al_2O_3 \cdot 3SiO_2)$ are abbreviated as a, b, c, I, II, III and IV, respectively. Therefore, the values of ΔG_1^M and ΔG_1^E for the following five reactions can be calculated by using Eqs. (15) and (13).

Fig. 1. Compositions on which a_{CaO} was determined in the Al_2O_3 -CaO-SiO₂ system.

Table 2. Values of ΔG_1^M and ΔG_1^E at 1773 K for the five reactions.

Reaction	ΔG_1^M / (J/mole)	ΔG_1^E / (J/mole)
$\frac{1}{2}a + \frac{1}{2}b = I$	-4042	6192
$\frac{1}{2}c + \frac{1}{2}II = I$	-18284	-8075
$\frac{1}{3}a + \frac{2}{3}II = III$	-233.0	9163
$\frac{4}{7}b + \frac{3}{7}III = IV$	6569	16652
$\frac{2}{7}I + \frac{2}{7}II + \frac{3}{7}b = IV$	7615	23514

Table 3. Values of γ_{CaS} and C_s and calculated and measured values of a_{CaO} .

Compound	γ_{CaS}	$\text{Log}C_s^{(9)}$	$a_{\text{CaO}}(\text{calc.})$	$a_{\text{CaO}}(\text{meas.})^{(10)}$
I	25.0	-3.46	0.054	0.03
II	10.4	-4.93	0.00078	0.001
III	12.7	-4.37	0.0035	0.002
IV	3.97 2.88	-3.94	0.0026 0.0019	0.005

$$\frac{1}{2}a + \frac{1}{2}b = I \quad \dots\dots\dots(16)$$

$$\frac{1}{2}c + \frac{1}{2}II = I \quad \dots\dots\dots(17)$$

$$\frac{1}{3}a + \frac{2}{3}II = III \quad \dots\dots\dots(18)$$

$$\frac{4}{7}b + \frac{3}{7}III = IV \quad \dots\dots\dots(19)$$

$$\frac{2}{7}I + \frac{2}{7}II + \frac{3}{7}b = IV \quad \dots\dots\dots(20)$$

The values at 1773 K are summarized in Table 2. Since γ_{CaS} for the binaries compounds a, b and c respectively is obtained as 120, 12 and 20,⁽⁸⁾ and assuming that the activity of CaS obeys Henry's law, the γ_{CaS} at the ternary compositions I, II, III and IV can be calculated by Eq. (12) where Eq. (20) was used to check the consistency of the calcula-

Fig. 2. Comparison of the activity coefficient of MnS calculated from the data of C_s and a_{MnO} and the one obtained from the MnS solubility,⁽¹¹⁾ which are denoted by closed and open circles, respectively.

tions. By using information of the $C_s^{(9)}$ along with the values presented above, the activity of CaO can be calculated by using the relationship presented in Eq. (10). Comparison between the calculated and the measured values⁽¹⁰⁾ respectively are found in Table 3. The agreement is reasonable, considering the above made assumptions and the accuracies of the experimental measurements for a_{CaO} and C_s .

4. γ_{MnS} in the MnO-SiO₂-TiO₂ System

To evaluate the activity of a metallic oxide in a slag system from the sulphide capacity of the slag using Eq. (8), the activity coefficient of the metallic sulphide is required. To deduce the activity coefficient of the sulphide from the solubility of the same, it is assumed that the activity of sulphide obeys Henry's law. This assumption is in the following section examined for the MnO-SiO₂-TiO₂ system. Figure 2 shows a comparison of the activity coefficient of MnS, γ_{MnS} , calculated from the data of C_s and a_{MnO} by using Eq. (8) and the one obtained from the MnS solubility⁽¹¹⁾ using the relation $\gamma_{\text{MnS}} = 1/x_{\text{MnS}}^{\circ}$ where x_{MnS}° is the solubility for the MnO-SiO₂-TiO₂ system.⁽¹²⁾ It can be seen that the values of γ_{MnS} obtained from the MnS solubility are 1 to 5 times smaller than the ones calculated from the data of C_s and a_{MnO} by employing Eq. (8). This result indicates that Henry's law does not hold because x_{MnS}° is very high ranging from 53 to 73 wt%.⁽¹¹⁾ Consequently, it is concluded that evaluation of a_{MnS} from C_s using Eq. (8) makes a large error in this system.

5. Relationship between $a_{\text{O}^{2-}}$ and C_s for Slags Containing Two Metallic Oxides

Although this evaluation method is only available for the slags containing one metallic oxide, it is interesting to consider the relationship between the activity of a metallic oxide and the sulphide capacity of a slag system containing two metallic oxides by using Eq. (6). Figure 3 shows the relationship between C_s and a_{MnO} for the MnO-SiO₂ system and BaO-MnO-SiO₂ system at low BaO content.⁽¹³⁾

When $\log C_s$ is plotted against $\log a_{\text{MnO}}$, a straight line

Fig. 3. Relationship between $\log C_s$ and $\log a_{\text{MnO}}$ for the MnO-SiO₂ system and BaO-MnO-SiO₂ system at low BaO content.¹³⁾

Fig. 4. Relationship between $\log C_s$ and $\log a_{\text{BaO}}$ for the BaO-MnO system.^{13,14)}

appears with a slope of unity for higher SiO₂ content of the BaO-MnO-SiO₂ system and the MnO-SiO₂ system as shown in Fig. 3. Since Eq. (6) is rewritten as

$$\log a_{\text{O}^{2-}} = \log C_s + \log \frac{\gamma_{\text{S}^{2-}}}{K} \cdot \frac{\sum x_i M_i}{100 M_s} \dots \dots \dots (21)$$

this relationship reflects that the second term of the right hand side in Eq. (21) should be constant over the entire composition range of the MnO-SiO₂ and BaO-MnO-SiO₂ systems respectively.¹³⁾ At higher BaO range, however, a straight line may not be drawn as shown in Fig. 3, suggesting that $a_{\text{O}^{2-}}$ is not proportional to a_{MnO} but is affected by BaO. Figure 4 illustrates the relationship between C_s and a_{BaO} for the BaO-MnO system^{13,14)} where BaO is considered to be more basic than MnO. It is found that the plot of $\log C_s$ vs. $\log a_{\text{BaO}}$ yields a straight line having a slope of unity. This clearly indicates that a_{BaO} rather than a_{MnO} is closely related with $a_{\text{O}^{2-}}$.

6. Summary and Conclusions

The correlation between the activity and sulphide capacity was developed for ternary systems. A method to evaluate the activity of a metallic oxide of a ternary slag system from the sulphide capacity of the same is presented. For this method, the activity coefficient of the metallic sulphide is required. The activity of CaO at some compositions in the CaO-Al₂O₃-SiO₂ ternary system was successfully evaluated from the sulphide capacity data and the activity coefficient of CaS in the CaO-SiO₂ and CaO-Al₂O₃ binary systems assuming that the Gibbs free energy of fusion for the ternary composition is additive of those for pure substances. The activity coefficients of CaS were obtained from the solubility of CaS assuming that the activity of CaS obeys Henry's law. Although the activity coefficient of the metallic sulphide is required in this method and was obtained from the solubility of the same, the solubility of metallic sulphides have been measured in few cases and some values may be too large to assume Henry's law. This limits extension of this evaluation method at this stage.

Acknowledgements

Support from the Swedish Foundation for International Cooperation in Research and Higher Education, STINT are gratefully acknowledged. The authors would also like to acknowledge Professor Seshadri Seetharaman, division of Metallurgy, The Royal Institute of Technology, Sweden for valuable comments, suggestions and fruitful discussions.

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