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MATHEMATICAL EXPRESSION OF SLAG-METAL REACTIONS IN STEELMAKING PROCESS BY QUADRATIC FORMALISM BASED ON THE REGULAR SOLUTION MODEL

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Synopsis: An attempt has been made quantitatively to describe the slag-metal reactions in steelmaking process by the relation of quadratic formalism based on the regular solution model. The approximate validity of the model was quite enough to formulate the oxygen distribution, the ferrous-ferric iron equilibrium, the manganese distribution, the phosphorus distribution, the hydroxyl capacity and the activities of components.

KEY WORDS: slag-metal reaction; steelmaking; quadratic formalism; regular solution model; oxygen distribution; ferrous-ferric iron equilibrium; manganese distribution; phosphorus distribution; hydroxyl capacity; thermodynamics; activity.

1. Introduction

During the past three decades, the available data for the physico-chemical properties of metallurgical slags have been exceedingly improved by the efforts of many investigators in the world. The selected values of activity and chemical properties for numerous binary, ternary and quaternary oxide melts have been compiled and published in Germany[1] and Japan[2]. However, useful data in multi-component slags are quite a few to describe the slag-metal reactions in steelmaking process. This paper will describe the outline of our recent studies on the application of regular solution model to formulate the activities of slag constituents, the capacities of slags and slag-metal reactions concerning steelmaking processes. The regular solution model has been proposed by J.Lumsden(1961)[3]. Recently, the approximate validity of the regular solution model has been proved for many kinds of silicate, phosphate and aluminate slags of multi-component systems by the extensive studies of Ban-ya and his co-workers[2,4-7]. The activity coefficient of component, i, in a multi-component regular solution is expressed by the following equations:

$$\Delta \overline{G}_i^E = \Delta \overline{H}_i = RT\ln\gamma_i \quad \cdots\cdots (1)$$

$$RT\ln\gamma_i = \sum_j \alpha_{ij}X_j^2 + \sum_j\sum_k(\alpha_{ij} + \alpha_{ik} - \alpha_{jk})X_jX_k \quad \cdots\cdots (2)$$

where X_i is cation fraction, and α_{ij} is the interaction energy between cations, *i.e.*, (i cation)-O-(j cation). The reference state of the activity in this case is taken to hypothetical pure liquid, which has regular nature.

Many experimental results showed us that the activity coefficient of silicate melts can be approximately expressed with the following Eq. (3), even if this melts is not strictly regular solution:

$$RT\ln\gamma_i = \sum_j \alpha_{ij}X_j^2 + \sum_j\sum_k(\alpha_{ij} + \alpha_{ik} - \alpha_{jk})X_jX_k + I' \quad \cdots\cdots (3)$$

where I' is the conversion factor of activity coefficient between hypothetical regular solution and real solution. In order to apply the regular solution model for silicate melts, one should know the next three matters of (1) the composition range in which the regular nature is satisfied, (2) the value of the interaction energy, and (3) the conversion factor for the reference state of the activity between regular and real solution. These three matters obtained are listed in **Tables 1, 2 and 3.**

Table 1. Interaction energy between cations of major components in steelmaking slag, α_{ij}(J).

i \ j	Fe^{2+}	Fe^{3+}	Mn^{2+}	Ca^{2+}	Mg^{2+}	Si^{4+}	P^{5+}	Al^{3+}
Fe^{2+}		-18660	+7110	-31380	+33470	-41840	-31380	-41000
Fe^{3+}	-18660		-56480	-95810	-2930	+32640	+14640	-161080
Mn^{2+}	+7110	-56480		-92050	+61920	-75310	-84940	-83680
Ca^{2+}	-31380	-95810	-92050		-100420	-133890	-251040	-154810
Mg^{2+}	+33470	-2930	+61920	-100420		-66940	-37660	-71130
Si^{4+}	-41840	+32640	-75310	-133890	-66940		+83680	-127610
P^{5+}	-31380	+14640	-84940	-251040	-37660	+83680		-261500
Al^{3+}	-41000	-161080	-83680	-154810	-71130	-127610	-261500	

Table 2. Interaction energy between cations of other components.

(*i* cation)-(*j* cation)	α_{ij} (J)	(*i* cation)-(*j* cation)	α_{ij} (J)
Li^{+} -Si^{4+}	- 142 130	H^{+}-Li^{+}	+ 1 500
Na^{+} -Fe^{2+}	+ 19 250	H^{+}-Na^{+}	+ 9 750
Na^{+} -Fe^{3+}	- 74 890	H^{+}-K^{+}	+ 13 520
Na^{+} -Si^{4+}	- 111 290	H^{+}-Mg^{2+}	+ 15 800
Na^{+} -P^{5+}	- 50 210	H^{+}-Ca^{2+}	+ 15 100
K^{+} -Si^{4+}	- 81 030	H^{+}-Mn^{2+}	- 8 230
Ti^{4+}-Ca^{2+}	- 167 360	H^{+}-Al^{3+}	- 24 400
Ti^{4+}-Mn^{2+}	- 66 940	H^{+}-Si^{4+}	+ 30 000
Ti^{4+}-Fe^{2+}	- 37 660	H^{+}-P^{5+}	+ 7 700
Ti^{4+}-Fe^{3+}	+ 1 260		
Ti^{4+}-Si^{4+}	+ 104 600		

Table 3. Conversion factors of activities.

Reaction	Free energy change (J)
$Fe_tO(l) + (1-t)Fe(s \text{ or } l) = FeO(R.S.)$	$\Delta G^0 = -\ 8\ 540 + 7.142T$
$SiO_2(\beta\text{-}tr) = SiO_2(R.S.)$	$\Delta G^0 = +\ 27\ 150 - 2.054T$
$SiO_2(\beta\text{-}cr) = SiO_2(R.S.)$	$\Delta G^0 = +\ 27\ 030 - 1.983T$
$SiO_2(l) = SiO_2(R.S.)$	$\Delta G^0 = +\ 17\ 450 + 2.820T$
$MnO(s) = MnO(R.S.)$	$\Delta G^0 = -\ 32\ 470 + 26.143T$
$MnO(l) = MnO(R.S.)$	$\Delta G^0 = -\ 86\ 860 + 51.465T$
$Na_2O(l) = 2NaO_{0.5}(R.S.)$	$\Delta G^0 = -\ 185\ 060 + 22.866T$
$CaO(s) = CaO(R.S.)$	$\Delta G^0 = +\ 18\ 160 - 23.309T$
$CaO(l) = CaO(R.S.)$	$\Delta G^0 = -\ 40\ 880 - 4.703T$
$MgO(s) = MgO(R.S.)$	$\Delta G^0 = +\ 34\ 350 - 16.736T$
$MgO(l) = MgO(R.S.)$	$\Delta G^0 = -\ 23\ 300 + 1.833T$
$P_2O_5(l) = 2PO_{2.5}(R.S.)$	$\Delta G^0 = +\ 52\ 720 - 230.706T$

2. Oxygen Distribution between Slag and Metal

The equilibrium relation of $FeO\text{-}Fe_2O_3\text{-}MnO\text{-}SiO_2\text{-}MgO\text{-}CaO$ slag with oxygen in metal can be written as follows by the model[4,8,9].

$$Fe(l) + \underline{O} = FeO(R.S.) \quad \cdots\cdots (4)$$

$$RT\ln K_O = RT\ln(X_{FeO}/a_O) + RT\ln\gamma_{FeO} \quad \cdots\cdots (5)$$

$$\Delta G^o = 128\ 100 - 57.99T\ (J) \quad \cdots\cdots (6)$$

$$\begin{aligned} RT\ln\gamma_{FeO} = & -18\ 660X^2_{FeO_{1.5}} + 7\ 110X^2_{MnO} - 41\ 840X^2_{SiO_2} + 33\ 470X^2_{MgO} \\ & - 31\ 380X^2_{CaO} + 44\ 930X_{FeO_{1.5}}\cdot X_{MnO} - 93\ 140X_{FeO_{1.5}}\cdot X_{SiO_2} \\ & + 17\ 740X_{FeO_{1.5}}\cdot X_{MgO} + 45\ 770X_{FeO_{1.5}}\cdot X_{CaO} + 40\ 580X_{MnO}\cdot X_{SiO_2} \\ & - 21\ 340X_{MnO}\cdot X_{MgO} + 67\ 780X_{MnO}\cdot X_{CaO} + 58\ 570X_{SiO_2}\cdot X_{MgO} \\ & + 60\ 670X_{SiO_2}\cdot X_{CaO} + 102\ 510X_{MgO}\cdot X_{CaO}\ (J) \quad \cdots\cdots (7) \end{aligned}$$

In Fig. 1, the oxygen contents in iron calculated by above equations of the regular solution model[8] were compared with the measured values for the typical measurements of previous works. From the results, it is confirmed that the oxygen content in liquid iron in equilibrium with slag can be estimated within the accuracy of ± 10% by the model.

The reference state of FeO activity in the model is taken to the hypothetical stoichiometric FeO of regular nature. However, the reference state of conventional iron oxide activity is the pure iron oxide in equilibrium with metallic iron. The conversion of the reference state is written as follows from Table 3[5,10]:

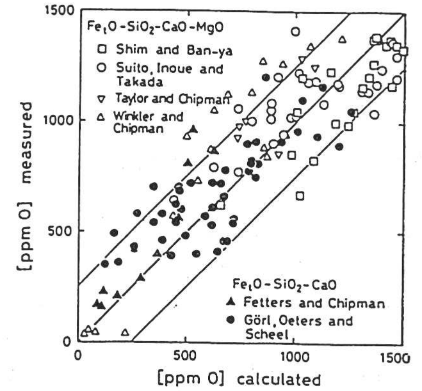

Fig. 1. Estimated values for oxygen contents by regular solution model and the measured values in liquid iron equilibrated with $Fe_tO\text{-}(CaO+MgO)\text{-}SiO_2$ slags.

$$Fe_tO(l) + (1 - t)Fe(s \text{ or } l) = FeO(R.S.) \quad \cdots\cdots (8)$$

$$\Delta G^o = -\ 8\ 540 + 7.142T\ (J) \quad \cdots\cdots (9)$$

$$RT\ln a_{Fe_tO(l)} = RT\ln a_{FeO(R.S.)} - 8\ 540 + 7.142T\ (J) \quad \cdots\cdots (10)$$

In Fig. 2, the activity of iron oxide, a_{Fe_tO}, in $Fe_tO\text{-}CaO\text{-}SiO_2$ ternary[9] in equilibrium with liquid iron estimated by the model was shown to compare with the experimental results of many previous investigators, who were referred to Fig. 1. An agreement of both measured and calculated values was excellent over the wide range of slag composition from acid side to basic side except for extremely FeO rich region of $N_{Fe_tO}>0.7$.

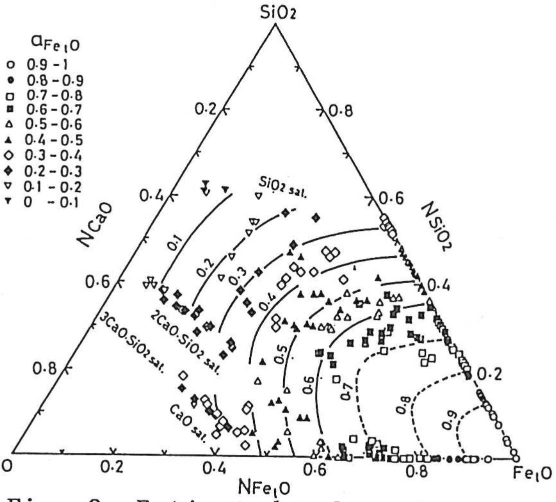

Fig. 2. Estimated values for $a_{Fe_tO(l)}$ by regular solution model and the measured values in Fe_tO-CaO-SiO_2 slags equilibrated with liquid iron at 1873K.

3. Ferrous-Ferric Iron Equilibrium in Slag

The quantitative treatment of the ferrous-ferric iron equilibrium in slag was very difficult due to the complicate variation by the slag composition and temperature. The Λ-ratio = Fe^{3+}/Fe^{2+} can be given by the model as follows[4,8]:

$$FeO_{1.5}(R.S.) = FeO(R.S.) + 1/4O_2(g) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(11)$$

$$RT\ln K_{Fe} = RT\ln(X_{FeO}/X_{FeO_{1.5}}) + 0.25RT\ln P_{O_2} + RT\ln(\gamma_{FeO}/\gamma_{FeO_{1.5}}) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(12)$$

$$\Delta G^{\circ} = 126\ 820 - 53.01T(J) \quad (13)$$

$$\log(Fe^{3+}/Fe^{2+}) = 6\ 625/T - 2.77 + 0.25\log P_{O_2} + (RT\ln\gamma_{FeO} - RT\ln\gamma_{FeO_{1.5}})/(19.1T) \quad \cdots\cdots\cdots(14)$$

It was confirmed that Eq. (14) quantitatively described the redox reactions of iron in slag.

4. Equilibrium of Manganese Distribution

The equilibrium relation of manganese distribution between slag and liquid iron can be written as follows[7]:

$$FeO(R.S.) + \underline{Mn} = Fe(l) + MnO(R.S.) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(15)$$

$$RT\ln K_{Mn} = RT\ln[X_{MnO}/(a_{FeO(R.S.)}\cdot a_{Mn})] + RT\ln\gamma_{MnO(R.S.)} \quad \cdots\cdots(16)$$

$$\Delta G^{\circ} = -141\ 400 + 66.28T\ (J) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(17)$$

In Fig. 3, the equilibrium constant of manganese distribution in Fe_tO-MnO-CaO-MgO-SiO_2 slag were plotted against the silica content to examine the validity of model. As seen in Fig. 3, the values of $\log K_{Mn}$ treated by the model were almost a constant value within experimental error over the wide range of slag composition.

The effect of temperature on the $\log K_{Mn}$ is expressed with Eq. (17). This equation was determined by the data reported by eight research groups.

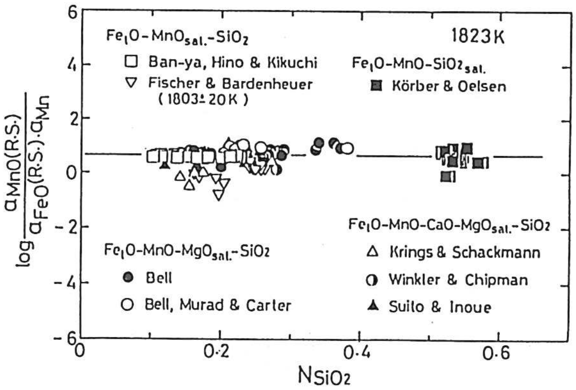

Fig. 3. Relation between equilibrium constant calculated by regular solution model and N_{SiO_2} at 1823K.

5. Equilibrium of Phosphorus Distribution

The equilibrium relation of phosphorus with slag can be written as follows[6,11]:

$$\underline{P} + 2.5\,\underline{O} = (PO_{2.5})(R.S.) \quad \cdots\cdots(18)$$

$$RT\ln K_{P1} = RT\ln[X_{PO_{2.5}}/(a_P\cdot a_O^{2.5})] + RT\ln\gamma_{PO_{2.5}}(R.S.) \quad \cdots\cdots(19)$$

$$\Delta G^\circ = -326\,520 + 162.88T \ (\sigma = 13\,810)\ (J) \quad \cdots\cdots(20)$$

The effect of temperature on the $\log K_{P1}$[6] treated by the model was shown in Fig. 4, in which the data reported by other five research groups. The results obtained by different kinds of slags and by many different investigators were in fairly good agreement with each other, and Eq.(20) was given.

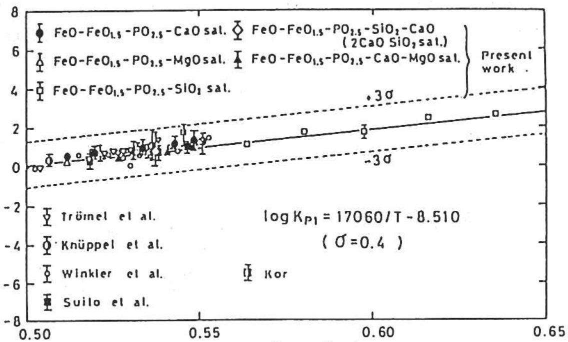

Fig. 4. Temperature dependence of $\log K_{P1}$.

The equilibrium relation of phosphorus in iron with iron oxide in slag can be derived as follows by the combination of Eqs. (6) and (20):

$$\underline{P} + 2.5(FeO)(\text{in slag}) = (PO_{2.5})(R.S.) + 2.5Fe(l) \quad \cdots(21)$$

$$\Delta G^\circ_{P2} = 6\,280 + 17.908T \ (\sigma = 13\,810)\ (J) \quad \cdots\cdots(22)$$

Figure 5 shows the comparison of the activity coefficient of P_2O_5 between measured and calculated values. In the past, the slag models, proposed by Flood and Grjøtheim [13], and Turkdogan and Pearson[12] were accurate enough to predict the phosphorus distribution for basic slag, but the models of the same idea were not successful to predict the oxygen distribution. However, in the case of the regular solution model, the distribution ratios of both oxygen and phosphorus can be estimated within the error of ± 10% over the wide range from basic slag to acid slag.

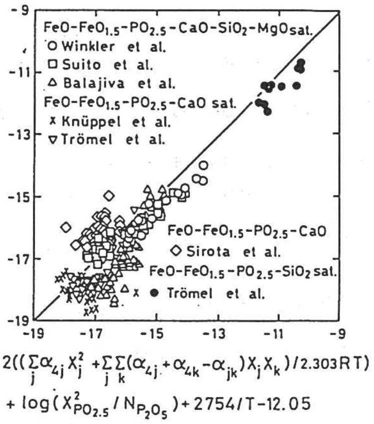

Fig. 5. Comparison between measured and calculated $\log\gamma_{P_2O_5}$.

6. Estimation of Hydroxyl Capacity

The equilibrium relation of water vapor solubility in silicate melts is written as follows by the model:

$$1/2H_2O(g) = HO_{0.5}(R.S.) \quad \cdots\cdots(23)$$

$$RT\ln K_{H_2O} = RT\ln X_{HO_{0.5}} - 1/2\log P_{H_2O} + RT\ln\gamma_{HO_{0.5}}(R.S.) \quad \cdots\cdots(24)$$

$$\Delta G^\circ_{H_2O} = -19\,800 + 26.32T\ (J)\ (1430 - 1873K) \quad \cdots\cdots(25)$$

Therefore, the hydroxyl capacity defined with mole fraction base, C'_{OH}, is expressed as follows:

$$\begin{aligned} RT\ln C'_{OH} &= RT\ln K_{H_2O} - RT\ln\gamma_{HO_{0.5}}(R.S.) \\ &= RT\ln K_{H_2O} - \sum_i \alpha_{H-i}X_i^2 - \sum_i\sum_j(\alpha_{H-i} + \alpha_{H-j} - \alpha_{ij})X_iX_j \quad (26) \end{aligned}$$

Figure 6 shows approximate validity of the model for the hydroxyl capacity of seven kinds of silicate melts.

7. Correction of the Interaction Energy with Other Physico- Chemical

Properties

The heat of mixing of multicomponent regular solution can be expressed is follows:

$$\Delta H^M = \sum_i \sum_j \alpha_{ij} X_i X_j \quad \cdots\cdots\cdots (27)$$

As a rough approximation of Eq. (27), the heat of formation of binary complex oxide, ΔH°_{298}, can be written as follows:

$$\Delta H^\circ_{298} \fallingdotseq \alpha_{ij} X_i X_j \quad \cdots\cdots\cdots (28)$$

Figure 7 shows the relationship between the heat of formation binary complex oxides[5], ΔH°_{298}, and the term of $\alpha_{ij}X_iX_j$ related to these complex oxides. A good correlation is found between them, especially in the range lower than $\Delta H^\circ_{298} = -41.8$ kJ. It is said that the bonding energy of (i cation)-(O)-(j cation) ion pair are affected by the valence and radius of cation. Therefore, **Fig. 8** shows the relationship of ionic radius and valence for $\alpha_{Fe^{2+}-M^{z+}}$ as one of the example of many interaction energies[9]. A good correlation was also found among the ionic radius, valence and interaction parameter except for Ti^{4+}.

8. Conclusion

It was confirmed that the regular solution model for silicate melts was valid to estimate the activities of slag constituents, the capacity of slag and the slag-metal reactions concerning steelmaking process.

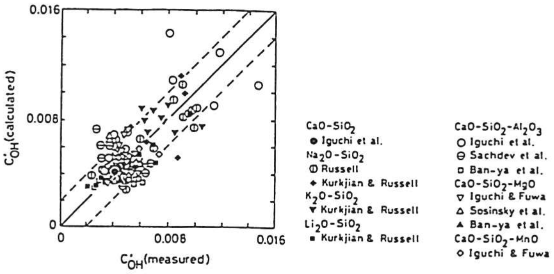

Fig. 6. Comparison of estimated values of C'_{OH} by regular solution model and the measured values in molten silicate slags.

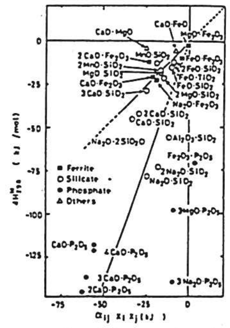

Fig. 7. Correlation between interaction energies and the heats of formation of complex oxides at 298K.

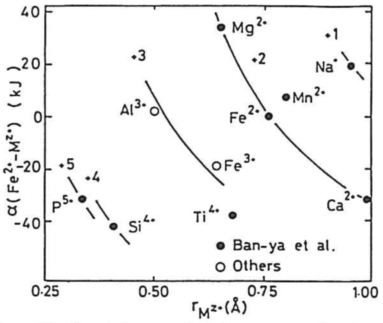

Fig. 8. Relation between interaction energies and cation radii.

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