Thermodynamic Properties of $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$, $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$, $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ and $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{SiO}_2-\text{Na}_2\text{O}$ Slags*

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Synopsis

The chemical equilibria of gas-slag reactions have been studied to clarify the effect of soda on the thermodynamic properties of slags in the hot metal treatment. The slags studied are the $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$ system (1 610 °C) equilibrated with $P_{\text{CO}_2}=1$ atm by using a Pt-crucible, the $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ system (1 400 °C), the $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ system (1 200 °C) and the $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{SiO}_2-\text{Na}_2\text{O}$ system (1 200 °C) equilibrated with $\text{H}_2\text{O}/\text{H}_2$ gas mixture by using a solid iron crucible. The influence of slag composition on the activity of iron oxide and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio has been determined. It has been clarified that the results can be expressed in terms of the Lumsden's regular solution model over a wide range of composition in the systems of $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$ and $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$. However, the model is not applicable to phosphate slags containing Na_2O . The iso-activity line for each component, iso- $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio lines and iso- P_{O_2} lines for the $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ slag in equilibrium with liquid iron at 1 400 °C have been calculated using the regular solution model.

I. Introduction

Many kinds of fluxes have been developed to eliminate phosphorus and sulphur in hot metal before steel-making process by ladle treatment. A special attention has been focused on soda ash among these fluxes because of its strong power of dephosphorization and desulphurization.^{1,2)} The studies of the physico-chemical properties of soda bearing slags, however, are very few due to experimental difficulties such as contamination of the vessel used and vaporization of soda.³⁾ In the present work, two series of measurements have been made to clarify the thermodynamic properties of soda bearing slags containing iron oxide. In the first series of experiments, the equilibrium of CO_2 with $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$ slag was studied by using a Pt crucible at 1 610 °C. The second series was on the equilibrium between $\text{H}_2\text{O}/\text{H}_2$ gas mixture and $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$, $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ or $\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags contained in a solid iron crucible at 1 200 °C or 1 400 °C. The results obtained were used to evaluate the effect of Na_2O on the activity of iron oxide and ferrous-ferric equilibrium in these slags. In view of the ionic theory of slags, approximate validity of the regular solution model proposed by Lumsden⁴⁾ was examined to estimate the activity of each component in these slags. From the results, it was confirmed that the regular solution model is satisfied over wide composition ranges in $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$

and $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ slags, but the model is not applicable to $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ and $\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags.

II. Experimental Procedure

Two series of experiments in the present work were made by the use of the same experimental apparatus and similar experimental procedure. Details of the experimental apparatus and techniques have been described in the previous paper,⁵⁾ and the outline is as follows:

The iron crucible containing the slag sample of 4.0 g was suspended with a Mo wire in a reaction tube and equilibrated with $\text{H}_2\text{O}/\text{H}_2$ gas mixtures at 1 200 °C or 1 400 °C for 7 hr. In the preliminary experiments, it was confirmed that the reaction time of 7 hr was enough to approach equilibrium. At the end of run, the crucible was lowered to the quenching section kept in an Ar atmosphere. After crushing the quenched sample, the contents of ferrous iron, total iron and other oxides in the sample were determined by chemical analysis. The sum total of each content determined by chemical analysis was within 100 ± 1 wt% for samples equilibrated with $\text{H}_2\text{O}/\text{H}_2$ gas mixtures, and was within 98.4 ± 1.6 wt% for $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$ slag melted in a CO_2 atmosphere. In the measurement of CO_2 -slag reaction, a special purification train for CO_2 was set to the apparatus, and the heating device was changed to the Keramax electric resistance furnace (8 kVA).

III. Experimental Results

1. Ferrous-Ferric Equilibrium in Slags

Since iron oxide in equilibrium with metallic iron is not a true stoichiometric ferrous oxide FeO as known from $\text{Fe}-\text{O}$ phase diagram, the following equilibria of ferrous-ferric ions can be expected in the gas-slag-metal system.

Gas-slag reaction:

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Slag-metal reaction:

It is interesting how the value of $\text{Fe}^{3+}/\text{Fe}^{2+}$ changes by the addition of other oxides to iron oxide.

1. System $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$

Figure 1 shows variation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$ slags equilibrated with $P_{\text{CO}_2}=1$ atm at 1 610 °C as a function of $N_{\text{Na}_2\text{O}}$. The ratios in $\text{Fe}_t\text{O}-\text{MnO}$ and $\text{Fe}_t\text{O}-\text{CaO}$ slags by Gurry and Darken⁶⁾ are also shown in Fig. 1 for comparison. It was found that Na_2O in slag increased the ratio more strongly than MnO and CaO .

2. System $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$

The solid lines in Fig. 2 show $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio observed in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ slags equilibrated with solid iron at 1 400 °C against $N_{\text{Fe}_t\text{O}}$ at each $N_{\text{Na}_2\text{O}}/N_{\text{SiO}_2}$ ratio. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio increased markedly with increasing $N_{\text{Na}_2\text{O}}/N_{\text{SiO}_2}$ at a given $N_{\text{Fe}_t\text{O}}$, and also increased slightly with increasing $N_{\text{Fe}_t\text{O}}$ at constant $N_{\text{Na}_2\text{O}}/N_{\text{SiO}_2}$ except for highly basic region. It meant that Na_2O and Fe_tO behave themselves as basic oxide in this system.

3. System $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$

Figure 3 shows experimental results on $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags equilibrated with metallic iron at 1 200 °C. The observed variation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio shown by solid lines is similar to that in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ slags, but it was recognized that the degree of variation by Na_2O addition was smaller than that in

iron sodium silicates.

Since the variation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio by the kinds of added oxides might be explained by formation of ferric complex anion from ferric ion, the ratio would be affected by the basicity of slags.

2. Activity of Iron Oxide in Slags

A principal reaction in this experiment is represented by Eq. (3), and the activity of iron oxide with reference to pure iron oxide in equilibrium with solid iron is obtained from Eq. (4) by applying the equilibrium constant and $\text{H}_2\text{O}/\text{H}_2$ gas ratio at a given temperature.

$$K_3 = P_{\text{H}_2\text{O}} / (P_{\text{H}_2} \cdot a_{\text{Fe}_t\text{O}}) \quad \dots\dots\dots(4)$$

where the equilibrium constant K_3 has been already confirmed in the previous work.⁵⁾

The activity of iron oxide in this paper was de-

Fig. 1. The ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in $\text{Fe}_t\text{O}-\text{MO}$ slags under $P_{\text{CO}_2}=1$ atm in the vicinity of 1 600 °C.

Fig. 2. The ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ slags in equilibrium with solid iron at 1 400 °C.

Fig. 3. The ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags in equilibrium with solid iron at 1 200 °C.

terminated based on two different reference states. The reference state of iron oxide designated with a_{FeO} is the pure liquid of a hypothetical stoichiometric FeO, and that with $a_{\text{Fe}_2\text{O}_3}$ is taken of the pure iron oxide in equilibrium with solid iron, where $N_{\text{Fe}_2\text{O}_3} = N_{\text{FeO}} + N_{\text{Fe}_2\text{O}_3}$. Thermodynamic data used in the present work are summarized in Table 1.

1. System $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$

Figure 4 shows iso-activity curves of Fe_tO in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ slags in equilibrium with solid iron at 1 400 °C. Activity of Fe_tO , $a_{\text{Fe}_t\text{O}}$ indicated a strong positive deviation from the ideality by the addition of Na_2O to $\text{Fe}_t\text{O}-\text{SiO}_2$ slags. This slag is the fundamental system for hot metal treatment, but activity data are very few in previous papers.^{7,8)}

2. System $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$

All the measurements for system $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ were made at 1 200 °C. Iso-activity curves of Fe_tO obtained are shown in Fig. 5. It is one of the important properties of liquid $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags that there is a wide area of miscibility gap. The region of miscibility gap determined by Olsen and Wiemer⁹⁾ is shown in Fig. 5, where point C_1 on the miscibility boundary is the critical point of the tie line of the two conjugate melts. It is very interesting that directions of contours of iso-activity of iron oxide change to the direction of $3\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ and the contours are almost parallel to the miscibility boundary. The tendency of the iso-activity contours is reasonable from the facts that the sodium phosphate is the most chemically stable compound in $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags, and that the activities of components in the two conjugate melts should be equal. The same tendency is re-

cognized in $a_{\text{Fe}_2\text{O}_3}$ in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{CaO}$ slags. The effect of addition of Na_2O to $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5$ binary slags on the activity of iron oxide is shown in Fig. 6 to compare with those of MgO and CaO .^{5,10)} For a given $N_{\text{Fe}_t\text{O}}$, the addition of Na_2O causes a greater in-

Fig. 5. Iso-activity curves of Fe_tO in $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags in equilibrium with solid iron at 1 200 °C.

Fig. 4. Iso-activity curves of Fe_tO in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{Na}_2\text{O}$ slags in equilibrium with solid iron at 1 400 °C.

Fig. 6. Comparison of Fe_tO activities in $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-0.1-N_{\text{MgO}}$, $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-0.1-N_{\text{CaO}}$ and $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-0.1-N_{\text{Na}_2\text{O}}$ slags at 1 400 °C.

Table 1. Standard free energies of the reactions.

Reactions	Free energy change (cal)	Refs.
$\text{Fe}_t\text{O}(\text{l}) + \text{H}_2(\text{g}) = \text{Fe}(\gamma) + \text{H}_2\text{O}(\text{g})$	$\Delta G^\circ = -7\,525 + 4.767\,T$	5)
$\text{Fe}_t\text{O}(\text{l}) + \text{H}_2(\text{g}) = \text{Fe}(\delta) + \text{H}_2\text{O}(\text{g})$	$\Delta G^\circ = -7\,265 + 4.607\,T$	5)
$\text{FeO}_{1.5}(\text{R.S.}) = \text{FeO}(\text{R.S.}) + 1/4\text{O}_2(\text{g})$	$\Delta G^\circ = 30\,310 - 12.67\,T$	4)
$\text{Fe}(\gamma) + \text{H}_2\text{O}(\text{g}) = \text{FeO}(\text{R.S.}) + \text{H}_2(\text{g})$	$\Delta G^\circ = 5\,485 - 3.06\,T$	4), 19), 20), 24)
$\text{Fe}(\delta) + \text{H}_2\text{O}(\text{g}) = \text{FeO}(\text{R.S.}) + \text{H}_2(\text{g})$	$\Delta G^\circ = 5\,225 - 2.90\,T$	4), 19), 20), 24)
$\text{Fe}(\text{l}) + 1/2\text{O}_2(\text{g}) = \text{FeO}(\text{R.S.})$	$\Delta G^\circ = -58\,391 + 12.90\,T$	4), 19), 20), 24)
$\text{Fe}(\text{l}) + 2\text{FeO}_{1.5}(\text{R.S.}) = 3\text{FeO}(\text{R.S.})$	$\Delta G^\circ = 2\,229 - 12.44\,T$	4), 19), 20), 24)

crease in $a_{\text{Fe}_t\text{O}}$ than do equivalent additions of MgO and CaO.

3. System $\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$

The activity of iron oxide in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags was determined at 1 200 °C. Iso-activity curves for $a_{\text{Fe}_t\text{O}}=0.45$ and 0.55 obtained are projected on the $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ phase diagram as shown in Fig. 7, respectively. The iso-activity curves of $a_{\text{Fe}_t\text{O}}$ in two figures of Fig. 7 move towards the $\text{Fe}_t\text{O}-\text{Na}_2\text{O}$ side with increasing SiO_2 contents in $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags.

According to the report by Oelsen and Maetz¹¹⁾ on the phase diagram of $\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{CaO}$, the region of miscibility gap becomes narrower with increasing SiO_2 contents in $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{CaO}$ slags as shown in Fig. 8. Since the same tendency of miscibility boundary can be expected even in $\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags, the variation of iso-activity contours of Fe_tO by the addition of SiO_2 in $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags might be explained from change of the miscibility region.

Fig. 7. Variation of iso-activity curves of $a_{\text{Fe}_t\text{O}}=0.45$ and $a_{\text{Fe}_t\text{O}}=0.55$ with addition of SiO_2 to $\text{Fe}_t\text{O}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ slags in equilibrium with solid iron at 1 200 °C.

IV. Discussion

One of the authors has reported that the regular solution model proposed by Lumsden could approximately be applied to express thermodynamic properties of $\text{Fe}_t\text{O}-\text{CaO}-\text{SiO}_2$ and $\text{Fe}_t\text{O}-\text{CaO}-\text{SiO}_2-\text{MgO}$ slags.¹²⁻¹⁷⁾ Therefore, the approximate validity of this model for soda bearing slags containing iron oxide was also discussed for further extension to the reactions in hot metal treatment.

The activity coefficient of a component in a multi-component regular solution is expressed by the following equation^{4,10,16,18)}:

$$RT \ln \gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \quad \dots \dots \dots (5)$$

where, X_j : cation fraction of component j in slag

α_{ij} : interaction energy between cations.

Sequence of subscripts is $i, j, k \dots$

1. Application to System $\text{FeO}-\text{Fe}_2\text{O}_3-\text{Na}_2\text{O}$

As an example of application of the regular solu-

Fig. 8. Phase diagrams of (a) system $\text{FeO}-\text{P}_2\text{O}_5-\text{Na}_2\text{O}$ and (b) system $\text{FeO}-\text{P}_2\text{O}_5-\text{CaO}-\text{SiO}_2$ in the vicinity of 1 400 °C.

tion model, the equilibrium reaction between ferrous and ferric ions in FeO-Fe₂O₃-Na₂O slags (1-2-4 component system) under $P_{\text{CO}_2}=1$ atm is written as follows⁴⁾:

$$RT \ln K_6 = RT \ln (\gamma_{\text{FeO}}/\gamma_{\text{FeO}_{1.5}}) + RT \ln (X_{\text{FeO}}/X_{\text{FeO}_{1.5}}) + 0.25RT \ln P_{\text{O}_2} \dots\dots\dots(7)$$

From $\alpha_{12}(\text{Fe}^{2+}-\text{Fe}^{3+}) = -4\,460$ cal,⁴⁾ the following relation is given:

$$\begin{aligned} (\alpha_{14}-\alpha_{24})X_{\text{NaO}_{0.5}} &= -30\,310 + 12.67T + 4.576T \log (X_{\text{FeO}_{1.5}}/X_{\text{FeO}}) \\ &\quad - 4\,460(X_{\text{FeO}}-X_{\text{FeO}_{1.5}})/X_{\text{SiO}_2} - 0.25 \times 4.576T \log P_{\text{O}_2} \\ &\equiv YA \dots\dots\dots(8) \end{aligned}$$

The left hand side of Eq. (8) is the unknown terms, and the right hand side can be calculated from the experimental data. If this solution formed the regular solution, the values of YA obtained from relation of Eq. (8) should be a linear function of cation fraction of NaO_{0.5}. Points of data obtained fit well upon a straight line passing through the origin as shown in Fig. 9.

2. Application to System FeO-Fe₂O₃-SiO₂-Na₂O

The following relation is given by the application of the regular solution model to equilibrium reaction between ferrous and ferric ions in FeO-Fe₂O₃-SiO₂-Na₂O slags (1-2-3-4 component system) under the given H₂O/H₂ gas mixtures.^{4),19-23)}

Fig. 9. Relation between YA and $X_{\text{NaO}_{0.5}}$ in FeO-FeO_{1.5}-NaO_{0.5} slags under $P_{\text{CO}_2}=1$ atm at 1 610 °C, and relation between YB and $X_{\text{NaO}_{0.5}}/X_{\text{SiO}_2}$ in FeO-FeO_{1.5}-SiO₂-NaO_{0.5} slags in equilibrium with solid iron at 1 400 °C.

$$\begin{aligned} (\alpha_{14}-\alpha_{24})X_{\text{NaO}_{0.5}}/X_{\text{SiO}_2} &= -(7\,656/X_{\text{SiO}_2}) \log (X_{\text{FeO}}/X_{\text{FeO}_{1.5}}) \\ &\quad - 4\,460(X_{\text{FeO}}-X_{\text{FeO}_{1.5}})/X_{\text{SiO}_2} + 9\,345/X_{\text{SiO}_2} \\ &\quad - (3\,828/X_{\text{SiO}_2}) \log (P_{\text{H}_2\text{O}}/P_{\text{H}_2}) + 17\,800 \\ &\equiv YB \dots\dots\dots(9) \end{aligned}$$

The experimental results calculated by Eq. (9) are also shown in Fig. 9. The points of data obtained in FeO-Fe₂O₃-SiO₂-Na₂O slags fit as well upon a straight line passing through the origin in the whole range of NaO_{0.5} higher than $X_{\text{NaO}_{0.5}}/X_{\text{SiO}_2}=0.67$ and except the near range of SiO₂ saturation. The following result was obtained from the slope of the lines for the two systems studied.

$$(\alpha_{14}-\alpha_{24}) = 22\,500 \text{ cal} \dots\dots\dots(10)$$

The deviation from the regular behaviour at low NaO_{0.5} contents might be explained from incomplete ionization of SiO₂ rich melt, which partially has the behaviour of covalent melts.

The equilibrium relation between H₂O/H₂ and FeO-Fe₂O₃-SiO₂-Na₂O slags in contact with metallic iron is expressed by the following equations^{4),19,20,24)}:

$$RT \ln K_{11} = RT \ln \gamma_{\text{FeO}} + RT \ln X_{\text{FeO}} - RT \ln (P_{\text{H}_2\text{O}}/P_{\text{H}_2}) \dots\dots\dots(12)$$

The unknown term is written as follows at 1 400 °C:

$$\begin{aligned} \alpha_{14}(1+X_{\text{NaO}_{0.5}}/X_{\text{SiO}_2})-\alpha_{34} &= -[7\,656/(X_{\text{NaO}_{0.5}}X_{\text{SiO}_2})] \log X_{\text{FeO}} \\ &\quad + 4\,460X_{\text{FeO}_{1.5}}(1-X_{\text{FeO}})/(X_{\text{NaO}_{0.5}}X_{\text{SiO}_2}) \\ &\quad + 10\,000(1-X_{\text{FeO}})/X_{\text{NaO}_{0.5}} \\ &\quad + 7\,800X_{\text{FeO}_{1.5}}/X_{\text{NaO}_{0.5}} - 373/(X_{\text{NaO}_{0.5}}X_{\text{SiO}_2}) \\ &\quad + [7\,656/(X_{\text{NaO}_{0.5}}X_{\text{SiO}_2})] \log (P_{\text{H}_2\text{O}}/P_{\text{H}_2}) \\ &\quad - (\alpha_{14}-\alpha_{24})X_{\text{FeO}_{1.5}}/X_{\text{SiO}_2} \\ &\equiv YC \dots\dots\dots(13) \end{aligned}$$

As shown in Fig. 10, a good linear relation was observed between YC and $(1+X_{\text{NaO}_{0.5}}/X_{\text{SiO}_2})$ in the range of $X_{\text{NaO}_{0.5}}/X_{\text{SiO}_2} \geq 0.67$ and except the near range of SiO₂ saturation. The following value was obtained from the slope of the straight line.

$$\alpha_{14}(\text{Fe}^{2+}-\text{Na}^+) = 4\,600 \text{ cal} \dots\dots\dots(14)$$

From the value of an intercept in Fig. 10 and Eq. (10), the values of the following interaction energy were obtained:

$$\alpha_{24}(\text{Fe}^{3+}-\text{Na}^+) = -17\,900 \text{ cal} \dots\dots\dots(15)$$

$$\alpha_{34}(\text{Si}^{4+}-\text{Na}^+) = -26\,600 \text{ cal} \dots\dots\dots(16)$$

3. Application to System FeO-Fe₂O₃-P₂O₅-Na₂O

The application of the regular solution model to the equilibrium relation between ferrous and ferric ions in FeO-Fe₂O₃-P₂O₅-Na₂O slags under given H₂O/H₂ gas mixtures gives the same equations as in

Fig. 10. Relation between YC and $1 + X_{NaO_{0.5}}/X_{SiO_2}$ in $FeO-FeO_{1.5}-SiO_2-NaO_{0.5}$ slags in equilibrium with solid iron at 1400 °C.

the case of system $FeO-Fe_2O_3-SiO_2-Na_2O$. The unknown term in Eq. (12) is expressed as follows at 1200 °C:

System $FeO-Fe_2O_3-P_2O_5-Na_2O$ (1-2-5-4)

$$\begin{aligned} & (\alpha_{14} - \alpha_{24}) X_{NaO_{0.5}}/X_{PO_{2.5}} \\ &= [8190 - 6740 \log(X_{FeO}/X_{FeO_{1.5}}) \\ & \quad - 3370 \log(P_{H_2O}/P_{H_2}) \\ & \quad - 4460(X_{FeO} - X_{FeO_{1.5}})/X_{PO_{2.5}} + 11000] \\ & \equiv YD \end{aligned} \quad (17)$$

Results obtained are shown in Fig. 11. Many points of data lie on a straight line passing through the origin, but the slope of the line is not equal to that for the above-mentioned systems of $FeO-Na_2O$ and $FeO-SiO_2-Na_2O$. It means that the interaction energies between iron and sodium ions in sodium phosphate are different from those in ferrites and iron silicates containing Na_2O and it might be caused by the difference in structure of the matrix in phosphate melts from that in silicate melts.

4. Application to Fe^{3+}/Fe^{2+} Ratio and P_{O_2} for $FeO-SiO_2-Na_2O$ Slags in Equilibrium with Liquid Iron

The iso- Fe^{3+}/Fe^{2+} ratio and P_{O_2} for $FeO-SiO_2-Na_2O$ slags in equilibrium with liquid iron can be calculated combining Eqs. (6) and (18).

In Fig. 12, the contents of ferric oxide $N_{Fe_2O_3}$ calculated by the model are compared with those measured for $FeO-Na_2O$ slag under $P_{CO_2}=1$ atm at 1610 °C, and for $FeO-SiO_2-Na_2O$ slag in equilibrium with solid iron at 1400 °C. Good agreement was found between them. This is the confirmation that the regular solution model is applicable to sodium silicates containing Fe_2O_3 .

The calculated iso- Fe^{3+}/Fe^{2+} ratio lines and iso- P_{O_2} lines for $FeO-SiO_2-Na_2O$ slags in equilibrium with

Fig. 11. Relation between YD and $X_{NaO_{0.5}}/X_{PO_{2.5}}$ in $FeO-FeO_{1.5}-PO_{2.5}-NaO_{0.5}$ slags in equilibrium with solid iron at 1200 °C.

Fig. 12. Relation between calculated and measured $N_{Fe_2O_3}$ contents in $FeO-Na_2O$ slags under $P_{CO_2}=1$ atm at 1610 °C, and that in $FeO-SiO_2-Na_2O$ slags in equilibrium with solid iron at 1400 °C.

liquid iron at 1400 °C are shown in Fig. 13, where dotted lines express the limits of the area in which the regular solution model is applicable. The variation of calculated Fe^{3+}/Fe^{2+} shows a good agreement with the measured ratios shown in Fig. 2, because the free energy of fusion of iron at 1400 °C, (267 cal²⁴), is so small that the variation of Fe^{3+}/Fe^{2+} in the slags equilibrated with liquid iron is similar to that equilibrated with solid iron.

5. Activities of Slag Constituents in $FeO-SiO_2-Na_2O$ Slags

The reference state of activity of each component in the regular solution model is taken as a hypothetical pure liquid in which the relation of the regular solution is assumed to be satisfied. However, in general, the pure substance of stable state at a given temperature is usually taken as a reference state of each component in slags. Therefore, it is necessary to convert activity values between the two different reference states. The details have been described in a

$$\Delta G_{25} = 6\,462 - 0.474T \text{ cal} \quad (1\,470 \sim 1\,723^\circ\text{C})$$

.....(26)

$$\text{SiO}_2(\text{l}) = \text{SiO}_2(\text{R.S.})$$

.....(27)

$$\Delta G_{27} = 4\,171 + 0.674T \text{ cal} \quad (> 1\,723^\circ\text{C})$$

.....(28)

3. Activity of Na₂O

Free energies of conversion between $a_{\text{Na}_2\text{O}}(\text{l})$ and $a_{\text{NaO}_{0.5}}(\text{R.S.})$ calculated by regular solution model was estimated by using free energies of formation of $2\text{Na}_2\text{O} \cdot \text{SiO}_2(\text{l})$, $\text{Na}_2\text{O} \cdot \text{SiO}_2(\text{l})$ or $\text{Na}_2\text{O} \cdot 2\text{SiO}_2(\text{l})$,^{36,37)} and are shown in Fig. 16. The following equations were selected for the conversion of activity of Na₂O by using free energy of formation of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2(\text{l})$ ³⁶⁾:

$$\text{Na}_2\text{O}(\text{l}) = 2\text{NaO}_{0.5}(\text{R.S.})$$

.....(29)

$$\Delta G_{29} = -44\,227 + 5.465T \text{ cal} \quad (1\,132 \sim 1\,470^\circ\text{C})$$

.....(30)

$$RT \ln a_{\text{Na}_2\text{O}}(\text{l}) = 2RT \ln a_{\text{NaO}_{0.5}}(\text{R.S.}) - 44\,227$$

$$+ 5.465T \text{ cal}$$

$$= 2(RT \ln X_{\text{NaO}_{0.5}} + RT \ln \gamma_{\text{NaO}_{0.5}})$$

$$- 44\,227 + 5.465T \text{ cal} \text{(31)}$$

In Fig. 17, the value of $a_{\text{Na}_2\text{O}}(\text{l})$ estimated by Eq. (31) is compared with those in other studies^{29–34,38–41)} for Na₂O–SiO₂ binary slag at 1 200 °C. Present results agree comparatively well with those of Frohberg *et al.*,³¹⁾ and Yamaguchi *et al.*³³⁾

4. Activities of Slag Constituents in Fe_tO–SiO₂–Na₂O Slags

As already described, it was confirmed that the regular solution model is applicable in some region in sodium silicate slags bearing iron oxides. Activities of slag constituents in Fe_tO–SiO₂–Na₂O slags, therefore, can be calculated on the assumption of the regular solution model by using the interaction energies obtained and Eqs. (21), (24), (26), (28) and (31). Figure 18 shows one example for the system in equilibrium with liquid iron at 1 400 °C, where the regular

solution model is applicable in the region bounded by dotted lines.

It was recognized that addition of Na₂O to Fe_tO–SiO₂ binary slags increased $a_{\text{Fe}_t\text{O}}(\text{l})$ exceedingly.

- ①

Rego, Sigworth & Philbrook³⁴⁾
- ②

Charles³⁰⁾
- ③

Frohberg, Caune & Kapoor³¹⁾
- ④

Yamaguchi, Imai & Goto³³⁾
- ⑤

Kohsaka, Sato & Yokokawa⁴⁰⁾
- ⑥

Neudorf & Elliott³²⁾
- ⑦

Pearce²⁹⁾
- ⑧

Holmquist³⁸⁾
- ⑨

Sanders & Haller³⁹⁾
- ⑩

Tsukihashi, Yukinobu, Hyodo, Werme & Sano⁴¹⁾
- ⑪

Present work

Fig. 17. Comparison of $a_{\text{Na}_2\text{O}}(\text{l})$ in Na₂O–SiO₂ slags at 1 200 °C.

Fig. 16. Conversion factor of Na₂O activity.

Fig. 18. Iso-activity curves of the components in Fe_tO–SiO₂–Na₂O slags in equilibrium with liquid iron at 1 400 °C.

Fig. 19. Correlation between interaction energies and the heats of formation of complex oxides at 25 °C.

Therefore, the addition of Na₂O is very useful in dephosphorization process of hot metal. The value of $a_{\text{Na}_2\text{O}}(l)$ is very low as below 10^{-5.5} in the dotted region, where amount of vaporization of Na₂O from the slags would be negligibly small. On the other hand, $a_{\text{SiO}_2}(\beta\text{-tr})$ changes drastically from 0.05 to 0.7 in the same area.

6. Correlation of Interaction Energy with the Heat of Formation

Since the heat of mixing in regular solution is expressed by Eq. (32), the heats of formation for complex oxides should correlate with the values of interaction energies between cations.

$$\Delta H^M = \sum_i \sum_j \alpha_{ij} X_i X_j \dots\dots\dots(32)$$

There are few data about ΔH^M due to very high melting points or unstable properties of oxides. In general, the heat of fusion of oxide is negligibly small compared with the heat of formation of a solid complex oxide from simple oxides, and temperature dependency of the heats of formation is fairly small.⁴²⁾ Therefore, the following equation is obtained approximately for binary system.

$$\Delta H^M(s) \simeq \alpha_{ij} X_i X_j \dots\dots\dots(33)$$

In Fig. 19, the heats of formation of complex oxides are plotted against the interaction energies between cations, obtained in the present work and our previous papers.^{5,10,12-18,25,28)} A good correlation is found between them as shown in Fig. 19. The relation between both values was represented by Eq. (33)

within the range of $\Delta H^M(s) = -10$ kcal. This fact may prove that the application of the regular solution model to silicate slags containing Na₂O, in which $|\Delta H^M(s)| < +10$ kcal, is limited in some region of slag composition.

V. Conclusion

Two series of measurements have been made to clarify the thermodynamic properties of sodium silicates and phosphates containing iron oxides. In the first experiment, the chemical equilibrium of Fe_tO–Na₂O slags with CO₂ was studied by using a platinum crucible at 1 610 °C. The second measurement was of the equilibrium between H₂O/H₂ gas mixtures and Fe_tO–SiO₂–Na₂O, Fe_tO–P₂O₅–Na₂O, or Fe_tO–SiO₂–P₂O₅–Na₂O slags contained in a solid iron crucible at 1 200 °C or 1 400 °C. From the results obtained, the influence of soda on the activity of iron oxide and Fe³⁺/Fe²⁺ ratio has been determined.

In view of the ionic theory, the approximate validity of the regular solution model for cations was examined to evaluate the thermodynamic properties of these slags. It was confirmed that the regular solution model was satisfied for Fe_tO–Na₂O and Fe_tO–SiO₂–Na₂O slags within experimental errors except for fairly FeO and SiO₂ rich region. However, the model was not applicable for the slags containing both P₂O₅ and Na₂O at the same time. The interaction energies between Na⁺ and cations were determined from the results obtained, and the iso-activity line for each component, iso-Fe³⁺/Fe²⁺ ratio lines and iso-P₂O₅ lines for Fe_tO–SiO₂–Na₂O slags in equilibrium with liquid iron at 1 400 °C have been calculated by using the regular solution model.

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