Activity of FeO in the Ternary System $\text{SiO}_2\text{--MgO--FeO}$ and Constitution of SiO_2^*

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Synopsis

Activity of FeO in the ternary system $\text{MgO--SiO}_2\text{--FeO}$ was measured by means of the levitation method of an induction furnace.

Activity of MgO in the binary system MgO--SiO_2 was calculated from the activity of FeO in this ternary system $\text{MgO--SiO}_2\text{--FeO}$.

Theoretical expressions derived for molecular size distributions in multichain polymers (polymer theory) were applied to this binary system MgO--SiO_2 , and the theoretical curve from the polymer theory fitted the calculated values of activities of MgO in the system MgO--SiO_2 , when the equilibrium constant of the polymer theory (K_{11}) is 0.01.

Application of the polymer theory to the ternary system $\text{MgO--SiO}_2\text{--FeO}$ seems to be possible with several assumptions.

I. Introduction

In a previous paper,¹⁾ theoretical expressions were derived for the most probable distribution of molecular sizes in branched polymers formed by the self-condensation of a multi-functional monomer.

Authors applied this theory to the calculation of activities in binary silicate melts.²⁾ But the activity of MgO in $\text{SiO}_2\text{--MgO}$ is not yet measured, because this system has high melting point in temperature. In this paper the activity of FeO in $\text{FeO--SiO}_2\text{--MgO}$ ternary system was measured, using this result, the activity of MgO in MgO--SiO_2 binary system was calculated, then was applied to the polymer theory. An attempt has been made to apply the polymer theory to the activity of FeO--MgO--SiO_2 ternary system.

II. Experimental

1. Materials

High-purity iron, designated AGL 20, was supplied by British Steel Corporation. Impurities apart from oxygen, were reported to be less than 0.05%. The oxygen and nitrogen impurities were 0.0971 and 0.0024% respectively by the vacuum analysis. FeO was prepared from the high-purity iron and Fe_2O_3 (Anachemica Chemicals).

Magnesium silicates with various molar ratios of MgO/SiO_2 were prepared from MgO (BDH Chemicals Ltd.) and SiO_2 (Mallinckrodt, AR) by sintering at 900°C for 4 hr.

Argon (Canada Liquid Air Co., Ltd.) was passed through titanium turnings at 880°C.

Helium (Airco) was used without purification.

2. Apparatus and Procedure

The levitation apparatus was similar to that used by previous works.³⁾

A sample of metal to be levitated was machined to the form of a cylinder of approximately 0.2 inch in diameter, with a cavity drilled along the axis.

It weighed about 1.0 g. A known weight of sintered magnesium silicate was inserted and a slightly tapered, tight-fitting stopper, machined from the same metal, was pressed into the cavity to encapsulate the oxide. The total weight of crucible and stopper was about 1.5 g and of magnesium silicate about 0.07 g in each experiment.

The procedure of levitation was described³⁾ previously. The sample of slag was obtained by quenching into water, and the sample of metal was obtained by vacuum suction.

III. Results

The activity of FeO was computed with the reference to the non-stoichiometric oxide in equilibrium with liquid iron as standard state.³⁾

$$\log [\%O]_{\text{sat}} = -6329/T + 2.734$$

The activity of FeO in the ternary system of $\text{SiO}_2\text{--MgO--FeO}$ is shown in Fig. 1.

IV. Discussion

1. The Activity of MgO--FeO System

The activity of FeO in the high MgO region was

Fig. 1. Isoactivity lines of FeO at 1900°C in the $\text{MgO--SiO}_2\text{--FeO}$ system

* Originally published in *Tetsu-to-Hagané*, **62** (1976), 176, in Japanese. English version received May 13, 1977.

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not obtained due to the high temperature of the melting point. So the activity of FeO in MgO–FeO system may be calculated from the following methods.

Darken⁴⁾ proposed a quadratic formalism that there is a linear relationship between the logarithm of the activity coefficient and mole fraction in both low and high mole fraction regions. If this relationship is applied to MgO–FeO system, the activity coefficient of FeO in the high MgO region is obtained and then the activity of FeO in this region is calculated. The activity of MgO is obtained by the Darken's equation

$$\ln \gamma_{\text{MgO}} = -\alpha_2 N_{\text{FeO}} \cdot N_{\text{MgO}} - \int_{N_{\text{MgO}}=1}^{N_{\text{MgO}}} \alpha_2 d(N_{\text{MgO}}) \dots \dots (1)$$

where, γ_{MgO} : the activity coefficient of MgO
 $\alpha_2 = \ln \gamma_{\text{FeO}} / N_{\text{MgO}}^2$
 $N_{\text{FeO}}, N_{\text{MgO}}$: mole fraction of FeO and MgO, respectively.

The activity of MgO is also calculated from the Gibbs–Duhem equation. Figure 2 shows a plot of N_{FeO} against the activities of FeO and MgO in the FeO–MgO binary system.

2. The Activity of MgO in MgO–SiO₂ System and the Equilibrium Constant of the Reaction in 2Mg₂SiO₄=Mg₃Si₂O₇+MgO

According to Darken⁵⁾ the activity of N_1 – N_3 system can be calculated if the activities between N_2 – N_1 , N_2 – N_3 and N_1 – N_2 – N_3 are known.

$$\begin{aligned} F^{xs} = & (1-N_2) \left[\int_1^{N_2} \bar{F}^{xs} / (1-N_2)^2 \cdot dN_2 \right]_{N_1/N_3} \\ & - N_1 \left[\int_1^0 \bar{F}^{xs} / (1-N_2)^2 dN_2 \right]_{N_3=0} \\ & - N_3 \left[\int_1^0 \bar{F}^{xs} / (1-N_2)^2 dN_2 \right]_{N_1=0} \dots \dots \dots (2) \end{aligned}$$

where, F^{xs} : mixing excess molar free energy
 $\bar{F}^{xs} = RT \ln \gamma_2$: excess molar free energy

From the data of the activity in MgO–SiO₂–FeO system, authors found the relationship between $\ln \gamma_{\text{FeO}} / (1-N_{\text{FeO}})^2$ and N_{FeO} to be a sixth power series within maximum error 3.6% in every ratio of $N_{\text{MgO}} / N_{\text{SiO}_2}$;

$$\begin{aligned} \frac{\ln \gamma_{\text{FeO}}}{(1-N_{\text{FeO}})^2} = & A + B N_{\text{FeO}} + C N_{\text{FeO}}^2 + D N_{\text{FeO}}^3 \\ & + E N_{\text{FeO}}^4 + F N_{\text{FeO}}^5 + G N_{\text{FeO}}^6 \dots \dots \dots (3) \end{aligned}$$

where A to G are coefficients.

By substituting for the calculated values in Eq. (2), the excess free energy of the MgO–SiO₂ system is calculated.

Figure 3 shows the excess free energy of MgO–SiO₂, compared with the excess free energy of CaO–SiO₂ by Darken.⁶⁾

$$RT \ln \gamma_{\text{MgO}} = F^{xs} + (1-N_{\text{MgO}})(dF^{xs}/dN_{\text{MgO}}) \dots \dots (4)$$

○: measured points
 The line of a_{FeO} is calculated values by the Darken's method⁴⁾.
 The line of a_{MgO} is calculated values from a_{FeO} by the Gibbs Duhem equation

Fig. 2. Activities of FeO and MgO for the system FeO–MgO

Fig. 3. Excess free energy chart for the system MgO–SiO₂ (1) at 1900°C, compared with the system CaO–SiO₂,⁶⁾ and (2) at 1600°C

Figure 4 shows the activity of MgO in the MgO–SiO₂ system from the results of Eq. (4), and the line is computed from the polymer theory¹⁾ of $K=0.01$. Figure 5 shows the ion fractions of SiO₄^{4–}, Si₂O₇^{6–}, Si₃O₁₀^{5–}, Si₄O₁₃^{10–} and Si₁₀O₃₁^{22–} against mole fraction of SiO₂ in the system MgO–SiO₂.

3. Discussion about the Activity of the Ternary System

If the equilibrium constant of reaction between SiO₄^{4–} and Si₂O₇^{6–} is known in metal oxide–SiO₂ binary system, the activity of the metal oxide is estimated by the polymer theory.¹⁾ But this theory can not be applied to the ternary system, because the mole fraction of cation is not unity in all regions.

We may assume the following conditions in the ternary system.

(1) The equilibrium constant (K_{11}) of the reaction $2\text{SiO}_4^{4-} \rightleftharpoons \text{Si}_2\text{O}_7^{6-} + \text{O}^{2-}$ in the polymer theory is constant for the given ratio of mole fraction of MgO

Circles are from excess molar free energies of mixing (Fig. 3).

The line is calculated from the polymer theory with $K_{11}=0.01$.

The broken line is after J. F. Elliott⁷⁾ (1 600°C).

Fig. 4. Activity of MgO plotted against mole fraction of MgO-SiO₂ at 1 900°C

and FeO in the SiO₂-MgO-FeO ternary system.

(2) Mg²⁺ cations associate with silicate anions stronger than Fe²⁺ cations, therefore a random mixing does not occur in this system. When y is a mole ratio of Fe₂SiO₄ and Mg₂SiO₄, y may be assumed;

$$\frac{y}{1-y} = \frac{\text{mole fraction of Fe}_2\text{SiO}_4}{\text{mole fraction of Mg}_2\text{SiO}_4} \approx \frac{K_{11} \text{ of MgO-SiO}_2 \text{ system}}{K_{11} \text{ of FeO-SiO}_2 \text{ system}} \quad \text{.....(5)}$$

(3) The activity of FeO in the FeO-MgO-SiO₂ ternary system is estimated from the following equation.

$$a_{\text{FeO}} = \gamma \cdot \mathcal{N}_{\text{Fe}^{2+}}^* \cdot \mathcal{N}_{\text{O}^{2-}}$$

where γ is an interaction coefficient between FeO and MgO in the MgO-FeO binary system. (Actually an activity coefficient of FeO in the FeO-MgO binary system will be used.)

$$\mathcal{N}_{\text{Fe}^{2+}}^* = \frac{\text{Ion fraction of "Free" Fe}^{2+}}{\text{Ion fraction of "Free" Fe}^{2+} + \text{Ion fraction of "Free" Mg}^{2+}} \quad \text{.....(6)}$$

"Free" means that the cations do not associate with silicate anions.

Now we show how to calculate the activity of FeO in the ternary system.

(i) In high SiO₂ regions

All of Mg²⁺ cations may be combined with silicate anions, because of high concentration of SiO₂.

"Free" $\mathcal{N}_{\text{Mg}^{2+}} \approx 0$, then $\mathcal{N}_{\text{Fe}^{2+}}^* \approx 1$

Also $\gamma=1$, because of no interaction between Fe²⁺ and Mg²⁺ cations.

Fig. 5. Ion fractions of SiO₄⁴⁻, Si₂O₇⁶⁻, Si₃O₁₀⁸⁻, Si₄O₁₃¹⁰⁻ and Si₁₀O₃₁²²⁻ plotted against mole fraction of silica for the system MgO-SiO₂

Therefore,

$$a_{\text{FeO}} = \mathcal{N}_{\text{O}^{2-}} \quad \text{.....(7)}$$

$\mathcal{N}_{\text{O}^{2-}}$ can be calculated from the polymer theory.

(ii) In low SiO₂ regions

It will be assumed that $\mathcal{N}_{\text{O}^{2-}}$ is unity, because of low concentration of SiO₂.

Therefore,

$$a_{\text{FeO}} \approx \gamma \mathcal{N}_{\text{Fe}^{2+}}^* \quad \text{.....(8)}$$

Then $\mathcal{N}_{\text{Fe}^{2+}}^*$ can be calculated from the following.

$$\begin{aligned} \text{Ion fraction of "Free" Fe}^{2+} &= \mathcal{N}_{\text{FeO}} - (2y\mathcal{N}_1 + 3y\mathcal{N}_2 + \dots + (x+1)y\mathcal{N}_x) \\ &= \mathcal{N}_{\text{FeO}} - y\Sigma(x+1)\mathcal{N}_x \quad \text{.....(9)} \end{aligned}$$

$$\mathcal{N}_{\text{SiO}_2} = \mathcal{N}_1 + 2\mathcal{N}_2 + \dots + x\mathcal{N}_x = \Sigma x \cdot \mathcal{N}_x \quad \text{.....(10)}$$

where $\mathcal{N}_{\text{FeO}}$ and $\mathcal{N}_{\text{SiO}_2}$ are mole fraction of FeO and SiO₂, respectively.

$\mathcal{N}_1, \mathcal{N}_2, \dots, \mathcal{N}_x$ are ion fraction of SiO₄⁴⁻, Si₂O₇⁶⁻, Si_xO_{3x+1}^{2(x+1)-}, respectively.

From the polymer theory¹⁾

$$\frac{\Sigma x \mathcal{N}_x}{\Sigma \mathcal{N}_x} = \frac{1}{1 - 3P_{\text{AA}}} \quad \text{.....(11)}$$

where P_{AA} is a probability to condense SiO⁻ with SiO⁻, and can be calculated from the value of K_{11} by the polymer theory.¹⁾ Equation (12) is obtained from Eqs. (9) and (11).

$$\begin{aligned} \text{Ion fraction of "Free" Fe}^{2+} &= \mathcal{N}_{\text{FeO}} - y\Sigma(x+1)\mathcal{N}_x \\ &= \mathcal{N}_{\text{FeO}} - y[\mathcal{N}_{\text{SiO}_2} + (1 - 3P_{\text{AA}})\mathcal{N}_{\text{SiO}_2}] \quad \text{.....(12)} \end{aligned}$$

Also

$$\begin{aligned} \text{Iron fraction of "Free" Mg}^{2+} &= \mathcal{N}_{\text{MgO}} - (1+y)[\mathcal{N}_{\text{SiO}_2} + (1 - 3P_{\text{AA}})\mathcal{N}_{\text{SiO}_2}] \quad \text{...(13)} \end{aligned}$$

Therefore

$$N_{Fe^{2+}}^* = \frac{[c/(1+c)] \cdot (1 - N_{SiO_2}) - \gamma[N_{SiO_2} + (1 - 3P_{AA})N_{SiO_2}]}{1 - 2N_{SiO_2} - (1 - 3P_{AA})N_{SiO_2}} \quad \dots\dots\dots(14)$$

where

$$C = N_{FeO}/N_{MgO}$$

Figure 6 shows the theoretical curves from Eqs. (7) and (8), compared with the experimental data.

V. Conclusion

The activity of FeO was measured in FeO-MgO-SiO₂ ternary system by using the levitation method.

From the activity of FeO, the activity of MgO-SiO₂ system was calculated. This activity line fits the theoretical curve from the polymer theory when the equilibrium constant of the polymer theory (K_{11}) is 0.01.

Application of the polymer theory to the ternary system MgO-SiO₂-FeO seems to be possible with several assumptions.

Acknowledgements

This work was done at the Atlantic Regional Laboratory, National Research Council of Canada. One of the authors (M. S.) wishes to express his gratitude to NRCC for the Fellowship.

The authors wish to thank Mr. G. Caines and Mr. J. Uher for chemical analysis of the samples.

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○: measured points

In the A regions, lines corresponds to $a_{FeO} = \gamma_{Fe^{2+}}$.

In the B regions, lines correspond to $a_{FeO} = N_{O^{2-}}$.

Fig. 6. Application of the polymer theory to the ternary system MgO-SiO₂-FeO at 1 900°C

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