Slag structure information derived from sulphide capacities

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Abstract:Slags are silicate melts that have been extensively used in the extraction and refining of metals. Structure and properties of slags have received a great deal of attention in the past decades. Thermophysical and thermochemical properties of slags depend directly on the structure of slags. For example, viscosity, one of the most important thermophysical properties of steelmaking slags, decreases with an increase in basic oxide content and with elevating temperature. This phenomenon corresponds to a breakdown of the silica network structure. It is found that sulfide capacity measurements also present an interesting path towards an understanding of the structure of slags in view of the relationship between temperature and sulfide capacity in logarithm. The reaction between sulphur in the gas and the basic oxide in the slag, especially at silica contents higher than the orthosilicate compositions involves the polymerization of silicates in order to supply the oxygen ions necessary for reactions with sulphur. The molar sulphide capacities C'_S = (mol%S)$(P_{O2}/P_{S2})^{1/2}$ on four binary systems, $MgO-SiO_2$, $CaO-SiO_2$, $MnO-SiO_2$ and $FeO-SiO_2$ are elucidated so as to compare the magnitudes of the basicities of four metallic oxides and to estimate the temperature dependencies of the basicities of metallic oxides. The enthalpy changes of the reaction $2O^- = O + O^{2-}$, *viz.* the silicate polymerization reaction (denoted as $\triangle H^o_{(8)}$) have been calculated from the slopes of the log C'_S versus $1/T$ curves for four binary silicates. The $\triangle H^o_{(8)}$ value is considered in the present work to be an index of the basicity of silicate melts. The basicities obtained on the basis of the $\triangle H^o_{(8)}$ values are in the order MgO < CaO < MnO < FeO, which are determined by two effects: (i) ionicity of chemical bonds between metallic and oxygen ions and (ii) clustering of metallic oxides in silicates. It is also found that the basicity of the $FeO-SiO_2$ system is larger at higher temperatures.

Keywords: Sulphide capacity, structure, basicity, iconicity of chemical bonds, clustering

1. Introduction

Slags are silicate melts that have been extensively used in the extraction and refining of metals. Structure and properties of slags have received a great deal of attention in the past decades. In steelmaking, for example, with higher demands on steel qualities, especially with respect to impurities such as sulphur and phosphorus as well as non-metallic inclusions in steels, understanding of the physics and chemistry of slags has become extremely important.

Thermophysical and thermochemical properties of slags depend directly on the structure of slags. For example, viscosity, one of the most important thermophysical properties of steelmaking slags, decreases with an increase in basic oxide content and with elevating temperature. This phenomenon corresponds to a breakdown of the silica network structure. Thermochemical properties such as activity of a component in the slag melt and slag capacities are also relevant to the structure. In this paper, the present authors focus on the relationship between sulphide capacity and structure.

The concept of sulphide capacity was first proposed by Fincham and Richardson [1] to quantify the desulphurizing capacity of slags, using the equilibrium reaction between molten slag and a gas phase with fixed sulfur and oxygen potentials,

$$\frac{1}{2}S_{2(g)}+O^{2-}=\frac{1}{2}O_{2(g)}+S^{2-} \qquad (1)$$

The sulphide capacity, C_s is thus defined as

$$C_s=(wt\%S)\left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2}=K\left(\frac{a_{O^{2-}}}{f_{S^{2-}}}\right) \qquad (2)$$

where wt%S is the mass of sulfur dissolved in slag, p_{O2} and p_{S2} are the partial pressures of oxygen and sulfur, respectively in the gas phase. Sulphide capacity is also equal to the relationship on the extreme right side of Eq. (2), where K stands for the equilibrium constant of ionic sulfur removal reaction, i.e., reaction (1), and a_{O2-} and f_{S2-} are the activity of oxygen ion and activity coefficient of sulfur ion in slag phase.

In view of the extreme importance of sulphide capacities of metallurgical slags, many efforts have been made by researchers [1-14] to obtain accurate sulphide capacity data for most of the slags used in the pyrometallurgical industries. Therefore, if the relationship between sulphide capacity and structure is theoretically deduced, vast amounts of sulphide capacity data could yield compositional and temperature dependences of slag structure.

A commonly used index of slag structure is the NBO/T ratio, i.e., the ratio of the number of non-bridging oxygen atoms to the number of tetrahedrally coordinated atoms (e.g. Si). The NBO/T ratio expresses the degree of depolymerization of silica network. Basicity is also considered to be a slag structure index as it is dependent on the activity of the free oxygen ions (a_{O2-}) in slags. Since the a_{O2-} values cannot be experimentally determined (ionic activities need also a clear definition of the standard state), several basicities have been defined, such as V ratio (i.e., (wt%CaO)/(wt%SiO_2)) and optical basicity [15]. Essentially, slag basicity should reflect the iconicity of chemical bonds between metallic and oxygen ions as well as the degree of depolymerization of silica network. Since sulphide capacity is proportional to the values of a_{O2-} and f_{S2-} is nearly constant in Eq. (1), sulphide capacity can be used as an index of slag basicity. In fact, it has been reported that there is a good correlation between sulphide capacity and optical basicity. [16] However, there are no indices described as a function of temperature, although basicity could be temperature-dependent. The aim of the present study is to elucidate the formerly reported temperature dependences of sulphide capacities on four binary systems, MgO-SiO_2, CaO-SiO_2, MnO-SiO_2 and FeO-SiO_2, so as to compare the magnitudes of the basicities of four metallic oxides and to estimate the temperature dependencies of the basicities of metallic oxides.

2. Principle

As shown in Eq. (1), wt%S is used to represent the amount of sulphur dissolved in slag. However, in relating sulphide capacities to slag structure, it would be more appropriate to adopt molar sulphide capacities instead of the traditional one based on the weight % of sulphur. Hence, molar sulphide capacity defined by the following equation is employed in the present paper.

$$C_S'=(mol\%S)\left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2}=K\left(\frac{a_{O^{2-}}}{f'_{S^{2-}}}\right) \qquad (3)$$

However, since the Kvalue in Eq. (3) as well as the terms a_{O2^-} and f'_{S2-} are functions of temperature, the temperature dependency of basicity cannot be directly related to the temperature dependency of the C'_S value. Hence, in the present paper, an attempt is made to obtain the temperature dependency of basicity from the C'_S data in the case of binary silicate systems. It is proposed to extend the same to higher order systems as a later part of the work.

The reaction between the sulphur molecule in the gas phase and a metallic oxide, MO, in the binary silicate melt MO-SiO_2 can be represented by the following reaction.

$$\frac{1}{2}S_{2(g)} + (MO)_{slag} = \frac{1}{2}O_{2(g)} + (MS)_{slag} \tag{4}$$

The standard Gibbs energy $\Delta G^o_{(4)}$ of the above reaction is given by

$$\Delta_r G^0_{(4)} = \Delta_r H^0_{(4)} - T\Delta_r S^0_{(4)} \tag{5}$$

where □${}_rH^o_{(4)}$ and □${}_rS^o_{(4)}$ are the standard enthalpy and entropy changes for the reaction (4), respectively. At the equilibrium state,

$$\Delta_r G^0 = -RT \ln K^0 \tag{6}$$

Applying the definition of molar sulphide capacity into Eqs. (5) and (6), log C'_S can be expressed by Eq. (7).

$$\log C_s^{'} = -0.522 \times 10^{-5} \times \Delta_r H^0 \times (\frac{10^4}{T}) + 0.0522 \times \Delta_r S^0 + \log(\frac{a_{MO}}{f_{MS}}) \tag{7}$$

It is known (as also shown in the later section) that log Cs (and also C'_s) is a linear function of 1/T for a number of slag systems. If sum of the second and the third terms of the right hand side of Eq. (7) is constant with respect to temperature, the standard enthalpy change, □${}_rH^o_{(4)}$, can be calculated from the slope of logC'_S versus $1/T$ curve using a Gibbs-Helmholtz relationship. However, in silicates with SiO_2 contents more than the orthosilicates, the following reaction takes place together with the reaction (4) [1].

$$2(\vdots Si - O^-) \leftrightarrow (\vdots Si - O - Si \vdots) + O^{2-} \tag{8}$$

Since it is known that the reaction (8) is endothermic [17], the apparent standard enthalpy change from experimental results, ${}_rH^o_{(4),\ app}$, obtained by the slope of log C'_S versus $1/T$ curve should be larger than the theoretical value for ${}_rH^o_{(4)}$ from thermodynamic calculations, as it would include the enthalpy for the polymerization of the silicate. In fact, the □ ${}_rH^o_{(4)}$ would correspond to the temperature dependencies of a_{MO} in the third term of the right hand side of Eq. (7) assuming that $\Delta_r S^o$ and f_{MS} are independent of temperature. The difference between □${}_rH^o_{(4),\ app}$ and □${}_rH^o_{(4)}$ is the enthalpy change, □$H^o_{(8)}$, for the reaction (8).

Let us consider the relationship between the □$H^o_{(8)}$ value and the type of metallic oxide in silicates. The reaction (8) may reflect the change in distribution of electrons in silicates: In the silica structure of the right hand side of reaction (8), electrons are more localized at specific oxygen ions, i.e., O^{2-}, and more unevenly distributed rather than the electrons in the left hand side. In other words, when the reaction (8) goes forward, the electron distribution becomes more uneven. The distribution of electrons is associated with the ionicity of chemical bonds between the metallic and oxygen ions in silicates: In the silicates having less basic metallic oxides, as for example FeO as compared to CaO, where the chemical bonds between metallic and oxygen ions tend to be more covalent, the electrons may be more uniformly distributed. As a consequence, the silicates with less basic metallic oxides may require larger thermal energy for the reaction (8) to be caused. On the contrary, the silicates with more basic metallic oxides may demand less thermal energy. Therefore, it is considered that the magnitude of $H^{o}_{(8)}$ is likely to be directly related to the basicity of silicates. Thus, it should also be possible to evaluate the temperature dependency of basicity from the temperature dependency of $H^{o}_{(8)}$.

3. Results

As mentioned earlier, log C_S or logC'_S versus $1/T$ curves have been found to be linear in specific temperature ranges, not only in the case of binary systems but also for various multi component silica systems by a number of researchers [1-14]. On the basis of previously reported experimental data, the molar sulphide capacities of the xMO-(1-x)SiO_2 systems (M = Mg, Ca, Mn and Fe, x the mole fraction) have been plotte d as a function of the reciprocal of temperature in Figure 1.

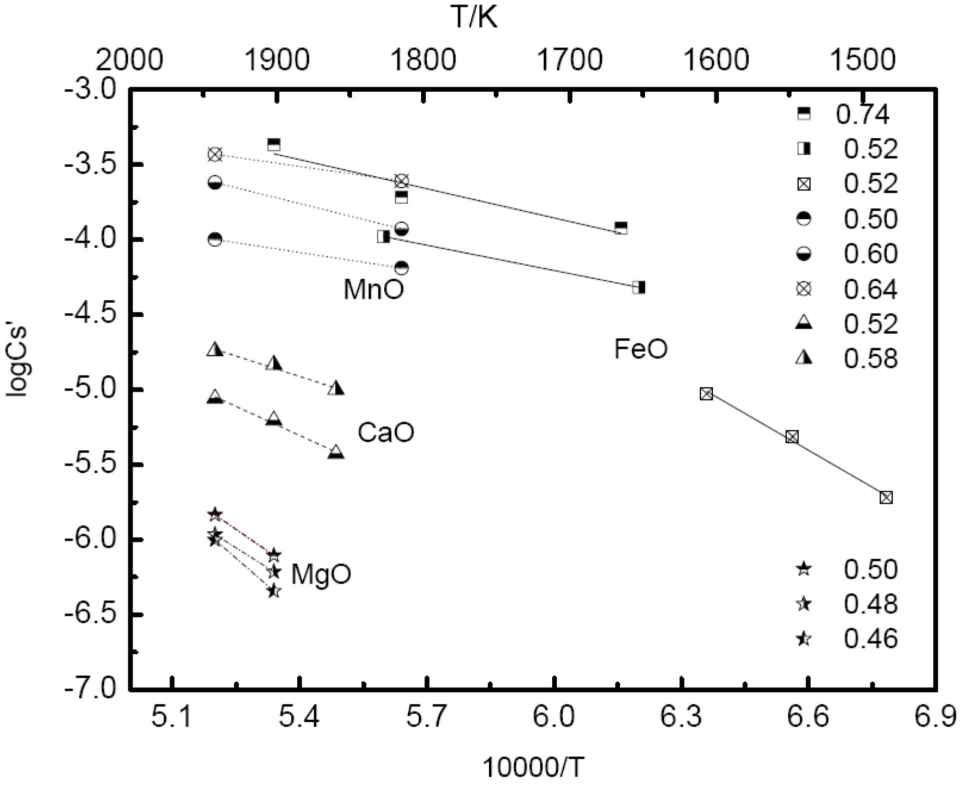

Figure 1. Relationship between log C'_S and reciprocal of temperature for the xMO-(1-x) SiO_2 (M=Mg, Ca, Mn and Fe) systems. The mole fractions of x are in the figure

In this figure, the corresponding compositions of silicates lie between metasilicates and orthosilicates region according to the data available. Table 1 summarizes the experimental temperature ranges and the references for the binary silicate data used in the present study.

It can be seen in Fig. 1 that the log C'_S versus $1/T$ curves are linear for the MgO-SiO_2, CaO-SiO_2, MnO-SiO_2 and FeO-SiO_2 systems. But in the case of the last-mentioned system, it is seen that the slope of the lines changes drastically with temperature. The slope is moderate and comparable to other binaries in the higher temperature region, i.e., in the temperature range between 1723 to 1923 K (steelmaking temperatures), while the slope is large at lower temperatures, *viz.*1473 -1623 K (copper making temperatures).

The □ $H^{o}_{(4),\ \mathrm{app}}$ values have been calculated from the slopes of the log C'_{S} versus $1/T$ curves and are shown in Table 2. This table also shows the standard enthalpy change for the reaction (4), $H^{o}_{(4)}$, and the enthalpy change for the reaction (8), $H^{o}_{(8)} = H^{o}_{(4),\ \mathrm{app}} -$ □ $H^{o}_{(4)}$. To obtain the standard enthalpy change of the reaction (4), the Raoult's standard state is used for all the elements and compounds in Eq. (4). It can be seen from Table 2 that all the values of □ $H^{o}_{(8)}$ are positive, which indicates that the reaction (8) is in fact endothermic.

Table 1 Literature survey of sulfide capacity for different binary silicates

system	Temperature range	Reference
CaO-SiO₂	1773K-1923K	[3]
	1823K-1923K	[4]
	1773K	[2]
MgO-SiO₂	1923K	[3]
	1923K	[6]
	1873-1923K	[8]
MnO-SiO₂	1773K-1923K	[6]
FeO-SiO₂	1773K	[3]
	1473K-1623K	[13]
	1623-1873K	[14]

Table 2 Temperature coefficients of gas-slag sulphur exchange reaction for various binary silicates at 1723K-1923K

System	x	$\Delta H_{(4),app}$/J/mol	$\Delta H^{\circ}_{(4)}$/J/mol	$\Delta H_{(8)}$=$\Delta H_{(4),app} - \Delta H^{\circ}_{(4)}$ kJ/mol
CaO-SiO₂	0.58 0.52	173754.8 247509.6	44464 44464	129 203
MgO-SiO₂	0.50	373754.8	119850	253.9
	0.48	342720.3	119850	222.8
	0.45	470689.7	119850	350.8
FeO-SiO₂	0.74	122605.4	109144	13.5
	0.52	130268.2	109144	21.1
	0.7 (lower temp)	356321.8	109144	247.2
MnO-SiO₂	0.53	134674.3	79062	55.6
	0.60	125478.9	79062	46.4
	0.63	82950.2	79062	3.9

* calculated by the reaction of $MO(l)+0.5S_2(g)=MS(l)+0.5O_2(g)$. Since there is no data for the fusion enthalpy of MgS, data in solid state is used.

4. Discussion

4.1 Magnitude of the $H^{o}_{(8)}$ values

As mentioned earlier in the principles section, in the view of the present authors, the magnitude of $H^{o}_{(8)}$ is an index of the basicity of silicates. The $H^{o}_{(8)}$ values are plotted as a function of the mole fractions of metallic oxides, x, in

Figure 2. As can be seen, the $H^{o}_{(8)}$ values monotonically decrease with an increase in *x* although the compositional range is quite narrow. This shows that the $H^{o}_{(8)}$ values are relevant to the basicities of silicates.

Before discussing the order of the $H^{o}_{(8)}$ values from the viewpoint of the basicity, it is necessary to evaluate the obtained $H^{o}_{(8)}$ value of the FeO-SiO_2 system more carefully. In the case of this system, it is to be noted that "FeO" is non-stoichiometric and, at the "FeO" end the composition would correspond to $FeO_{1+\delta}$. With the addition of SiO_2, the extent of non-stoichiometry would decrease. In view of this, $H^{o}_{(8)}$ value of the FeO-SiO_2 system is likely to be affected by the change in non-stoichiometry of FeO, due to the removal of excess oxygen. The decrease in non-stoichiometry is an endothermic reaction [17]. In order to obtain the impact of the decrease in the excess oxygen values on the enthalpy change occurring due to the polymerization of the silicate corresponding to reaction 8, the enthalpy change due to oxygen loss in the FeO-SiO_2 system was estimated in the present work from the results of Darken and Gurry [17]. These authors measured the enthalpy of formation of vacancies in FeO by gas equilibrium data introduction of oxygen in the lattice from gas phase as -282.45kJ/mol (which is exothermic).

In the present discussion, the excess oxygen and vacancies would diminish with the polymerization of the silicate and the effect will be the reverse of Eq. (9), which will be endothermic, adding to the already endothermic effect of reaction (8).

$$2Fe^{2+} + \frac{1}{2}O_{2(g)} = 2V_{(Fe)} + Fe^{3+}_{I} + Fe^{3+}_{Fe} + O^{2-}_{(O)} \qquad (9)$$

Accordingly, the enthalpy change of the redox pair of Fe^{2+}/Fe^{3+} is approximately 141.2kJ/mol. As can be found in the literature, the concentration of Fe^{3+} in 0.7FeO-0.3SiO_2 is around 4wt% [13], i.e. the enthalpy caused by decreasing non-stoichiometry of FeO is evaluated as 4.09kJ. On the other hand, at the metasilicate composition, the extent of non-stoichiometery of FeO in FeO-SiO_2 system may be very insignificant. Thus, the □ $H^{o}_{(8)}$ value of the FeO-SiO_2 system due to the reaction (8) may not be seriously affected by the change in the non-stoichiometry of FeO due to silicate polymerization and would be close to the values listed in Table 2.

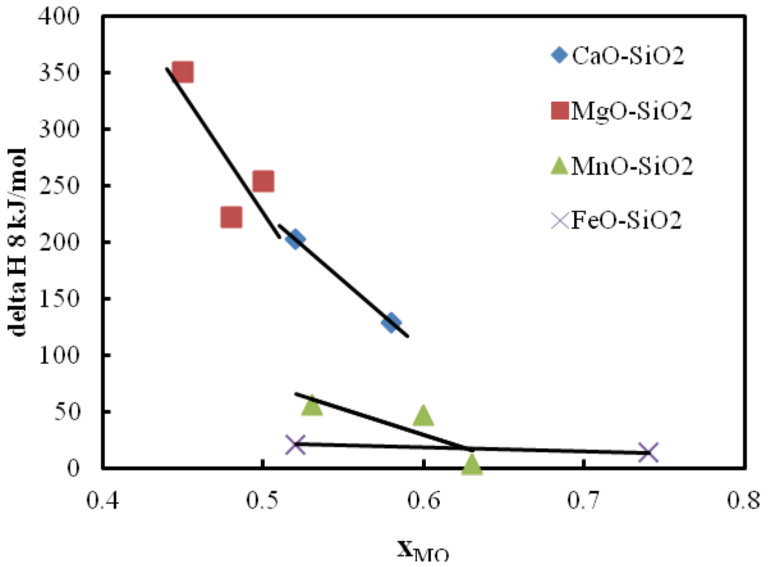

Fig.2 Relationship between $H^{o}_{(8)}$ and mole fraction of MO for the *x*MO-(1-*x*) SiO_2 (M=Mg, Ca, Mn and Fe) systems

The $H^{o}_{(8)}$ values at x nearly equal to 0.5 are compared for the four binary systems. The magnitude of the $H^{o}_{(8)}$ values are in the hierarchy of MgO > CaO > MnO > FeO over the temperature range between 1723 and 1923 K, which implies that the basicities increase in the order MgO < CaO < MnO < FeO according to the authors' definition of basicity. However, the theoretical optical basicities deduced from the electron densities are in the order MgO < FeO < MnO < CaO [18]. Let us consider this contradiction.

The optical basicities and the basicities based on the present definition are compared for the silicates having an identical NBO/T ratio, where the types of metallic oxides only influence the basicities. The optical basicity originally defined by Duffy and Ingram [14] expresses the electron donor power. According to the definition of the optical basicity, this property is mainly relevant to the ionicity of chemical bonds between metallic and oxygen ions. On the other hand, the present basicity concept, i.e., the □ $H^{o}_{(8)}$ values, may reflect the uniformity of electron distribution. In silicates having smaller values of $H^{o}_{(8)}$, electrons are more locally sited in the silicates so that the O^{2-} ions could be produced with less thermal energy. Localization of electrons may be relevant to

(i) ionicity of chemical bonds between metallic and oxygen ions and

(ii) clustering of metallic oxides in silicates. In fact, clustering of metallic oxides correspond to the clustering of non-bridging oxygen ions, O^{-}, which may easily produce O^{2-} and O^{0} from $2O^{-}$ by exchange of electrons.

The clustering of metallic oxides in silicates may be evaluated by the size of the miscibility gap: The miscibility gaps actually appear in mixtures of silica with the alkaline earth oxides and the oxides of other metals such as zinc, manganese, lead, and iron, both ferrous and ferric at higher silica content region below the critical temperatures[19]. The size of the miscibility gap tends to increase with the ratio of ion charge to ion radius (z/r) for the metal cation although there are some exceptions. In fact, the miscibility gaps are reported to be in the order CaO < MgO < FeO for the binary silicates [19]. Since the ionic radius of Mn^{2+} is in between those of Ca^{2+} and Fe^{2+}, the size of the miscibility gap of MnO could also be in between those of CaO and FeO. On the other hand, the ionicity of chemical bonds between metallic and oxygen ions may be in the order MgO < FeO < MnO < CaO according to the optical basicity. The basicity defined by the magnitude of the □ $H^{o}_{(8)}$ values is determined by both factors, resulting in the order MgO < CaO < MnO < FeO.

The clustering of metallic oxides in silicates may also be evaluated by the Gibbs energy of mixing of MO and SiO_2 and/or the activity coefficient of MO, □$_{MO}$, in addition to the aforementioned miscibility gaps. Toop and Samis [20, 21] have shown how the Gibbs energy of mixing is related to the equilibrium of reaction (8). Masson [22, 23] has correlated the equilibrium constant of reaction (8), $K_{(8)}$, with a_{MO} for the linear and branched chains based on some assumptions.

$$K_{(7)} = \frac{[O^{2-}][O^{0}]}{[O^{-}]^{2}} \tag{10}$$

For linear chains

$$\frac{1}{N_{SiO_2}} = 2 + \frac{1}{1-a_{MO}} - \frac{1}{1+a_{MO}\left(\frac{1}{k_{11}}-1\right)} \tag{11}$$

For branched chains

$$\frac{1}{N_{\mathrm{SiO_2}}} = 2 + \frac{1}{1 - a_{\mathrm{MO}}} - \frac{3}{1 + a_{\mathrm{MO}}\left(\frac{3}{k_{11}} - 1\right)} \qquad (12)$$

These equations indicate that, as the a_{MO} value in the MO-SiO_2 system at the same silica content is larger, i.e., as MO has poorer affinity with SiO_2, the value of $K_{(8)}$ becomes larger. Masson has also shown that the system with higher value of $K_{(8)}$ consists of larger variety of anionic species, Si_nO_{3n+1}. This means that in the silicate systems with higher value of $K_{(8)}$, metallic oxides are less uniformly distributed (i.e., metallic oxides are clustering) making large variety of anionic species, which supports the reasoning by the present authors. Masson has calculated the value of $K_{(8)}$ for various binary silicates from the activity data. Table 3 shows the $K_{(8)}$ values for the binary silicates, MO-SiO_2 (M = Mg, Ca, Mn and Fe). It can be seen that the $K_{(8)}$ values increase in the order CaO < MgO < MnO < FeO although $K_{(8)}$ of MgO should be taken as a lower value than 0.01 at lower temperatures. The $K_{(8)}$ values seems to have the same order as that of the size of the miscibility gap. The $K_{(8)}$ value and the size of the miscibility gap may be correlated with each other, and both are relevant to the $H^{o}_{(8)}$ value in a similar manner.

Table3 Suggested equilibrium constant values $K_{(8)}$ for various binary silicates [23]

System	$K_{(8)}$	T / K
CaO-SiO_2	0.0016	1873
MgO-SiO_2	0.01	2173
FeO-SiO_2	0.7	1573
FeO-SiO_2	1	1873
MnO-SiO_2	0.25	1773

4.2 Temperature dependences of the $H^{o}_{(8)}$ values for the FeO-SiO_2 system

It is found that the $H^{o}_{(8)}$ value of the FeO-SiO_2 system is smaller at higher temperatures, corresponding to that the basicity of the FeO-SiO_2 system is larger at higher temperatures. In fact, the $K_{(8)}$ values for the FeO-SiO_2 system are 0.7 at 1573 K and 1 at 1873 K (see Table 3) [23]. This trend is in accordance with that of the $H^{o}_{(8)}$ value. Larger basicity at higher temperatures may stem from the serious breakdown of the silica network structure occurring at higher temperatures.

5. Conclusions

The temperature dependences of previously reported sulphide capacities on four binary systems, MgO-SiO_2, CaO-SiO_2, MnO-SiO_2 and FeO-SiO_2 are elucidated so as to compare the magnitudes of the basicities of four metallic oxides and to estimate the temperature dependencies of the basicities of metallic oxides. The enthalpy changes of the reaction $2O^{-} = O + O^{2-}$ (denoted as $H^{o}_{(8)}$) have been calculated from the slopes of the log C'_{S} versus $1/T$ curves for four binary silicates, where C'_{S} is the molar sulphide capacity, $C'_{S} = (\mathrm{mol\%S})(P_{O2}/P_{S2})^{1/2}$. The $H^{o}_{(8)}$ value is considered to be an index of the basicity of silicates. The $H^{o}_{(8)}$ values for four binary silicates were compared and discussed as follows:

(1) The $H^{o}_{(8)}$ values monotonically decrease with an increase in the mole fraction of metallic oxide in spite of the narrow compositional range. This shows that the $H^{o}_{(8)}$ values are relevant to the basicities of silicates.

(2) The $H^{o}_{(8)}$ values at x nearly equal to 0.5 are compared for the four binary systems. The magnitude of the $H^{o}_{(8)}$ values are in the hierarchy of MgO > CaO > MnO > FeO over the temperature range between 1723 and 1923 K,

which implies that the basicities increase in the order MgO < CaO < MnO < FeO.

(3) It is considered that the $H^{o}_{(8)}$ values reflect the uniformity of electron distribution which is affected by both (i) ionicity of chemical bonds between metallic and oxygen ions and (ii) clustering of metallic oxides in silicates. The clustering of metallic oxides can be evaluated by the size of the miscibility gap of silicates or the equilibrium constant of the reaction $2O^{-} = O + O^{2-}$ deduced by Masson.

(4) It is found that the □ $H^{o}_{(8)}$ value of the $FeO\text{-}SiO_2$ system is smaller at higher temperatures, corresponding to that the basicity of the $FeO\text{-}SiO_2$ system is larger at higher temperatures.

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