Thermodynamic Model For Ternary Silicate Systems

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A thermodynamic model has been developed for the representation of ternary liquid silicate systems $\text{SiO}_2\text{--AO--BO}$, where A and B are metals such as Ca, Fe, Mn, *etc.* It is based on a structural model which assumes that each metallic oxide produces the depolymerization reaction $\text{O}^\circ + \text{O}^{2-} = 2\text{O}^-$ with a characteristic free energy change. The model can calculate the properties of ternary systems solely from data of the binary sub-systems. No ternary terms are required.

The model is used to calculate the activities of the components in complex silicates such as $\text{SiO}_2\text{--FeO--CaO}$ where the behavior of Fe^{2+} is very different from that of Ca^{2+} in the silicate structure. This model has been also used to calculate the activities in the systems $\text{SiO}_2\text{--MgO--FeO}$, $\text{SiO}_2\text{--MgO--CaO}$, $\text{SiO}_2\text{--MgO--MnO}$, $\text{SiO}_2\text{--NaO--MgO}$ and $\text{SiO}_2\text{--Na}_2\text{O--CaO}$. Good agreement is obtained between calculated and experimental results.

KEY WORDS: molten silicates, ternary systems, thermodynamic model.

1. Introduction

In recent years, the structural model developed by Lin and Pelton¹⁾ for silicate systems MO--SiO_2 ($\text{M}=\text{Ca}, \text{Mn}, \text{Mg}, \text{Fe}, \text{etc.}$) was examined in more depth for binary systems.²⁾ A more general empirical expression for enthalpy was written, and an empirical nonconfigurational excess entropy was added. It was also shown that the structural model can be used to predict sulfide capacities of the melts.³⁾ This model is based on the depolymerization reaction of SiO_2 :

or, in shorthand notation:

where O^{2-} is a free oxygen ion, O° is a bridge oxygen bonded to two silicon atoms, and O^- is an oxygen singly bonded to one silicon atom.

The earlier structural model for binary silicate melts was extended to ternary systems $\text{SiO}_2\text{--AO--BO}$ assuming that random mixing of cations A^{2+} and B^{2+} occurs when the oxides AO and BO behave in a similar way with silicate.⁴⁾ If the AO--SiO_2 and BO--SiO_2 binary systems exhibit similar thermodynamic behavior, that is comparable free energies of mixing, the properties of the ternary $\text{SiO}_2\text{--AO--BO}$ can be extrapolated from those binary systems in a straightforward fashion. This condition is found in the $\text{SiO}_2\text{--MnO--MgO}$ and $\text{SiO}_2\text{--FeO--MnO}$ systems where the activities and liquidus temperatures calculated solely from data on the binary sub-systems are in good agreement with measured ternary data.

In binary silicate systems, AO--SiO_2 and BO--SiO_2 , with very different mixing free energy, the oxides AO and BO would behave in a very different way with silicate. For example, the free energies of the FeO--SiO_2 system are very far from those of CaO--SiO_2 . This means that Ca^{2+} and Fe^{2+} must play a different role in the silicate network. The cations Ca^{2+} will be found associated to the O^- species and the cations Fe^{2+} will be close to the free oxygen ions O^{2-} . In this case, the random mixing can not be longer be assumed and the previously developed model⁴⁾ for ternary systems would fail.

The aim of the present article is to develop a model for ternary silicates systems $\text{SiO}_2\text{--AO--BO}$, where A and B are metals such as Ca, Fe, Mn, *etc.*, which takes into account the different behavior of the cations in the silicate structure.

2. Binary Equations

A detailed development was given previously.²⁾ Only a brief summary will be presented here. The structural model assumes that every silicon atom is bonded to four oxygen atoms. Thus, mass balance considerations require that:

$$N_{\text{O}^\circ} = 2X_{\text{SiO}_2} - \frac{N_{\text{O}^-}}{2} \dots\dots\dots (3)$$

$$N_{\text{O}^{2-}} = X_{\text{MO}} - \frac{N_{\text{O}^-}}{2} \dots\dots\dots (4)$$

where X_{MO} and X_{SiO_2} are the mole fractions of the components and N_{O° , $N_{\text{O}^{2-}}$ and N_{O^-} are the numbers of moles of the various oxygen species per mole of solution. The configurational entropy is calculated by assuming a tetrahedral quasi lattice in which the sites are occupied by O^{2-} ions and Si

atoms (each associated with four oxygen atoms bonded to it):

$$\Delta S^C = -R \left[X_{\text{SiO}_2} \ln \left(\frac{X_{\text{SiO}_2}}{X_{\text{SiO}_2} + N_{\text{O}^{2-}}} \right) + N_{\text{O}^{2-}} \ln \left(\frac{N_{\text{O}^{2-}}}{X_{\text{SiO}_2} + N_{\text{O}^{2-}}} \right) \right] \\ - R \left[N_{\text{O}^{\circ}} \ln \left(\frac{N_{\text{O}^{\circ}}}{N_{\text{Si-Si}}} \right) + (N_{\text{Si-Si}} - N_{\text{O}^{\circ}}) \ln \left(\frac{N_{\text{Si-Si}} - N_{\text{O}^{\circ}}}{N_{\text{Si-Si}}} \right) \right] \quad (5)$$

where $N_{\text{Si-Si}}$ is the number of moles of neighboring Si-Si pairs per mole of solution:

$$N_{\text{Si-Si}} = \frac{4X_{\text{SiO}_2}}{2} \left(\frac{X_{\text{SiO}_2}}{X_{\text{SiO}_2} + N_{\text{O}^{2-}}} \right) \quad (6)$$

The structural model assumes that Reaction (1) is associated with a Gibbs energy change containing an enthalpic (ω) and entropic (η) term:

$$\Delta H = \left(\frac{N_{\text{O}^{\circ}}}{2} \right) \omega \quad (7)$$

$$S^{\text{nc}} = \left(\frac{N_{\text{O}^{\circ}}}{2} \right) \eta \quad (8)$$

Finally, ω and η are expanded as polynomials:

$$\omega = \omega_0 + \omega_1 X_{\text{SiO}_2} + \omega_2 X_{\text{SiO}_2}^2 + \dots \quad (9)$$

$$\eta = \eta_0 + \eta_1 X_{\text{SiO}_2} + \eta_2 X_{\text{SiO}_2}^2 + \dots \quad (10)$$

The coefficients ω_i and η_i are the parameters of the model which are obtained by optimization of the data. Given a composition, X_{SiO_2} , and values of the parameters ω_i and η_i , the actual value of $N_{\text{O}^{\circ}}$ can be calculated by minimizing the Gibbs energy at constant X_{SiO_2} , ω and η :

$$\Delta G = \Delta H - T(\Delta S^C + S^{\text{nc}}) \quad (11)$$

$$2 \left[\frac{\partial \Delta G}{\partial N_{\text{O}^{\circ}}} \right]_{X_{\text{SiO}_2}, \omega, \eta} \\ = (\omega - \eta T) - RT \left[\ln \left(\frac{N_{\text{O}^{2-}}}{1 - X_{\text{MO}} + N_{\text{O}^{2-}}} \right) + \left(\frac{N_{\text{O}^{\circ}}}{N_{\text{Si-Si}}} \right) \right. \\ \left. - \left(1 + \frac{N_{\text{Si-Si}}}{1 - X_{\text{MO}} + N_{\text{O}^{2-}}} \right) \ln \left(\frac{N_{\text{Si-Si}} - N_{\text{O}^{\circ}}}{N_{\text{Si-Si}}} \right) \right] = 0 \quad (12)$$

Substitution of Eqs. (3), (4) and (6) into Eq. (12) gives an equation in terms of X_{MO} (or X_{SiO_2}) and $N_{\text{O}^{\circ}}$, which can be solved numerically at a fixed composition and for given values of the parameters ω_i and η_i to give $N_{\text{O}^{\circ}}$. This value can then be substituted back into Eqs. (3), (4), (5), (7) and (8) to give ΔS and ΔH .

3. Binary Metallic Oxide Systems

The main goal of this paper is to apply the model to analyse SiO_2 -AO-BO ternary systems. Thus, a model is

necessary to represent the thermodynamic properties of the liquid binary metallic oxides (AO-BO). In this work the following expression was chosen:

$$G_{\text{AO-BO}}^E = X_{\text{AO}} X_{\text{BO}} [(a_1 + a_2 T) + (b_1 + b_2 T) X_{\text{BO}} + (c_1 + c_2 T) X_{\text{BO}}^2] \quad (13)$$

where a_i , b_i and c_i are constant parameters.

4. Ternary Equations

Let us consider the general SiO_2 -AO-BO ternary system where A and B are divalent cations. It is assumed that there are 5 kind of oxygens:

1. O° : Bridge oxygens
2. O_A^{2-} : "Free oxygens ions" introduced in the system by the AO species
3. O_B^{2-} : "Free oxygens ions" introduced in the system by the BO species
4. O_A^{-} : Broken bridges for the AO species
5. O_B^{-} : Broken bridges for the BO species

That is, there are two depolymerization reactions given by:

The mass balance considerations requires now that:

$$N_{\text{O}^{\circ}} = 2X_{\text{SiO}_2} - \frac{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}}}{2} \quad (16)$$

$$N_{\text{O}_A^{2-}} = X_{\text{AO}} - \frac{N_{\text{O}_A^{-}}}{2} \quad (17)$$

$$N_{\text{O}_B^{2-}} = X_{\text{BO}} - \frac{N_{\text{O}_B^{-}}}{2} \quad (18)$$

Combination of Eqs. (17) and (18) gives:

$$N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} = (X_{\text{AO}} + X_{\text{BO}}) - \frac{N_{\text{O}_A^{-}} + N_{\text{O}_B^{-}}}{2} \quad (19)$$

The number of moles of neighboring Si-Si pairs per mole of solution ($N_{\text{Si-Si}}$) in the ternary system is expressed by:

$$N_{\text{Si-Si}} = \frac{4X_{\text{SiO}_2}}{2} \left(\frac{X_{\text{SiO}_2}}{X_{\text{SiO}_2} + N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}}} \right) \quad (20)$$

4.1. Configurational Entropy

The expression of the entropy is obtained making two statistical distributions:

$$S^C = S_I^C + S_{II}^C \quad (21)$$

Where S_I^C is estimated through the distribution of O_A^{2-} , O_B^{2-} and Si in a quasilattice:

$$S_I^C = -R \left\{ N_{\text{O}_A^{2-}} \ln \left(\frac{N_{\text{O}_A^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) \right. \\ \left. + N_{\text{O}_B^{2-}} \ln \left(\frac{N_{\text{O}_B^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) \right\}$$

$$+X_{\text{SiO}_2} \ln \left(\frac{X_{\text{SiO}_2}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) \dots\dots\dots(22)$$

S_{II}^c is estimated through the distribution of O° over the neighboring Si-Si pairs:

$$S_{\text{II}}^c = -R \left\{ N_{\text{O}^\circ} \ln \left(\frac{N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) + (N_{\text{Si-Si}} - N_{\text{O}^\circ}) \ln \left(\frac{N_{\text{Si-Si}} - N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \right\} \dots\dots\dots(23)$$

4.2. Excess Free Energy

The excess free energy expression for the ternary system is obtained by the addition of the interaction energy terms ($\omega - \eta T$) for each bridge breaking reaction, Eqs. (14) and (15), which are known in the two binary systems (AO-SiO₂ and BO-SiO₂) from the binary optimizations. This expression also must include the contribution of the excess free energy for the AO-BO binary system, $G_{\text{AO-BO}}^E$, which is multiplied by the fraction of free oxygen ions in the quasi lattice whose sites are occupied by O^{2-} ions and Si atoms.

$$G^E = \frac{N_{\text{O}_A^{2-}}}{2} (\omega - \eta T)_{\text{AO}} + \frac{N_{\text{O}_B^{2-}}}{2} (\omega - \eta T)_{\text{BO}} + \left(\frac{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) G_{\text{AO-BO}}^E \dots\dots\dots(24)$$

The Gibbs free energy of mixing is then obtained joining the expressions (22) to (24)

$$\begin{aligned} \Delta g^{\text{mix}} = & RT \left\{ N_{\text{O}_A^{2-}} \ln \left(\frac{N_{\text{O}_A^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) \right. \\ & + N_{\text{O}_B^{2-}} \ln \left(\frac{N_{\text{O}_B^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) \\ & + X_{\text{SiO}_2} \ln \left(\frac{X_{\text{SiO}_2}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) + N_{\text{O}^\circ} \ln \left(\frac{N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \\ & + (N_{\text{Si-Si}} - N_{\text{O}^\circ}) \ln \left(\frac{N_{\text{Si-Si}} - N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \left. \right\} + \frac{N_{\text{O}_A^{2-}}}{2} (\omega - \eta T)_{\text{AO}} \\ & + \frac{N_{\text{O}_B^{2-}}}{2} (\omega - \eta T)_{\text{BO}} + \left(\frac{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) G_{\text{AO-BO}}^E \dots\dots\dots(25) \end{aligned}$$

This expression is thermodynamically consistent with the Gibbs-Duhem and Gibbs-Helmholtz equations. Equation (25) reduces to the respective expressions for the binary sub-systems:

a) If $X_{\text{AO}} = 0$ or $X_{\text{BO}} = 0$

$$\Delta g^{\text{mix}} = RT \left\{ N_{\text{O}^{2-}} \ln \left(\frac{N_{\text{O}^{2-}}}{N_{\text{O}^{2-}} + X_{\text{SiO}_2}} \right) \right.$$

$$\begin{aligned} & + X_{\text{SiO}_2} \ln \left(\frac{X_{\text{SiO}_2}}{N_{\text{O}^{2-}} + X_{\text{SiO}_2}} \right) + N_{\text{O}^\circ} \ln \left(\frac{N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \\ & + (N_{\text{Si-Si}} - N_{\text{O}^\circ}) \ln \left(\frac{N_{\text{Si-Si}} - N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \left. \right\} + \frac{N_{\text{O}^\circ}}{2} (\omega - \eta T) \dots\dots\dots(26) \end{aligned}$$

b) If $X_{\text{SiO}_2} = 0$

$$N_{\text{O}_A^{2-}} = X_{\text{AO}}, N_{\text{O}_B^{2-}} = X_{\text{BO}}, \text{ and } \Delta g^{\text{mix}} = RT [X_{\text{AO}} \ln(X_{\text{AO}}) + X_{\text{BO}} \ln(X_{\text{BO}})] + G_{\text{AO-BO}}^E \dots\dots\dots(27)$$

The expression of Δg^{mix} depends on two parameters ($N_{\text{O}_A^{2-}}$ and $N_{\text{O}_B^{2-}}$ or $N_{\text{O}_A^{2-}}$ and $N_{\text{O}_B^{2-}}$). Their values will be calculated by minimizing the expression of the free energy. Choosing the first pair of parameters one obtains:

$$\left(\frac{\partial \Delta g^{\text{mix}}}{\partial N_{\text{O}_A^{2-}}} \right)_{X_{\text{SiO}_2}, X_{\text{BO}}, N_{\text{O}_B^{2-}}} \dots\dots\dots(28)$$

$$\left(\frac{\partial \Delta g^{\text{mix}}}{\partial N_{\text{O}_B^{2-}}} \right)_{X_{\text{SiO}_2}, X_{\text{AO}}, N_{\text{O}_A^{2-}}} \dots\dots\dots(29)$$

Minimizing Δg^{mix} with respect to $N_{\text{O}_A^{2-}}$ one obtains:

$$\begin{aligned} \frac{\partial \Delta g^{\text{mix}}}{\partial N_{\text{O}_A^{2-}}} = & RT \left\{ \ln \left(\frac{N_{\text{O}_A^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) \ln \left(\frac{N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \right. \\ & + \left(\frac{\partial N_{\text{Si-Si}}}{\partial N_{\text{O}_A^{2-}}} - 1 \right) \ln \left(\frac{N_{\text{Si-Si}} - N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \left. \right\} \\ & - (\omega - \eta T)_{\text{AO}} + \left(\frac{X_{\text{SiO}_2}}{(N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2})^2} \right) G_{\text{AO-BO}}^E \dots\dots\dots(30) \end{aligned}$$

where

$$\frac{\partial N_{\text{Si-Si}}}{\partial N_{\text{O}_A^{2-}}} = \frac{-2(X_{\text{SiO}_2})^2}{(N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2})^2} \dots\dots\dots(31)$$

Now minimizing Δg^{mix} with respect to $N_{\text{O}_B^{2-}}$ one obtains:

$$\begin{aligned} \frac{\partial \Delta g^{\text{mix}}}{\partial N_{\text{O}_B^{2-}}} = & RT \left\{ \ln \left(\frac{N_{\text{O}_B^{2-}}}{N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2}} \right) + \ln \left(\frac{N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \right. \\ & + \left(\frac{\partial N_{\text{Si-Si}}}{\partial N_{\text{O}_B^{2-}}} - 1 \right) \ln \left(\frac{N_{\text{Si-Si}} - N_{\text{O}^\circ}}{N_{\text{Si-Si}}} \right) \left. \right\} \\ & - (\omega - \eta T)_{\text{BO}} + \left(\frac{X_{\text{SiO}_2}}{(N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2})^2} \right) G_{\text{AO-BO}}^E \dots\dots\dots(32) \end{aligned}$$

where

$$\frac{\partial N_{\text{Si-Si}}}{\partial N_{\text{O}_B^{2-}}} = \frac{-2(X_{\text{SiO}_2})^2}{(N_{\text{O}_A^{2-}} + N_{\text{O}_B^{2-}} + X_{\text{SiO}_2})^2} \dots\dots\dots(33)$$

Table 1. Energy parameters, ω and η , for the bridge breaking reaction in binary silicate systems²⁾ (ω in J mol⁻¹ and η in J mol⁻¹ K⁻¹).

SYSTEM	ω and η parameters
MnO-SiO ₂	$\omega = -56,143 - 1,791 X_{\text{SiO}_2} + 116,820 X_{\text{SiO}_2}^3$ $\eta = -15.11 + 18.638 X_{\text{SiO}_2}^3$
MgO-SiO ₂	$\omega = -55,140 - 76,333 X_{\text{SiO}_2} + 245,570 X_{\text{SiO}_2}^3$ $\eta = -47.99 X_{\text{SiO}_2} + 18.638 X_{\text{SiO}_2}^3$
FeO-SiO ₂	$\omega = 6,770 - 122,724 X_{\text{SiO}_2} + 183,040 X_{\text{SiO}_2}^2 + 106,539 X_{\text{SiO}_2}^4$ $\eta = -34.59 X_{\text{SiO}_2} + 87.366 X_{\text{SiO}_2}^3$
CaO-SiO ₂	$\omega = -57,738 - 258,739 X_{\text{SiO}_2} + 262,548 X_{\text{SiO}_2}^2 + 89,325 X_{\text{SiO}_2}^6$ $\eta = -35.5 X_{\text{SiO}_2} + 70.71 X_{\text{SiO}_2}^4$
Na ₂ O-SiO ₂	$\omega = -90,841 - 473,168 X_{\text{SiO}_2} + 297,835 X_{\text{SiO}_2}^2$ $\eta = -31.38$

Since Eqs. (30) and (32) are both equal to zero and given that $\partial N_{\text{Si-Si}} / \partial N_{\text{O}_A} = \partial N_{\text{Si-Si}} / \partial N_{\text{O}_B}$, we can reduce the number of unknowns through the resulting expression:

$$N_{\text{O}_A} = (N_{\text{O}_B}) \exp\left(\frac{-\Delta e}{RT}\right) \dots\dots\dots(34)$$

where $\Delta e = (\omega - \eta T)_{\text{BO}} - (\omega - \eta T)_{\text{AO}}$.

Thus, it is required to solve only a non-linear equation with one unknown in order to estimate the amount of different kind of oxygens as well as the mixing free energy.

This model is also applied to systems of the type SiO₂-A₂O-BO, for example SiO₂-Na₂O-MgO, in the silica rich region. In this case, we assume A⁺ cations associate in pairs and remain so in the silicate structure.

5. Applications

The test of the model have been made for the following ternary systems SiO₂-FeO-CaO, SiO₂-FeO-MgO, SiO₂-MgO-CaO, SiO₂-MnO-MgO, SiO₂-Na₂O-MgO and SiO₂-Na₂O-CaO. The parameters ω_i and η_i for the binary silicate systems MO-SiO₂ (M=Fe, Ca, Mg, Mn, Na₂) are given in **Table 1**²⁾ and the parameters of the excess free energy for the binary liquid metallic oxides AO-BO are shown in **Table 2**.^{4,5)}

5.1. SiO₂-FeO-CaO

Activities of FeO in the liquid phase were determined by Timucin and Morris⁶⁾ at 1823 K by equilibration of the melts, held in thin-walled platinum crucibles, with CO/CO₂ mixtures. The experimental and calculated activities of FeO, shown in **Fig. 1**, are in good agreement, especially between 0.4 and 0.8.

5.2. SiO₂-FeO-MgO

The calculated curves of activities of FeO at 1873 K

Table 2. Excess free energy for the liquid binary metallic oxide systems.

$$G^E = X_{\text{AO}} X_{\text{BO}} [(a_1 + a_2 T) + (b_1 + b_2 T) X_{\text{BO}} + (c_1 + c_2 T) X_{\text{BO}}^2] \text{ J/mol}$$

SYSTEM	a ₁	a ₂	b ₁	c ₁	Ref.
MgO-MnO	2810	0.0	0.0	0.0	4
CaO-MnO	15924	0.0	0.0	0.0	5
FeO-MnO	0.0	0.0	0.0	0.0	4
MgO-CaO	24311	0.0	-14490	0.0	5
MgO-FeO	7531	0.0	0.0	0.0	4
FeO-CaO	-107294	41.84	0.0	-17442	5

b₂ and c₂ are equal to zero for all the systems

Fig. 1. Calculated and experimental⁶⁾ iso-activity curves of FeO at 1823 K in liquid SiO₂-FeO-CaO solution (liquid standard state).

plotted in **Fig. 2** are consistent with the concentration dependence of the experimental data obtained by Ban-ya *et al.*⁷⁾ by equilibration of the melts with H₂/H₂O mixtures.

5.3. SiO₂-MgO-CaO

Activities of SiO₂ in the liquid phase (relative to the solid as standard state) were determined by Rein and Chipman⁸⁾ at 1873 K by measuring the distribution of Si between the slag and an Fe-Si-C alloy saturated either with graphite or SiC. The experimental activities of SiO₂ are shown in **Fig. 3** along with the calculated values by the model. The Gibbs energy of fusion of pure SiO₂ was taken as⁹⁾:

$$\Delta G_{\text{fusion}}^{\circ}(\text{SiO}_2) = 9581.36 - 4.8003T \text{ J/mol} \dots\dots(35)$$

5.4. SiO₂-MnO-MgO

In **Fig. 4** is shown the comparison between calculated activities of MnO at 1923 K (relative to the solid as standard state) and the experimental values measured by Metha and Richardson.¹⁰⁾ In this experimental work the slags contain-

Fig. 2. Calculated and experimental⁷⁾ iso-activity curves of FeO at 1873 K in liquid SiO₂-FeO-MgO solution (liquid standard state).

Fig. 3. Calculated and experimental⁸⁾ iso-activity curves of SiO₂ at 1873 K in liquid SiO₂-MgO-CaO solution (solid standard state).

ing manganese oxide were brought into equilibrium with thin strips of platinum metal at controlled partial pressure of oxygen, obtained from mixtures of carbon dioxide, hydrogen and nitrogen. The Gibbs energy of fusion of pure MnO was taken as⁹⁾:

$$\Delta G_{\text{fusion}}^{\circ}(\text{MnO}) = 54392.0 - 25.71454T \text{ J/mol} \dots (36)$$

5.5. SiO₂-Na₂O-MgO

The model has been also used to estimate the thermodynamic properties of ternary silicate systems with a monovalent cation in the silica rich region. The activities of Na₂O were measured by Rego *et al.*¹¹⁾ at 1673 K by a gas phase equilibration technique to generate Na₂O isoactivity data at high-silica compositions in this system. The experimental and calculated activities of Na₂O shown in Fig. 5 are in good agreement.

Fig. 4. Calculated and experimental¹⁰⁾ iso-activity curves of MnO at 1923 K in liquid SiO₂-MnO-MgO solution (solid standard state).

Fig. 5. Calculated and experimental¹¹⁾ iso-activity curves of Na₂O at 1673 K in liquid SiO₂-Na₂O-MgO solution (liquid standard state).

5.6. SiO₂-Na₂O-CaO

The activities of Na₂O were also measured by Rego *et al.*¹¹⁾ at 1673 K in the silica rich region of the SiO₂-Na₂O-CaO system. The experimental and calculated activities of Na₂O are shown in Fig. 6. Agreement is well within the uncertainties.

6. Discussion

The amount of different kind of oxygens in the SiO₂-FeO-CaO predicted by the model at 1823 K and $X_{\text{SiO}_2} = 0.35$ is shown in Fig. 7. Although the experimental evidence is scarce it is clear that there is a complete breakdown of the polymeric structure by the CaO and FeO basic oxides at this composition of SiO₂. This Figure also shows that the cations Ca²⁺ are associated to the O⁻ and the amount of O_{Ca}²⁻ is negligible along all the composition range, whereas cations Fe²⁺ are partially associated to the O⁻ species and free oxygen ions O_{Fe}²⁻. In this way the

Fig. 6. Calculated and experimental¹¹⁾ iso-activity curves of Na₂O at 1673 K in liquid SiO₂-Na₂O-CaO solution (liquid standard state).

Fig. 7. Concentration of oxygen species in the SiO₂-FeO-CaO system calculated by the model at 1823 K and $X_{\text{SiO}_2} = 0.35$.

model takes into account the non random mixing of cations in the silicate structure.

The characteristic “c” shape of the FeO activity curves in the SiO₂-FeO-CaO system at 1823 K, shown in Fig. 8, is explained by the amount of broken bridges (O_{Ca}^- and O_{Fe}^-) produced by the bridge breaking reactions, Eqs. (14) and (15). The bold line separates the regions where the FeO contributes to the breaking oxygen bridges, *i.e.* where $N_{\text{O}_{\text{Fe}}} = 0$ and $N_{\text{O}_{\text{Fe}}} > 0$, which corresponds with the sharp change in the slope of the curves.

When extended to SiO₂-Na-O-MgO and SiO₂-Na₂O-CaO, the model gives a good representation of the thermodynamic data in the acid region ($X_{\text{SiO}_2} > 0.50$). This supports to the assumption of the model, that in the silica rich region, two cations Na⁺ are associated with each broken oxygen bridge.

7. Conclusions

The earlier structural model^{1,2)} for binary silicate melts has been extended to ternary systems for the representation of liquid silicate systems SiO₂-AO-BO, where A and B are

Fig. 8. Activities of FeO (liquid standard state) and range of concentration where the FeO contributes to the breaking oxygen bridges in the SiO₂-FeO-CaO system at 1823 K.

metals such as Ca, Fe, Mn, etc. The model assumes that each metallic oxide produces the depolymerization reaction $\text{O}^\circ + \text{O}^{2-} = 2\text{O}^-$ with a characteristic free energy change. The model can calculate the properties of ternary systems solely from data of the binary sub-systems. No ternary terms are required.

The model is used to calculate the activities of the components in complex silicates such as SiO₂-FeO-CaO where the behavior of Fe²⁺ is very different from that of Ca²⁺ in the silicate structure. This model has been also used to calculate the activities in the systems SiO₂-MgO-FeO, SiO₂-MgO-CaO, SiO₂-MgO-MnO, SiO₂-Na₂O-CaO and SiO₂-Na₂O-MgO. Good agreement is obtained between calculated and experimental results.

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