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Activities of Ions in Silicate Melts

G. W. Toop and C. S. Samis

The problem of determining the degree of polymerization of silicate anions in both acid and basic silicate melts has been investigated in order to apply ionic theory to binary and ternary silicate slags. With an examination of structure and equilibria in silicate melts, it was found that polymerization in acid and basic slags may be expressed in terms of an equilibrium constant involving singly-bonded oxygen, doubly-bonded oxygen, and free-oxygen ions in the melt. For appropriate values of the equilibrium constant, it was found that integral molar-free energy of mixing curves may be calculated that are close to, or equal to, those of various binary silicate melts. This indicated that the integral free energy of mixing of a binary silicate melt may arise solely from the interaction of oxygen ions and silica. This observation was supported mathematically by the application of ionic forms of the Gibbs-Duhem equation to silicate systems. The ionic Gibbs-Duhem equations were used to calculate cationic and anionic free energies of mixing and the activities of Fe²⁺, Ca²⁺, and O²⁻ ions in the CaO-FeO-SiO₂ system at 1600°C. A method was developed for determining the most probable silicate anions present in acid and basic silicate melts.

The ionic character of fused oxides and silicates has become widely accepted with experimental measurements of electrical conductivity, electron transport, viscosity, and expansivity. The common slag forming oxides, FeO, MnO, CaO, MgO, PbO are considered to ionize and to contribute metal cations and oxygen anions to the melt. Silicon, on the other hand, is a complexing agent which exhibits strong tetrahedral coordination with oxygen to form discrete chain-type ions, ring-type ions, and complex ring-type ions, depending on the type and concentration of metal oxides present.

The question of the degree of polymerization of complex silicate anions, particularly in acid slags, can completely obscure evaluation of anionic concentrations in the melt. A satisfactory solution to this problem must precede any successful application of ionic theory to slags.

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EQUILIBRIUM IN SILICATE MELTS

Any attempt to describe equilibria in silicate melts is complicated by the fact that the structure of the melt changes with composition. Since the reaction by which equilibrium polymerization is established is expected to be the same for all silicate compositions, it follows that any proposed equilibrium reaction should be of general form and should not involve specific silicate anions.

Fincham and Richardson, recognizing that oxygen in silicate melts occurs in only three forms, singly bonded O₁, doubly bonded O₂, and free oxygen ions O₃, have suggested a simple and probable equilibrium reaction,

$$2 \text{O}_1 = \text{O}_2 + \text{O}_3$$  [1]

Eq. [1] is a fundamental result of the charge balance required by the tetrahedral coordination of oxygen with silicon, and when any silicate anions associate to form higher polymers plus oxygen ions, the overall reaction reduces to Eq. [1].

Under equilibrium conditions, an equilibrium constant \( k \) may be written according to Eq. [1],

$$k = \frac{[\text{O}_2][\text{O}_3]}{[\text{O}_1]^2}$$  [2]

where \([\text{O}_1]\), \([\text{O}_2]\), and \([\text{O}_3]\) are the equilibrium number of moles of singly bonded oxygen, doubly bonded oxygen, and free oxygen ions per mole of slag. It is proposed that \( k \), as defined in Eq. [2], is constant at a given temperature and characteristic of the cations present in any binary or ternary silicate melt.

For one mole of any binary or ternary silicate melt involving basic metal oxides which contribute 1 O²⁻ ion per molecule, it may be shown that,

$$N_{\text{SiO}_2} \text{ moles of silica}$$

and

$$(1 - N_{\text{SiO}_2}) \text{ moles of O}^{2-} \text{ ions}$$

combine to form the silicate anions of the melt plus free oxygen ions, assuming complete dissociation of the basic metal oxides. A charge balance gives the following expression,

$$2[\text{O}_1] + [\text{O}_1] = 4N_{\text{SiO}_2} = \text{number of silicon bonds}$$  [3]

which may be rearranged to give the number of doubly bonded oxygen atoms in one mole of slag,

$$[\text{O}_1] = \frac{4N_{\text{SiO}_2} - [\text{O}_1]}{2}$$  [4]

Material balance considerations give the number of free oxygen ions per mole of slag.

THE METALLURGICAL SOCIETY OF AIME
Fig. 1—Equilibrium values of \( (O^+) \), \( (O^-) \), and \( (O^{2-}) \) vs \( N_{SiO_2} \) for \( k \) equal to 0.06.

\[
(O^{2-}) = (1 - N_{SiO_2}) - \frac{(O^-)}{2} = \frac{2 - 2N_{SiO_2} - (O^-)}{2}
\]

Eqs. [4] and [5] may be inserted into Eq. [2] to give an equation in \( (O^-) \) in terms of \( k \) and \( N_{SiO_2} \),

\[
4k = \frac{[4N_{SiO_2} - (O^-)][2 - 2N_{SiO_2} - (O^-)]}{(O^-)^2}
\]

A series of quadratic equations in the standard form,

\[ a(O^-)^2 + b(O^-) + c = 0 \]

may be derived from Eq. [6] and values of \( (O^-) \), \( (O'^-) \), and \( (O^{2-}) \) may be calculated for various values of \( N_{SiO_2} \) and \( k \), see Fig. 1.

The values of \( (O^-) \), \( (O'^-) \), and \( (O^{2-}) \) obtained for any value of \( k \), satisfy the material and charge balance of the slag and the problem of determining the total number of anions in the melt is reduced to one of determining how silicon, \( (O^-) \) and \( (O'^-) \) are assembled at any slag composition to form discrete silicate anions. This problem will be treated later. The significant feature of Fig. 1 to be noted at this point is that the \( (O^-) \) curve exhibits the characteristic shape of an integral free energy of mixing curve of a binary silicate melt, and that singly bonded oxygen atoms \( (O^-) \) are the product of reaction [1]. It is thus apparent from Eq. [1] that when 1 mole of oxygen ions (in pure liquid basic oxide, MO) reacts with 1 mole of doubly bonded oxygen atoms (in pure liquid SiO\(_2\)) to form 2 moles of singly bonded oxygen atoms (in pure liquid M\(_2\)SiO\(_4\)), the standard molar free energy change \( \Delta G^0 \) in calories, divided by 4.575 \( T \), should be given by

\[
\frac{\Delta G^0}{4.575 \ T} = - \log \frac{1}{k} = \log k
\]

But, the actual number of moles of oxygen ions that have reacted in the melt is \( (O^-)/2 \) moles. Hence, the free energy change due to Eq. [1] per mole of liquid silicate formed, should be given approximately by

\[
\frac{\Delta G_{\text{mix}}}{4.575 \ T} = \frac{(O^-)}{2} \log k
\]

The free energy of mixing given by Eq. [8] was calculated for various values of \( k \) and the corresponding values of \( (O^-)/2 \). The results are shown in Fig. 2 where comparison is made with the measured integral free energy of mixing liquid PbO and liquid SiO\(_2\) at 1100\(^{\circ}\)C\(_6\) and the calculated integral free energy of mixing liquid CaO and liquid SiO\(_2\) at 1800\(^{\circ}\)C\(_{11}\).

The calculated free energy curves of Fig. 2 are remarkably similar to the characteristic free energy of mixing curves of binary silicate melts even though \( k \) is expressed in concentration terms \( (O^2^-) \), \( (O^-) \), and \( (O'^-) \) per mole of slag, and should technically be expressed as a thermodynamic equilibrium constant in terms of \( a_{O^2^-}, a_{O'^-}, \) and \( a_{O^-} \). Fig. 2 indicates that the free energy of mixing of a binary silicate melt may arise entirely from the interaction of oxygen ions and silica and it follows that the activity of oxygen ions \( a_{O^2^-} \) should therefore be equal to the activity of the basic metal oxide in the expression for the binary integral molar free energy of mixing

\[
(1 - N_{SiO_2}) \log a_{O^2^-} + N_{SiO_2} \log a_{SiO_2} = \frac{\Delta G_{\text{binary}}}{4.575 \ T}
\]

Under this condition, the effect of different cations in binary silicate melts would be to allow greater or less polymerization and hence less or greater interaction between oxygen ions and silica.

Fig. 2 gives the first indication of what value of the equilibrium constant \( k \) might be used for a given binary silicate melt. According to Fig. 2 values of the constant \( k \) have been proposed for some common binary silicate systems and are shown in Table I.

Clearly, the implication that the free energy of mixing of a binary silicate melt may be entirely anionic, defines a new model with which to treat silicate melts and a detailed thermodynamic examination of binary and ternary silicate melts was undertaken in order to determine if such a model is feasible.
APPLICATION OF IONIC GIBBS-DUHÉM EQUATIONS TO SILICATE MELTS

It is interesting to investigate how the foregoing structural model may be supported by a strictly thermodynamic development. For this purpose the CaO-FeO-SiO₂ system is chosen for illustration. The activities of CaO, FeO, and SiO₂ refer to the pure liquid oxides at 1600°C.

For the expression of ionic fractions of positive and negative ions the equations of Temkin⁷ have been used, i.e.,

\[ N_{M^{2+}} = \frac{n_{M^{2+}}}{\text{sum of positive ions}} \]  \[ N_{O^{2-}} = \frac{(O^{2-})}{\text{sum of negative ions}} \]  \[ \text{[10]} \]

For example, the cation fraction of Fe²⁺ ions in CaO-FeO-SiO₂ melts is given by,

\[ N_{Fe^{2+}} = \frac{N_{FeO}}{N_{FeO} + N_{CaO}} - \frac{N_{FeO}}{1 - N_{SiO₂}} \]  \[ \text{[12]} \]

Introducing the ionic definition⁸ of the activity of CaO and FeO, the expression for the integral molar free energy of mixing of CaO-FeO-SiO₂ melts may be written,

\[ N_{CaO} \log a_{Ca^{2+}} a_{O^{2-}} + N_{FeO} \log a_{Fe^{2+}} a_{O^{2-}} + N_{SiO₂} \log a_{SiO₂} = \frac{\Delta G^{\text{mix}}}{4.575 T} \]  \[ \text{[13]} \]

or

\[ N_{CaO} \log a_{Ca^{2+}} + N_{FeO} \log a_{Fe^{2+}} + (1 - N_{SiO₂}) \times \log a_{O^{2-}} + N_{SiO₂} \log a_{SiO₂} = \frac{\Delta G^{\text{mix}}}{4.575 T} \]  \[ \text{[14]} \]

Differentiating Eq. [14] gives Eq. [15] and Eq. [16] (the Gibbs-Duhem equation) below,

\[ dN_{CaO} \log a_{Ca^{2+}} + dN_{FeO} \log a_{Fe^{2+}} + d(1 - N_{SiO₂}) \times \log a_{O^{2-}} + dN_{SiO₂} \log a_{SiO₂} = \frac{d\Delta G^{\text{mix}}}{4.575 T} \]  \[ \text{[15]} \]

and,

\[ N_{CaO} \ d \log a_{Ca^{2+}} + N_{FeO} \ d \log a_{Fe^{2+}} + (1 - N_{SiO₂}) \times d \log a_{O^{2-}} + N_{SiO₂} \ d \log a_{SiO₂} = 0 \]  \[ \text{[16]} \]

Now, a basic assumption is made which makes the application of Eq. [16] fundamentally consistent with the proposed structural model. It is assumed that the sum of the cationic terms of Eq. [16] is equal to zero and the sum of the anionic terms is equal to zero along composition paths in the CaO-FeO-SiO₂ system where the ratio \( (N_{Ca^{2+}}/N_{Fe^{2+}}) \) is constant, that is, along straight lines joining the SiO₂ apex of the ternary diagram with the FeO-CaO binary side, i.e.,

\[ [N_{CaO} \ d \log a_{Ca^{2+}} + N_{FeO} \ d \log a_{Fe^{2+}} = 0 \]  \[ \text{[17]} \]

Differentiating Eq. [14] gives Eq. [15] and Eq. [16] (the Gibbs-Duhem equation) below,

\[ dN_{CaO} \log a_{Ca^{2+}} + dN_{FeO} \log a_{Fe^{2+}} + d(1 - N_{SiO₂}) \times \log a_{O^{2-}} + dN_{SiO₂} \log a_{SiO₂} = \frac{d\Delta G^{\text{mix}}}{4.575 T} \]  \[ \text{[15]} \]

and,

\[ N_{CaO} \ d \log a_{Ca^{2+}} + N_{FeO} \ d \log a_{Fe^{2+}} + (1 - N_{SiO₂}) \times d \log a_{O^{2-}} + N_{SiO₂} \ d \log a_{SiO₂} = 0 \]  \[ \text{[16]} \]

Now, a basic assumption is made which makes the application of Eq. [16] fundamentally consistent with the proposed structural model. It is assumed that the sum of the cationic terms of Eq. [16] is equal to zero and the sum of the anionic terms is equal to zero along composition paths in the CaO-FeO-SiO₂ system where the ratio \( (N_{Ca^{2+}}/N_{Fe^{2+}}) \) is constant, that is, along straight lines joining the SiO₂ apex of the ternary diagram with the FeO-CaO binary side, i.e.,

\[ [N_{CaO} \ d \log a_{Ca^{2+}} + N_{FeO} \ d \log a_{Fe^{2+}} = 0 \]  \[ \text{[17]} \]

\[ \text{Table I. Proposed Values of the Equilibrium Constant } k \text{ for Various Binary Silicate Systems} \]

<table>
<thead>
<tr>
<th>System</th>
<th>( k )</th>
<th>Number of Compounds</th>
<th>Temperature of Melt °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO-SiO₂</td>
<td>0.35</td>
<td>0</td>
<td>1100</td>
</tr>
<tr>
<td>FeO-SiO₂</td>
<td>0.17</td>
<td>1</td>
<td>1600</td>
</tr>
<tr>
<td>ZnO-SiO₂</td>
<td>0.06</td>
<td>1</td>
<td>1300</td>
</tr>
<tr>
<td>PbO-SiO₂</td>
<td>0.04</td>
<td>2</td>
<td>1100</td>
</tr>
<tr>
<td>CaO-SiO₂</td>
<td>0.0017</td>
<td>2</td>
<td>1600</td>
</tr>
</tbody>
</table>
and,
\[
(1 - N_{SiO_2}) \frac{d}{dN_{SiO_2}} \log a_{O^2-} + N_{SiO_2} \frac{d}{dN_{SiO_2}} \log a_{SiO_2} = 0 \]  \[ \text{[18]} \]

There are three reasons for making this assumption. Primarily, the application of Eqs. [17] and [18] to the CaO-SiO₂ and FeO-SiO₂ binary systems (limiting cases of the composition paths mentioned) predicts exactly the structural results derived earlier. Applying Eq. [18] to the CaO-SiO₂ system gives,
\[
a_{O^2-} = a_{CaO} \]  \[ \text{[19]} \]
and applying Eq. [17] to the CaO-SiO₂ system gives,
\[
a_{Ca^{2+}} = 1 = N_{Ca^{2+}} \]  \[ \text{[20]} \]
Similarly, in the FeO-SiO₂ system,
\[
a_{O^2-} = a_{FeO} \]  \[ \text{[21]} \]
and,
\[
a_{Fe^{2+}} = 1 = N_{Fe^{2+}} \]  \[ \text{[22]} \]
Secondly, this assumption provides a definition of the "standard states" of the ions Ca²⁺, Fe²⁺, and O²⁻ consistent with Temkin's expression of ionic fractions. The usual definition of a standard state of a component is that state in which the activity of the component is unity and in which the mole fraction of the component is unity. If this definition is adopted for the standard states of ions, it is apparent that Eq. [20] defines a standard state for calcium cations as pure liquid solutions of CaO and SiO₂ in all proportions. A similar standard state may be defined for ferrous ions in FeO-SiO₂ melts. The activity of both Ca²⁺ and Fe²⁺ ions is therefore equal to one when their ionic fraction is equal to one. To be consistent with this result, the activity of oxygen ions aO²⁻, is defined as unity in the CaO-FeO binary system since Temkin's ionic fraction of oxygen ions in this system is unity. According to the above definitions, the product of the cation activity and the oxygen ion activity gives the activity of the metal oxide with respect to pure liquid oxide. Thirdly, some interesting evidence of the validity of Eqs. [17] and [18] may be obtained with the calculation of cationic and anionic activities and free energies of mixing in the CaO-FeO-SiO₂ system.

Dividing Eq. [17] by \((1 - N_{SiO_2})\) gives,
\[
[d \log a_{Fe^{2+}} = - \frac{N_{Ca^{2+}}}{N_{Fe^{2+}}} \log a_{Ca^{2+}} ] \frac{d}{dN_{Ca^{2+}}/N_{Fe^{2+}}} \]  \[ \text{[23]} \]
Integrating Eq. [23] from the CaO-FeO binary toward the silica apex of the CaO-FeO-SiO₂ ternary along composition paths of constant \(N_{Ca^{2+}}/N_{Fe^{2+}}\) gives,
\[
\log a_{Fe^{2+}} \text{ ternary} = - \log a_{Fe^{2+}} \text{ CaO-FeO} = - \frac{N_{Ca^{2+}}}{N_{Fe^{2+}}} \times [ \log a_{Ca^{2+}} \text{ ternary} - \log a_{Ca^{2+}} \text{ CaO-FeO} ] \]  \[ \text{[24]} \]
In the CaO-FeO binary system,
\[
N_{Fe^{2+}} = N_{FeO} \text{ and } N_{Ca^{2+}} = N_{CaO} \]
and since \(a_{O^2-}\) is defined as unity in CaO-FeO melts,
\[
a_{Fe^{2+}} = a_{FeO} \]  \[ \text{[25]} \]
and Eq. [24] may be written as follows for constant \(N_{Ca^{2+}}/N_{Fe^{2+}}\),
\[
N_{Fe^{2+}} \log a_{Fe^{2+}} + N_{Ca^{2+}} \log a_{Ca^{2+}} \text{ ternary} = \left[ N_{FeO} \log a_{FeO} + N_{CaO} \log a_{CaO} \right] \text{ CaO-FeO} = \frac{\Delta G^{\text{mix}}_{\text{CaO-FeO}}}{4.575 T} N_{Ca^{2+}}/N_{Fe^{2+}} \]  \[ \text{[25]} \]
Multiplying Eq. [25] by \((1 - N_{SiO_2})\) gives,
Fig. 4—Cationic and anionic free energy of mixing of CaO-FeO-SiO_2 melts at 1600°C, vs N_{Fe^{2+}} in the ternary for N_{SiO_2} equal to 0.40, 0.50, and 0.60.

\[
\left[ N_{Fe^{2+}} \log a_{Fe^{2+}} + N_{Ca^{2+}} \log a_{Ca^{2+}} \right]_{ternary} = (1 - N_{SiO_2}) \left[ \frac{\Delta G_{mix}^{mix}}{4.575 T} \right] \frac{N_{Ca^{2+}}/N_{Fe^{2+}}}{4.575 T} \]  

and introducing Eq. [26] into Eq. [14], the integral molar free energy of mixing in the CaO-FeO-SiO_2 system may be written,

\[
(1 - N_{SiO_2}) \left[ \frac{\Delta G_{mix}^{mix}}{4.575 T} \right] \frac{N_{Ca^{2+}}/N_{Fe^{2+}}}{4.575 T} + (1 - N_{SiO_2}) \times \log a_{O^{2-}} + N_{SiO_2} \log a_{SiO_2} = \frac{\Delta G_{mix}^{mix}}{4.575 T} \]  

It is thus apparent from Eq. [27] that, under the assumption made, the integral molar free energy of mixing is made up of a cationic and an anionic portion. The free energy of mixing cations is equal to \(1 - N_{SiO_2}\) times the free energy of mixing in the CaO-FeO binary for the same ratio \(N_{Ca^{2+}}/N_{Fe^{2+}}\). The free energy of mixing anions comes from the interaction of oxygen ions and silica,

\[
(1 - N_{SiO_2}) \log a_{O^{2-}} + N_{SiO_2} \log a_{SiO_2} \]  

\[
\frac{\Delta G_{mix}^{mix}}{4.575 T} \]  

The cationic and anionic free energies of mixing as derived above were calculated from the summary of Elliott\(^{10}\) for the CaO-FeO-SiO_2 system. Elliott’s work provides a complete, mathematically consistent set of data at 1600°C and it was used to illustrate the shapes of the cationic and anionic free energy curves across the ternary field for constant values of \(N_{SiO_2}\).

The integral molar free energy of mixing in the CaO-FeO-SiO_2 system was obtained by adding the ideal free energy of mixing to Elliott’s\(^{10}\) values of the excess integral free energy. The results were plotted as \(\Delta G_{mix}^{mix}/4.575 T vs N_{Fe^{2+}}\) for various constant values of \(N_{SiO_2}\). The cationic free energy of mixing given by Eq. [26] was then subtracted from the \(\Delta G_{mix}^{mix}/4.575 T\) curves and the difference plotted to give the anionic free energy of mixing curves. The results are shown in Figs. 3 and 4.

The free energy curves of Figs. 3 and 4 closely resemble the free energy of mixing curves deduced by Richardson\(^{13}\) on the basis of ideal mixing of silicates. There is a difference however, and this difference is clear. Whereas Richardson takes the ternary cationic contribution to the free energy of mixing to be \((1 - N_{SiO_2})\) times the ideal molar free energy of mixing the two cations, the free energy of mixing cations given by Eq. [26] is \((1 - N_{SiO_2})\) times the actual molar free energy of mixing cations in the CaO-FeO binary for the same ratio \(N_{Ca^{2+}}/N_{Fe^{2+}}\), and thus account is taken of a constant cation-cation interaction in the CaO-FeO-SiO_2 system along composition paths of constant \(N_{Ca^{2+}}/N_{Fe^{2+}}\).

As pointed out by Richardson, deviations from ideal mixing in ternary silicate melts appear for values of \(N_{SiO_2}\) below about 0.42. These deviations in the application of the ideal mixing principle could arise if, in the ternary, the cationic free energy of mixing is more negative than ideal due to cation-cation interaction, and the anionic free energy of mixing is less negative than ideal, i.e., below a straight line joining the free energy of mixing curves of the two silicate binaries for constant \(N_{SiO_2}\), see Figs. 3 and 4.

The activity of the individual ions Ca^{2+}, Fe^{2+}, and O^{2-} in the CaO-FeO-SiO_2 system may now be calculated. Applying Eq. [15] along composition paths in the CaO-FeO-SiO_2 ternary where \(N_{SiO_2}\) is constant, and noting that,

\[
[dN_{CaO} = -dN_{FeO} = (1 - N_{SiO_2}) dN_{Fe^{2+}}]_{N_{SiO_2}} \]  

gives,
Rearranging the terms of Eq. [25] gives,
\[
\log \frac{a_{\text{Ca}^{2+}}}{a_{\text{Fe}^{2+}}} = \frac{-d\Delta G^\text{mix}}{4.575 T} \left[ \frac{1}{1 - N_{\text{SiO}_2}} \right] N_{\text{SiO}_2} \tag{29}
\]
Substituting Eq. [29] into Eq. [30] gives,
\[
\log a_{\text{Fe}^{2+}} \text{ternary} = \left[ \frac{\Delta G^\text{mix}_{\text{CaO-FeO}}}{4.575 T} \right] N_{\text{Ca}^{2+}}/N_{\text{Fe}^{2+}} + \frac{1 - N_{\text{Fe}^{2+}}}{1 - N_{\text{SiO}_2}} \frac{d\Delta G^\text{mix}}{4.575 T} N_{\text{SiO}_2} \tag{31}
\]
and a mathematically similar equation may be derived for ternary values of \(a_{\text{Ca}^{2+}}\).

Ternary values of \(a_{\text{Fe}^{2+}}\) were calculated from Eq. [31] by determining the slope of the tangent to the integral free energy of mixing curves of Figs. 3 and 4, and the values of the free energy of mixing in the CaO-FeO binary for the same value of \(N_{\text{SiO}_2}\). The results are shown in Fig. 5. Values of \(a_{\text{Ca}^{2+}}\) in the ternary were then obtained by Eq. [29] and the results are given in Fig. 6. According to the standard states defined earlier, Fig. 5 shows that the activity of \(\text{Fe}^{2+}\) ions remains constant at unity throughout the FeO-SiO\(_2\) binary where \(N_{\text{Fe}^{2+}} = 1\). Similarly, Fig. 6 shows that the activity of the \(\text{Ca}^{2+}\) ion is unity in the CaO-SiO\(_2\) binary where \(N_{\text{Ca}^{2+}} = 1\). The behavior of \(a_{\text{Fe}^{2+}}\) and \(a_{\text{Ca}^{2+}}\) in the ternary shows the widely postulated result that in CaO-FeO-SiO\(_2\) melts, the \(\text{Ca}^{2+}\) ions are closely associated (low activity) with the silicate groups and tend to "free" the \(\text{Fe}^{2+}\) ions. This is shown in Fig. 5 where the activity of \(\text{Fe}^{2+}\) ions, with respect to FeO-SiO\(_2\) melts, is raised substantially (even though \(N_{\text{Fe}^{2+}}\) decreases) as CaO is added to FeO-SiO\(_2\) melts in the acid region of the ternary. This is in accord with the behavior of \(a_{\text{FeO}}\) which also increases (even though \(N_{\text{FeO}}\) decreases) in the ternary for values of \(N_{\text{SiO}_2}/N_{\text{CaO}}\) greater than 0.5, as CaO is added to FeO-SiO\(_2\) melts, i.e., along straight composition paths joining the FeO-SiO\(_2\) binary with the CaO apex of the ternary.

Ternary values of \(a_{\text{O}^{2-}}\) were calculated with the use of Fig. 5 and Elliott's ternary values of \(a_{\text{FeO}}\),
\[
a_{\text{O}^{2-}} = \frac{a_{\text{FeO}}}{a_{\text{Fe}^{2+}}} \tag{32}
\]
and the results, which could also be obtained by integrating Eq. [18], are shown in Fig. 7. The isoactivity lines for \(\text{O}^{2-}\) ions sweep smoothly across the ternary field showing that the activity of oxygen ions is high in FeO-SiO\(_2\) melts and low in CaO-SiO\(_2\) melts for the same value of \(N_{\text{SiO}_2}\). This result may be deduced from Eq. [2] and Table I which show that a high value of \(k\) (FeO-SiO\(_2\) melts) gives more available \(\text{O}^{2-}\) ions than a low value of \(k\) (CaO-SiO\(_2\) melts).

The reasons for postulating that Eq. [16] may be divided into cationic and anionic terms to form Eqs. [17] and [18] will now be more clear. Before Eq. [16], the Gibbs-Duhem equation, may be solved for the activities of \(\text{Ca}^{2+}\), \(\text{Fe}^{2+}\), and \(\text{O}^{2-}\) ions, standard states for these ions must be defined. The division of Eq. [16] into cationic and anionic terms provides a definition of ionic standard states consistent with the interpretation of silicate melts.
given here and consistent with Temkin's expression of ionic fractions. It should also be noted that the use of Eqs. [17] and [18] along the composition paths mentioned and hence with the use of Figs. 5, 6, and 7, to calculate the molecular terms,

$$\Delta G_{\text{mix}} = \Delta G_{\text{cations}} + \Delta G_{\text{anions}}$$

gives precisely the same values for the terms $$\Delta G_{\text{cations}}$$, $$\Delta G_{\text{anions}}$$, and so forth, that would be obtained from any other ternary application of the Gibbs-Duhem equation, for example that of Darken or Schuhmann. The fact that the cationic and anionic activities and free energies of mixing as derived here are in accord with current concepts of ionic interactions in silicate melts, provides an interesting correlation between these concepts and the application of the Gibbs-Duhem equation to ternary systems.

**DETERMINATION OF THE NUMBER OF SILICATE ANIONS IN SILICATE MELTS**

It has been shown above that some significant thermodynamic relationships may be derived from the calculated values of singly bonded oxygen ($$O^-$$), doubly bonded oxygen ($$O^2$$), and free oxygen ions.
(O^+) and the equilibrium constant k by which they are related in silicate melts. However, it is of interest structurally to determine how silicon, (O^0) and (O^7) are assembled at any slag composition to form discrete silicate anions.

With the use of the triangular ternary phase diagram shown in Fig. 8, it was found that silicate anions can be arranged into a linear polymerization pattern if silicon is always considered to be tetrahedrally coordinated with four oxygen atoms. The plot was made by placing the constituents of the anions, silicon Si(IV), singly bonded oxygen O^-, and doubly bonded oxygen O^+ at the corners of the ternary diagram and all conceivable silicate anions fall on a straight line joining pure silica with the most highly ionized form, SiO_4^-.

It should be noted that Fig. 8 is not a phase diagram in the ordinary sense but is a graphical illustration of the proportions of Si(IV), O^- and O^+ in any discrete silicate anion.

With the use of Fig. 8, a useful polymerization diagram may be derived in which each discrete silicate anion has a specific position. This is done by taking the linear ionic plot of Fig. 8 and plotting it as the abscissa against the number of silicon atoms per ion, see Fig. 9. Of the three coordinates of Fig. 8, the proportion of singly bonded oxygen atoms in any silicate anion, varying from zero to 0.8, and given by,

\[
\frac{O^-}{O^- + O^+ + Si(IV)} = \text{proportion of singly bonded oxygen atoms in any silicate anion}
\]  

and if this is equated to the proportion of singly bonded oxygen atoms in one mole of melt

\[
\frac{(O^-)}{(O^-) + (O^0) + N_{SiO_2}} = \text{proportion of singly bonded oxygen atoms in one mole of melt}
\]

was used numerically as the abscissa in Fig. 9. But, for various values of N_{SiO_2} and k, the proportion of singly bonded oxygen atoms in one mole of a silicate melt may be obtained,

In order to evaluate the most probable number of silicate anions present in one mole of slag for any value of k, the most probable number of silicon atoms per ion must be divided into N_{SiO_2}. For this purpose a choice must be made of the most probable polymerization path, through the points of Fig. 9, that a silicate melt would follow as increasing amounts of silica are added to a basic metal oxide. This choice must be made between the two limiting polymerization paths possible. On one hand, the silicate anions could polymerize to form long chains along the points shown as "chain ions" in Fig. 9. On the other hand, the silicate anions could polymerize to form the maximum number of discrete ions along the points in Fig. 9 having the lowest number of silicon atoms per ion. For two reasons, the authors have drawn curve A as the most probable polymerization path. First, curve A is approximately the mean path between the two limiting polymerization paths mentioned. Secondly, the shape of curve A may be deduced from viscosity data which indicates that the size of silicate groups in silica-rich melts, decreases rapidly with the addition of a basic metal oxide, and the discrete silicate anions formed then decrease gradually in size through the moderately acid to the highly basic melts. Since the number of silicon atoms per
ion is a measure of the size of the silicate anions present, curve A was drawn so that the number of silicon atoms per ion decreases sharply through the SiO₂-rich side of Fig. 9 and then declines gradually through the moderately acid to the highly basic melts.

An example of the use of curve A is shown as dotted lines in Fig. 9. For 1 mole of an MO-SiO₂ type silicate melt (for \( k = 0.005 \)) containing 0.63 moles of SiO₂, the average number of silicon atoms per silicate anion is shown to be approximately 9, from curve A. Hence, the silicate anions present would most probably consist of double-ring anions containing 8 to 10 silicon atoms per ion, i.e., Si₈O₂₀³⁻ or Si₁₀O₂₆¹⁰⁻ with some single-ring anions, possibly Si₄O₁₂⁶⁻ or Si₆O₁₆¹⁰⁻ and some triple-ring anions, i.e., Si₁₂O₃₈⁻ to Si₁₈O₅₆¹⁰⁻. The most probable number of these silicate anions present would be 0.63/9 = .07 mole per mole of slag.

It should be noted that the determination of the number of silicate anions with the use of Fig. 9 is quite insensitive to the position of curve A over a wide range of silicate compositions. This is because the silica-rich end of the curve will, in general, terminate at an immiscibility gap for many of the common silicate systems and many of the lower values of \( N_{SiO_2} \) shown in Fig. 9, lie under the basic metal oxide-rich end of the curve where its position is most certain.

SUMMARY

The equilibrium equation,

\[
k = \frac{(O^+)(O^-)}{(O^-)^2}
\]

has been solved for the number of free oxygen ions \( (O^+) \), doubly bonded oxygen atoms \( (O^\circ) \), and singly bonded oxygen atoms \( (O^-) \) per mole of MO-SiO₂ type silicate melts. For appropriate values of the equilibrium constant \( k \), integral molar free energy of mixing curves have been calculated that are close to, or equal to, measured free energies of mixing in various binary silicate melts. The implication that the free energy of mixing of a binary silicate melt is entirely anionic, is supported mathematically by the application of ionic forms of the Gibbs-Duhem equation to binary and ternary silicate systems.
Cationic and anionic free energies of mixing and the activities of Fe\(^{2+}\), Ca\(^{2+}\), and O\(^{2-}\) ions have been calculated in the CaO-FeO-SiO\(_2\) system at 1600°C. The results agree well with current concepts of ionic free energies of mixing and cation-cation interactions in the ternary system.

A method has been developed for determining the degree of polymerization and the most probable silicate anions present in basic and acid silicate melts.

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REFERENCES


A Study of Basic Brick from Various Copper Smelting Furnaces

G. R. Rigby

Used basic brick taken from copper anode furnaces, reverberatory furnace roofs, and copper converters have been examined by chemical analysis, petrographical examination, and X-ray diffraction techniques. In the anode furnace roof, brick absorb copper and copper oxides, whilst in the reverberatory roof, iron oxide with smaller amounts of alumina and silica are absorbed. Chemical reactions in the converter are most complex since the brick absorb both a copper-copper oxide slag and a fayalite-magnetite slag.

Changes taking place in basic brick after use in copper smelting furnaces have received attention from C. Burton Clark and J. Spotts McDowell, who examined brick taken from copper converters, and by G. R. Rigby and B. G. Hamilton who examined brick from copper anode furnaces. This paper describes the changes taking place in basic brick from all types of copper smelting furnaces and discusses the major reasons for lining wear.

A) METHODS OF EXAMINING SAMPLES

A variety of used brick have been taken from the following positions in various furnaces, a) roofs, reverberatory arches, and bottoms of copper anode furnaces, b) roofs of copper reverberatory furnaces.

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| Table I. Analyses Of Used Brick From Copper Anode Furnace: Fitted Chrome-Magnesia Type |
|-----------------------------------|------------------|------------------|------------------|------------------|
| Sample                           | First Inch Of Working Face | Unstacked Brick At Cold Face | First Inch Of Working Face | Unstacked Brick At Cold Face |
| Percent                          | SiO\(_2\)          | Fe\(_2\)O\(_3\) | Al\(_2\)O\(_3\) | Cr\(_2\)O\(_3\) | CaO | MgO | LOI | LOI | CuO* | CuO* | SO\(_3\) | SO\(_3\) | |
|                                  | 7.6 | 4.5 | 8.3 | 6.3 | 2.3 | 25.4 | 2.9 (g) | 39.5 | 1.3 | 6.5 | 10.7 | 21.5 | 19.8 | 1.5 | 0.5 | 0.2 | 0.7 | 0.7 | 5.2 | 12.2 | 15.1 | 14.9 | 0.7 | 23.4 | 34.0 | 21.8 | NIl | NIl | |
|                                  | 4.1 | 5.2 | 12.2 | 25.2 | 1.6 | 34.0 | 21.8 | NIl | NIl | |

*Including some metallic copper.