A STATISTICAL MECHANICAL THEORY FOR MOLTEN SILICATE SOLUTIONS

Milton Blander and Ira Bloom
Argonne National Laboratory
Argonne, IL 60439-4837

ABSTRACT

A statistical mechanical theory for molten silicates has been deduced that takes into account the silicate structures and the configuration dependence of the free energy of breaking Si-O-Si bridging bonds with O^{2-} ions. Thermodynamic properties of binary solutions can be described in terms of a structural model with four equilibrium constants \( K_i \) for breaking bridges on silicons already having \( i \) broken bonds attached. The theory provides a realistic means to relate structural and thermodynamic data.

INTRODUCTION

Recent work on modeling the solution properties of molten silicates have been based on an ad hoc modification of quasichemical theory.\(^1\)-\(^{10}\) It can be used to predict the properties of multicomponent silicates from those of the constituent binaries when silica is the only acidic component. However, when another acidic component, such as alumina, is in the molten solution, this approach is not flexible enough to provide this capability. In such cases, one requires ad hoc ternary interaction terms in the energy parameters of the theory and empirical predictions of the properties of multicomponent systems can be made from the subsidiary ternaries.\(^10\) Many other silicate solution properties such as sulfide or phosphate capacities can not be treated directly by the quasichemical approach and require separate models to make predictions of these quantities a priori. This inflexibility of the quasichemical theory arises because it is not a true model of a silicate solution. The purpose of this paper is to discuss a structural model for silicates that can ultimately incorporate all the above types of thermodynamic properties of silicates in a realistic manner and provide a means for representing and predicting the properties of all multicomponent systems from those of lower order systems.

This structural model is a generalization of a model proposed by Lin and Pelton,\(^11\) that is more general than the works of Masson;\(^12\) Gaskell;\(^13\) Fincham and Richardson;\(^14\) Toop and Samis;\(^15\) Frohberg et al.;\(^16\) Flood and Knapp;\(^17\) Førland;\(^18\) and Niwa and Yokokawa.\(^19\) The Lin-Pelton model incorporated fundamental concepts that were proposed by these workers and reduced to the equations of Flood and Knapp,\(^17\) and of Førland\(^18\) in different ranges of concentration.
The fundamental model starts with the conjectures of Fincham and Richardson. In pure silica, the silica network consists of four coordinated silicons singly connected by bridging nearest-neighbor oxygen atoms, which are thus two-coordinated. Addition of an oxide, MO, to silica cuts a bridging bond as follows:

\[ Si-O-Si + O^{2-} \rightleftharpoons 2SiO^- \]  

(1)

or, in shorthand notation:

\[ O + O^{2-} \rightleftharpoons 2O^- \]  

(2)

In the model, it is assumed that the cation of the added oxide binds to the two SiO\(^-\) ends of the cut bond. Lin and Pelton then calculated the entropy by assuming random mixing of bridges with cut bridges, a concept proposed by Forland. In addition, they incorporate a general form of a proposal by Flood and Knapp, which suggests that the entropy of mixing of basic solutions (high in MO, low in silica) can be calculated by assuming a random distribution of O\(^{2-}\) and SiO\(_4^{4-}\) anions. As the solution becomes more acidic, the SiO\(_4^{4-}\) ions polymerize. Masson showed that the Flory polymer model described such solutions at concentrations less than 50 m/o silica, a concentration above which the Flory model is certainly inadequate because of the formation of three-dimensional and cyclic polymers of bridged silica tetrahedra. The Lin-Pelton model combined all these concepts in a self-consistent manner by assuming random mixing of bridges and cut bridges and also of O\(^{2-}\) with the silica tetrahedra.

Although this model was a conceptual generalization and permitted one to describe silicate mixtures at all concentrations, it failed to fit data in binary systems without an ad hoc assumption concerning the energy parameter in the theory; this assumption was similar to the one also made later in the modified quasichemical theory, that the energy parameter is a function of composition. In reality, the energy parameter should be a function of the configurations of the bridges and cut bridges about the silicon atoms. By not taking this configuration dependence into account, one loses potentially important advantages of a true theory for silicates, such as the ability to obtain useful structural information from analyses of thermodynamic data, more reasonable entropic terms, and the ability to deduce physically and structurally meaningful values of the energies and free energies of cutting bridge bonds.

Here, the configuration dependence of the energy of cutting a bridging bond is incorporated into a theory for silicates. In the model discussed below, the energy (or free energy) of bridge breaking is a function of the number of broken bridges already attached to the silicon atoms. Since the bridges and cut bridges span two silicon atoms, each "bond" can be distinguished by a two-number index which specifies the number of broken bonds on each of the two silicon atoms connected by the bridge, cut or uncut. Thus, the
two types of bridges (cut and uncut) mixed randomly in the Lin-Pelton model become two classes with 10 types of uncut bridges and 10 types of cut bridges.

Partition Function for the Model

The model considers silicates to contain silicon atoms tetrahedrally coordinated by oxygens. In pure SiO₂, these oxygens are considered to be all bridging oxygens connecting two silicons, so that for n_{Si} atoms, the number of bridges, b_{00}, is equal to 2n_{Si}. The b signifies a bridge and the subscript, 00, signifies that the bridges in question connect two silicons, each with zero cut bridges. At all other concentrations of silica mixed with a basic oxide, MO, there is a distribution of ten types of uncut bridges and the number of bridges of each type are designated b_{ij}, where i,j = 0,1,2,3. In addition, there are also ten types of cut bridges with the number of such bridges designated as c_{i+1,j+1}, where i,j = 0,1,2,3. The bridges and cut bridges form a three-dimensional network of 2n_{Si} total species (bridges and cut bridges which mix randomly in the simplest approach considered here). The statistical factor for this is given in Eq. 3.

\[ S_1 = \frac{(2n_{Si})!}{\Pi_{i=0}^{3} \Pi_{j=0}^{3} (b_{ij})! \Pi_{i=0}^{3} \Pi_{j=0}^{3} (c_{i+1,j+1})!} \]  

(3)

One must be careful in the determination of b_{ij} and c_{ij} to correct for the fact that each bond is counted twice in this notation.

In addition to mixing in the network of bridges, and cut bridges, there is also a statistical factor for the mixing of oxide ions with silicon. In basic solutions, this is equivalent to the simple mixing of O^{2-} with SiO_{4}^{4-} ions, and in somewhat acidic solutions of \( X_{SiO_{2}} < 0.5 \), it is equivalent to the mixing of O^{2-} with polymeric anions, as described by Masson’s model based on Flory’s polymer theory. This statistical factor, which was generalized by Lin and Pelton to apply for all concentrations, is given by,

\[ S_2 = \frac{(n_{Si} + n_{O^{2-}})!}{n_{Si}! n_{O^{2-}}!} \]  

(4)

where n_{Si} is the number of silicons in the melt and n_{O^{2-}} is the number of oxide ions which are free and are not associated with a cut bridge.

One still has to define local partition functions for the relevant entities in the model. The symbols p_{ij} and q_{ij} are defined as the local partition functions for the bridges and the cut bridges, respectively, which span two atoms that have i and j cut bridges. We define q_{O^{2-}} as the local partition function for the free oxide ion and define the molten
silicate mixture as having \( n_{Si} \) moles of SiO\(_2\) and \( n_{MO} \) moles of the oxide, MO. The moles of "free" oxide is thus given by the following:

\[
n_{O^2-} = n_{MO} - \sum_i \sum_j c_{ij}
\]

(5)

where the sum is calculated so that each bond is, in effect, counted once. The total partition function, \( Q \), is therefore given by,

\[
Q = \frac{(2n_{Si})! (n_{Si} + n_{O^2-})!}{\prod_i \prod_j b_{ij}^{n_{Si}} c_{i+1,j+1}^{n_{O^2-}}} \prod_i \prod_j p_{ij}^{b_{ij}} q_{ij}^{c_{i+1,j+1}} n_{O^2-}^{n_{O^2-}}
\]

(6)

In order to obtain a usable thermodynamic equation from this partition function, we maximize \( \ln(Q) \) with respect to the variables \( b_{ij} \) and \( c_{i+1,j+1} \). The results of the calculation are the equilibrium constants for the bridge-breaking reactions in Eqs. 1 and 2, given as follows:

\[
K_{i+1,j+1} = \frac{q_{i+1,j+1}}{p_{ij} q_{O^2-}} = \frac{c_{i+1,j+1}}{b_{ij} X_{O^2-}}
\]

(7)

where \( X_{O^2-} = n_{O^2-}/(n_{Si} + n_{O^2-}) \). Since the ratio \( c_{i+1,j+1}/b_{ij} \) is unitless, one may use any self-consistent concentration scale for the uncut bridges and cut bridges. It is not necessary to choose such a scale until we have simplified the equations.

The double summations in some of the expressions (e.g., Eq. 5) and the double subscripts present difficulties in the calculation because there are twenty different species. We can eliminate the double summations and subscripts by performing partial summations and separating the local partition functions for adjacent pairs of silicons (\( p_{ij} \) and \( q_{i+1,j+1} \)) into the more localized partition functions for individual silicons. This reduces the number of terms and simplifies the equations considerably.

If the partition function for the uncut (\( p_{ij} \)) and cut (\( q_{ij} \)) are solely a function of \( i \) and \( j \) such that \( p_{ij} = p_{ij} \) and \( q_{ij} = q_{ij} \) (i.e., the bond free energies are additive), and if we perform partial summations of the terms in \( \ln(Q) \) such as \( \Sigma_i \Sigma_j p_{ij} \ln(b_{ij}) \) and \( \Sigma_i \Sigma_j q_{ij} \ln(p_{ij}) \), we can deduce equilibrium constants \( K_{i+1} \) for the formation of a silicon species with \( i+1 \) cut bonds from one with \( i \) cut bonds.

\[
K_{i+1} = \frac{q_{i+1}}{p_{ij}^{0.5} q_{O^2-}^{0.5}} = \frac{(i+1)n_{i+1}^{0.5}}{(4-i)n_i^{0.5} X_{O^2-}^{0.5}} \quad i = 0,1,2,3
\]

(8)
where \( n_i \) is the number of silicons with \( i \) cut bonds. In addition, Eq. 5 for \( n_{O^2-} \) becomes

\[
n_{O^2-} = n_{MO} - \sum_{i=0}^{4} \frac{in_i}{2}
\]

and we can eliminate one of the variables, \( n_i \), with the equation

\[
\sum_{i=0}^{4} n_i = n_{Si}
\]

Calculations of the partial molar chemical potentials are made by taking a partial derivative of \( \ln(Q) \) with respect to \( n_{Si} \) and \( n_{MO} \) to obtain

\[
\frac{\mu_{SiO_2} - \mu_{SiO_2}^0}{RT} = \ln a_{SiO_2} = \ln X_{Si} + 2 \ln \frac{b_{00}}{2n_{Si}}
\]

\[
= \ln X_{Si} + 2 \ln \frac{16n_0^2}{4n_{Si} \sum (4-i)n_i}
\]

and

\[
\frac{\mu_{MO} - \mu_{MO}^0}{RT} = \ln a_{MO} = \ln X_{O^2-}
\]

These equations have a physically meaningful interpretation. In Eq. 11, \( X_{O^2-} \) is the activity of the basic oxide and is also the concentration of "free" oxide ions (not part of a cut bridge bond) that mix with silicons. It is defined as follows:

\[
X_{O^2-} = \frac{n_{O^2-}}{n_{Si} + n_{O^2-}} = 1 - X_{Si}
\]

The term \( X_{Si} \) in Eq. 10 is the concentration of Si in the mixture of Si and \( O^2- \) and \( b_{00}/2n_{Si} \) is the fraction of the total number of bridges that are uncut bridges between two silicons having no cut bridges attached. These are, of course, the only type of bridges present in the standard state of pure silica, so that the properties of these bonds are related to the properties of the standard state. The term \( \ln b_{00}/2n_{Si} \) is multiplied by 2 because there are two bonds per silicon in the melt. The term \( b_{00} \) is calculable from knowledge of the parameters \( n_i \), which, in turn, are calculable from the four equilibrium constants, \( K_{i+1} \) (\( i = 0,1,2,3 \)). Conversely, one can deduce these constants from a knowledge of the activities of SiO\(_2\) (or MO) as a function of composition.
DISCUSSION

Equations 8-11 provide the capability for realistically determining the thermodynamic properties of binary molten silicates. Analyses of measurements in terms of the theory can provide values of the four formation constants, $k_1$, $k_2$, $k_3$, $k_4$, for cutting Si-O-Si bridges. These, in turn provide information on local structures and on the relative stabilities of the different configurations about silicon atoms. In addition, the theory is flexible enough to permit one to describe the solubility of a solute MX (e.g., X is a sulfide, phosphate or carbonate) by simple multiplication of the partition function in Eq. 6 by the factor $q_n^{n}(n_{Si}+n_{O}^{2}+n_{x})/(n_{Si}+n_{O}^{2})/n_{x}$. An analogous, but more complex, procedure can be used to describe solutions containing alumina. This theory has the fundamental capability for a general description of the thermodynamic properties of molten silicates. Some of the assumptions in the theory can be generalized. For example, we have assumed that the distribution of silicon species among the bonds is not preferential, so that all cut bonds have the same probability for being connected to a particular silicon species. One can generalize the theory to take into account steric or other factors which might lead to a preferential distribution of the pairs of silicons connected by bonds. Thus, the probabilities and concentrations ratios such as $b_{ij}b_{0ij}(b_{0ij})^{2}$ could be made higher or lower than calculated by this simple form of the model. At the current stage of development, such complexity is not warranted. In any case, the theory we present should lead to a more realistic representation of silicate structures than prior models, and the results can be compared with structural data (e.g., NMR measurements on glasses).

References

1. M. Blander and A. D. Pelton, "Computer Assisted Analysis of the Thermodynamic Properties of Slags in Coal Combustion Systems," ANL/FE-83-9, Argonne National Laboratory, Argonne, IL (Sept. 1983).

2. A. D. Pelton and M. Blander, Proc. 2nd Intl. Symp. on Metall. Slags and Fluxes, H. A. Fine and D. R. Gaskell, Eds., pp. 281-294, TMS-AIME, Warrendale, PA (1984).

3. M. Blander and A. D. Pelton, Ibid., pp. 295-304.

4. M. Blander and A. D. Pelton, Mineral Matter and Ash in Coal, K. S. Vorres, Ed., Am. Chem. Soc. Symp. Ser. 301 186-194 (1986).

5. A. D. Pelton and M. Blander, Metall. Trans., 17B, 805-15 (1986).

6. M. Blander and A. D. Pelton, Geochim. Cosmochim. Acta, 51, 85-95 (1987).
7. A. D. Pelton and M. Blander, CALPHAD J. 12, 97-108 (1988).
8. A. D. Pelton, G. Eriksson and M. Blander, Proc. 3rd Int. Symp. on Metall. Slags and Fluxes, pp. 66-69, Inst. of Metals, London (1989).
9. P. Wu, G. Eriksson, A. D. Pelton, and M. Blander, J. Iron and Steel Inst. of Japan, 33, 26-35 (1993).
10. G. Eriksson and A. D. Pelton, Metall. Trans., 24B, 817-825 (1993).
11. P. L. Lin and A. D. Pelton, Metall. Trans., 10B, 667-675 (1979).
12. C. R. Masson, J. R. Smith and S. G. Whiteway, Can. J. Chem., 48, 1456-64 (1970); C. R. Masson, Glass 1977, Proc. 11th Intl. Congress on Glass, Vol. 1, pp. 3-41, J. Gotz, Ed., Prague (1977).
13. D. R. Gaskell, Metall. Trans., 8B, 131-145 (1977).
14. C. J. B. Fincham and F. D. Richardson, Proc. Royal Soc., 223, 40 (1954).
15. G. W. Toop and C. S. Samis, Trans. TMS-AIME, 224, 878-87 (1962).
16. G. M. Frohberg, M. L. Kapoor and G. M. Nichotra, Arch. Eisenhuetttenwes, 45, 213-18 (1974).
17. H. Flood and W. J. Knapp, J. Am. Ceram. Soc., 46, 61 (1963).
18. T. Førlund, Fused Salts, B. R. Sundheim, Ed., Chap. 3, McGraw-Hill, NY, (1964).
19. K. Niwa and T. Yokokawa, Trans. Jpn. Inst. Met., 10, 3-7 (1969).