An Interacting Pair Model for Alkaline Binary and Ternary Liquid Silicates: Application to the Systems Na$_2$O-K$_2$O-SiO$_2$ and Na$_2$O-Cs$_2$O-SiO$_2$

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Among all the available models describing the structure of molten silicates, that of Pelton et al. allows accurate fitting of the experimental data of the free energies in the binary systems MO-SiO$_2$, with M = Fe, Mn, Pb, and Ca. An extension to the ternary systems MO-M'O-SiO$_2$, where M and M' are alkaline metals, is proposed. A statistical treatment of the configurations of the solution gives a meaning to the new parameters. The mixed alkaline effect is quite well shown by the application of the model to the ternary systems K$_2$O-Na$_2$O-SiO$_2$ and Cs$_2$O-Na$_2$O-SiO$_2$, in particular, in the calculation of the configurational entropy.

I. INTRODUCTION

Numerous thermodynamic models of oxide melts are available in the literature. In particular, for molten silicates, a review of these structural models has been published by Gaskell in 1981.[1] Chronologically, the theoretical representations developed by Toop and Samis,[2] Gaskell, Mason and co-workers,[3,4,5] Kapoor et al.[6,7,8], Yokokawa and Niwa,[9,10] and then Lin and Pelton[11] can be mentioned. The models describing the liquid as polymerized silicate anions represent correctly the viscosity of the melts. For most of the descriptions, the basic idea is the gradual depolymerization of the three-dimensional network of pure silica by the modifying oxides. Following the pioneers Fincham and Richardson,[12] the polymerization-depolymerization reactions can be reduced to the simplest equilibrium $O^{n-} + O^{2+} = 2 O^{n-}$, where the double bounded O$^n$ atom represents the bridging oxygens between the silicon atoms in the tetrahedral network of silica, O$^{2+}$ the free oxygens provided by the modifying oxide, and O$^{-}$ the nonbridging oxygens resulting from the depolymerization reaction.

Although no structural details are initially introduced, the model of Lin and Pelton[11] permits description of the distribution of the chain lengths in the entire concentration range and in agreement with the results of structural models. This model is particularly efficient to represent the thermodynamic quantities of silicate melts, and its mathematical simplicity can be considered as a quality. The enthalpy of mixing is then described by the following expression: $\Delta H = n_o/2 (A x_{Si} + B x_M + C x_{Si} x_{M})$ in which $x_{Si}$ denotes the silica concentration and $x_M$ the modifying oxide M$_2$O concentration in the melt; $n_o$ is the number of singly bounded oxygen O$^{-}$ per mole of binary silicate M$_2$O-SiO$_2$. The three adjustable parameters $A$, $B$, and $C$ are fitted to experimental data and thus do not a priori hold any physical significance. In this work, the model that differs from that of Pelton in the expression of the enthalpy is developed for ternary systems by giving a statistical meaning to the parameters.

II. BINARY SYSTEMS

A. Model

It is supposed that only configurational properties act in the mixing process. In addition, neither volume nor accommodation effects have been taken into account. The introduction of the modifying ionized oxide $2M^+$, O$^{-2}$ in the pure silica network breaks the -Si-O$^0$-Si- bonds, which transform into two ionic entities -Si-O$^-$-O$^+$-Si-. Two singly bonded oxygen O$^-$ appear instead of one bridging oxygen O$^0$. Let $n_{Si}$ be the number of silicon atoms and $n_M$ the number of M$_2$O molecules. The resulting enthalpies and entropies of reaction vary significantly with the nature of the cation M$^+$. It is assumed that the melt contains the anions O$^{-2}$ and O$^-$, the divalent cation M$^+$ or pairs of monovalent cations M$^-$-M$^-$, and the O$^-$ and Si atoms. It is also considered that only the O$^{-2}$ and Si atoms occupy the sites of a random network in the liquid (Zachariassen hypothesis), the cohesion of which is ensured by the short-range bonds between the species (Figure 6). For 1 mole of solution, the total number of the lattice sites is $N = N_{x_{Si}} + n_{o-2}$, where $N$ is the Avogadro’s number and $n_{o-2}$ is the number of the free oxygen anions on the network, which is obviously smaller than the total initial number of O$^{-2}$ in the modifying oxide represented by $N(1 - x_{Si})$ in the case of the monovalent metal. The concentration of the species $i$ on the lattice is denoted $x_i = n_i/N$. Let $n_{o-}$ be the number of the bridging oxygen and $n_o$ the number of O$^-$ provided by the reaction $O^{2+} + O^{-} = 2 O^-$. The mass balance in oxygen imposes the equality $n_{o-2} + n_{o-} + n_O^- = N(1 + x_{Si})$. The mass balance in silicon induces $N x_{Si} = N x_{Si}$ and the charge balance $n_{o+} + 2n_{o-} = 2N (1 - x_{Si})$. With the notations that have been chosen and from the former balances, the number of the O$^-$ anions equals $2(N - N)$. The solution is described as pairs. The statistical counting is thus applied to O$^{-2}$-O$^{-2}$, Si-O$^{-2}$, and the two kinds of pairs of the silicon atoms: -Si-(O$^-$)-Si- and -Si-O$^+$(Si-. No long-range order is considered and each atom forms Z/2 pairs with its Z nearest neighbors.

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From the former relations, it can be deduced that \( 4N \chi_{Si} = n_{Si} + 2n_{O} \), which translates into the fact that a silicon atom that is connected to only some oxygen atoms presents a coordination number of four. This coordination number of four is also assumed for the O\(^{2-}\) anions. A network corresponding to 1 mole of the solution holds \( 1/2NZ \) pairs; an average configuration of such a solution is described in Table I. According to the hypothesis of Bragg and Williams, the number of pairs is calculated in the random approximation; thus, the probability of finding a pair \( i-j \) equals \( 2x_{x} \chi_{x} \) and a pair \( i-i, \) \( \chi_{i} \). To each pair \( (i,j) \) is assigned a short-range bond energy \( E_{ij} \), which is assumed to be independent of the temperature. Considering that the pairwise interactions are additive, the total configurational energy of the solution can be written as the sum of the various pair energies. The standard states represented by the pure oxides in the undercooled liquid state are described in the same manner. It can be verified that the total number of pairs remains constant over the reaction and equals \( 1/2NZ \). The potential energy and the corresponding configurational partition function of the solution can be written as

\[
\phi = n_{O}^{o}E_{Si-O}^{o} + (1/2NZ\chi_{Si}^{2} - n_{O}^{o})E_{Si-Si}^{-} + (1/2NZ\chi_{O}^{2} - E_{O}^{-2} - \omega^{-2})\}

\[
\Omega = g(n_{O}^{o}, n_{O}^{-}, n_{Si}) \exp (-\phi/RT)
\]

As previously calculated by Lin and Pelton,\(^{11}\) the degeneracy is first calculated over the possibilities of the interchange of the atoms on the lattice without changing the energy. Following the Bragg and Williams hypothesis, the atoms of the same nature are indistinguishable; then, the first term of the degeneracy is \( (n_{Si} + n_{O}^{-})! \). The second cause of the degeneracy is the possibility of exchanging pairs of Si atoms. The total number of pairs Si-Si is given by \( 1/2NZ\chi_{Si} \). There are two kinds of such pairs (Table I), the numbers of which are respectively \( n_{Si} \) and \( 1/2NZ\chi_{Si} - n_{Si} \). Finally, the greatest number of configurational states is given by

\[
g = \frac{(n_{Si} + n_{O}^{-})!}{(n_{Si})! (n_{O}^{-})! (n_{Si})! (1/2NZ\chi_{Si} - n_{Si})!}
\]

For the pure oxides SiO\(_{2}\) and M\(_{2}O\) in the liquid standard state, the molar potential energies are calculated from the equations

\[
\phi_{SiO_{2}} = 1/2NZ\chi_{Si}E_{Si-O}^{o} \quad \text{(in pure SiO\(_{2}\));}
\]

\[
\Omega_{SiO_{2}} = \exp (-\phi_{SiO_{2}}/RT)
\]

\[
\phi_{M_{2}O} = 1/2NZ(1 - x_{M})E_{O}^{-2} - \omega^{-2} \quad \text{(in pure M\(_{2}O\));}
\]

\[
\Omega_{M_{2}O} = \exp (-\phi_{M_{2}O}/RT)
\]

The molar free energy of mixing can be written as

\[
\frac{\Delta G}{RT} = \ln \left( \frac{\Omega_{SiO_{2}}\Omega_{M_{2}O}}{\Omega} \right)
\]

\[
\Delta G = \phi - \phi_{SiO_{2}} - \phi_{M_{2}O} - RT \ln g
\]

The configurational entropy is \( \Delta S = k \ln g \). Assuming that the pair energies \( E_{Si-Si} \) and \( E_{O}^{-2} - \omega^{-2} \) are identical in the mixture and in the reference states, the enthalpy of formation per mole of solution \( x_{Si} \) SiO\(_{2}\) (1 - \( x_{Si} \)) M\(_{2}O\) can be written as

\[
\Delta H = \phi - \phi_{SiO_{2}} - \phi_{M_{2}O} = (n_{O}^{o} - 1/2NZ\chi_{Si})E_{Si-O}^{o} + (1/2NZ\chi_{O}^{2} - n_{O}^{o})E_{Si-Si}^{-} + (1/2NZ\chi_{O}^{2} - \omega^{-2}) \]

\[
+ 1/2NZ(\chi_{O}^{2} - \omega^{-2}) - N(1 - x_{Si})/N) E_{O}^{-2} - \omega^{-2}
\]

Taking into account the relations previously exposed, the relation can be decomposed in

\[
\Delta H = (n_{O}^{o} - 1/2NZ\chi_{Si})/2 \]

\[
+ Z_{x}N_{x}E_{Si-O}^{o} + (1/2NZ\chi_{Si})E_{Si-Si}^{-} + n_{O}^{o}E_{O}^{-2} - \omega^{-2} \]

\[
- n_{O}^{o} - 1/2NZ\chi_{O}^{2} - \omega^{-2}) E_{Si-Si}^{-} \]

\[
+ 1/2NZ(\chi_{O}^{2} - \omega^{-2}) + 1/2NZ\chi_{Si}E_{Si-O}^{o} - \omega^{-2}
\]

Thus, for \( Z = 4, \)

\[
\Delta H = n_{O}^{o}/2 \]

\[
+ Z_{x}N_{x}E_{Si-O}^{o} - 2E_{O}^{-2} - \omega^{-2} \]

\[
+ 2N_{x}\chi_{O}^{2} - (2E_{Si-Si}^{-} - E_{O}^{-2} - \omega^{-2} - E_{Si-Si}^{-} \omega^{-2})
\]

Let \( W = N(E_{Si-O}^{o} - E_{Si-Si}^{-} - 2E_{O}^{-2} - \omega^{-2}) \) and \( w = N(2E_{Si-Si}^{-} - E_{O}^{-2} - \omega^{-2}) \) and let these quantities be constant over all the concentration range. If \( x_{O}^{o} \) and \( x_{O}^{-} \) represent, respectively, the O\(^{2-}\) and the O\(^{2-}\) concentrations in 1 mole of the melt \( n_{O}^{o} = N_{x}x_{O}^{o}, n_{O}^{-} = N_{x}x_{O}^{-} \), then

\[
\Delta H = \frac{x_{O}^{o}}{2} W + 2x_{Si} \frac{x_{O}^{-}}{x_{O}^{o} + x_{Si}} w
\]

The mixing enthalpy contains two parts describing the binding energy between the silicon atoms and the oxygen anions. It corresponds, on the one hand, to the enthalpy of formation of the orthosilicate in accordance to the reaction, SiO\(_{2}\) + 2M\(_{2}O\) \( \rightleftharpoons \) M\(_{2}SiO\(_{4}\) with the enthalpy change \( W \) and, on the other hand, to the energy of intercalation of the free oxygens into the network of silica as -Si-O-O-Si- + O\(^{2-}\) \( \rightarrow \) -Si-O-O-Si- + O\(^{2-}\) - O-Si- with the enthalpy change \( w \). The second part only becomes significant in the M\(_{2}O\)-rich domain. The molar-free energy referred to the simple oxides SiO\(_{2}\) and M\(_{2}O\) in the liquid state is written as

\[
\Delta G = \frac{x_{O}^{o}}{2} W + 2x_{Si} \frac{x_{O}^{-}}{x_{O}^{o} + x_{Si}} \ln \left( \frac{x_{O}^{o}}{x_{O}^{o} + x_{Si}} + x_{Si} \right)
\]

\[
+ RT \left( x_{Si} \ln \frac{x_{Si}}{x_{O}^{o} + x_{Si}} + x_{O}^{o} \ln \frac{x_{O}^{o}}{x_{O}^{o} + x_{Si}} + x_{O}^{o}\right)
\]

\[
\ln \left( \frac{x_{O}^{o}}{x_{Si} - x_{O}^{o}} + x_{Si} \ln \frac{x_{Si}}{x_{Si} - x_{O}^{o}} \right)
\]

with the Stirling approximation for great numbers.

**B. Calculation of the Equilibrium**

The equilibrium corresponds to the minimum of the free energy change, i.e., \( \frac{\partial \Delta G}{\partial (x_{O}^{o}/2)} = 0 \). Then,