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# ANALYSES AND PREDICTIONS OF THE THERMODYNAMIC PROPERTIES AND PHASE DIAGRAMS OF SILICATE SYSTEMS*

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# ANALYSES AND PREDICTIONS OF THE THERMODYNAMIC PROPERTIES AND PHASE DIAGRAMS OF SILICATE SYSTEMS

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## SYNOPSIS

Molten silicates are ordered solutions which can not be well represented by the usual polynomial representation of deviations from ideal solution behavior (i.e. excess free energies of mixing). An adaptation of quasichemical theory which is capable of describing the properties of ordered solutions represents the measured properties of binary silicates over broad ranges of composition and temperature. For simple silicates such as the $MgO$-$FeO$-$SiO_2$ ternary system, in which silica is the only acid component, a combining rule generally leads to good predictions of ternary (and probably higher order) solutions from those of the binaries. In basic solutions, these predictions are consistent with those of the conformal ionic solution theory. Our results indicate that our approach could provide a potentially powerful tool for representing and predicting the properties of multicomponent molten silicates.

KEY WORDS: Molten silicates, solution theory, solution thermodynamics, $MgO$-$FeO$, $MgO$-$SiO_2$, $FeO$-$SiO_2$, $MgO$-$FeO$-$SiO_2$

## INTRODUCTION

The thermodynamic properties of ordered solutions such as liquid silicates can not be well represented over wide ranges of temperature and composition with the standard polynomial expressions for the the excess free energies of mixing. In highly ordered binary solutions there is a tendency for the enthalpies of mixing versus concentration curves to be "V" shaped and for the total entropies of mixing to be "m" shaped. These characteristics require one to represent the properties of silicates with equations which will have these characteristic properties for strongly interacting binary pairs (e.g., $Na_2O$-$SiO_2$) but which will reduce to the polynomial representaion for weakly interacting binary pairs [1], [2], [3], [4]. In this paper, we discuss a modification of quasichemical theory which has these characteristics and which has been specifically adapted for use with silicates. Our purpose is to illustrate the significance of this approach which allows one to (a) represent the properties of binary silicate systems over wide ranges of temperature and composition with a relatively small number of parameters (less than seven) and (b) predict the properties of multicomponent silicates from those of the corresponding binaries when silica is the only acid component. Such predictions are based on a combining rule which has been shown to be consistent with the predictions of the conformal ionic solution theory in basic silicate solutions [4], [5], [6].

The importance of properly representing ordering (and association) has been amply illustrated for phase relations in ionic systems [5], [6], where the influence of non-random mixing on phase diagrams is often significant. For example, without taking ordering (or association) into account, one would incorrectly predict ternary miscibility gaps in the LiF-KCl quasi-binary system [5] and in basic compositions of e.g., the $Na_2O$-$FeO$-$SiO_2$ system. Phase diagrams are sensitive not only to the absolute values of the free energies of mixing but also to their concentration derivatives.

The outline of this paper is as follows: This INTRODUCTION will be followed by a section on QUASICHEMICAL EQUATIONS which describes the basis for our calculations, followed by a section on a new analysis of the $MgO$-$FeO$ and $MgO$-$SiO_2$ BINARY SYSTEMS to illustrate the methods and the types of data which go into the calculation of the energy parameters in the quasichemical equations. In a section on TERNARY SYSTEMS, the results of a calculation of the ternary system $FeO$-$MgO$-$SiO_2$ will be presented to illustrate the predictive capability of our methods. A final CONCLUSION section follows.

## QUASICHEMICAL EQUATIONS

The quasichemical theory [7], is a well known approximation for the solution chemistry of binary and higher order systems which, for very negative values of the energy of interaction of two of the components, has the characteristic properties of ordered solutions. If one considers a simple binary mixture of the two pure liquids, A and B, the theory focusses on the energy change for making some A-B bonds in the mixture by the loss of A-A and B-B bonds in the original pure liquids. For silicates, these bonds are between next nearest neighbor pairs.

$$\text{A-A} + \text{B-B} \rightleftarrows \text{A-B} \tag{1}$$

If this energy change is very negative relative to -RT, then the mixture will be ordered. In a general sense, one can consider this energy change to be temperature dependent and represented by $(\omega-\eta T)$. If the total number of atoms of A or B is designated as $n_A$ and $n_B$ then the mole fractions of A and B are $X_A=n_A/(n_A+n_B)$ and $X_B=n_B/(n_A+n_B)$. One also defines the number of A-A, B-B and A-B bonds, $n_{AA}$, $n_{BB}$ and $n_{AB}$ and generally, for simplicity, the coordination of the atoms is taken as a constant, Z. Thus $Zn_A = 2n_{AA} + n_{AB}$ and $Zn_B = 2n_{BB} + n_{AB}$ and the bond fractions $X_{ij}$ are defined as $X_{ij} = n_{ij}/(n_{AA}+n_{BB}+n_{AB})$. In order for the entropy of mixing of a perfectly ordered solution to have the expected value of zero, one must choose an unrealistic value of $Z=2$. With these definitions, one calculates a bond equilibrium constant

$$X_{AB}^2/(X_{AA}X_{BB}) = 4\exp[-2(\omega-\eta T)/RT] \tag{2}$$

an enthalpy of mixing

$$\Delta H = X_{AB}\omega/2 \tag{3}$$

a non-configurational entropy of mixing, $\Delta S^{nc}$

$$\Delta S^{nc} = X_{AB}\eta/2 \tag{4}$$

and the configurational entropy, $\Delta S^{c}$, is given by

$$\begin{aligned}\Delta S^{c} &= -R(X_A\ln X_A+X_B\ln X_B)\\ &+R[X_{AA}\ln(X_{AA}/X_A^2)+X_{BB}\ln(X_{BB}/X_B^2)+X_{AB}\ln(X_{AB}/2X_AX_B)]\end{aligned} \tag{5}$$

Although these equations reproduce the properties of ordered liquids, they must be adapted to the properties of silicates. For example, the quasichemical theory is symmetric and the composition of maximum ordering (i.e., the composition of the minima in the total entropy and enthalpy of mixing for a strongly ordered AB pair is at $X_A = X_B = 0.5$ whereas in silicates such as in, e.g., the $CaO$-$SiO_2$ system, it is expected at $X_{CaO} = 2/3$. In order to accomplish this, the concentration scale is altered from mole fractions to equivalent fractions (e.g., $Y_{CaO} = n_{CaO}/(n_{CaO}+2n_{SiO2})$) and component "coordination numbers" $b_AZ$ and $b_BZ$ are chosen to provide a value of the entropy of mixing very close to zero for a perfectly ordered binary mixture at the most ordered composition. For self consistency, $Z=2$ and $b_{SiO2}$ was always taken to be 1.3374 and CaO, FeO, MgO etc. were taken to be half that value, so that the ratio $b_A/b_B$ was also equal to the ratio of the number of equivalents per mole. Thus, equations (3), (4) and (5) were modified by multiplying the r.h.s. of Eqs. (3) and (4) and the last term on the r.h.s. of Eq. (5) by $b_AX_A+b_BX_B$ and substituting the equivalent fractions $Y_A$ and $Y_B$ for $X_A$ and $X_B$ in Eq. (2) and in the last term in brackets in Eq.(5).

In addition, the quasichemical theory is based on the commonly used assumption that pair bond energies are additive and are all the same for each of the different A-A, B-B and A-B pairs. Real systems can be much better represented by configuration dependent energies. However, early attempts to represent bond energies in this manner were far too complex and, consequently, we substituted concentration dependent energies by representing $\omega$ and $\eta$ in Eq.(2) by a polynomial in powers of the equivalent fraction of silica. Although recent progress has been made in deducing suitable equations for configuration dependent energies, this development requires considerably more work.

## BINARY SYSTEMS

We will illustrate the methods used to perform calculations [8] for one ternary system, the MgO-FeO-$SiO_2$ system, and in this section, we will exhibit some of the calculations for two of the three subsidiary binary systems, MgO-FeO, and MgO-$SiO_2$ [9], [10]. The results of such calculations are the primary input for the prediction of the solution properties of the ternary system.

In the most recent work on the FeO-MgO system [11], [12], the oxygen potentials in the binary solid solutions have been remeasured [12] and the resultant activities of FeO and the earlier solidus data [13] have been shown to be well represented by one parameter in a regular solution model for the solid [9, 10]

$$g^E(\text{sol}) = 10175 X_{FeO} X_{MgO} \text{ Jmol}^{-1} \tag{6}$$

and by a value of $\omega = 3347 \text{ Jmol}^{-1}$ for the binary liquid in the quasichemical model.

The data for the binary MgO-$SiO_2$ system have been used to perform an optimized simultaneous analysis of all the data for this binary using the quasichemical equations [8], [9], 10]. This includes liquidus data [14], [15], [16], miscibility gap data [17], [18], [19], activities of MgO and $SiO_2$ [20], [21], [22], and data on the free energy functions and enthalpies of formation at 298 K of the binary compounds [23], [24]. Not all these data were self consistent. As a result, an assessment of the data was made and based on more recent work [16], the reports of solid solutions of silica in periclase and periclase in forsterite [15], were discounted. The careful work of Hageman and Oonk [19], on the miscibility gap was given precedence in this analysis. The result was a total of three terms in the polynomial for $\omega$ and two terms in the polynomial for $\eta$. These parameters were obtained by a non-linear least squares technique which we developed [8].

A test of the self consistency of our equations in representing data over a wide range of temperatures and compositions is to reverse the optimization procedure so as to back calculate the input data. For the data on activities and free energies (and enthalpies) of formation of compounds, the calculated values were well within the uncertainties in the measurements. Because liquidus temperatures are extremely sensitive to very small errors in these last quantities, we changed the enthalpies of formation at 298 K of $Mg_2SiO_4$ and $MgSiO_3$ [23], by -3206 and 453 $\text{Jmol}^{-1}$ respectively in order to reproduce the measured melting or peritectic points. These changes are well within the known uncertainties in $\Delta H^o_{298}$ [24].

The calculated phase diagram exhibited in Figure 1 is in good agreement with the measured data also shown in the Figure and illustrates the ability of our equations to represent data in such ordered systems. A similar optimization was performed on data for the FeO-$SiO_2$ system. This general capability for representing the thermodynamic properties of such binary ordered solutions is an important prerequisite for any useful method for representing and predicting the properties of multicomponent silicates.

## TERNARY SYSTEMS

In this section we will discuss the method for calculating the properties of the relatively simple ternary systems in which the only "acidic" component is silica and in which the basic components are monovalent or divalent oxides. For such systems, a relatively simple asymmetric combining rule generally leads to good predictions of the solution properties of ternary systems (and presumably higher order systems) which in basic compositions are consistent with the predictions of the conformal ionic solution theory [3], [4], [5], [6]. For most other systems (e.g. the CaO-$Al_2O_3$-$SiO_2$ system), ternary correction terms were needed to represent the properties accurately.

The asymmetric combining rule is very simply stated in words. If one considers a ternary system A-B-C in which silica is component C, then the interaction "energy" terms ($\omega$-$\eta$T) for each of the binary pairs AC or BC are only a function of $Y_C$ in the ternary and are independent of the variable $Y_A$ at constant values of $Y_C$. In addition, the interaction energy term for the AB pair for any one value of $Y_A/(Y_A+Y_B)$ is the same as the corresponding value in the binary system AB. With this approximation substituted into the quasichemical equations for ternary systems [3], [4], we have shown that (a) The solution properties of ternary (and presumably higher order) systems in which silica is the only acid component are predicted *a priori* solely from the binary properties. For example, activities of components and phase diagrams were correctly predicted within the uncertainties in the measurements. (b) An important property related to association and ordering is predicted in basic solutions. Without this property, one would incorectly predict miscibility gaps in e.g., quasi binary systems such as FeO-$Na_4SiO_4$, MnO-$Na_4SiO_4$ and FeO-$Ca_2SiO_4$. To illustrate the predictions of the asymmetric approximation we give the calculated phase diagram of the ternary MgO-FeO-$SiO_2$ system in Figure 2 which is in excellent agreement with measurements.

## CONCLUSIONS

Modified quasichemical equations can be used to predict the properties of simple ternary (and presumably higher order) silicate systems from those of the subsidiary binaries. For more complex silicates, ternary interaction terms are necessary to describe ternary properties. The properties of multicomponent silicates can be predicted from the properties of the lower order binary or ternary systems. Further studies are needed to test the utility of these predictions which could provide a potentially powerful tool for representing and predicting the properties of multicomponent molten silicate systems. We have already optimized and evaluated a large number of binary and ternary systems and performed calculations for multicomponent systems [9], [10], [25].

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