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AN APPROACH TO THERMOCHEMICAL MODELING OF NUCLEAR WASTE GLASS

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ABSTRACT
    This initial work is aimed at developing a basic understanding of the phase equilibria and solid solution behavior of the constituents of waste glass. Current, experimentally determined values are less than desirable since they depend on measurement of the leach rate under non-realistic conditions designed to accelerate processes that occur on a geologic time scale. The often-used assumption that the activity of a species is either unity or equal to the overall concentration of the metal can also yield misleading results. The associate species model, a recent development in thermochemical modeling, will be applied to these systems to more accurately predict chemical activities in such complex systems as waste glasses.

INTRODUCTION

    High-level nuclear and transuranic wastes are currently foreseen as being incorporated in a host glass for permanent disposal. A large number of glasses have been explored, with borosilicate glass as the typical base composition. Prediction of the long-term stability of these waste forms requires an accurate understanding of the chemical activity of the constituent species. These are necessary for determining volatility, leaching behavior, and corrosion reactions. However, accurate thermochemical values for the constituents of glasses require a global model for the glass phase. To date, such a model is lacking, requiring the use of experimental simulation or oversimplistic assumptions. Figure 1 is a schematic of the leaching process from glass. It can be seen that any assumption regarding the activity of a species in the glass will directly influence the eventual concentration in the leachate. This illustrates the dependence of leachate concentrations on the assumption of activity for a metal oxide constituent of the glass and the need for an accurate understanding of species chemical potentials. Unfortunately, because of the lack of a suitable model for the thermochemistry of glasses, it has been necessary to either assume a metal oxide is present at unit activity or that it has an activity equal to the overall concentration of the metal in the glass. These approaches can

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lead to highly misleading results. Accurate predictions of leaching from a chemically complex nuclear waste glass requires accurate thermodynamic activities of its component oxides.
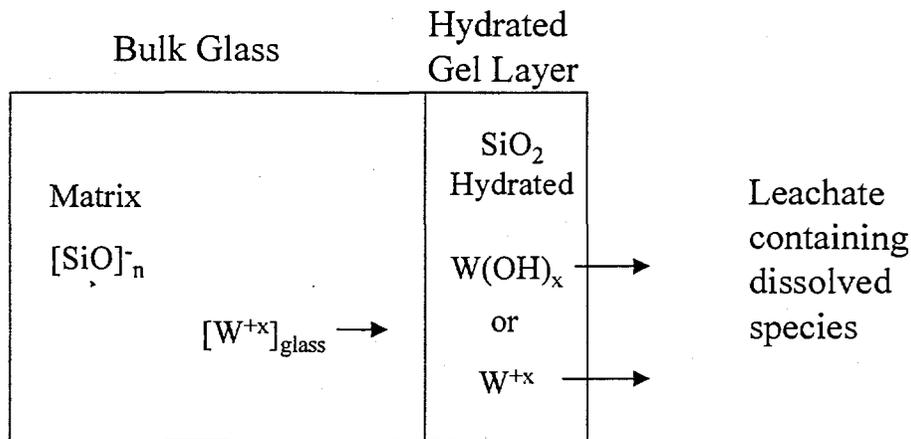

Fig. 1. Schematic of the leaching process from glass. The concentration of the leached waste species is dependent on the activity of the ion, [W^{+x}], in the glass.

The work presented in this paper covers initial efforts in developing a comprehensive model for waste glass compositions. The effort is focussed on producing an accurate, easy to understand and use thermochemical representation for describing the stability of waste glasses. The model must be able to generate accurate values for thermodynamic activities of glass components as a function of temperature and glass composition.

The approach used here utilizes the common description of a glass as a supercooled liquid solution phase. It therefore requires developing an accurate model for the complex oxide liquid phase. This requires a critically assessed thermodynamic database consistent with the model for binary and ternary combinations of the major components in a typical waste glass. These systems can then be combined to represent the thermodynamic behavior of complex, multicomponent glass systems.

SOLUTION MODEL

An associate model developed in the 1980s was used to represent the thermochemical behavior of liquid oxide solutions. With an accurate model of the liquid solution, the supercooled liquid therefore represents the chemically complex nuclear waste glass. The model was initially utilized for complex solutions by Hastie, Bonnell, and co-workers (2-5). A review of much of their research incorporating this model is given in Bonnell and Hastie (5). Pantano, Spear and co-workers also used the model for predicting and explaining interface reactions in fiber-reinforced glass-matrix composite systems (6-8), and the behavior of tin and iron in float glass systems (9-10). Other thermodynamic models have been used to represent nuclear waste glass, most notably the modified quasichemical model of Pelton, Blander and co-workers (11-12) who initially used it to represent molten slag phases, and later nuclear materials, including waste glass (13). The associate model, however, is substantially easier for non-specialists to

understand and use, and yet the model still accurately represents the limiting thermodynamic activities of components in these metastable glass phases.

Energies of interaction between end-member component oxides beyond those of ideal mixing often exist. These are considered explicitly in representations such as the quasichemical model (14). The use of interaction energies in such an approach results in a significant multiplication of terms making it cumbersome to develop relationships for complex systems. These energies are included in the associate model by adding "associate species," with their respective formation energies, to the solution. Thus the complex interaction terms are simply embodied in additional species in the solution. For example, in using the associate model for the $Na_2O-Al_2O_3$ binary oxide system examined in this paper, an ideal liquid solution phase was created from the liquid components $Na_2O(l)$ and $Al_2O_3(l)$ along with a $NaAlO_2(l)$ associate liquid species. In calculating the equilibrium state of the liquid phase containing the three species, the minimization of the total free energy determines the relative mole fractions of the species. As the system is treated as an ideal solution, the activities are by definition equivalent to the species mole fraction. The resulting activities of these species can be used to predict leaching behavior, corrosion reactions, and other important phenomena.

THERMODYNAMIC DATA AND CALCULATIONS

The thermodynamic computer program ChemSage™ (15), thermodynamic data from the SGTE database, 1996 update (16), estimated thermodynamic data, and phase diagrams from Phase Diagrams for Ceramists (17) and other sources (18-20) were used in our assessments and calculations. Unavailable data which had to be estimated included fusion enthalpies and entropies, enthalpies of formation at 298 K, absolute entropies at 298 K, and heat capacity (Cp) equations for temperatures from 298 to ~3000 K. Trends in chemical reaction values were used as described by Spear (21) for entropies and heat capacities. Enthalpies of formation were derived by adjusting values until the computed phase diagram stability regions were consonant with those of accepted, published diagrams. All values were assessed to determine if they would yield reasonable thermodynamic and phase relations over wide ranges of temperature and composition.

Data for the $Na_2O-Al_2O_3$ System

A search of the SGTE database (16) for the $Na_2O-Al_2O_3$ system revealed that it did not contain values for the fusion of $NaAlO_2$, nor any data for $\beta''-Al_2O_3$ [Na_2O - 6•Al_2O_3] and $\beta-Al_2O_3$ and [Na_2O -11•Al_2O_3]. These data were estimated, including fusion enthalpies and entropies, enthalpies of formation at 298K, absolute entropies at 298K, and Cp equations for temperatures from 298 to ~3000K. A liquid phase which produced a good thermodynamic fit of the binary phase diagram (17,18), however, required only three liquid species: Na_2O, Al_2O_3, and $NaAlO_2$. Additional associate species when included in the solution phase did not improve the fit to the phase diagram.

Data for the Na_2O-SiO_2 System

Thermodynamic data for crystalline phases in the Na_2O-SiO_2 system were available from the SGTE database (16), but a liquid solution phase had to be developed and all of the system data refined by manually optimizing it with respect to the binary temperature-composition phase diagram (17,19). Species in the liquid solution included:

Na$_2$O, Si$_2$O$_4$, Na$_{1.6}$Si$_{0.4}$O$_{1.6}$, Na$_{1.33}$Si$_{0.67}$O$_2$, NaSiO$_{2.5}$. (Note that these formulae have the same atom ratios as the typically denoted crystalline phase formulae: Na$_2$O, SiO$_2$, Na$_4$SiO$_4$, Na$_2$SiO$_3$, Na$_2$Si$_2$O$_5$.) Each associate species in the liquid phase was written so that

$$a \text{ Na} + b \text{ Si} = 2/\text{formula unit}$$

where the number of metals per formula unit equals 2. This general rule was followed for each system studied since it gives equal weight to all liquid species in the solution with regard to the entropy of mixing, and resulted in the best fits of the phase diagrams. The fundamental reasons for why better phase diagram fits were obtained when the sum of the non-oxygen atoms equaled 2/formula unit rather than 1/formula unit is not understood.

Data for the SiO$_2$-Al$_2$O$_3$ System

The SiO$_2$-Al$_2$O$_3$ system data were taken from the SGTE database (16), but the data for the mullite liquid associate required adjustment to give the best fit of the phase diagram (17,20). The liquid species included Si$_2$O$_4$. Al$_2$O$_3$, and Al$_{1.5}$Si$_{0.5}$O$_{3.25}$.

RESULTS AND DISCUSSION

Na$_2$O-Al$_2$O$_3$ System

Figure 2(a) is the calculated phase diagram for this system after fitting the liquid associate thermodynamic data to reproduce the melting temperatures of its stoichiometric crystalline phases. Figure 2(b) contains plots of the calculated activities of the liquid species (Na$_2$O, Al$_2$O$_3$, NaAlO$_2$) as a function of composition at 1200°C. The values were computed by suppressing the formation of crystalline phases and only then computing the thermochemical equilibrium state of the system. In this way the activities of the associates in the supercooled liquid can be represented. Since the associate solution model assumes ideal mixing behavior, the activities are numerically equal to the mole fractions of the respective species in the liquid solution phase. From Fig. 2(b) it is apparent that the associate NaAlO$_2$(l) dominates the liquid phase at Al$_2$O$_3$ mole fractions from about 0.25 to 0.75, and is almost unity at its stoichiometric composition in the glass. This indicates that the liquid solution energy in this composition range is dominated by the formation energy of the associate species, with very little contribution from the ideal mixing term. The strong association energy of NaAlO$_2$(l) causes the Na$_2$O(l) activity to be lowered from about 10^{-1} to 10^{-6} as the composition of the liquid changes from the Na$_2$O-rich side to the Al$_2$O$_3$-rich side of the NaAlO$_2$ liquid composition. A similar, but opposite effect occurs with the Al$_2$O$_3$(l) activity as this composition region is traversed.

Na$_2$O-SiO$_2$ System

Figure 3(a) is the calculated phase diagram for this system after fitting the liquid associate thermodynamic data to reproduce the melting temperatures of its stoichiometric crystalline phases. The calculated activities of the liquid species (Na$_2$O, Si$_2$O$_4$, Na$_{8/5}$Si$_{2/5}$O$_{8/5}$, Na$_{4/3}$Si$_{2/3}$O$_2$, NaSiO$_{5/2}$) are plotted in Fig. 3(b) as a function of composition at 1200°C. Again, the activities are calculated at 1200°C with the formation of crystalline
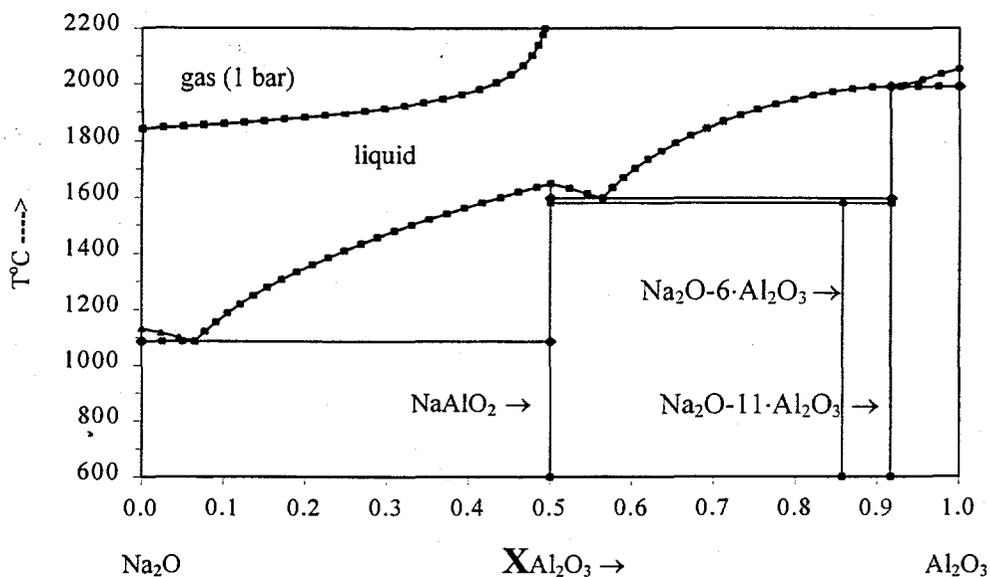
Fig. 2(a). Calculated phase diagram for the Na_2O-Al_2O_3 system using ChemSage™ (15), optimizing the thermodynamic data for the liquid phase to reproduce the melting temperatures (17,18) of the stoichiometric compound phases.
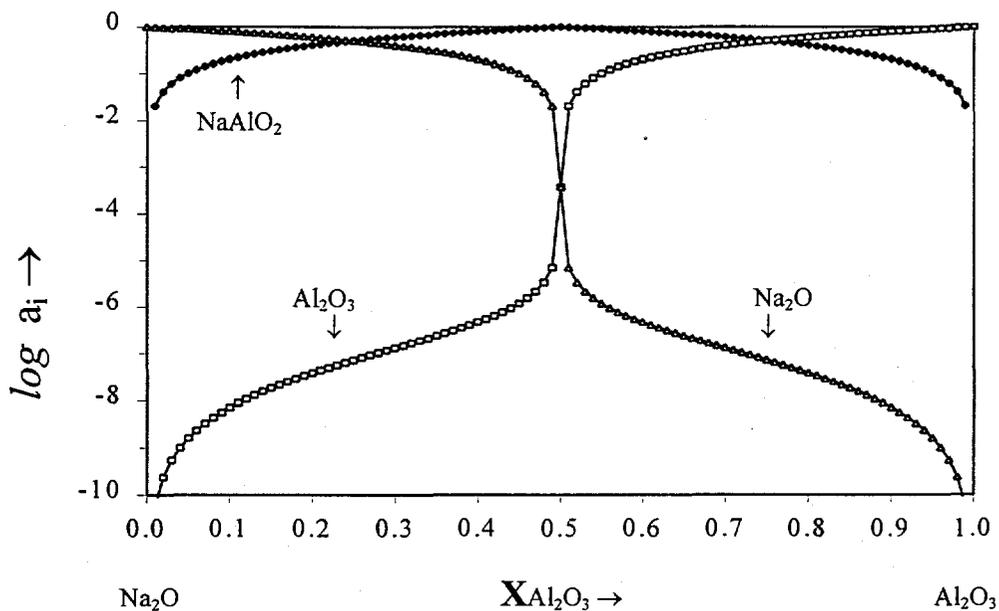

Fig. 2(b). Calculated activities of Na_2O, Al_2O_3, and $NaAlO_2$ liquid species at 1200°C for the Na_2O-Al_2O_3 system using ChemSage™ (15) using the thermodynamic data which produced the phase diagram in Fig. 2(a). The formation of equilibrium crystalline phases was suppressed.
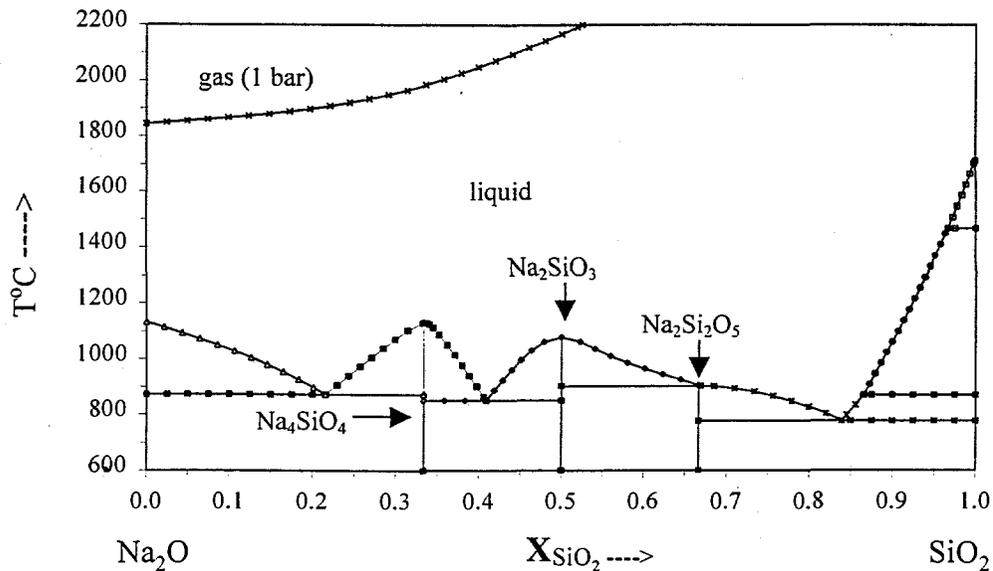
Fig. 3(a). Calculated phase diagram for the Na_2O-SiO_2 system using ChemSage™ (15), optimizing the thermodynamic data for the liquid phase to reproduce the melting temperatures (17,19) of the stoichiometric compound phases.
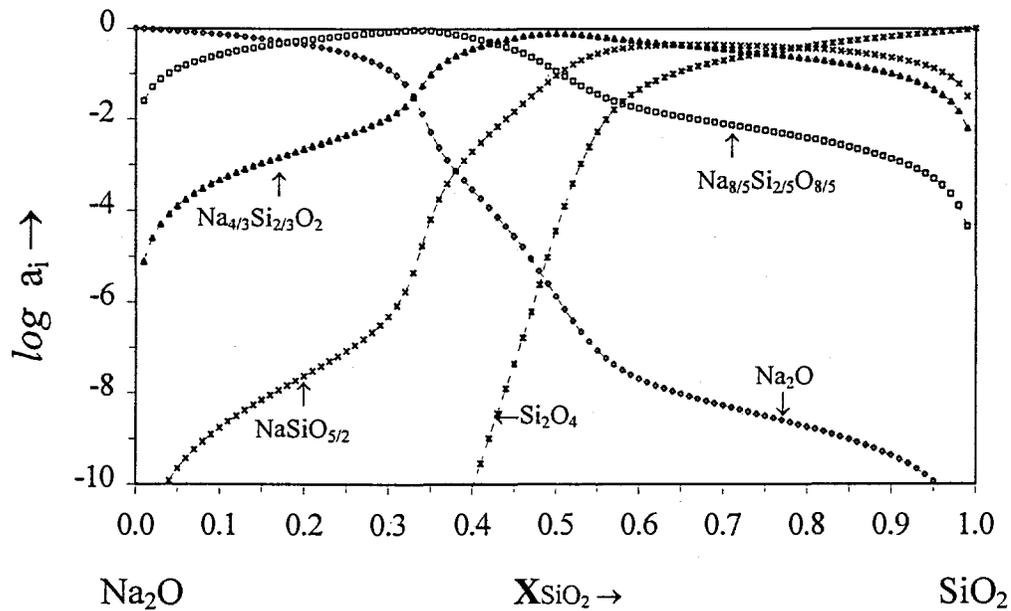

Fig. 3(b). Calculated activities of Na_2O, Si_2O_4, $Na_{8/5}Si_{2/5}O_{8/5}$, $Na_{4/3}Si_{2/3}O_2$, and $NaSiO_{5/2}$ liquid species at 1200°C for the Na_2O-SiO_2 system using ChemSage™ (15) using the thermodynamic data which produced the phase diagram in Fig. 3 (a). The formation of equilibrium crystalline phases was suppressed.

phases suppressed so that these activities represent those in a supercooled liquid phase. The liquid associates dominate the liquid phase at SiO_2 mole fractions of from 0.2 to 0.8, with two of the associates attaining almost unit activities at liquid compositions corresponding to their respective stoichiometric compositions. The third associate, $NaSiO_{5/2}$, is not as stable as the other two, and thus does not dominate the liquid solution energy at its composition. As is seen from Fig. 3(b), the strong association energies of the liquid associate species in this system cause the component activities of Na_2O and Si_2O_4 to remain at very low values except near the compositional extremes.

SiO_2-Al_2O_3 System

Figure 4(a) gives the calculated phase diagram for this system after fitting the liquid associate thermodynamic data to reproduce the melting temperatures of its stoichiometric crystalline phases. Figure 4(b) is a plot of the calculated activities of the liquid species (Si_2O_4, Al_2O_3, $Al_{1.5}Si_{0.5}O_{3.25}$) at 1200°C. Note the difference in the activity scale (3 orders of magnitude) as compared to the other two systems discussed in this paper (10 orders of magnitude). The liquid species Si_2O_4 and Al_2O_3 dominate the liquid phase, even at the stoichiometric composition of mullite. The weak association energy of $Al_{1.5}Si_{0.5}O_{3.25}(l)$ results in appreciable mixing energy in the liquid at all compositions. This may be the result of the need to decrease the stability of the liquid mullite species in order to obtain an accurate melting temperature.

CONCLUSIONS

As demonstrated in the current work, as well as in previous studies, the associate model is a simple and accurate means for representing the activities of the constituent species of oxide melts and glasses. The approach of developing a critically assessed thermodynamic database for binary and ternary combinations of the major components in a typical waste glass is continuing with assessments of other binary alkali and alkaline earth silicates, aluminates, and borates. At the same time, the database being created will be used for producing datasets for assessments of ternary and higher order systems so that the importance of ternary associate species on the liquid solution stability can be determined. These data will then be combined to predict the thermodynamic behavior of the more complex glass systems used for high-level nuclear and transuranic wastes. In the case of leaching from a waste form, the activity of the each of the more important (higher activity) species, whether single oxide and associate species, should be used in the calculation of the equilibrium hydration reaction. This procedure should give the most accurate result with regard to equilibrium concentrations of leaching constituents.
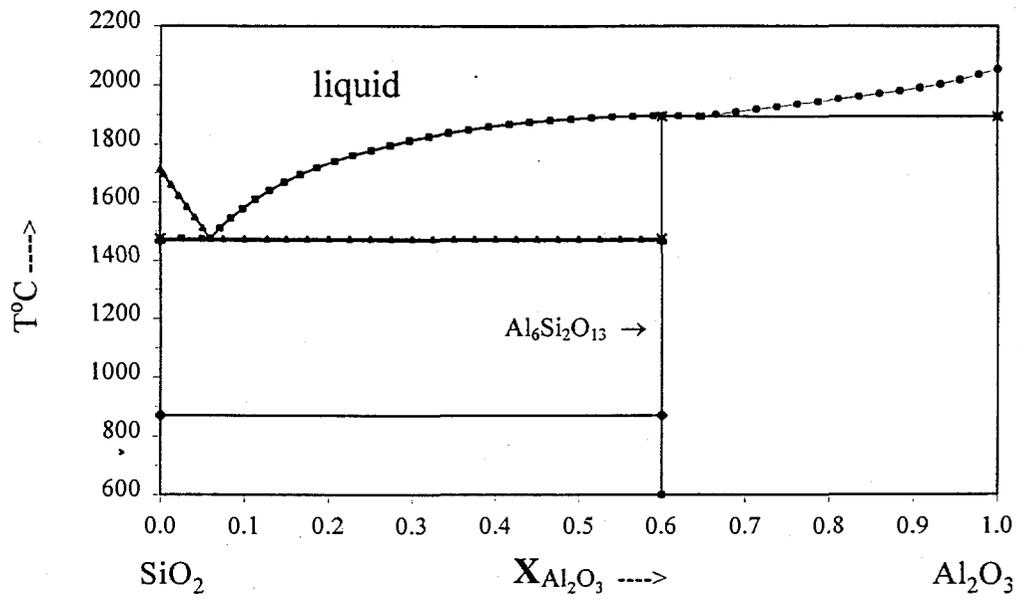
Fig. 4(a). Calculated phase diagram for the SiO_2-Al_2O_3 system using ChemSage™ (15), optimizing the thermodynamic data for the liquid phase to reproduce the melting temperatures (17,20) of the stoichiometric mullite phase.
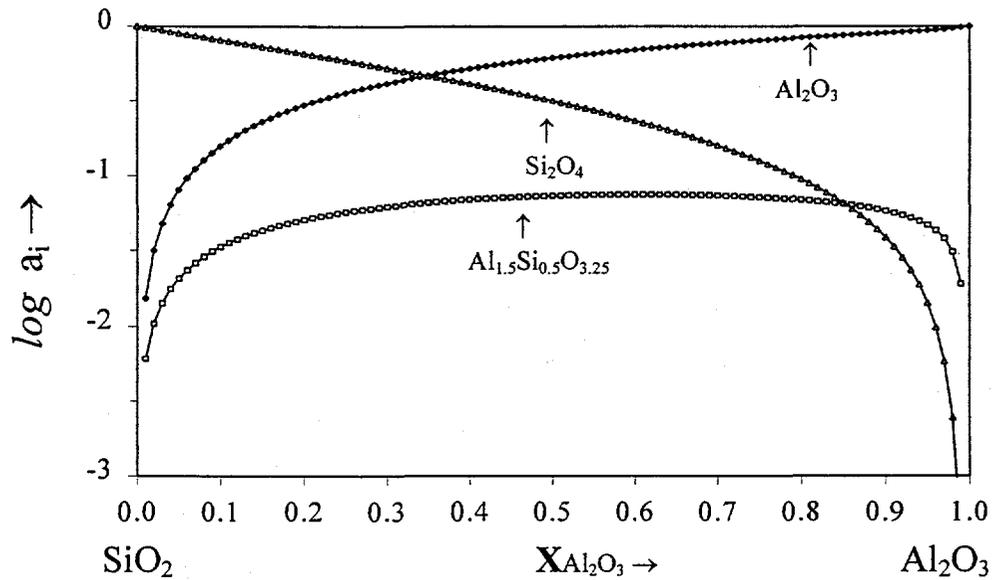

Fig. 4(b). Calculated activities of Si_2O_4, Al_2O_3, and $Al_{1.5}Si_{0.5}O_{3.25}$ liquid species at 1200°C for the SiO_2-Al_2O_3 system using ChemSage™ (15) and the thermodynamic data which produced the phase diagram in Fig. 4 (a). The formation of equilibrium crystalline phases was suppressed.

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