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THERMOCHEMICAL MODELING OF NUCLEAR WASTE GLASS*

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The development of assessed and consistent phase equilibria and thermodynamic data for major glass constituents used to incorporate high-level nuclear waste is discussed in this paper. The initial research has included the binary Na_2O-SiO_2, Na_2O-Al_2O_3, and SiO_2-Al_2O_3 systems. The nuclear waste glass is assumed to be a supercooled liquid containing the constituents in the glass at temperatures of interest for nuclear waste storage. Thermodynamic data for the liquid solutions were derived from mathematical comparisons of phase diagram information and the thermodynamic data available for crystalline solid phases. An associate model is used to describe the liquid solution phases. Utilizing phase diagram information provides very stringent limits on the relative thermodynamic stabilities of all phases which exist in a given system.

Keywords: glass modeling, thermochemical modeling, nuclear waste glass, associate solution model, Na_2O-Al_2O_3, Na_2O-SiO_2, Al_2O_3-SiO_2, thermodynamics of glass

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THERMOCHEMICAL MODELING OF NUCLEAR WASTE GLASS

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The development of assessed and consistent phase equilibria and thermodynamic data for major glass constituents used to incorporate high-level nuclear waste is discussed in this paper. The initial research has included the binary Na_2O-SiO_2, Na_2O-Al_2O_3, and SiO_2-Al_2O_3 systems. The nuclear waste glass is assumed to be a supercooled liquid containing the constituents in the glass at temperatures of interest for nuclear waste storage. Thermodynamic data for the liquid solutions were derived from mathematical comparisons of phase diagram information and the thermodynamic data available for crystalline solid phases. An associate model is used to describe the liquid solution phases. Utilizing phase diagram information provides very stringent limits on the relative thermodynamic stabilities of all phases which exist in a given system.

INTRODUCTION

Current efforts in developing long term storage for high level nuclear waste include incorporating the waste into a glass form. An example composition for such a complex, multicomponent nuclear waste glass is given in Table 1. The present paper discusses results of a research project aimed at developing an accurate, easy to understand and use, thermochemical model for describing the thermodynamic stability of high level waste glasses. More specifically, the model must be able to generate accurate values for thermodynamic activities of glass components as a function of temperature and glass composition. A major concern with radioactive waste storage is the possibility of leaching active components from the waste if it comes into contact with ground water. Accurate predictions of leaching from a chemically complex nuclear waste glass requires accurate thermodynamic activities of its component oxides.

Since a glass can be described as a supercooled liquid solution phase, developing an accurate model for representing the thermodynamic properties of oxide liquid phases is critical to understanding the limiting chemical behavior of the nuclear waste glass. Our approach is to first develop a critically assessed thermodynamic database for binary and ternary combinations of the major components in a typical waste glass. These data can then be combined to represent the thermodynamic behavior of complex multicomponent glass systems.

Table 1: An Examples of Components in High Level Radioactive Waste Glass Ellison and Navrotsky (1)

major	mol%	trace	mol%
SiO_2	54.82	U_3O_8	0.167
Li_2O	9.66	ThO_2	0.047
Na_2O	9.24	Cr_2O_3	0.052
B_2O_3	7.55	CuO	0.363
Fe_2O_3	2.86	$CaSO_4$	0.037
FeO	2.84	$BaSO_4$	0.116
K_2O	2.69	NaCl	0.213
Al_2O_3	2.56	Na_2SO_4	0.055
MgO	2.20		
MnO	1.88	**subtotal trace**	**1.050**
CaO	1.13		
NiO	0.78	**others**	
TiO_2	0.74	Group A	
		Tc, Se, Te, Rb, & Mo	
subtotal major	**98.95**	Group B	
		Ag, Cd, Cr, Pd, Tl, La, Ce	
		Pr, Pm, Nd, Sm, Sn, Sb, Co	
		Zr, Nb, Eu, Np, Am, Cm	

GENERAL DESCRIPTION OF LIQUID SOLUTION MODEL

We use an associate model to represent the thermodynamic properties of liquid solutions which we then supercool to represent the chemically complex nuclear waste glass. The model was utilized for complex solutions by Hastie, Bonnell and co-workers (2-5) in the 1980's. 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 developed by Pelton, Blander and co-workers (11-12) to represent molten slag phases, and later nuclear materials, including waste glass (13). We have chosen to develop and use an associate model for liquid solutions related to nuclear waste glass because it is easy for nonspeciallists to understand and use, and yet the model still accurately represents the limiting thermodynamic activities of components in these metastable equilibrium glass phases.

Energies and Activities in the Associate Liquid Solution Model

Nonideal energies often exist when mixing end-member component oxide species to form a solution. Such energies are included in the associate model by adding "associate species" with their respective formation energies to the solution. For example, in using the associate model for the Na_2O-Al_2O_3 binary oxide system examined in this paper, we created an ideal liquid solution phase from liquid components $Na_2O(l)$ and $Al_2O_3(l)$ along with a $NaAlO_2(l)$ associate liquid species.

The associate species formation energy is readily obtained from considerations of the congruent melting reaction

$$NaAlO_2(s) = \text{“}NaAlO_2(l)\text{”} \qquad \Delta G = 0 \quad \text{at } T_{fusion} \qquad [1a]$$

which is at equilibrium at the congruent melting temperature of the crystalline phase. Thus,

$$\Delta G_{NaAlO_2(s)} = \Delta G^{\circ}_{NaAlO_2(s)} = \Delta G_{\text{“}NaAlO_2(l)\text{”}} \qquad [1b]$$

The free energy and standard free energy of the solid are identical since the pure stoichiometric solid phase is defined as having unit activity. The same may not be true for the liquid phase in equilibrium with this solid at its congruent melting temperature. The "$NaAlO_2(l)$" is written within quotation marks since the liquid solution is composed of Na_2O, Al_2O_3 and $NaAlO_2$ liquid species with a constraint that the liquid composition be identical to the solid phase composition in equation [1] at the congruent melting temperature. The relative amounts of each liquid species ($a_i = Y_i$, i.e. activity is equal to mole fraction, in an ideal solution) are determined by the equilibrium reaction

$$Na_2O(l) + Al_2O_3(l) = 2\ NaAlO_2(l) \qquad K_{eq} = \{Y_{NaAlO_2(l)}\}^2/\{Y_{Na_2O(l)}\ Y_{Al_2O_3(l)}\} \qquad [1c]$$

much as one would consider a homogeneous, equilibrium mixture of gas molecules. More detail is given below with regard to energies and activities in this model.

As with the total energy of a homogeneous ideal gaseous solution, the energy of a homogeneous ideal liquid solution which is comprised of associate species can be represented by the equation

$$\Delta G_{liq} = \sum n_i\ \Delta G_i(l) = \sum n_i\ \{\Delta G_i^{\circ}(l) + RT\ ln\ Y_i(l)\} \qquad [2]$$

where $\Delta G_i(l)$ is the free energy of formation of the *ith* liquid species, n_i is its number of moles in the liquid solution, $\Delta G_i^{\circ}(l)$ is its standard free energy of formation, and $Y_i(l)$ is the mole fraction of species i in the liquid solution.

In the Na_2O-Al_2O_3 system, the formation of one mole of each of these liquid species from pure reference components $Na_2O(l)$ and $Al_2O_3(l)$ can be represented by the general chemical equation

$$X\ Na_2O(l,a=1) + (1-X)\ Al_2O_3(l,a=1) = (Na_2O)_X \bullet (Al_2O_3)_{1-X}(l,solution) \quad [3]$$

where X is the mole fraction of Na_2O in the product liquid species. In the liquid composed of the three species Na_2O, Al_2O_3 and $NaAlO_2$, the formation reactions for these liquid species from the pure liquid components are:

$$Na_2O(l,a=1) = Na_2O(l, solution) \quad [4a]$$

$$Al_2O_3(l,a=1) = Al_2O_3(l,solution) \quad [5a]$$

$$1/2\ Na_2O(l,a=1) + 1/2\ Al_2O_3(l,a=1) = NaAlO_2(l,solution) \quad [6a]$$

and their respective free energy equations are

$$\Delta G_{Na_2O(l)} = RT\ ln\ Y_{Na_2O(l)} \quad [4b]$$

$$\Delta G_{Al_2O_3(l)} = RT\ ln\ Y_{Al_2O_3(l)} \quad [5b]$$

$$\Delta G_{NaAlO_2(l)} = \Delta G^\circ_{NaAlO_2(l)} + RT\ ln\ Y_{NaAlO_2(l)} \quad [6b]$$

where Y_i is the species mole fraction in the solution. Since the associate model assumes ideal mixing of all solution species (activity coefficients = 1), the activity of each species is identical to its mole fraction. The sum of the three Y_i's in equations [4b-6b] is equal unity since only these three species comprise the liquid solution phase.

The standard free energy for reaction [4a], $\Delta G^\circ_{Na_2O(l)}$, is zero since it is equal to the energy change for the standard state reaction which, by definition, has unit activities for all of its reactants and products

$$Na_2O(l,a=1) = Na_2O(l, a=1) \quad [4c]$$

The same is true for liquid species Al_2O_3, but *not* for liquid species $NaAlO_2$. The standard state reaction for the latter species is

$$1/2\ Na_2O(l,a=1) + 1/2\ Al_2O_3(l,a=1) = NaAlO_2(l,a=1) \quad [6c]$$

and its standard reaction energy can be related, in the associate solution model, to the nonideal mixing portion of a liquid solution in which only end-member Na_2O and Al_2O_3 components are mixed to form the solution. Each species mole fraction in the liquid solution can be determined from (a) the bulk liquid composition, (b) the fact that the sum of the liquid species mole fractions must equal unity, (c) the assumption of ideal solution behavior, and (d) the equilibrium constant given by reaction [1c] above.

THERMODYNAMIC CALCULATIONS AND DATA

The thermodynamic computer program ChemSage™(14), thermodynamic data from the SGTE database, 1996 update (15), estimated thermodynamic data, and phase diagrams from Phase Diagrams for Ceramists (16) and other sources (17-19) were used in our assessments and calculations. Unavailable data which had to be estimated included

fusion enthalpies and entropies, enthalpies of formation at 298K, absolute entropies at 298K, and Cp equations for temperatures from 298--3000K. We used trends in chemical reaction values as described by Spear (20) for entropies and heat capacities, and then used the forced fitting of phase diagrams for generating enthalpy of formation values. In all cases values were tested to give reasonable thermodynamic and phase diagram information over wide ranges of temperature and compositions. More details on the estimation techniques will be published later.

Data for Na_2O-Al_2O_3 System

A search of the SGTE database (15) 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 β"-Al_2O_3 [Na_2O - 6•Al_2O_3] and β-Al_2O_3 and [Na_2O -11•Al_2O_3]. We estimated these data, which included fusion enthalpies and entropies, enthalpies of formation at 298K, absolute entropies at 298K, and Cp equations for temperatures from 298--3000K. A liquid phase which produced a good thermodynamic fit of the binary phase diagram (16,17) included only three liquid species: Na_2O, Al_2O_3, and $NaAlO_2$. Additional associate species were tried, but did not improve the thermodynamic description of the liquid phase.

Data for Na_2O-SiO_2 System

Thermodynamic data for crystalline phases in the Na_2O-SiO_2 system were available from the SGTE database (15), but a liquid solution phase had to be developed and all of the system data refined by optimizing it with respect to the binary temperature-composition phase diagram (16,18). Species in the liquid solution included: Na_2O, Si_2O_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_2O, SiO_2, Na_4SiO_4, Na_2SiO_3, $Na_2Si_2O_5$.) Each associate species in the liquid phase was written so that

$$a\ \mathrm{Na} + b\ \mathrm{Si} = 2\ \mathrm{mol/formula}$$

This general rule was followed for each system studied since it gives equal weight to all liquid species in the solution, and the best fittings of the phase diagrams were obtained following this procedure. The fundamental reasons explaining why better phase diagram fits were obtained when the sum of the non-oxygen atoms equaled 2 mol/formula rather than 1 mol/formula is not yet understood.

Data for SiO_2-Al_2O_3 System

The Al_2O_3-SiO_2 system data were taken from the SGTE database (15), but the data for mullite liquid associate was again adjusted to give the best fit of the phase diagram (16,19). The liquid species included Si_2O_4. Al_2O_3, and $Al_{1.5}Si_{0.5}O_{3.25}$ (mullite composition with number of atoms of Al plus Si equal to two in the associate).

RESULTS AND DISCUSSION

Na_2O-Al_2O_3 System

Figure 1(a) gives the calculated temperature-composition phase diagram for this system after optimization of the liquid associate thermodynamic data to reproduce the melting temperatures of its stoichiometric crystalline phases. Figure 1(b) shows the calculated activities of the liquid species (Na_2O, Al_2O_3, $NaAlO_2$) as a function of composition for a constant temperature of 1200°C. These activities are calculated relative to the respective pure liquid species at 1200°C. Since our 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. The formation of crystalline phases was suppressed so that these activities represent those in a supercooled liquid phase (glass). The associate $NaAlO_2(l)$ dominates the liquid phase at Al_2O_3 mole fractions from about 0.25 to 0.75, and is almost unity at its stoichiometric composition. This shows that the liquid solution energy in this composition range is dominated by the formation energy of the associate species, with very little energy from the ideal mixing term. The strong association energy of $NaAlO_2(l)$ causes the $Na_2O(l)$ activity to be lowered from about 10^{-1} to 10^{-6} as the composition of the liquid changes from the Na_2O-rich side to the Al_2O_3-rich side of the $NaAlO_2$ liquid composition. A similar, but opposite effect occurs with the $Al_2O_3(l)$ activity as this composition region is traversed.

Na_2O-SiO_2 System

Figure 2(a) gives the calculated temperature-composition phase diagram for this system after optimization of the liquid associate thermodynamic data to reproduce the melting temperatures of its stoichiometric crystalline phases. Figure 3(b) shows the calculated activities of the liquid species (Na_2O, Si_2O_4, $Na_{8/5}Si_{2/5}O_{8/5}$, $Na_{4/3}Si_{2/3}O_2$, $NaSiO_{5/2}$) as a function of composition for a constant temperature of 1200°C. As above, these activities are calculated relative to the respective pure liquid species at 1200°C, and the formation of crystalline phases was suppressed so that these activities represent those in a supercooled liquid phase (glass). The liquid associates dominate the liquid phase at SiO_2 mole fractions of about 0.2 to 0.8, with two of the associates attaining almost unit activities (mole fractions of unity) 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 completely dominate the liquid solution energy at its composition. As is seen from Figure 2(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 attain very low values.

SiO_2-Al_2O_3 System

Figure 3(a) gives the calculated temperature-composition phase diagram for this system after optimization of the liquid associate thermodynamic data to reproduce the melting temperatures of its stoichiometric crystalline phases. Figure 3(b) shows the calculated activities of the liquid species (Si_2O_4, Al_2O_3, $Al_{1.5}Si_{0.5}O_{3.25}$) as a function of composition for a constant temperature of 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). As above, the activities are calculated relative to the respective pure liquid species at 1200°C, and the formation of crystalline mullite was suppressed so that these activities represent those in a supercooled liquid phase (glass). 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. In order to calculate an accurate melting temperature for mullite while optimizing the liquid solution data, the stability of the associate $Al_{1.5}Si_{0.5}O_{3.25}(l)$ had to be decreased because of the ideal mixing contributions to the liquid solution energy.

Sensitivity of Phase Diagrams to Relative Thermodynamic Stabilities of Phases

Calculating the phase equilibria of a system from the thermodynamic properties of the phases in the system is a critical test (a) of the relative consistency of a set of free energies of formation for all crystalline and liquid phases in a system, and (b) for the models used to represent the solution phase energies.

As a test of the relative sensitivity of phase diagram data to the thermodynamic data for the phases in a system, the enthalpy of formation of $Na_2SiO_3(s)$ was varied, and the phase diagram of the Na_2O-SiO_2 system recalculated and compared with the phase diagram shown in Figure 2(a). First, the compound was made less stable by 3.5 kJ/mol, and then it was made more stable by 3.5 kJ/mol. The changes in the calculated diagram were significant. Lowering the stability of $Na_2SiO_3(s)$ caused its melting temperature to decrease by about 80 degrees, and increasing its stability caused its melting temperature to increase by close to the same amount. Increasing the $Na_2SiO_3(s)$ stability also resulted in the disappearance of $Na_2Si_2O_5(s)$ as a stable phase in the system. Comparisons of the respective activity plots from these calculations showed negligible changes among the species activities. Therefore, little uncertainty in calculated species activities is expected from the current modeling studies, even if the phase diagram data are approximate.

The above sensitivity calculations show that optimizing the relative thermodynamic data of all phases in a system by forcing consistency with even an approximate phase diagram should result in very precise data. The accuracy of the data will depend on the accuracy of the best known values for an intermediate phase in a given system. If the thermodynamic data for one phase are known quite well, then those values should not be allowed to change during the optimization process, and all other values should be adjusted to be consistent with these "best thermodynamic values" and the best phase diagram information for the system.

Even in complex systems with many components, such as a high level nuclear waste glass, interactions of components in the liquid phase can occur primarily between two, or at most three chemically different nearest neighbor oxide components. Thus, critical assessments of thermodynamic and phase equilibria data for the binary and ternary systems are of most concern. These assessments will produce reliable thermodynamic

data for the binary and ternary liquid associate species which represent the important interaction terms in even the most complex nuclear waste glass.

SUMMARY

The above discussed results support the use of an associate solution model for developing a glass database capable of generating accurate values for the thermodynamic activities of glass components in high level nuclear waste glass. This easy to understand and use thermochemical model for describing the limiting stability of glass systems as a function of temperature and composition will hopefully be applied in developing a better understanding of the processing, and then ultimately the limiting behavior of high level nuclear waste glass during its long term storage. A major concern of the possible leaching of active components from the waste glass can be more accurately addressed by using the component activities calculated with this model.

Our 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 such as those used in the storage of high level nuclear wastes.

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Figure 1 (a) Calculated phase diagram for Na_2O-Al_2O_3 system using ChemSage™ (14), optimizing the thermodynamic data for the liquid phase to reproduce the melting temperatures (16,17) of the stoichiometric compound phases.

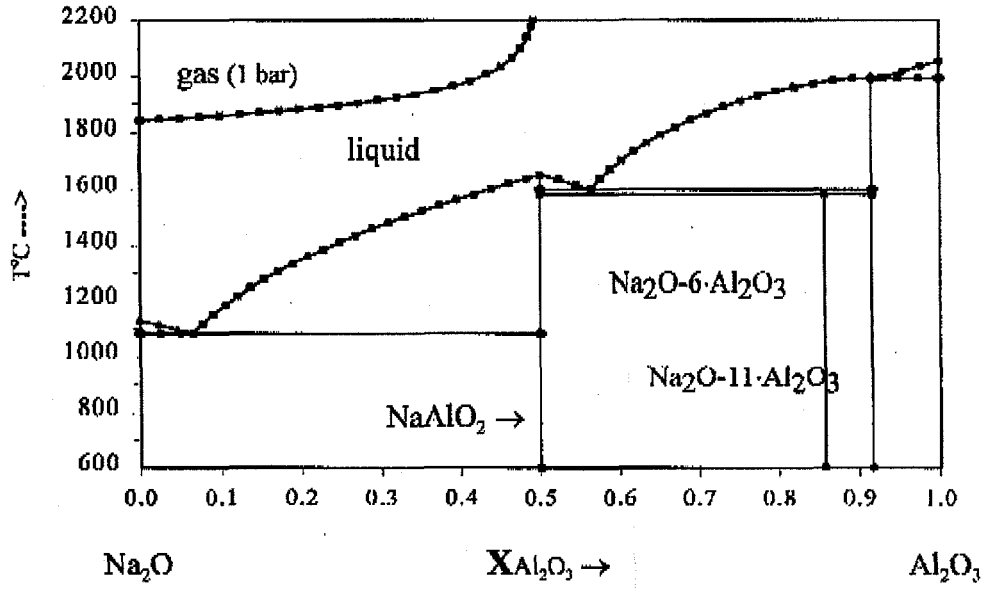


Figure 1 (b) Calculated activities of Na_2O, Al_2O_3, and $NaAlO_2$ liquid species at 1200°C for Na_2O-Al_2O_3 system using ChemSage™ (14) using the thermodynamic data which produced the phase diagram in Figure 1(a). The formation of equilibrium crystalline phases was suppressed.

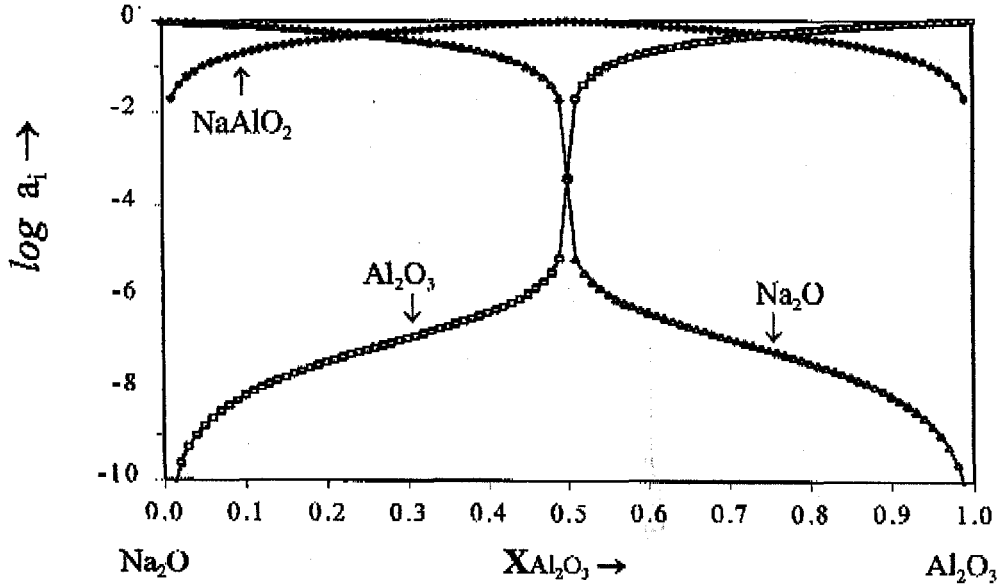


Figure 2 (a) Calculated phase diagram for Na_2O-SiO_2 system using ChemSage™ (14), optimizing the thermodynamic data for the liquid phase to reproduce the melting temperatures (16,18) of the stoichiometric compound phases.

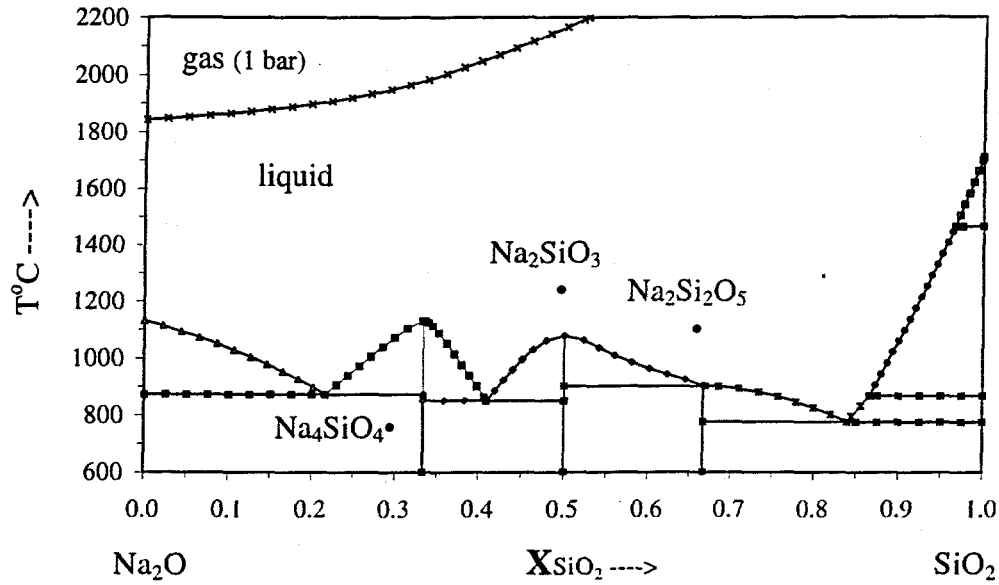


Figure 2 (b) Calculated activities of Na_2O, Si_2O_4, $Na_{8/5}Si_{2/5}O_{8/5}$, $Na_{4/3}Si_{2/3}O_2$, and $NaSiO_{5/2}$ liquid species at 1200°C for Na_2O-SiO_2 system using ChemSage™ (14) using the thermodynamic data which produced the phase diagram in Figure 2 (a). The formation of equilibrium crystalline phases was suppressed.

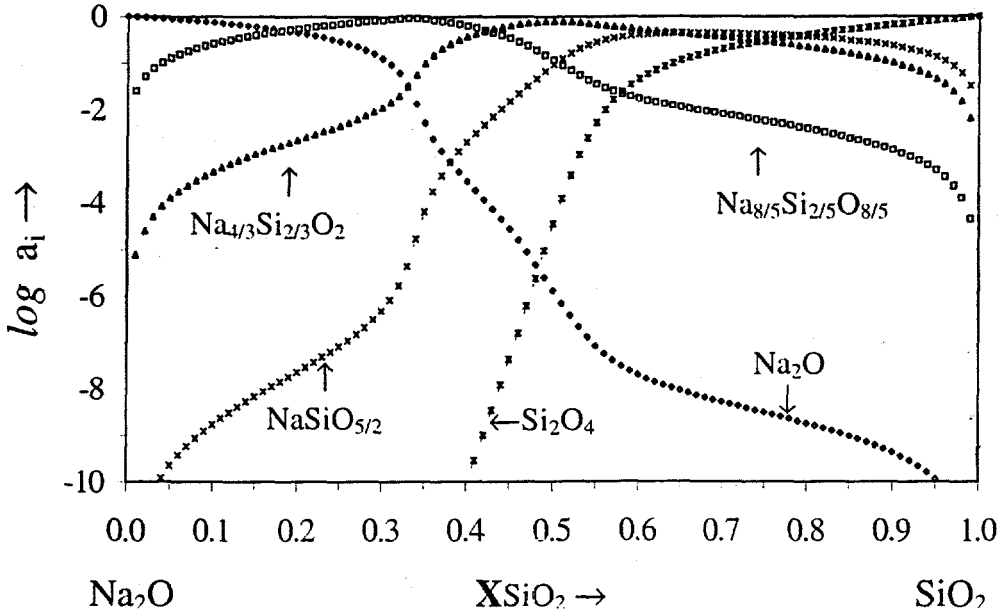
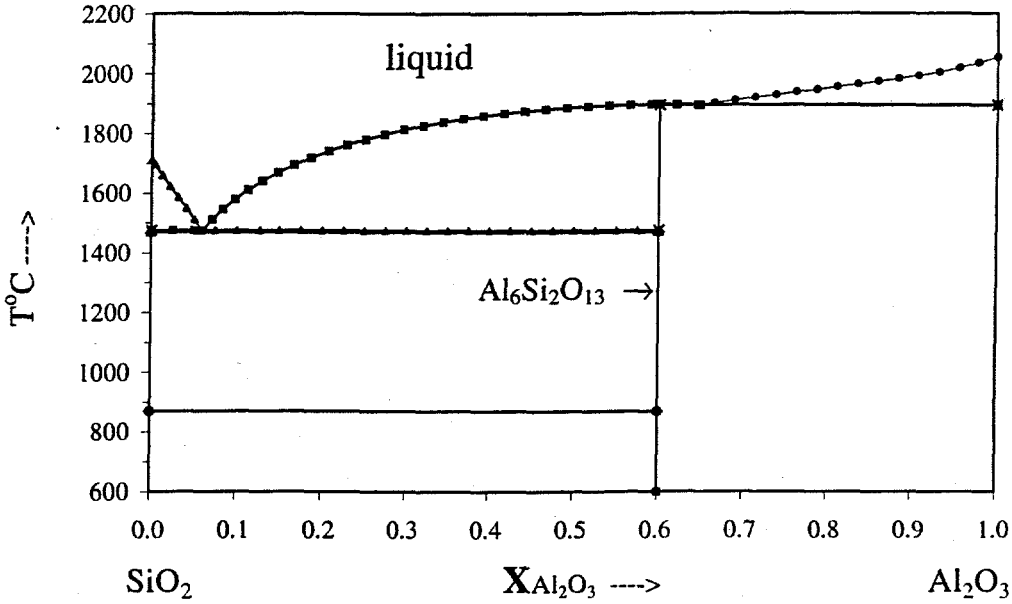


Figure 3 (a) Calculated phase diagram for SiO_2-Al_2O_3 system using ChemSage™ (14), optimizing the thermodynamic data for the liquid phase to reproduce the melting temperatures (16,19) of the stoichiometric mullite



phase.

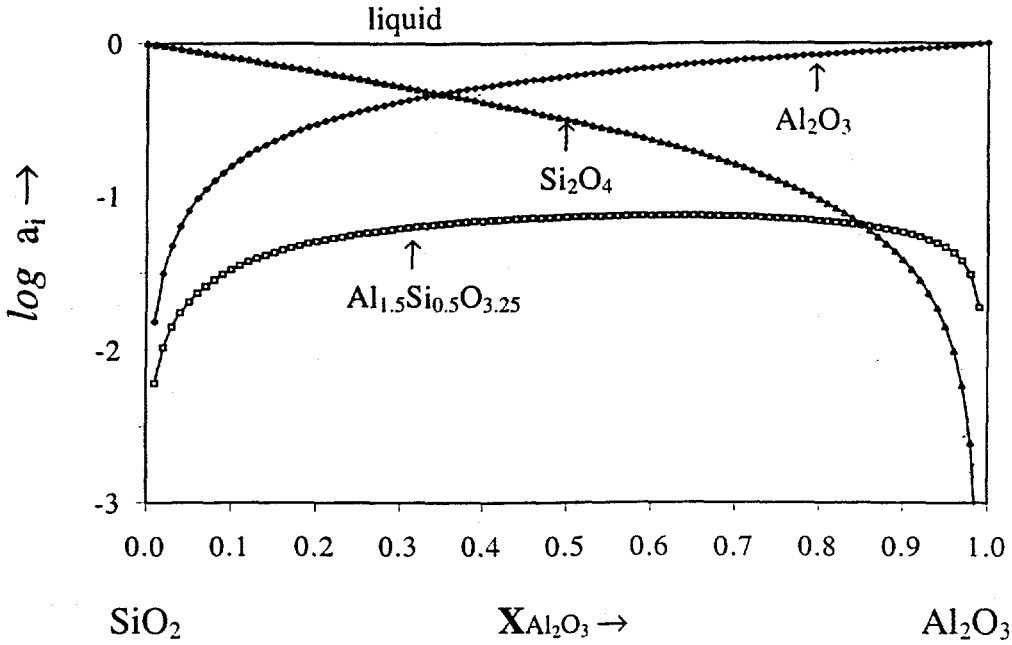



Figure 3 (b) Calculated activities of Si_2O_4, Al_2O_3, and $Al_{1.5}Si_{0.5}O_{3.25}$ liquid species at 1200°C for SiO_2-Al_2O_3 system using ChemSage™ (14) and the thermod gas (1 bar) hich produced the phase diagram in Figure 3 (a). The formation of equilibrium crystalline phases was suppressed.