

Thermochemical Modeling of Oxide Glasses

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A modified associate species approach is used to model the liquid phase in oxide systems. The relatively simple technique treats oxide liquids as solutions of end-member and associate species. The model is extended to representing glasses by treating them as undercooled liquids. Equilibrium calculations using the model allow the determination of species activities, phase separation, precipitation of crystalline phases, and volatilization. In support of nuclear waste glass development, a model of the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system has been developed that accurately reproduces its phase equilibria. The technique has been applied to the $\text{CaO}-\text{SiO}_2$ system, which is used to demonstrate how two immiscible liquids can be treated.

I. Introduction

OXIDE glass materials have been in use for millennia; however, glass remains a highly enigmatic material. For example, the chemical thermodynamics of oxide melts, slags, and glasses have been difficult to model because of strong interactions between constituents, particularly with SiO_2 . Thus, unlike many metal alloys, simple solution models do not accurately reproduce the thermodynamic and phase relations in most oxide liquid systems. Although lacking long-range order, oxide-glass materials have very specific short-range/cluster periodicity that is a function of composition. Even oxide liquids exhibit short-range order, and specific coordinations have been observed experimentally and computed using molecular dynamics.¹

The past two decades have seen the emergence of two successful approaches for modeling chemical thermodynamic behavior and, thus, the phase relations of complex oxide systems. These approaches are the techniques of Pelton and Blander and their co-workers^{2,3} and those of Spear and his collaborators.⁴ Pelton and Blander pioneered the modified quasi-chemical model to describe the short-range order in these liquids. This model involves determining the interactions, or bonding, between second-nearest-neighbor metals. The energy change in establishing those bonds or interactions is represented by a mathematical expansion in composition having temperature-independent and temperature-dependent terms. For multicomponent systems, these compositions typically must be determined by fitting the phase equilibria and other properties for each constituent binary system as well as some

ternary and quaternary systems. The result has been a multiplication of terms that makes the systems quite complex, but the technique has done an admirable job of representing the phase equilibria and chemical thermodynamics (activities) of the systems. Pelton and Blander have successfully modeled 18 constituent oxide systems within significant compositional ranges. For the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system, the difference between computed and experimental invariant point temperatures range from 0° to 52°C, with the large differences trending toward higher Na_2O compositions.⁵

The second approach has been termed the modified associate species model. The original associate species model was first expanded for complex oxide solutions by Hastie, Bonnell, and co-workers^{6–9} in the 1980s in an attempt to thermodynamically describe slag systems. The basis for this approach is that the complex oxide solutions can be represented by an ideal solution of end-member species and intermediate associate species. A review of much of their research incorporating this model is given in Bonnell and Hastie.⁹ Pantano, Spear, and co-workers used the model for predicting and explaining interface reactions in fiber-reinforced glass-matrix composite systems^{10,11} and the behavior of tin and iron in float-glass systems.^{12,13}

The associate species approach is attractive because it (i) accurately represents the thermodynamic behavior of very complex chemical systems over wide temperature and composition ranges, (ii) accurately predicts the activities of components in metastable equilibrium glass phases, (iii) allows logical estimation of unknown thermodynamic values with an accuracy much greater than that required for predicting useful engineering limits on thermodynamic activities in solutions, and (iv) is relatively easy for nonspecialists in thermochemistry to understand and use. Ideally mixing associate species accurately represents the solution energies in which end-member components exhibit attractive forces. The modification to the associate species model, hence the term “modified” associate species model, is the incorporation of positive solution model constants to represent any positive interaction energies in a solution. With these constants, it is possible to accurately represent reported immiscibility in solution phases (e.g., liquid–liquid immiscibility common in many SiO_2 -containing systems). The result is simple, well-behaved equations for free energies that can be confidently extrapolated and interpolated to unstudied temperature and composition ranges.

High-level nuclear and transuranic wastes are currently foreseen as being incorporated in a host glass for permanent disposal. Many glasses have been explored, with borosilicate glass as the typical base composition. Glass compositions are under development—at Pacific Northwest National Laboratory, Savannah River Laboratory, and other sites—that allow dissolution of the waste species in a glass matrix. Issues of glass stability are important in that the glass must remain mechanically intact and retain a low leach rate on exposure to moisture. A somewhat opposing goal is to maximize waste loading of the glass, with a significant economic gain associated with incremental increases in waste content. In support of the nuclear waste glass development effort a model of

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the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system has been developed using the modified associate species approach.

II. Modified Associate Species Model

The associate species solution model uses intermediate “chemical species” with their corresponding thermodynamic data to represent the negative nonideal mixing of the end-member components in a system, i.e., the heat of mixing or attractive forces/ordering between constituents. For example, liquid $\text{NaAlO}_2(l)$ and $\text{Na}_2\text{Al}_4\text{O}_7(l)$ species ideally mix with end-member $\text{Na}_2\text{O}(l)$ and $\text{Al}_2\text{O}_3(l)$ to represent the liquid phase in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ binary system. Although $\text{NaAlO}_2(l)$ and $\text{Na}_2\text{Al}_4\text{O}_7(l)$ may not exist as chemical entities that can be isolated and characterized, these species in the model can accurately represent the negative interaction energies that occur between Na_2O and Al_2O_3 in an oxide liquid solution. Such fictive species, when they are required, are selected for inclusion in the model when it is apparent that the phase equilibria cannot be represented only with species of the same stoichiometry as condensed phases. The compositions of the fictive species are typically dictated by the compositional region of the phase diagram where there is a need for a better “fit.”

The ideal mixing contribution to the partial free energy is $RT \ln Y_i$, where Y_i is the mole fraction of the liquid species i in the solution. The value of Y_i can vary, depending on the assumed stoichiometry of the species, even if the metal:nonmetal ratio remains constant; e.g., it is half as large for the same Na_2O content if the formula is written Na_4O_2 instead of Na_2O . In the approach of this work, it is therefore specified that all liquid associate species have formulas that contain two non-oxygen atoms per mole to allow equal weighting of each species with regard to its ideal mixing entropic contribution. Thus, the $\text{Na}_2\text{Al}_4\text{O}_7(l)$ species noted above is actually $\text{Na}_{2/3}\text{Al}_{4/3}\text{O}_{7/3}(l)$ or $\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)$ in the terminology used in the current work.

This procedure has been adopted during the optimization process when phase-diagram information has been mathematically compared with thermodynamic data to obtain internally consistent sets of data for a given chemical system. It has been determined that, for all systems (aluminates, borates, silicates, aluminosilicates, etc.), the thermochemical data can be more easily optimized when liquid associate species contain two non-oxygen atoms per species rather than one atom. As noted, this approach influences the ideal mixing energy of the solution phase, but the implications of its use are not yet fully understood. However, for very stable liquid associate species, no ideal mixing energy (ideal mixing entropy) exists at the composition of that associate, because a single associate species makes up the entire liquid solution at that composition. This aspect of the modified associate species model produces mixing behavior identical to that of the quasi-chemical model of Pelton and Blander^{2,3} at the composition of the one intermediate liquid species used in the latter model, because their model treats the system as consisting of a single species with variable composition.

Complex, multicomponent system models are built up in a manner similar to that used by Pelton and Blander.^{2,3} Binary and ternary constituent systems are modeled so that they accurately represent the experimentally determined phase equilibria. The various associates of these binary and ternary systems then can be included in a single ideal solution for many constituent oxides, allowing equilibria to be easily computed and chemical activities derived. Where liquid immiscibilities exist in the binary and ternary systems, such that some interaction terms are necessary to accommodate repulsive energetic relationships, these too can be represented in commonly used data files. Unlike the modified quasi-chemical model, these interaction terms have not required more than two terms of an expansion, which include temperature dependencies. Fitting the phase diagram can be accomplished manually (i.e., trial and error), obviating the need for sophisticated optimization routines.

(1) $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ System

A fundamental oxide system that is useful for illustrating the associate species approach is $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$. In using the associate species model to represent the thermodynamic properties of the liquid phase in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ binary oxide system, it is necessary to create an ideal liquid solution phase from end-member liquid components $\text{Na}_2\text{O}(l)$ and $\text{Al}_2\text{O}_3(l)$, and intermediates (associate species) $\text{NaAlO}_2(l)$ and $\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)$. Although the utility of including the $\text{NaAlO}_2(l)$ associate species is apparent from its existence in the system as a crystalline phase, the additional use of $\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)$, which has no crystalline counterpart, is necessary to accurately reproduce the phase relations in the compositional region near $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3 = 1:2$. The initial thermochemical values for the $\text{NaAlO}_2(l)$ species that are used when starting the phase diagram/thermodynamic data optimization are derived from the crystalline phase, whereas the $\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)$ species initial values are estimated using techniques described by Spear *et al.*⁴

This initial free energy of formation of the associate species, $\text{NaAlO}_2(l)$, is readily determined from considerations of the congruent melting reaction



where ΔG is the total free energy change for the reaction and T_{fusion} , the melting temperature. The 298 K heat of formation, $\Delta H_{f,298}$, for $\text{NaAlO}_2(l)$ is the 298 K heat of formation for $\text{NaAlO}_2(s)$ plus the heat of fusion, and the 298 K entropy of the solid is similarly adjusted to give the liquid species entropy by adding the entropy of fusion. The result is, that, at T_{fusion} ,

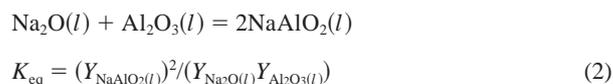
$$\begin{aligned} \Delta G_f(\text{NaAlO}_2(s)) &= \Delta G_f^\circ(\text{NaAlO}_2(s)) \\ &= Y_{\text{Na}_2\text{O}} \Delta G_f(\text{Na}_2\text{O}(l)) \\ &\quad + Y_{\text{NaAlO}_2} \Delta G_f(\text{NaAlO}_2(l)) \\ &\quad + Y_{\text{Na}_2\text{Al}_4\text{O}_7:1/3} \Delta G_f(\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)) \\ &\quad + Y_{\text{Al}_2\text{O}_3} \Delta G_f(\text{Al}_2\text{O}_3(l)) \end{aligned} \quad (1b)$$

where ΔG_f is the free energy of formation and ΔG_f° is the standard free energy of formation. The free energy and standard free energy of formation of the solid are identical, because the pure stoichiometric solid phase is defined as having unit activity, $a = 1$. The same may not be true for the liquid phase in equilibrium with this solid, because the liquid solution is composed of $\text{Na}_2\text{O}(l)$, $\text{Al}_2\text{O}_3(l)$, $\text{NaAlO}_2(l)$, and $\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)$ liquid species with the constraint that the liquid composition be identical to that of the solid-phase composition at the congruent melting temperature. Because the liquid solution is ideal, the following type of equation holds for each liquid species. $\text{NaAlO}_2(l)$ is used as an example, where Y_{NaAlO_2} is the mole fraction (activity) of this species in the liquid solution.

$$\Delta G_f(\text{NaAlO}_2(l)) = \Delta G_f^\circ(\text{NaAlO}_2(l)) + RT \ln Y_{\text{NaAlO}_2} \quad (1c)$$

Minimization of the total free energy determines the equilibrium state and the relative mole fractions of the species. Because the liquid phase is treated as an ideal solution, the activities of the liquid associate species are by definition equivalent to their mole fractions, $a_i = Y_i$, and these activities can be used to predict properties such as leaching behavior, corrosion reactions, and other important phenomena.

Chemical reactions and associated equilibrium constants can be used in determining the relative amounts of each species,



much as one would consider a homogeneous, equilibrium mixture of gaseous molecules. The activity values (mole fraction values) of these species at any given system composition can be inserted into Eq. (2) to calculate the value of K_{eq} at this temperature. Each system

composition results in the same value of K_{eq} at a given temperature for this reaction, because, for a given chemical reaction, K_{eq} is dependent only on temperature and not composition.

As noted above, equilibrium calculations that treat the end-member liquid species plus the associate species as an ideal solution allow complete description of the system. Therefore, it is possible to compute the phase relations and determine a phase diagram. ChemSageTM¹⁴ is the primary tool for developing an assessed, internally consistent thermodynamic database, and for subsequent calculations of the equilibrium chemical behavior of the systems and drawing phase diagrams. The needed thermodynamic data are obtained from the literature and sources such as the assessed SGTE substance database¹⁵ associated with ChemSage and from estimates, and then simultaneously comparing and optimizing sets of phase equilibria and thermodynamic data. A primary source of phase-diagram information is the set of volumes *Phase Diagrams for Ceramists*,¹⁶ plus literature that includes reports of previously optimized thermochemical data.

Typically, the thermodynamic values for the associate species are not sufficiently refined as to allow accurate reproduction of the phase diagram. Melting and other transition temperatures are very sensitive to thermodynamic values, and, therefore, small differences can result in significantly skewed phase equilibria. Thus, the initial thermodynamic properties of the associate species, derived as described by Spear *et al.*,⁴ are modified to calculate phase relations that match those of the experimentally determined phase diagram. This generally involves adjusting the heat of formation to be several to tens of kilojoules per mole more positive or negative.

The chemical thermodynamic data set generated for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ system allows the final computed phase diagram to be drawn by ChemSage,¹⁴ as depicted in Fig. 1(a). The diagram compares exceedingly well with the experimentally reported phase relations.¹⁷

All solution energies can be described by the summation of the ideal and excess free energies (G_{exs}), and, for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ associate species model, the excess free energy over the composition space is plotted in Fig. 1(b) for the liquid at 1200°C. For the associate species model, the excess free energy is represented by the associate species formation energies (multiplied by their concentrations), similar to an ideal gaseous solution with intermediate species between the end members. In the common practice of using a polynomial expression to represent the excess free energy for mixing only the two end members—the simple case being a regular solution—the plot has to be fit with the constants in the polynomial. The ideal mixing entropy value is slightly different in the two cases, because the number and concentrations of mixing species are different.

The ChemSage¹⁴ software also computes the individual activities of the species, and, for the liquid/glass species, these are plotted in Fig. 1(c) for 800°C. The calculations have been performed such that independent crystalline phases in the system have been computed to exist in appropriate phase fields; thus, the nonvarying activities in Fig. 1(c) are the result of two-phase regions where all degrees of freedom are fixed. In contrast, calculations constrained such that no crystalline phases form, as is

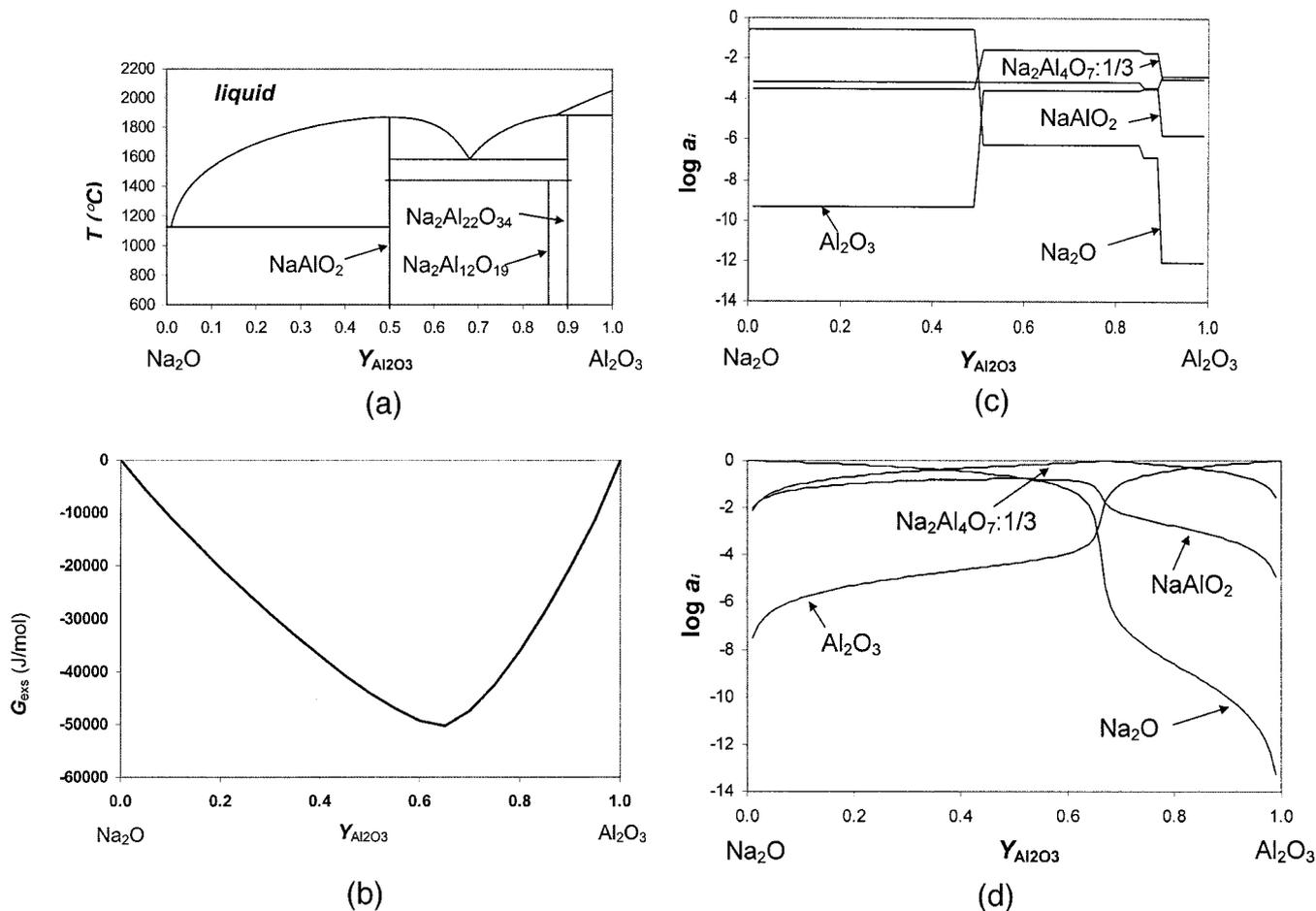


Fig. 1 (a) Computed phase diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ system. (b) Excess free energy (G_{exs}) plotted as a function of composition for the associate species representation of the liquid $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ over the composition space at 1200°C. (c) Computed activities for the species in the associate species model for the glass phase in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ system at 800°C, where all crystalline phases are allowed to form. In the presence of two phases at constant temperature, all lines are horizontal, because all degrees of freedom are fixed. (d) Computed activities for the species in the associate species model for the glass phase in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ system at 800°C, where no crystalline phases are allowed to form. Curves vary continuously because of the presence of only the single glass phase.

the case for an undercooled liquid forming a glass, result in activities that vary smoothly (Fig. 1(d)).

The activities plotted in Fig. 1(d) are illustrative of the relative stability, at least within the associate species model assumption, of the species in the glass. For this system, the end-member species, $\text{Na}_2\text{O}(l)$ and $\text{Al}_2\text{O}_3(l)$, have only high activities near the terminal compositions and, therefore, are not controlling chemical behavior over much of the compositional region. The most important species is the associate $\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)$, which has a high activity over almost the entire compositional range, approaching unity at a $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ ratio of 1:2, the species nominal composition that also coincides with the liquid eutectic composition between NaAlO_2 and $\text{NaAl}_5\text{O}_{14}$. As noted earlier, this indicates that the glass exhibits a high degree of interaction between the component oxides and, thus, is not well represented by an ideal mixture of the end members.

(2) CaO-SiO_2 System

The CaO-SiO_2 system is more complex to model and is a good example of treating liquid-liquid immiscibility using the modified associate species approach. As noted above, such immiscibility requires the solution to be treated as nonideal, having positive interaction energies. The liquid for the CaO-SiO_2 system contains the end-member species $\text{Ca}_2\text{O}_2(l)$ and $\text{Si}_2\text{O}_4(l)$ plus the associate species $\text{Ca}_2\text{SiO}_4:2/3(l)$ (i.e., $\text{Ca}_{4/3}\text{Si}_{2/3}\text{O}_{8/3}$), $\text{Ca}_3\text{SiO}_5:1/2(l)$ (i.e., $\text{Ca}_{3/2}\text{Si}_{1/2}\text{O}_{5/2}$), and $\text{CaSiO}_3(l)$. Again, the unusual stoichiometries are required to maintain 2 non-oxygen gram-atoms per mole of each species.

Figure 2(a) contains the computed phase diagram for the CaO-SiO_2 system, using parameters derived from the modified associate species model. The liquid-liquid immiscibility region requires the inclusion of nonideal interaction terms, determined by trial and error, between $\text{CaSiO}_3(l)$ and $\text{Si}_2\text{O}_4(l)$, such that the excess free energy, G_{exs} , is

$$G_{\text{exs}} = X(1 - X)[(141000 - 65T) + (-10000 - 10T)(1 - 2X)] \quad (3)$$

where X is the mole fraction of $\text{Si}_2\text{O}_4(l)$ and T the absolute temperature (in kelvin). Given the great sensitivities of phase

equilibria to thermodynamic values, the phase diagram is well reproduced using this model.¹⁸

The chemical activities at 800°C of the species in the glass solution in the absence of crystalline phases have been computed and are plotted in Fig. 2(b). At high CaO contents, the species $\text{Ca}_2\text{O}_2(l)$ and $\text{Ca}_3\text{SiO}_5:1/2(l)$ are dominant. In the high- SiO_2 region, the results of the positive interaction energies between CaSiO_3 and Si_2O_4 are apparent in their high activities, which approach unity. There are two glass phases present because of the immiscibility, thus constraining all the degrees of freedom and resulting in all activities being constant over this immiscible region.

(3) $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ System

In developing the thermodynamic data file for the quaternary $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ system, the thermodynamic and phase diagram data for six binary ($\text{Na}_2\text{O-Al}_2\text{O}_3$, $\text{Na}_2\text{O-B}_2\text{O}_3$, $\text{Na}_2\text{O-SiO}_2$, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-SiO}_2$, and $\text{B}_2\text{O}_3\text{-SiO}_2$) and four ternary ($\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$, $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$, and $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$) subsystems have been examined. A significant fraction of the needed thermochemical information has not been measured or reported; therefore, a set of procedures for estimating or calculating the information has been developed.⁴ In all cases, the complete set of thermochemical information for a system is refined and tested to give reasonable thermodynamic and phase diagram information over wide ranges of temperature and composition (Tables I and II). Although many phases contain significant homogeneity ranges, in the current effort only mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}\text{-Al}_6\text{B}_{1.33}\text{O}_{11}$) and nepheline ($\text{NaAlO}_2\text{-NaAlSiO}_4\text{-NaAlSi}_2\text{O}_6$) have been modeled as solid solutions over particular compositional ranges important to the proposed applications of the storage of nuclear waste in glass. Using the associate species approach for these crystalline solid solutions, successful models for the phases have been developed. Nepheline is treated as an ideal solution of NaAlSiO_4 , $\text{NaAlSi}_2\text{O}_6$, and NaAlO_2 . Mullite is assumed to be composed of $\text{Al}_6\text{B}_{1.33}\text{O}_{11}$ and $\text{Al}_6\text{Si}_2\text{O}_{13}$, because these compositions represent compositional bounds for the phase. The phases and species contained in the data file are listed in Table III.

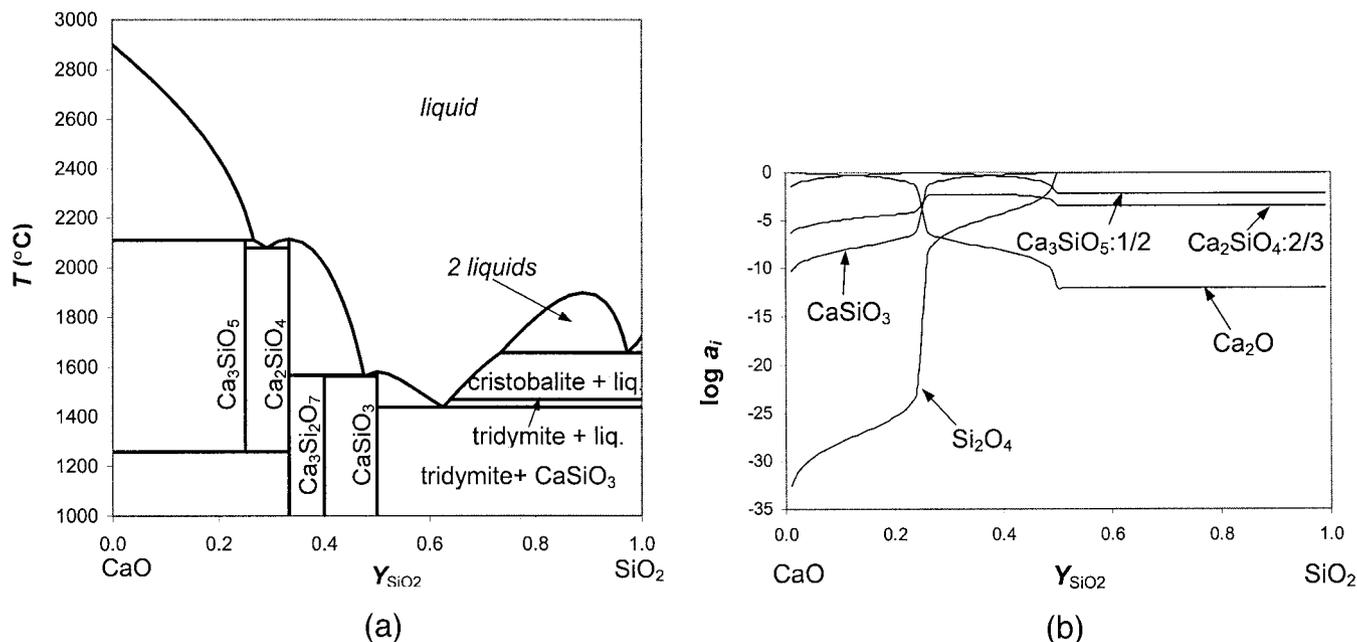


Fig. 2. (a) Computed phase diagram for the CaO-SiO_2 system, including representation of the two immiscible liquids region. (b) Computed activities for the species in the associate species model for the glass phase in the CaO-SiO_2 system at 800°C, where no crystalline phases are allowed to form. Curves vary continuously because of the presence of only the single glass phase at low SiO_2 content, but are invariant at high SiO_2 contents because of the presence of a second glass phase eliminating a degree of freedom.

Table I. Thermodynamic Data for Condensed Solutions in Na₂O–Al₂O₃–B₂O₃–SiO₂

Species	$\Delta H_{f,298}^{\circ}$ (J/mol)	S_{298}° (J/(mol·K))	T (K)	$C_p = a + bT + cT^2 + d/T^2$ (J/(mol·K))			
				a	b ($\times 10^3$)	c ($\times 10^6$)	d ($\times 10^{-5}$)
Nepheline associate solution							
NaAlSiO ₄	–2,147,700	120.000	1000	158.115	42.175	–15.270	–59.685
			1525	171.657	13.245	0	–57.615
			1799	171.657	13.245	0	–57.615
			3000	234.304	0	0	0
				$\Delta H_{trans}^{\circ}(1525 \text{ K}) = 6,100$			
NaAlSi ₂ O ₆	–3,055,000	160.000	1000	229.746	44.056	–15.270	–98.745
			1600	243.286	15.125	0	–96.675
			3000	320.076	0	0	0
NaAlO ₂	–1,111,000	64.500	1000	86.485	40.295	–15.270	–20.625
			1923	100.027	11.365	0	–18.555
			3000	148.532	0	0	0
Mullite associate solution							
Al ₆ Si ₂ O ₁₃	–6,850,000	244.900	2163	495.730	34.900	0	–189.450
			3000	748.936	0	0	0
Al ₆ B _{1.33} O ₁₁	–5,921,100	193.333	900	390.490	79.813	0	–120.703
			2223	438.937	31.140	0	–111.330
			3000	663.859	0	0	0
Liquid associate solution							
Na ₂ O(l)	–370,284	108.989	1023	55.480	70.210	–30.540	–4.140
			1243	82.563	12.350	0	0
			1405	82.563	12.350	0	0
			3500	104.600	0	0	0
				$\Delta H_{trans}^{\circ}(1023 \text{ K}) = 1,757$			
				$\Delta H_{trans}^{\circ}(1243 \text{ K}) = 11,924$			
Al ₂ O ₃ (l)	–1,564,604	98.679	2327	117.490	10.380	0	–37.110
			3000	192.464	0	0	0
B ₂ O ₃ (l)	–1,248,941	87.938	723	57.030	73.010	0	–14.060
			3000	129.700	0	0	0
Si ₂ O ₄ (l)	–1,793,592	101.658	1996	143.260	3.760	0	–78.120
			3000	171.544	0	0	0
Al ₆ Si ₂ O ₁₃ :1/4(l)	–1,600,000	99.430	2163	123.932	8.725	0	–47.362
			3000	187.234	0	0	0
NaAlO ₂ (l)	–1,000,000	107.000	1000	86.485	40.295	–15.270	–20.625
			1923	100.027	11.365	0	–18.555
			3000	148.532	0	0	0
Na ₂ Al ₄ O ₇ :1/3(l)	–1,234,000	95.000	1000	96.820	30.323	–10.180	–26.120
			1923	105.848	11.037	0	–24.740
			3000	163.176	0	0	0
Na ₄ B ₂ O ₅ :1/3(l)	–761,000	102.500	913	55.997	71.143	–20.360	–7.447
			3000	112.967	0	0	0
NaBO ₂ (l)	–938,630	99.500	1000	56.255	71.610	–15.270	–9.100
			1240	106.132	6.175	0	0
			3000	117.150	0	0	0
Na ₂ B ₄ O ₇ :1/3(l)	–1,050,000	88.600	1015	56.513	72.078	–10.180	–10.753
			3000	121.333	0	0	0
Na ₂ B ₈ O ₁₃ :1/5(l)	–1,143,900	85.000	1089	56.720	72.450	–6.108	–12.076
			3000	124.680	0	0	0
Na ₄ SiO ₄ :2/5(l)	–785,540	117.004	1000	73.036	56.920	–24.436	–18.936
			1393	94.702	10.632	0	–15.624
			3000	112.332	0.752	0	–15.624
Na ₂ SiO ₃ :2/3(l)	–980,800	116.366	1000	84.740	48.060	–20.360	–28.800
			1363	102.795	9.487	0	–26.040
			3000	117.487	1.253	0	–26.040
Na ₂ Si ₂ O ₅ :1/2(l)	–1,199,000	113.875	1147	99.370	36.985	–15.270	–41.130
			3000	123.930	1.880	0	–39.060
			1000	105.410	28.117	–10.180	–39.790
NaAlSiO ₄ :2/3(l)	–1,373,150	110.000	1525	114.438	8.830	0	–38.410
			1799	114.438	8.830	0	–38.410
			3000	156.203	0	0	0
			1000	114.873	22.028	–7.635	–49.372
NaAlSi ₂ O ₆ :1/2(l)	–1,500,000	105.000	1600	121.643	7.562	0	–48.337
			3000	160.038	0	0	0
			1000	114.873	22.028	–7.635	–49.372

Interaction Parameters for Liquid Species[†]

$$G_{\text{exs}} = X(1 - X)[A_0 + A_1T] + B_0(1 - 2X) \text{ (J)}$$

Species 1	Species 2	A ₀	A ₁	B ₀
Al ₂ O ₃ (l)	Si ₂ O ₄ (l)	30,000	0	0
B ₂ O ₃ (l)	Si ₂ O ₄ (l)	16,000	0	0
Al ₆ Si ₂ O ₁₃ :1/4	Si ₂ O ₄ (l)	30,000	0	0
Na ₂ B ₈ O ₁₃ :1/5	Si ₂ O ₄ (l)	55,000	–28.0	0
Na ₂ Si ₂ O ₅ :1/2	Si ₂ O ₄ (l)	10,000	0	–11,400
NaAlSi ₂ O ₆ :1/2	Si ₂ O ₄ (l)	5,000	0	0
Na ₂ B ₄ O ₇ :1/3	B ₂ O ₃ (l)	16,000	0	0
Na ₂ B ₈ O ₁₃ :1/5	B ₂ O ₃ (l)	14,000	0	0

[†]X is the mole fraction of the species 2 in the solution.

Table II. Thermodynamic Data for Crystalline Species in Na₂O–Al₂O₃–B₂O₃–SiO₂ System

Species [†]	$\Delta H_{f,298}^{\circ}$ (J/mol)	S_{298}° (J/(mol·K))	T (K)	$C_p = a + bT + cT^2 + d/T^2$ (J/(mol·K))			
				a	b ($\times 10^3$)	c ($\times 10^6$)	d ($\times 10^{-5}$)
Crystalline solids							
Na ₂ O	–417,982	75.040	1023	55.480	70.210	–30.540	–4.140
			1243	82.563	12.350	0	0
			1405	82.563	12.350	0	0
Al ₂ O ₃	–1,675,692	50.940	2327	117.490	10.380	0	–37.110
			4000	192.464	0	0	0
			3500	104.600	0	0	0
B ₂ O ₃	–1,273,500	53.970	723	57.030	73.010	0	–14.060
			3000	129.700	0	0	0
SiO ₂ (cris)	–906,377	46.029	1996	71.630	1.880	0	–39.060
			3000	85.772	0	0	0
SiO ₂ (trid)	–907,257	45.524	1996	71.630	1.880	0	–39.060
			3000	85.772	0	0	0
SiO ₂ (quar)	–908,758	44.207	1996	71.630	1.880	0	–39.060
			3000	85.772	0	0	0
NaAlO ₂	–1,111,000	64.500	1000	86.485	40.295	–15.270	–20.625
			1923	100.027	11.365	0	–18.555
			3000	148.532	0	0	0
Na ₂ Al ₁₂ O ₁₉	–10,685,000	369.750	1000	760.420	132.490	–30.540	–226.800
			2000	787.503	74.630	0	–222.660
			3000	1259.384	0	0	0
NaAl ₉ O ₁₄	–7,873,000	262.000	1000	556.445	81.800	–15.270	–169.065
			2273	569.985	52.900	0	–166.995
			3000	918.390	0	0	0
Na ₃ BO ₃	–1,396,100	147.800	948	111.735	141.820	–45.810	–13.240
			3000	221.750	0	0	0
Na ₄ B ₂ O ₅	–2,370,500	220.400	913	167.990	213.430	–61.080	–22.340
			3000	338.900	0	0	0
NaBO ₂	–972,700	72.500	1000	56.255	71.610	–15.270	–9.100
			1240	106.132	6.175	0	0
			3000	117.150	0	0	0
Na ₂ B ₄ O ₇	–3,267,000	190.000	1015	169.540	216.230	–30.540	–32.260
			3000	364.000	0	0	0
NaB ₃ O ₅	–2,292,200	117.000	1039	113.285	144.620	–15.270	–23.160
			3000	246.850	0	0	0
Na ₂ B ₈ O ₁₃	–5,895,000	280.000	1089	283.600	362.250	–30.540	–60.380
			3000	623.400	0	0	0
NaB ₅ O ₈	–3,593,400	165.000	1058	170.315	217.630	–15.270	–37.220
			3000	376.550	0	0	0
NaB ₉ O ₁₄	–6,159,200	272.000	955	284.375	363.650	–15.270	–65.340
			3000	635.950	0	0	0
Na ₄ SiO ₄	–2,095,630	195.811	1000	182.590	142.300	–61.080	–47.340
			1393	236.756	26.580	0	–39.060
			3000	280.830	1.880	0	–39.060
Na ₆ Si ₂ O ₇	–3,676,200	317.000	1000	309.700	214.390	–91.620	–90.540
			1393	390.949	40.810	0	–78.120
			3000	457.060	3.760	0	–78.120
Na ₂ SiO ₃	–1,555,500	119.000	1000	127.110	72.090	–30.540	–43.200
			1363	154.193	14.230	0	–39.060
			3000	176.230	1.880	0	–39.060
Na ₂ Si ₂ O ₅	–2,475,200	165.000	1147	198.740	73.970	–30.540	–82.260
			3000	247.860	3.760	0	–78.120
Na ₆ Si ₈ O ₁₉	–9,241,573	585.000	1147	739.480	225.770	–91.620	–324.900
			3000	886.840	15.040	0	–312.480

[†](cris) is cristobalite, (trid) is tridymite, and (quar) is quartz.

The accuracy of the complex system model is particularly reflected in the ability to reproduce the phase relations of the ternary systems. A computed pseudobinary phase diagram spanning the nepheline to SiO₂ compositional region is shown in Fig. 3 as an example of the capability of the modeling approach. Again, for such a remarkably simple model, the agreement is excellent with only minor discrepancies in some composition limits.¹⁹

III. Application to High-Level Nuclear Waste Glass

An issue in nuclear waste glass processing is the equilibrium melting temperature for the material. It is necessary to process the glass at a sufficiently high temperature to properly melt the constituents so as to produce a homogeneous glass. It is also

desirable to use compositions with lower equilibrium melt temperatures to simplify the process and decrease the likelihood that crystalline phases precipitate during cooling. It is thus important that the liquidus behavior of the base-glass system be well understood so that temperatures at which crystalline phases can precipitate are known. An important issue in the processing of nuclear waste glass is preventing the precipitation of crystalline phases as the glass cools from the melt, because some of these phases can decrease the stability of the glass and increase the leach rate of radionuclides from the waste form.

(1) Modeling Liquidus Temperature

The liquidus temperature is very sensitive to thermodynamic values, and, as such, complex compositions are difficult to

Table III. Phases and Their Associate Species Utilized in the Modified Associate Species Model for the Na₂O–Al₂O₃–B₂O₃–SiO₂ System[†]

Glass	Crystalline solution phases	Crystalline phases	
Na ₂ O	Mullite:	Na ₂ O	Na ₃ B ₈ O ₁₃
Al ₂ O ₃	Al ₆ B _{1.33} O ₁₁	Al ₂ O ₃	NaB ₅ O ₈
B ₂ O ₃	Al ₆ Si ₂ O ₁₃	B ₂ O ₃	NaB ₉ O ₁₄
Si ₂ O ₄	Nepheline:	SiO ₂ (cris)	Na ₄ Si ₄ O ₇
Al ₆ Si ₂ O ₁₃ :1/4(l)	NaAlSiO ₂	SiO ₂ (trid)	Na ₆ Si ₃ O ₇
NaAlO ₂	NaAlSi ₂ O ₆	SiO ₂ (quar)	Na ₂ Si ₂ O ₃
Na ₂ Al ₂ O ₇ :1/3(l)	NaAlO ₂	NaAlO ₂	Na ₂ Si ₂ O ₅
Na ₄ B ₂ O ₅ :1/3(l)		Na ₂ Al ₁₂ O ₁₉	Na ₆ Si ₈ O ₁₉
NaBO ₂		NaAl ₃ O ₁₄	NaAlSiO ₄
Na ₂ B ₄ O ₇ :1/3(l)		Na ₃ BO ₃	NaAlSi ₂ O ₈
Na ₂ B ₈ O ₁₃ :1/5(l)		Na ₄ B ₂ O ₅	
Na ₄ Si ₄ O ₄ :2/5(l)		NaBO ₂	
Na ₂ Si ₂ O ₃ :2/3(l)		Na ₃ B ₄ O ₇	
Na ₂ Si ₂ O ₅ :1/2(l)		NaB ₃ O ₅	
NaAlSiO ₄ :2/3(l)			
NaAlSi ₂ O ₆ :1/2(l)			

[†]Fixed stoichiometric crystalline phases in the quaternary system are also listed.

accurately model. Reasonable estimates of liquidus temperatures as well as trends in liquidus temperature as a function of composition can be obtained using the associate species model. Figure 4 is a plot of the variation in the predicted liquidus with composition determined from the modified associate species model for Na₂O–Al₂O₃–B₂O₃–SiO₂ and the crystalline phases in equilibrium with the liquid. This is an example of the type of useful information the modified associate species model can produce in support of efforts such as nuclear waste glass processing. The liquidus temperature varies irregularly as compositional regions are traversed, but, not unexpectedly, the temperature increases markedly at higher Al₂O₃ and SiO₂ contents.

(2) Nepheline Precipitation

A problem in waste glass production for certain composition regions has been identified at the Pacific Northwest National Laboratory as the precipitation of a nepheline phase during the cooling of nuclear waste glass.²⁰ This phenomenon weakens the network structure by removing the glass formers Al₂O₃ and SiO₂. The result is that nepheline precipitation in nuclear waste glass limits waste species loading. It has been observed that compositions rich in Al₂O₃ and Na₂O are particularly prone to precipitating nepheline. The rapid kinetics of nepheline formation in the cooling glass suggests that an equilibrium thermodynamic model can provide useful insights with regard to the compositional parameters governing its precipitation.¹⁷

It has been observed that the precipitation of nepheline occurs during glass cooling in the absence of other crystalline phases.¹⁷ It

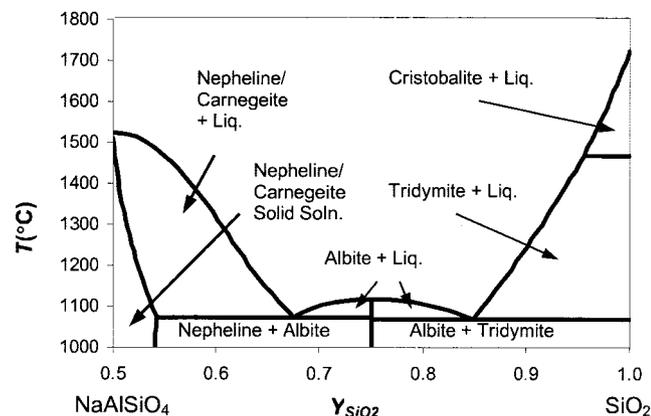


Fig. 3. Computed pseudobinary phase diagram for NaAlSiO₄–SiO₂.

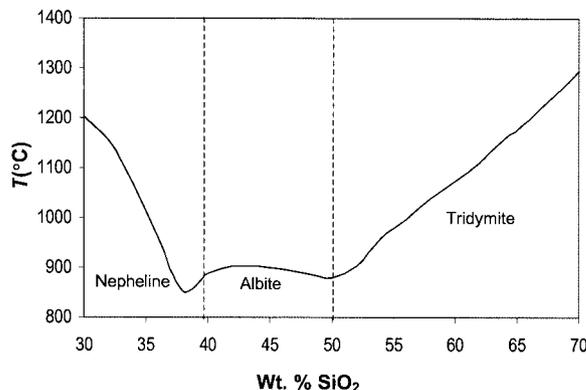


Fig. 4. Computed liquidus curve for Na₂O–Al₂O₃–B₂O₃–SiO₂ containing 30 wt% B₂O₃ over the compositional region range 30–70 wt% SiO₂ and for which the weight percent values for Na₂O and Al₂O₃ are equal (dashed lines delineate regions where the indicated crystalline phases are computed to be present with the liquid at the liquidus temperature).

is thus possible to model this behavior using pseudoequilibrium calculations in which nepheline and the glass/liquid phase are the only phases allowed to form, i.e., with all other crystalline phases eliminated in the calculations. The thermochemical computations, therefore, indicate either the glass alone is present or the glass is present in equilibrium with nepheline.

The composition space for the ternary oxide Na₂O–Al₂O₃–SiO₂ system has been explored at 600°C with no B₂O₃ present and with 30 wt% B₂O₃ present. The 600°C temperature is selected, because it is below any likely liquidus and represents an elevated temperature in a cooling glass “log.” The results are shown in the section of a ternary diagram in Fig. 5, with the binary oxides and the nepheline composition indicated.

Apparent from the calculated results is the wide compositional range over which nepheline is stable. Important for the selection of waste compositions is the observation that the stability region decreases to lower SiO₂ content with increasing B₂O₃ content.

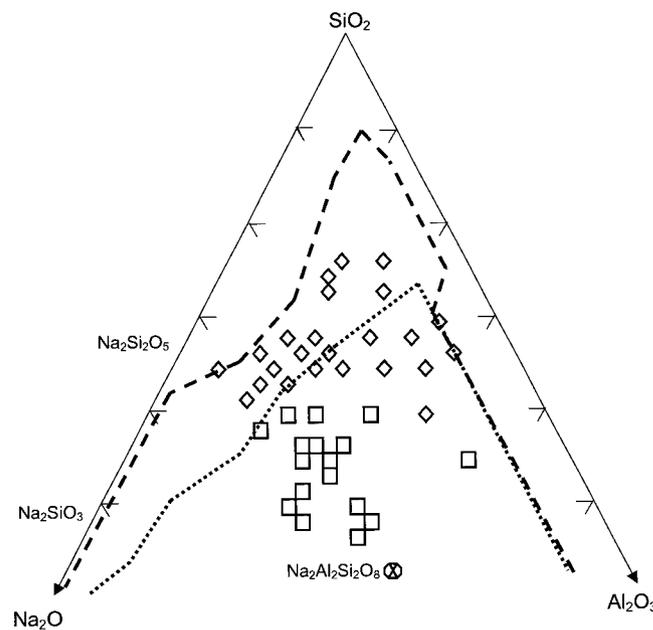


Fig. 5. Section of a Na₂O–Al₂O₃–SiO₂ ternary composition space (in wt%) indicating the region in which nepheline is computed to be stable in the presence of the glass at 600°C (---) without B₂O₃ present and with (···) 30 wt% B₂O₃ present. Experimental values from Li *et al.*¹⁷ indicate relative compositions (◇) where nepheline was not observed and (□) where the phase precipitated.

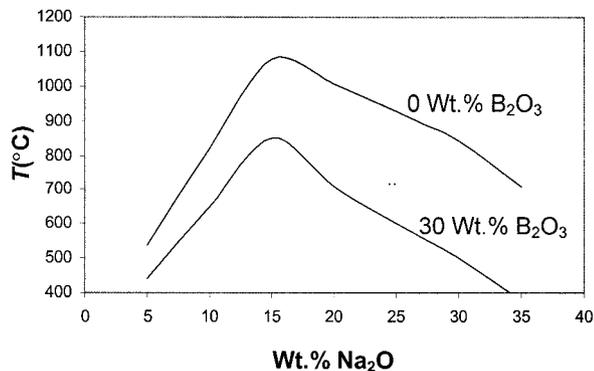


Fig. 6. Maximum computed temperatures (formation temperatures) at which nepheline is observed to form in the presence of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ glass with the other crystalline phases constrained from forming. Compositional ranges include that with no B_2O_3 present and with 30 wt% B_2O_3 present. Remaining composition is 60 wt% SiO_2 , with the remaining 40 wt% consisting of the Na_2O content indicated on the plot and the balance Al_2O_3 .

Experimental results¹⁷ are also shown on the diagram, and they agree reasonably well with the results of the calculations. However, in the experimental work, a variety of B_2O_3 contents have been used that span the 0–30 wt% range, and the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system also contains other components representative of practical waste compositions, such as Li_2O , K_2O , CaO , and Fe_2O_3 . Thus, the comparison between experiment and modeling results is only approximate.

To aid in controlling nepheline precipitation, it is useful to know the thermodynamic predictions of temperature at which this phase can form as the glass cools. Figure 6 is a plot of the calculated formation temperatures in the presence of the glass phase over a compositional range with no B_2O_3 present and with 30 wt% B_2O_3 present. The remaining composition in the calculations consists of 60 wt% SiO_2 ; the remaining 40 wt% is the Na_2O content indicated on the plot and the balance Al_2O_3 . Only glass and nepheline phases are computationally allowed to form. The curves thus indicate the maximum temperature that nepheline can be expected to precipitate from the glass during cooling. The calculations illustrate that the presence of B_2O_3 significantly decreases the formation temperature, as does minimizing Na_2O or Al_2O_3 . The latter also has been observed experimentally.¹⁷ Minimizing the precipitation temperature limits nepheline formation, because kinetics/diffusion are slower at the lower temperatures.

IV. Conclusions

The modeling of oxide glasses and melts is a difficult problem. The strong interactions between constituents prevent simple solution models that typically involve nonideal mixing of end-member components from successfully describing the phase relations and thermochemistry of these systems. The modified associate species model is used as an alternative to the relatively complex quasi-chemical approach. The modified associate species technique uses ideal solutions for much of the descriptions of the oxide solutions, needing to rely only on simple excess free-energy expressions for treating liquid–liquid immiscibility.

A relatively accurate model has been developed for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system that reproduces important melting points and liquidus lines and surfaces. The effort has required the reassessment of thermochemical data for this fundamental system to accurately reproduce the phase relations. The model includes representations of the specific homogeneity ranges in mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}-\text{Al}_6\text{B}_{1.33}\text{O}_{11}$) and nepheline ($\text{NaAlO}_2-\text{NaAlSi}_4\text{O}_{14}$) that are of current interest. Other important binary and ternary oxide systems are currently being modeled with the objective of including them in a global model that has many

components, of which the $\text{CaO}-\text{SiO}_2$ system described in this paper is one. That system well demonstrates the ability of the modified associate species methodology to treat such complexities as liquid–liquid immiscibility.

The modified associate species approach is beginning to be applied to practical problems, such as describing nuclear waste glass. It has provided valuable insights with regard to liquidus temperatures for designing waste glass compositions. The model has been applied to the issue of nepheline precipitation in cooling glass, indicating compositional controls that can minimize or eliminate this problem. Future issues to be addressed include a basic understanding of the phase equilibria and solid solution of waste glasses that incorporate other critical waste constituents, including sulfur, chromium, iron, phosphorus, actinides, and rare earths. Commercial glasses and problems associated with glass melting, production, and use also need to be addressed in future efforts.

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