Role of basicity and tetrahedral speciation in controlling the thermodynamic properties of silicate liquids, part 1: The system CaO-MgO-Al$_2$O$_3$-SiO$_2$

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Abstract—Activity coefficients of oxide components in the system CaO-MgO-Al$_2$O$_3$-SiO$_2$ (CMAS) were calculated with the model of Berman (Berman R. G., "A thermodynamic model for multicomponent melts with application to the system CaO-MgO-Al$_2$O$_3$-SiO$_2$," Ph.D. dissertation, University of British Columbia, 1983) and used to explore large-scale relationships among these variables and between them and the liquid composition. On the basis of Berman's model, the natural logarithm of the activity coefficient of MgO, $\ln(\gamma_{MgO}^{Liq})$, and $\ln(\gamma_{MgO}^{Liq}/\gamma_{SiO_2}^{Liq})$ are nearly linear functions of $\ln(\gamma_{CaO}^{Liq})$. All three of these variables are simple functions of the optical basicity Λ with which they display minima near $\Lambda \sim 0.54$ that are generated by liquids with low ratios of nonbridging to tetrahedral oxygens (NBO/T) (<0.3) and a mole fraction ratio, $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$, in the range 4 to 20. Variations in $\ln(\gamma_{CaO}^{Liq})$ at constant Λ near the minimum are due mostly to liquids with $(X_{CaO}^{Liq} + X_{MgO}^{Liq})/X_{Al_2O_3}^{Liq} < 1$. The correlations with optical basicity imply that the electron donor power is an important factor in determining the thermodynamic properties of aluminosilicate liquids.

For a constant NBO/T, $\ln(\gamma_{CaO}^{Liq}/\gamma_{Al_2O_3}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ form curves in terms of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$. The same liquids that generate minima in the Λ plots are also associated with minima in $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ as a function of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$. In addition, there are maxima or sharp changes in slope for NBO/T > 0.3, which occur for $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ranging from ~ 0 to ~ 6 and increase with increasing NBO/T. The systematic variations in activity coefficients as a function of composition and optical basicity reflect underlying shifts in speciation as the composition of the liquid is changed. On the basis of correlations among the activity coefficients, it is likely that the use of CaO, an exchange component such as SiMg$_{-1}$ and two of MgO, CaAl$_2$O$_4$, or MgAl$_2$O$_4$ would yield significant savings in the number of parameters required to model the excess free energy surface of liquids over large portions of CMAS relative to the use of oxide end members.

Systematic behavior of thermodynamic properties extends to small amounts of other elements dissolved in otherwise CMAS liquids. For example, $\ln(X_{Fe^{2+}}^{Liq}/X_{Fe^{3+}}^{Liq})$ at constant oxygen fugacity is linearly correlated with $\ln(\gamma_{CaO}^{Liq})$. Similarly, $\ln(C_S)$, where C_S is the sulfide capacity is linearly correlated at constant temperature with each of the optical basicity, $\ln(a_{CaO}^{Liq})$ and $\ln(\gamma_{CaO}^{Liq})$, although the correlation for the latter breaks down for low values of Λ. The well-known systematic behavior of sulfide capacity as a function of optical basicity for systems inside as well as outside CMAS suggests that $\ln(\gamma_{CaS}^{Liq})$ is also a simple function of optical basicity and that the relationships observed among the activity coefficients in CMAS may hold for more complex systems. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Knowledge of the thermodynamic properties of silicate liquids is essential for the modeling of igneous processes as well as for optimizing compositions and synthesis conditions for the production of commercial glasses and slags. Variations in the thermodynamic properties are also played out in the structure and rheology and in the magnitude of liquid properties such as diffusivity and electrical conductivity so that the study of one property often leads to insights that are applicable to another. It is possible, for example, to constrain the configurational entropy and enthalpy of a liquid by determining the viscosity or studying the speciation of a melt through nuclear magnetic resonance (NMR) (Richet and Bottinga, 1995; Lee and Stebbins, 1999). Similarly, by measuring the enthalpy of mixing for a series of compositions, some constraints can be placed on corresponding variations in the speciation of the liquid (e.g., Navrotsky, 1995). In principle, a similar potential for cross pollination exists for the activity coefficients of oxide components in the liquid because the activity coefficients reflect underlying variations in the excess free energy, which must in turn incorporate responses to variations in the liquid structure.

Although it is possible to derive the excess free energy from activity coefficients (e.g., Lupis and Elliott, 1967), models for the thermodynamic properties of multicomponent systems are usually developed by postulating a specific functional form for the excess free energy and then fitting coefficients by means of a mixture of calorimetric data and phase equilibria (Berman, 1983; Ghiorso et al., 1983, Berman and Brown, 1984; 1994; Hallstedt et al., 1994). Activity coefficients are then obtained through differentiation of the excess free energy function. This procedure is flexible but prone to systematic errors, and it generally requires that a large number of parameters be fit when modeling multicomponent systems. Also, the calibrations tend to be system specific so that a parameterization that works well for natural magma compositions will generally fail in simple subsystems. If simplifying correlations exist among the activity coefficients or between the activity coefficients and composition that extend from simple to more complex systems, then it

may be possible to construct better models for the thermodynamic properties with a smaller number of arbitrary constants. Because variations in the activity coefficients are likely in part to reflect underlying structural features of the liquids, identifying correlations among them may also help to guide the interpretation of data on the physical properties of silicate melts and glasses and highlight desirable compositions for future work.

In this study, the model of Berman (1983) is used to evaluate the activities of end-member oxides in the system CaO-MgO-Al_2O_3-SiO_2 (CMAS). Magmatic liquids are considered in part 2. CMAS is an important starting point from a theoretical perspective because it is an example of the simplest system to contain two cations that are normally considered network modifiers (Ca, Mg) and two that are generally thought of as network formers (Al, Si). Thus, CMAS can be expected to have many of the complications to be found in natural magmatic liquids but compositional variables that influence the behavior of the system may be more readily isolated. Previous efforts thematically similar to this work (e.g., Ryerson, 1985; Longhi, 1987) have either been applied to binary systems or very restricted, multiply saturated portions of more complex systems. The study of CMAS also has immediate practical benefits because most Ca-, Al-rich inclusions from carbonaceous chondrites and many slags used in the making of steel have bulk compositions that are well represented by CMAS (Wark and Lovering, 1982; Sosinsky and Sommerville, 1986).

In the following discussion, the solution model used for the liquids is first introduced. Possible variations in activity coefficients are then considered that reflect the ability of the medium to donate electrons (i.e., the basicity) or a sensitivity to the Si/Al ratio and overall degree of polymerization as expressed by the number of nonbridging to tetrahedral oxygens (NBO/T). The latter can for CMAS liquids be calculated from the following: (e.g., Mysen et al., 1984; Mills, 1993)

$$NBO/T = \frac{2(X_{CaO}^{Liq} + X_{MgO}^{Liq} - X_{Al_2O_3}^{Liq})}{X_{SiO_2}^{Liq} + 2X_{Al_2O_3}^{Liq}}. \quad (1)$$

Finally, implications of correlations involving activities and activity coefficients for predicting the solubility of volatile species and the ratios of multivalent species (e.g., Fe^{2+}/Fe^{3+}) are assessed for examples in which the concentrations of additional elements in otherwise CMAS melts are low.

2. RESULTS AND DISCUSSION

2.1. Model of Berman (1983)

The activity-composition model of Berman (1983) has been used effectively to explore the role of liquids in the primitive solar nebula (Yoneda and Grossman, 1995; Ebel and Grossman, 2000; Grossman et al., 2000). Because this model is also the basis of the present study, a brief overview is provided before considering results of calculations. A much more thorough exposition is given by Berman and Brown (1984) for the system CaO-Al_2O_3-SiO_2 and by Berman (1983) for CMAS (see also de Capitani and Brown, 1987). The basic idea is to use calorimetric data and exchange reactions between coexisting solids and liquids or pairs of liquids to constrain the excess free energy, G_{excess}, of the liquid. The activity coefficient of a

specific oxide component relative to its standard state can be derived from G_{excess} through suitable differentiation and the resulting expression for the functional form used by Berman (1983) is given by Berman and Brown (1984).

For a solid coexisting with a CMAS liquid, one or more statements of equilibrium can be written in the form

$$\sum_{i=1}^{4} \rho_i [\mu_i^{o, Liq} + RTln (X_i^{Liq} \gamma_i^{Liq})] = \mu_{solid}^o + RTlna_{solid} \quad (2)$$

where ρ_i is the stoichiometric coefficient for oxide i in the formation reaction of the solid phase from the liquid oxides (e.g., for $2MgO_{(Liq)} + SiO_{2(Liq)} = Mg_2SiO_{4(forsterite)}$, $\rho_{MgO} = 2$, $\rho_{SiO_2} = 1$, and $\rho_{CaO} = \rho_{Al_2O_3} = 0$). In Eqn. 2, μ_{solid}^o and $\mu_i^{o, Liq}$ are the standard state chemical potentials of the solid phase and of oxide i in the liquid, a_{solid} is the activity of the solid relative to the end-member phase in its standard state, and γ_i^{Liq} is the activity coefficient of oxide component i in the liquid. In this work, lime, periclase, corundum, and high cristobalite at temperature and 1 atm are used as standard states for oxide components in the melt. Eqn. 2 is used to test for saturation with respect to solid phases in Berman's (1983) database, assuming that $a_{solid} = 1$. This approach was required because Berman (1983) restricted consideration of solids to end members. For most liquids considered in this study (1600°C), there are no solid solutions in CMAS for which serious errors in predicting supersaturation are expected. A few calculations were performed for 1800°C, where Ca solubility in olivine and Al solubility in spinel may lead to overestimating liquid stability for small regions of composition space and the stability of melilite is underestimated for calculations at 1400°C. As noted below, ignoring metastability for all possible liquid compositions can lead to large errors. Given the large volume of stable liquid composition space explored in the calculations and the large scale variations in thermodynamic properties being considered, it is, however, unlikely that incorporating a few liquids that are metastable with respect to some solid solution within a large collection of stable liquids has a significant effect on the results of this study.

An important consideration for the present work is that there is no implicit assumption in Berman's (1983) model regarding how the structure or other properties of the liquid interplay with the thermodynamic properties nor of what the relative values of activity coefficients among the oxides might be for a liquid of arbitrary composition. It is the large database of phase equilibria and calorimetry obtained over the last century that provides a ground truth for the calculated excess free energy surface. Systematic order of magnitude variations of the activities or activity coefficients, either with each other or with a specific compositional variable, thereby reflect underlying variations in the excess free energy surface for the liquids and are not artifacts of the model or optimization procedures. Chamberlin and coworkers (Chamberlin et al., 1992; Chamberlin, 1994) showed experimentally that relative values of activities for the oxides given by the model of Berman (1983) are approximately correct. The model activities of SiO_2 were systematically high by ~25% for the region of composition space explored through their experiments and those for Al_2O_3 were systematically low by ~25%. Because this work is primarily concerned with larger

scale changes in the *relative* values of activity coefficients, systematic errors of the type described by Chamberlin and coworkers are not particularly important.

2.2. Role of Basicity

At its most fundamental level, the thermodynamic properties of aluminosilicate liquids can be thought of as arising from acid–base equilibria (e.g., Duffy and Ingram, 1976; Duffy, 1993; Duffy, 1996a; Hallstedt et al., 1994) in the sense that acids accept electrons and bases donate them. In CMAS, CaO and MgO act as electron donors (i.e., bases), and SiO_2 acts as an acid. Alumina is amphoteric in that it acts like a base in the absence of other bases (i.e., in the Al_2O_3-SiO_2 binary) but will generally act as an acid in the presence of Ca, Mg, or both. Operationally, the acid–base interactions are probably best considered from the perspective of oxygen. When oxygen is in a free state as O^{2-}, its ability to donate negative charge is at a maximum. This ability is modestly impeded when the oxygen is coordinated to a relatively nonpolarizing cation such as Ca and greatly impeded upon coordination with one or more highly polarizing cations such as Si^{4+}. Oxygen in the latter environment is less able to act as a base towards any other nearby cations because the Si^{4+} draws negative charge (i.e., the "basicity" is lowered). The effective basicity of a specific liquid therefore depends on the number and identity of the cations to which the oxygen is coordinated.

In this study, the optical basicity Λ is used as a starting point for correlating the thermodynamic properties of silicate melts in CMAS. The optical basicity is convenient because it is readily calculated given a bulk composition (e.g., Mills, 1993) and is correlated to other measures of basicity such as the sulfide, carbide, carbonate, and phosphate capacities (e.g., Wagner, 1975; Sosinsky and Sommerville, 1986; Tsao and Katayama, 1986; Gaskell, 1989; Young et al., 1992; Singh and Ghosh, 1994) and to redox reactions involving polyvalent cations (e.g., Baucke and Duffy, 1991; Duffy, 1996b; Yang and Belton, 1998). Thermodynamic parameters that correlate with the optical basicity may therefore be thought of as being sensitive to the mean basicity of the melt.

The concept of optical basicity in its current form was developed by Duffy and Ingram (1971, 1973, 1975, 1976) as a way to describe the spectral shift in the ultraviolet region that is observed when a small amount ($\sim 10^{-3}$ M) of a $d^{10}s^2$ probe ion (e.g., Pb^{2+}) is placed into a medium containing polarizing cations. The more electrons are donated by neighboring oxygens to the probe ion (i.e., as the basicity of the medium increases), the greater the observed frequency shift. Duffy and Ingram (1976) defined the optical basicity as

$$\Lambda = \frac{\nu_{\text{free ion}} - \nu_{\text{glass}}}{\nu_{\text{free ion}} - \nu_{\text{CaO}}}$$

where ν_i refers to the frequency of the $^1S_0 \rightarrow {}^3P_1$ transition for the probe ion measured in i, and $\nu_{\text{free ion}}$ represents the hypothetical frequency of the ion in a completely unperturbed environment. The optical basicity is therefore a measure of how good an electron donor the oxygen in a given medium is relative to oxygen in CaO. Largely on the basis of data in Duffy and Ingram (1971), Duffy and Ingram (1973) showed that

optical basicity for a variety of media including oxides, glasses and molten salts with Λ ranging from 0.3 to 1.0, is linearly related to Pauling's electronegativity. For CMAS, this leads to (Mills, 1993)

$$\Lambda = \frac{X_{CaO}^{Liq} + 0.78X_{MgO}^{Liq} + 1.8X_{Al_2O_3}^{Liq} + 0.96X_{SiO_2}^{Liq}}{X_{CaO}^{Liq} + X_{MgO}^{Liq} + 3X_{Al_2O_3}^{Liq} + 2X_{SiO_2}^{Liq}}. \quad (3)$$

Note that the calculation of optical basicity via Eqn. 3 requires only the bulk composition.

2.3. Correlations with Optical Basicity in CMAS

A temperature of 1600°C was selected for most calculations because liquids are stable over much of the system but the temperature is not so high that extrapolation of Berman's model, which is based mostly on phase equilibria acquired at temperatures at or below 1600°C, becomes excessive. It is worth noting, however, that the correlations discussed below exist at both higher and lower temperatures, so the conclusions are not sensitive to the use of a representative temperature. For 1600°C, accepted liquids have mole fractions of oxides in the range of 0 to 0.71 for CaO, 0 to 0.55 for MgO, 0 to 0.45 for Al_2O_3, and 0 to 0.95 for SiO_2. Liquids supersaturated with respect to one or more solid phases (calculated by Eqn. 2) were rejected because the correlations described below are degraded if certain metastable liquid compositions are used, most notably those supersaturated with respect to an oxide end member. Because the results for these same liquids, if obtained at higher temperatures where they are stable, are consistent with those for other stable liquids, it is likely that extrapolation of Berman's (1983) model into the metastable liquid region sometimes leads to inaccurate predictions of the activities.

The natural logarithm of the activity coefficient of CaO in CMAS liquids at 1600°C is plotted against the optical basicity in Figure 1a. Values of $\ln(\gamma_{CaO}^{Liq})$ for stable liquids over the entire system fall within the region outlined by the calculations. The somewhat irregular outline in the linear portion of the plot primarily reflects the stability limits for liquids in CMAS relative to various solid phases. For most liquids, $\ln(\gamma_{CaO}^{Liq})$ increases approximately linearly with Λ, a relationship that suggests that the activity coefficient of CaO is generally a good indicator of basicity. This is not a surprising result. Steelworkers have long known that one way to increase the basicity of a slag was to add lime, and other researchers have noted that the activity of CaO in binary systems is a good measure of the basicity (e.g., Wagner, 1975; Reddy and Blander, 1987; Nilsson et al., 1994). The limitations of using this correlation are, however, apparent both in the existence of a minimum at $\Lambda \sim 0.54$ and in the factor of several variations in γ_{CaO}^{Liq} at constant optical basicity, even in the linear portion of the figure, that expand to more than an order of magnitude near the minimum.

The variations in $\ln(\gamma_{CaO}^{Liq})$ at constant optical basicity near the minimum of Figure 1a primarily reflect varying Si/Al and (Ca + Mg)/Al ratios. Figure 1b shows calculated values of $\ln(\gamma_{CaO}^{Liq})$ at constant Si/Al plotted as a function of optical basicity. There are two features of note. First, compositions near the minimum ($\Lambda = 0.54$) are characterized by relatively high Si/Al ratios (values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ are in the range 4 to 20 for $\Lambda < 0.54$) with $\ln(\gamma_{CaO}^{Liq})$ generally increasing with increas-
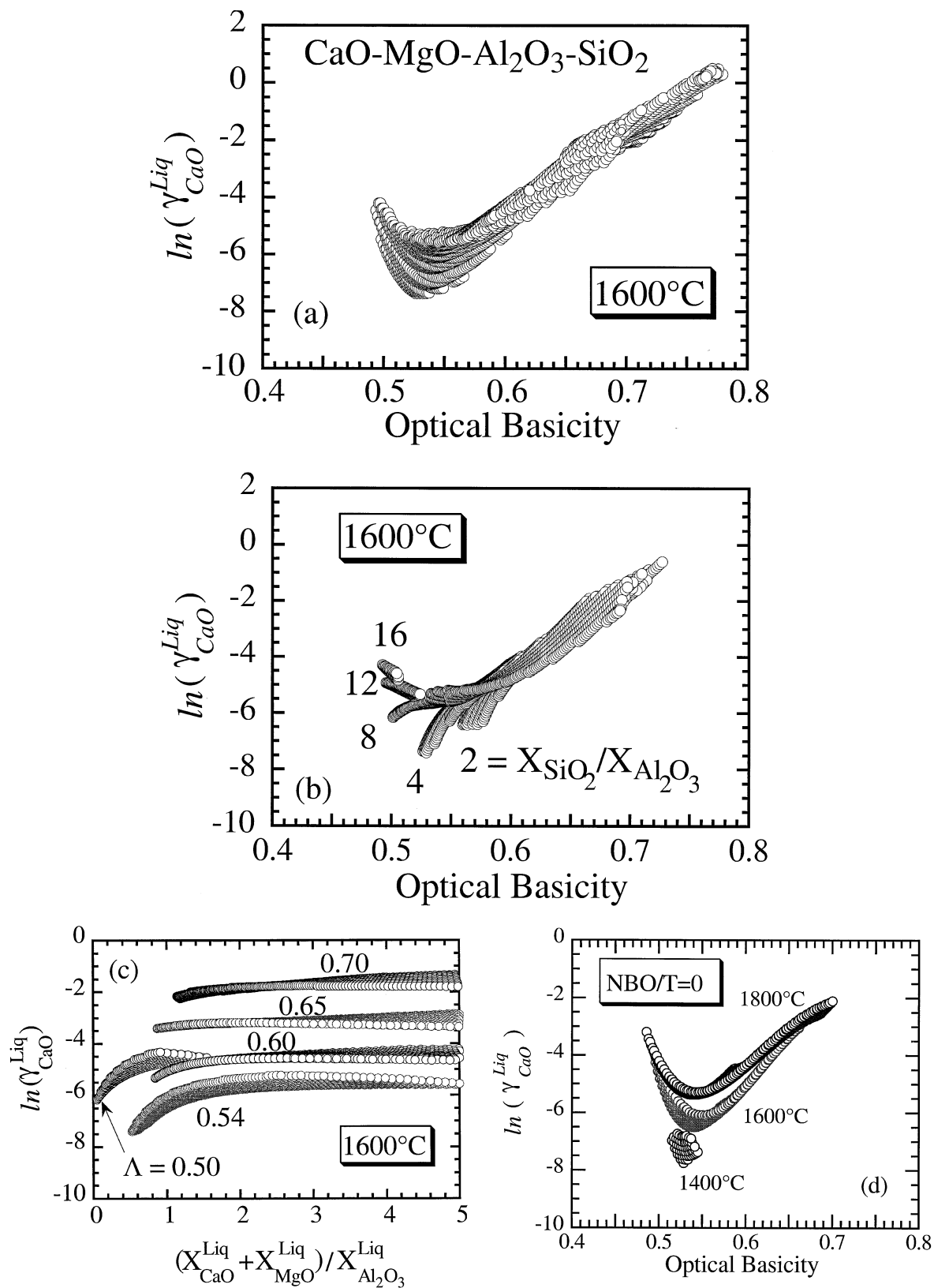
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Fig. 1. Variation of $\ln(\gamma_{CaO}^{Liq})$ with optical basicity in the system CMAS. (a) 1600°C, variable NBO/T. Each symbol in this and subsequent figures refers to a calculated result for one liquid composition. (b) Effect of Si/Al ratio at 1600°C. Values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ are indicated. (c) Effect of $(X_{CaO}^{Liq} + X_{MgO}^{Liq})/X_{Al_2O_3}^{Liq}$ ratio at 1600°C and constant optical basicity. Values of Λ are indicated. (d) Effect of temperature for liquids with NBO/T = 0. Temperatures are indicated adjacent to the curves.

ing Si/Al at constant Λ. Second, the curves for constant Si/Al cross over for optical basicities between 0.55 and 0.65 and merge so that at optical basicities exceeding ~0.65, the Si/Al effect is muted. There is nevertheless a sharp increase in $\ln(\gamma_{CaO}^{Liq})$ with increasing Si/Al at the lowest values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ at any given Λ. Variations of $\ln(\gamma_{CaO}^{Liq})$ at low (Ca + Mg)/Al ratios (Fig. 1c) are important contributors to expanding the range in $\ln(\gamma_{CaO}^{Liq})$ for low values of Λ. Near the minimum at $\Lambda = 0.54$, values of $\ln(\gamma_{CaO}^{Liq})$ increase sharply with increasing base to Al ratios for $(X_{CaO}^{Liq} + X_{MgO}^{Liq})/X_{Al_2O_3}^{Liq} < \sim 1.5$, whereas for $(X_{CaO}^{Liq} + X_{MgO}^{Liq})/X_{Al_2O_3}^{Liq} > \sim 1.5$, these variables are virtually independent of each other. These effects also appear to be expressed in the variation of $\ln(\gamma_{CaO}^{Liq})$ with temperature (Fig. 1d). For optical basicities near $\Lambda = 0.54$, $\ln(\gamma_{CaO}^{Liq})$ increases with temperature, rising by as much as a factor of twenty over 400°C. The position of the minimum is not strongly affected but the range in $\ln(\gamma_{CaO}^{Liq})$ near $\Lambda = 0.54$ decreases with increasing temperature even though the volume of composition space for stable liquids is simultaneously increasing. For liquids near $\Lambda = 0.54$, the melt becomes much more basic, as measured by $\ln(\gamma_{CaO}^{Liq})$, as the temperature increases. On the other hand, the temperature effect is quite modest for $\Lambda > \sim 0.65$ at NBO/T = 0 and reconnaissance calculations for other values of NBO/T show that a small temperature dependence is characteristic for $\Lambda > \sim 0.65$ to 0.70.

Minima in the solubility of carbon (Park and Min, 1999b), silver (Park and Min, 1999a), and platinum (Nakamura et al., 1998) and maxima in Fe^{2+}/Fe^{3+} (Sumita et al., 1982) in slag liquids as a function of optical basicity have invariably been attributed to changes in speciation (e.g., Ag^+ vs. Ag^{2-} or C^- vs. C_2^{2-}). At least for silver, a valence change is supported by corresponding changes in the solubility as a function of oxygen fugacity (e.g., Park and Min, 1999a). Redox reactions are not responsible for variations in Λ for CMAS liquids but the same principle, that a change in speciation is involved in producing the observed minimum in $\ln(\gamma_{CaO}^{Liq})$, is likely to hold. As noted above, relatively high Si/Al ratios characterize liquid compositions near the minimum in Figure 1a. These liquids also have a low total content of normal bases ($X_{CaO}^{Liq} + X_{MgO}^{Liq} < 0.18$), low NBO/T ($< \sim 0.3$), and values of ($X_{CaO}^{Liq} + X_{MgO}^{Liq})/X_{Al_2O_3}^{Liq}$ generally < 5 (Fig. 1c). There is also a strong temperature dependence (Fig. 1d), consistent with an ordering reaction involving Ca (i.e., the melt tends to become more disordered with increasing temperature). Moreover, the decreasing $\ln(\gamma_{CaO}^{Liq})$ with increasing optical basicity on the low Λ side of the minimum, even as X_{CaO}^{Liq} is increased, probably indicates complexation of the Ca. Certainly, one can propose specific ordering reactions to explain these observations (e.g., those involving destabilization of Al-Si clusters due to preferential short-range ordering of Ca and Al). It should be kept in mind, however, that many possible microscopic variations in speciation are consistent with a given set of macroscopic thermodynamic properties. This creates an inherent ambiguity unless there are formal microscopic constraints, the development of which lies outside the scope of the present study. Therefore, the details must remain murky and it is simply concluded that the minimum in Figure 1a hints at a fundamental shift in speciation near $\Lambda = 0.54$.

Up to this point, attention has been restricted to the activity coefficient of Ca because it is a direct measure of nonideality in

the liquid but, ultimately, it is the activities that determine the stability of the liquid and partitioning of elements between phases. Figure 2 shows that there is a good correlation between $\ln(a_{CaO}^{Liq})$ and optical basicity for $\Lambda > \sim 0.6$, comparable in quality to that exhibited by $\ln(\gamma_{CaO}^{Liq})$ (Fig. 1a), but that variations in $\ln(a_{CaO}^{Liq})$ at constant Λ increase dramatically at lower values of Λ. In part, the correlation for high Λ reflects the relatively small range in X_{CaO}^{Liq} at constant Λ for these liquids so that variations in a_{CaO}^{Liq} are dominated by variations in γ_{CaO}^{Liq}. At low and constant Λ, γ_{CaO}^{Liq} is even more variable than at high Λ (Fig. 1a) and this is superimposed on order of magnitude variations in X_{CaO}^{Liq} even for the restricted range in composition (i.e., $X_{CaO}^{Liq} \geq 0.01$) imposed on the calculation.

The excess free energy for stable liquids in CMAS is not correlated with optical basicity. It would be highly desirable to evaluate possible correlations involving excess enthalpies and entropies or the temperature dependence of activity coefficients with Λ as it is ultimately entropic contributions to the free energy that stabilizes liquids relative to solids. There may, for example, be a hint of changing configurational contributions in the decreasing range in $\ln(\gamma_{CaO}^{Liq})$ as temperature is increased for liquids with NBO/T = 0 and $\Lambda \sim 0.54$ (Fig. 1d). However, one weakness of solution models for liquids that are based primarily on phase equilibria from liquidus surfaces is that although they can do a fairly good job of predicting the free energies, they are not well suited to quantitatively separating contributions from the enthalpy and entropy. Attention was therefore restricted to a search for additional activity coefficients or combinations of activity coefficients characterized by strong correlations with the optical basicity and this yielded two functions, $\ln(\gamma_{MgO}^{Liq}/\gamma_{SiO_2}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq})$. Values of the former are shown plotted against the optical basicity in Figure 3a. As with $\ln(\gamma_{CaO}^{Liq})$, there is a generally positive correlation for liquids with $\Lambda > \sim 0.54$ and a negative correlation for liquids with $\Lambda < \sim 0.54$. Liquid compositions associated with the minimum also show the same characteristics as for $\ln(\gamma_{CaO}^{Liq})$ with relatively high $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ (4 to 20 for $\Lambda < 0.54$), a low total content of normal bases ($X_{CaO}^{Liq} + X_{MgO}^{Liq} < 0.18$) and low NBO/T ($< \sim 0.3$). This points to a common source for the minima in Figures 1a and 3a.

As might be expected given the similar functional dependencies shown in Figures 1a and 3a, $\ln(\gamma_{CaO}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq}/\gamma_{SiO_2}^{Liq})$ are strongly correlated (Fig. 3b). Note that for liquids with NBO/T $> \sim 0.5$, the correlation is roughly linear. Although there is overlap, compositions with lower NBO/T yield a more arcuate trend, the tail being formed by liquids with $\Lambda < 0.54$. An essentially linear trend between $\ln(\gamma_{CaO}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq}/\gamma_{SiO_2}^{Liq})$ appears to be a fundamental relationship in aluminosilicate melts as it is also observed for magmatic liquids (at constant alkali contents) with a much larger number of components.

From Figure 3c, there is a broad linear correlation between $\ln(\gamma_{CaO}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq})$. This presumably reflects the competition by Ca and Mg for similar sites in the melt that is played out through their differing field strengths and ionic radii. On the other hand, there is, at most, a weak correlation between $\ln(a_{MgO}^{Liq}/a_{SiO_2}^{Liq})$ or $\ln(a_{MgO}^{Liq})$ and either the optical basicity, $\ln(a_{CaO}^{Liq})$ or $\ln(\gamma_{CaO}^{Liq})$. A correlation between the logarithms of activity coefficients speaks to the form of the excess free energy surface and, presumably, speciation in the liquid (i.e., it
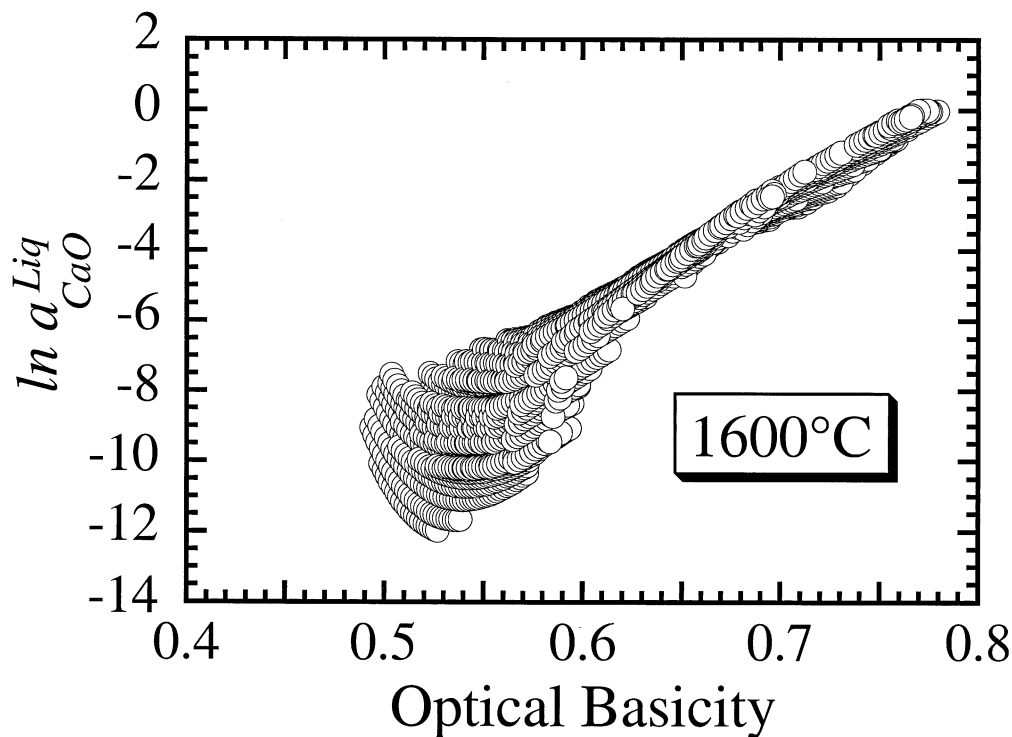
Fig. 2. Variation of $\ln(a_{CaO}^{Liq})$ with optical basicity for $X_{CaO}^{Liq} \geq 0.01$ in the system CMAS at 1600°C. Note that the bulge near $\Lambda = 0.54$ would extend downward if lower values of X_{CaO}^{Liq} were considered by an amount consistent with the difference $\ln(X_{CaO}^{Liq}) - \ln(0.01)$.

is a reflection of homogeneous equilibrium within the melt). A corresponding correlation for the activities would imply either external buffering through the presence of additional phases (i.e., heterogeneous equilibria would be involved) or a restricted range of liquid compositions. Because the oxide contents of liquids examined in the present study range from zero to levels sufficient to saturate the melt with respect to end-member oxides, strong correlations involving pairs of oxide activities were not expected.

The dramatic importance that the Si/Al ratio can have on the thermodynamic properties of CMAS liquids is illustrated in Figure 4 in which $\ln(a_{SiO_2}^{Liq})$ is plotted against the optical basicity. There is a strong negative correlation for compositions with a constant value of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ but the total variation in $\ln(a_{SiO_2}^{Liq})$ at constant Λ can be quite large (actually infinitely large because $\gamma_{SiO_2}^{Liq}$ is constant for sufficiently dilute solutions so that $a_{SiO_2}^{Liq}$ is proportional to $X_{SiO_2}^{Liq}$). There also appears to be a fairly good negative correlation for all liquids with $\Lambda < {\sim}0.7$ independent of Si/Al. This latter correlation is, however, largely an artifact of the phase relations because at 1600°C liquids with low values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ are unstable at low values of Λ and many with high values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ are at or close to silica-saturation. The negative correlation for liquids with constant $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq} \leq 1$ is real although this partly stems from the fact that imposing a low value of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ greatly restricts possible values of $X_{SiO_2}^{Liq}$ (i.e., variations in $\ln(\gamma_{SiO_2}^{Liq})$ are the underlying cause of the correlations). Meraikib (1997) found that both the activity and activity coefficient of silica are linearly correlated with Λ for the suite of 30 slags he

studied and, given the restricted range in $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ (4.3 to 5.4) and Λ (0.65 to 0.67) encompassed by his data, results depicted in Figure 4 are consistent with his observations.

2.4. Role of Tetrahedral Speciation

So far, the primary focus in this work has been on relationships between measures of basicity and the thermodynamic properties of silicate melts in the CMAS system. Even the best correlations involving the optical basicity or $\ln(\gamma_{CaO}^{Liq})$ are, however, sensitive to tetrahedral speciation. This can be seen in Figure 1b, where liquid compositions on the low Λ side of the minimum were restricted to high Si/Al ratios. It shows up again in Figure 3b, where the correlation between $\ln(\gamma_{CaO}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq}/\gamma_{SiO_2}^{Liq})$ shifts with the NBO/T ratio. Through Figure 4, it was shown that there is a negative correlation between $\ln(a_{SiO_2}^{Liq})$ at constant Si/Al and the optical basicity. Other workers have been aware that optical basicity might be sensitive to tetrahedral speciation and this has led to efforts to calculate group optical basicities for polymerized anions such as SiO_4^{4-} (e.g., Duffy and Ingram, 1976; Sommerville and Masson, 1992) and "corrected" optical basicities designed to be sensitive to degree of polymerization (Mills, 1993). However, these exercises have not been particularly useful.

In this section, relationships involving activity coefficients and a general measure of the degree of polymerization are explored. Products of activity coefficients are emphasized because they may reflect underlying short-range order in the liquids involving network forming and network modifying cat-
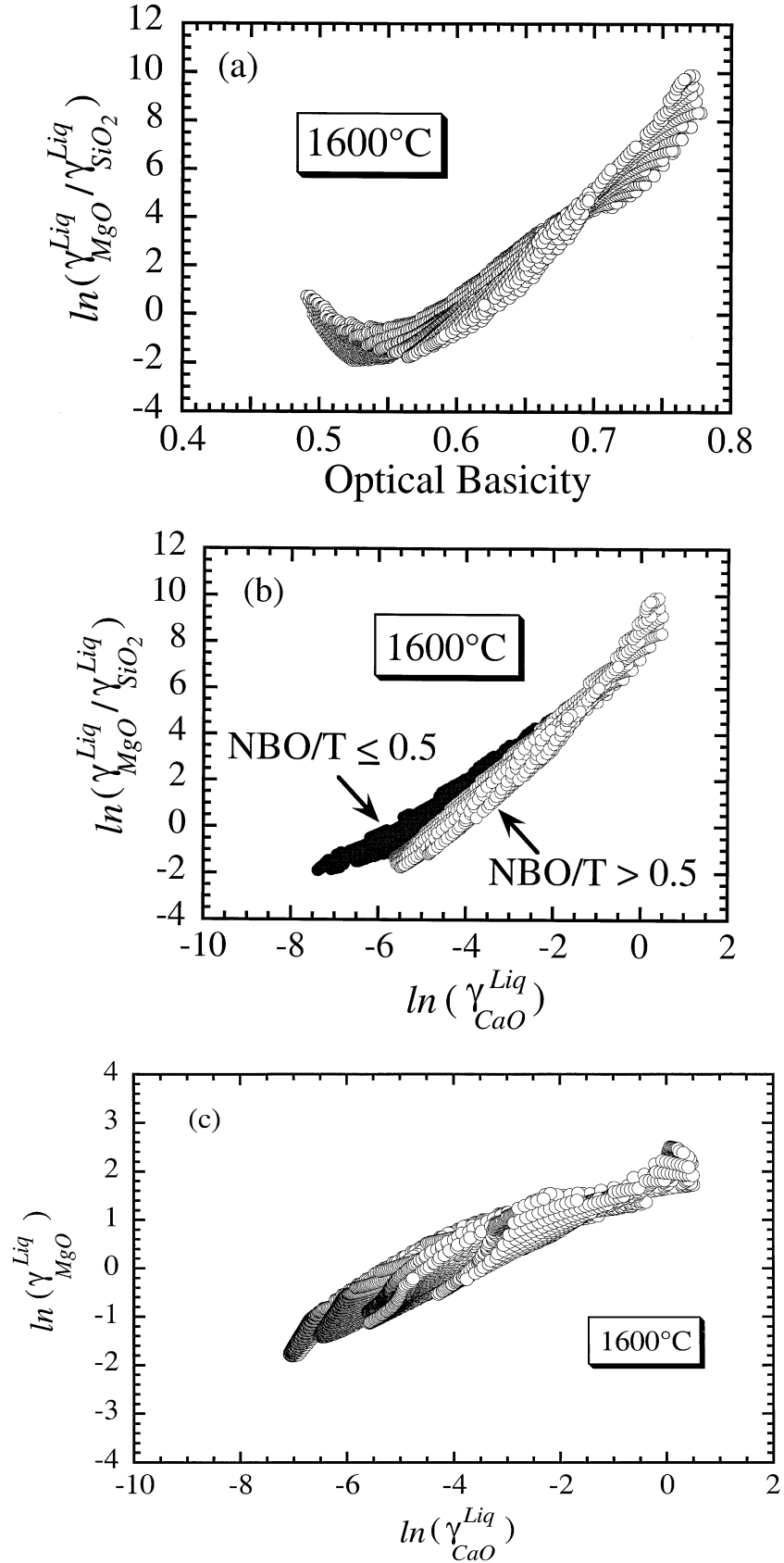
Fig. 3. Relationships involving $\ln(\gamma_{SiO_2}^{Liq}/\gamma_{MgO}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq})$ in the system CMAS at 1600°C. (a) Variation of $\ln(\gamma_{SiO_2}^{Liq}/\gamma_{MgO}^{Liq})$ with optical basicity. (b) Variation of $\ln(\gamma_{SiO_2}^{Liq}/\gamma_{MgO}^{Liq})$ with $\ln(\gamma_{CaO}^{Liq})$. (c) Variation of $\ln(\gamma_{MgO}^{Liq})$ with $\ln(\gamma_{CaO}^{Liq})$.
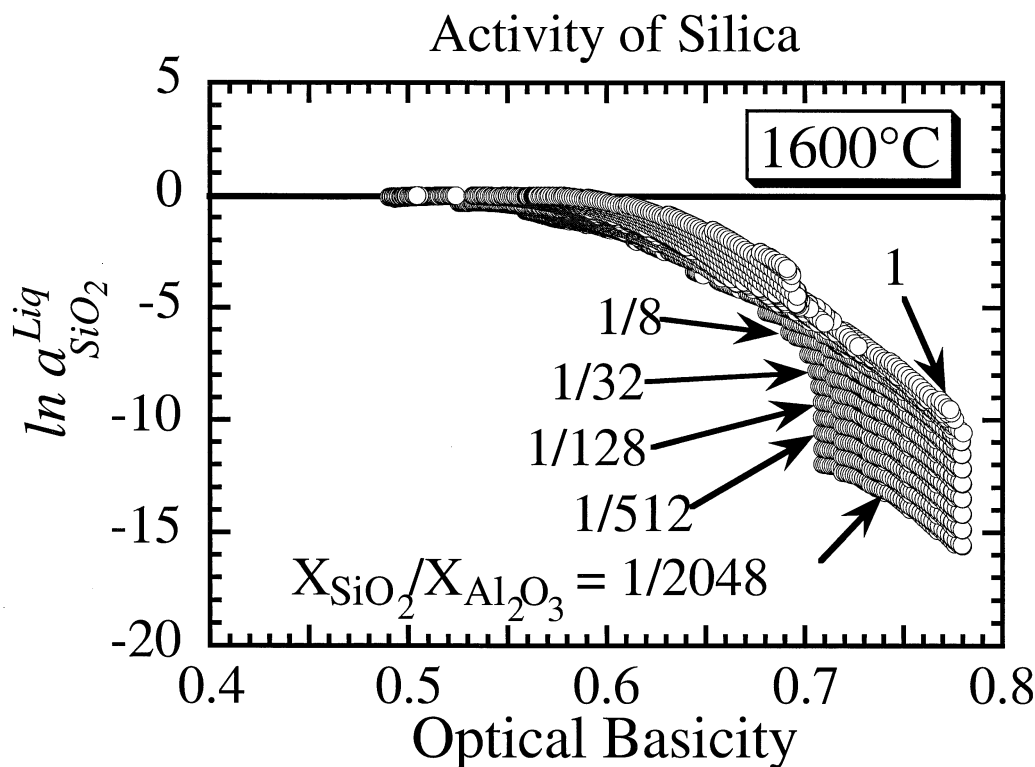
Activity of Silica

Fig. 4. Relationship between $\ln(a_{SiO_2}^{Liq})$ and optical basicity at 1600°C. Selected values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ are indicated next to the curves.

ions and because such products may point the way towards more efficient composition variables for thermodynamic modeling than are the end-member oxides. The NBO/T ratio (Eqn. 1) is used for this purpose although this is done with the knowledge that the parameter is a crude filter that fails to capture many aspects of the structural state of the liquid. The true degree of polymerization in a given liquid is dictated by homogeneous equilibria among the many species that are present in the melt and NBO/T can't express this speciation quantitatively. Note from Eqn. 1 that liquids with NBO/T < 0 are possible, basically reflecting compositions in which there is insufficient CaO + MgO to charge balance all of the aluminum in tetrahedral coordination. Liquids with an NBO/T = 0 are fully compensated so that all tetrahedra can be charge balanced but there are no divalent cations in excess of this amount to act as network modifiers. Such melts are nominally fully polymerized although there is good NMR evidence (e.g., Stebbins and Xu, 1997; Lee and Stebbins, 1999) that significant concentrations of nonbridging oxygens are in fact present in these liquids. At the other end of the spectrum, liquids with NBO/T = +4 are nominally completely depolymerized, the tetrahedral species residing entirely in isolated tetrahedra. At 1600°C, stable CMAS liquids encompass an NBO/T range of −0.2 to +4.0. As noted above, these values of NBO/T can not be equated directly to corresponding degrees of polymerization but it is nevertheless a reasonable expectation that stable liquids in CMAS at 1600°C range from highly polymerized to highly depolymerized.

Figure 5a shows values of $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ as a function of

$X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ at constant NBO/T in the range −0.1 to 1.0. Values of $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ form an undulating surface in NBO/T (i.e., the figure can be thought of as a projection from NBO/T). Curves for NBO/T < +0.3 (illustrated by NBO/T = −0.1 and 0.0 in the figure) show a minimum near $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ = 5, which migrates to higher values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ with increasing NBO/T. Liquid compositions near the minima in Figure 5a are the same as those near the minima of Figures 1a and 3a and, presumably, reflect the same phenomenon. For curves with NBO/T > 0.2, a maximum develops at low values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$, which migrates to higher values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ with increasing NBO/T. This can also be seen in Figure 5b. For NBO/T > ~0.3 and constant $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$, $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ for siliceous compositions increases with increasing NBO/T. As might be anticipated on the basis of Figure 3c, $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ shows a similar behavior (Fig. 6) though the minima are less prominent and the maxima tend to occur at higher values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$.

Figure 7 shows $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ for specified values of NBO/T plotted against $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$. The prominent maximum for NBO/T in the range 0.5 to 3 corresponds to maxima or changes in slope observed in Figures 5 and 6 at low to moderate values of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$, perhaps indicating that competition between Ca and Mg is involved. This would be consistent with expectations based on relative basicity and it is reflected in the relative enthalpies of solution for Ca and Mg (as well as for other alkali and alkaline earth cations) as pointed out by Roy and Navrotsky (1984) and as discussed below. On the
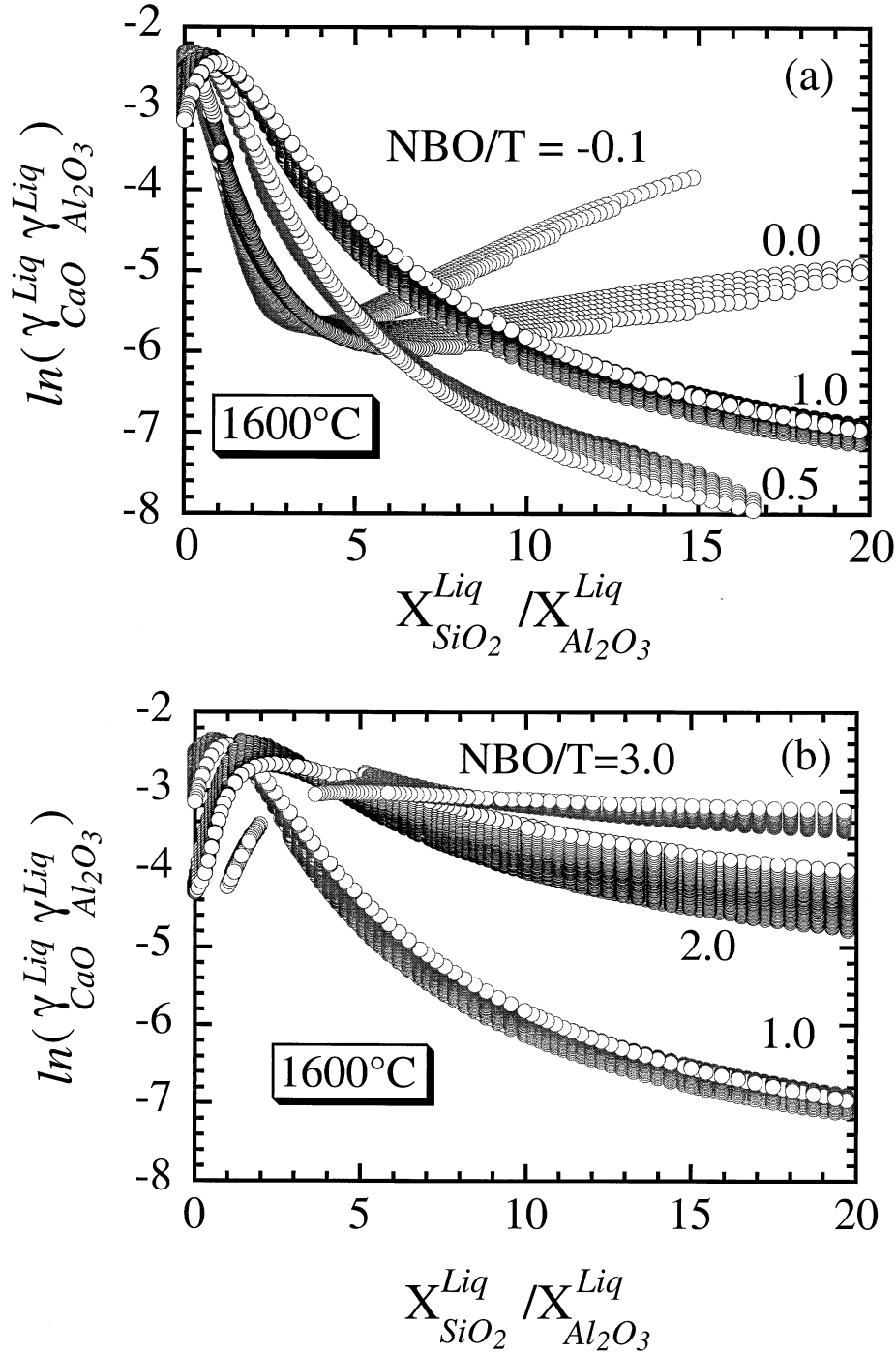
Fig. 5. Relationships involving $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ and $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ at 1600°C. Values of NBO/T are indicated next to the curves. (a) NBO/T ≤ 1. (b) NBO/T ≥ 1.

other hand, the minima observed for low NBO/T (Figs. 5a and 6a) are not reflected in significant slope changes in Figure 7.

Neutral components other than end-member oxides are in common use for modeling silicate liquids (Bottinga and Richet, 1978; Bottinga et al., 1981; Björkman, 1985; Ghiorso et al., 1994), reflecting either a desire to minimize required data for modeling or assumptions regarding speciation in the melt. The existence of correlations involving the combinations of activity coefficients for oxide components in CMAS also suggests that simplifications in modeling for this system can be achieved by the use of an alternative set of components. CaO and possibly MgO appear to be desirable end members on the basis of Figure 3c, but chemical potentials involving alumina and silica would probably be more efficiently modeled by the use of an exchange component such as $SiMg_{-1}$ and one or both of $CaAl_2O_4$ and $MgAl_2O_4$.
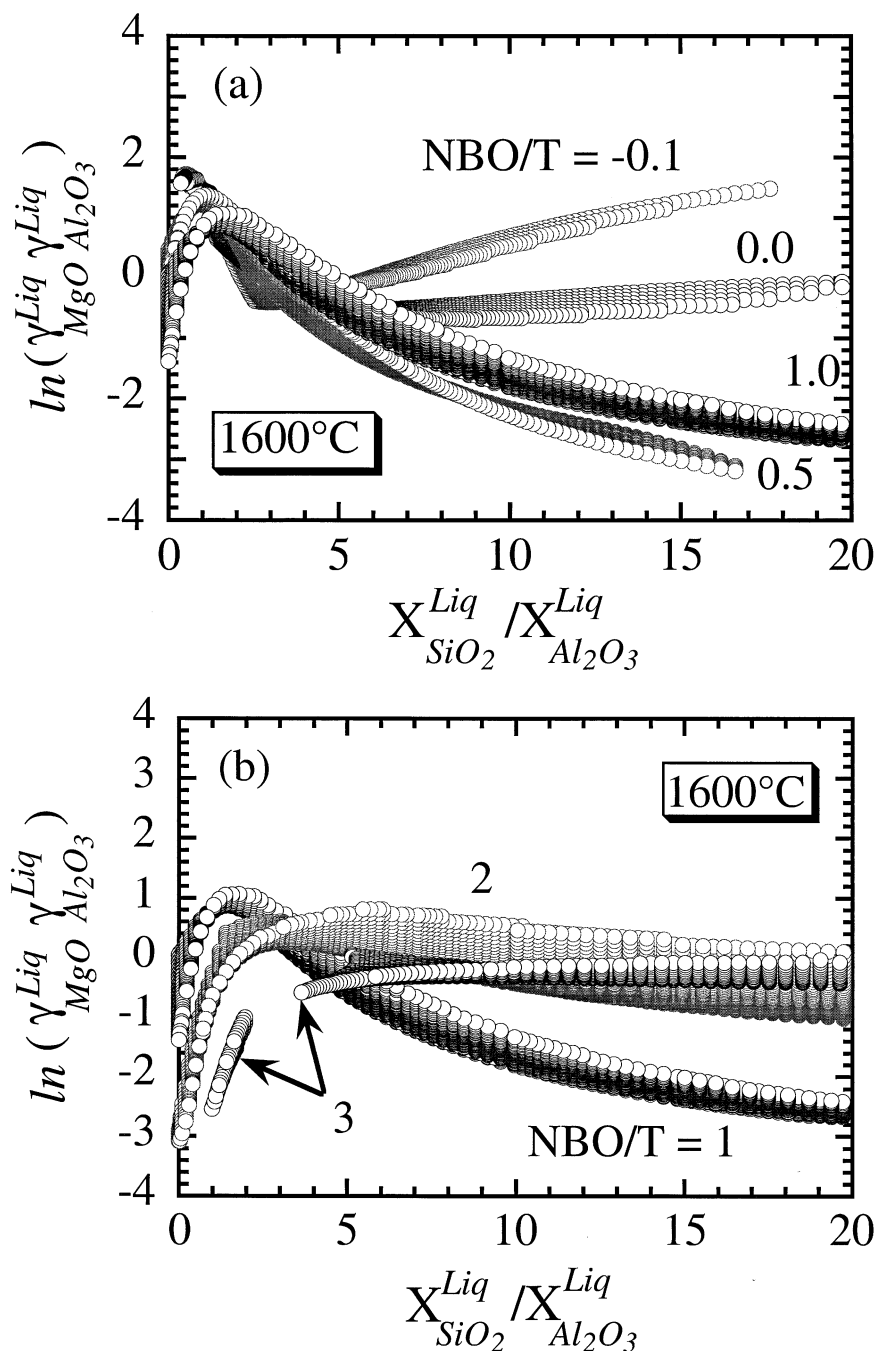
Fig. 6. Relationships involving $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ and $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ at 1600°C. Values of NBO/T are indicated next to the curves. (a) NBO/T $\leq$ 1. (b) NBO/T $\geq$ 1.

2.5. Relationships with Other Properties of CMAS Liquids

A general pattern that emerges from the above analysis is one of strong correlations involving the activity coefficients of oxides in CMAS liquids and important shifts in these parameters that can be tied to specific regions of composition space. In this section, systematic observations on other properties of CMAS liquids and glasses are considered. The intent is to look for additional insight into sources of variations in the activity

coefficients and to explore possible predictive correlations. Enthalpy of solution data, which has a direct thermodynamic connection to the activity coefficients, are considered first followed by assessments of spectroscopic information, variations in valence, and sulfide capacity. Possible relationships with the viscosity are not considered in this work. The viscosity involves a thermally activated process that depends on species whose concentrations may be weakly attuned to even large-scale shifts in the activity coefficients of the end-member
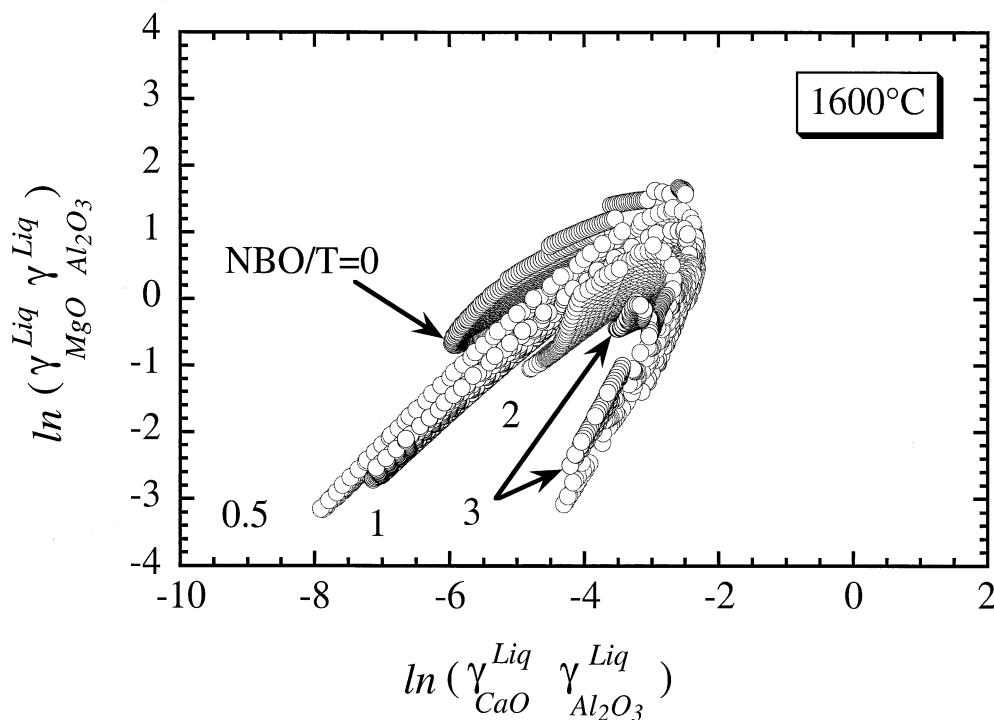
Fig. 7. $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ vs. $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ at 1600°C. Values of NBO/T are indicated.

oxides. The reader is, however, referred to a series of articles by Seetharaman and coworkers (Seetharaman and Du Sichen, 1994; Seetharaman et al., 1999, 2000) in which empirical relationships between excess free energies of liquids and the activation energies for viscosity are used in fitting available viscosity data for metallic and silicate liquids and to articles of Bottinga and coworkers (e.g., Richet, 1984; Richet et al., 1993; Bottinga et al., 1995; Richet and Bottinga, 1995; Bottinga and Richet, 1996) in which relationships between viscosity and configurational entropy are pursued.

Navrotsky and coworkers (Navrotsky et al., 1980, 1982; Roy and Navrotsky, 1984) obtained heats of solution for glasses in a suite of binary joins of the type $M_{\nu/2}^{\nu+}Al_2O_4 - SiO_2$ (NBO/T = 0), where M refers to an alkali or alkaline earth cation of charge ν. In effect, they were studying relative enthalpies for the substitution $Si^{4+} = Al^{3+} + (1/\nu)M^{\nu+}$ as a function of the network modifying cation. These authors were able to isolate two features in the enthalpy of solution data that may also be manifested in the activity coefficients. First, there is a pronounced curvature in the heat of solution data for $CaAl_2O_4$-SiO_2 and, especially, $MgAl_2O_4$-SiO_2 for $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ~3 to 20 that Navrotsky et al. (1985) attributed to incipient metastable immiscibility. For NBO/T = 0, which is the pertinent value for these joins, there is a minimum in $\ln(\gamma_{CaO}^{Liq})$ at $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ~ 4 to 6 (cf. Figs. 1a and 1b), in $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ at $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ~5 to 7 (Fig. 5a) and in $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ at $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ~7 to 10 (Fig. 6a), which may be distant reflections of the same phenomenon. The second feature in the calorimetric data is a maximum near $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq} = 2$. There are no corresponding maxima in the NBO/T = 0 curves for $\ln(\gamma_{CaO}^{Liq}\gamma_{Al_2O_3}^{Liq})$ or $\ln(\gamma_{MgO}^{Liq}\gamma_{Al_2O_3}^{Liq})$, although maxima near $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ~ 1 appear for NBO/T > ~ 0.2 and the position of the maximum migrates

to higher $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ with increasing NBO/T. Navrotsky et al. (1985) suggested that the maximum in their enthalpy of solution data might imply that Al-O-Si linkages are enthalpy-stabilized relative to Al-O-Al and Si-O-Si linkages and later molecular orbital calculations of Tossell (1993) are consistent with such an assertion. If these arguments are correct, then the somewhat different positions of the maxima exhibited in Figures 5 and 6 may reflect the influence of configurational contributions to the free energy of mixing.

Spectroscopic techniques provide information on the speciation in silicate liquids, which is the bridge between macroscopic and microscopic descriptions of the thermodynamic properties. As with calorimetry, considerable emphasis in spectroscopic studies of CMAS glasses and liquids has been placed on the joins $CaAl_2O_4$-SiO_2 and $MgAl_2O_4$-SiO_2. On the basis of Raman spectroscopy, McMillan and coworkers (McMillan and Piriou, 1982, 1983a,b; McMillan et al., 1982; Sato et al., 1991) suggested that near $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ~ 2, the melt is highly ordered but that in more aluminous liquids, there is local clustering of Si-rich and Al-rich regions and some coordination disorder for the aluminum (also seen in liquids whose compositions are Al-rich relative to the $CaAl_2O_4$-SiO_2 join; Sato et al., 1991). Such an interpretation could be consistent with both calorimetric evidence for incipient immiscibility of the aluminous compositions and in the maxima observed in the heat of solution data near $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ ~ 2. Correlations noted above with respect to the activity coefficient as a function of $X_{SiO_2}^{Liq}/X_{Al_2O_3}^{Liq}$ (Figs. 1b, 5a, 6a) may also be consistent with these observations although detailed comparisons would require systematic spectroscopic data off the charge-compensated joins.

Raman spectroscopy of glasses can yield some broad-brush information on structural variations in aluminosilicate liquids

but the spectra are complex and difficult to interpret. Early efforts to apply NMR spectroscopy to CMAS liquids were also rather qualitative (Murdoch et al., 1985; Sato et al., 1991; McMillan and Kirkpatrick, 1992), although evidence for highly coordinated Al in aluminous compositions was unambiguous. Recent advances in NMR spectroscopy have, however, begun to yield quantitative constraints on speciation (Stebbins and Xu, 1997; Stebbins et al., 1999). For example, Stebbins and Xu (1997) were able to show that several percent of the oxygen in two glasses close in composition to $CaAl_2Si_2O_8$ were non-bridging compared with a few tenths of a percent expected on the basis of charge compensation (i.e., for NBO/T = 0, the nominal fraction of nonbridging oxygens is zero). Similarly, Lee and Stebbins (1999) studied a series of glasses along the join $CaAl_2O_4$-SiO_2 and showed that Al-avoidance was only partially obeyed (i.e., the glasses were not completely ordered). They also used their results to fit a quasichemical model for the Al-Si speciation data, from which they were able to extract the contribution of Al-Si disorder to the configurational entropy and enthalpy. They concluded that disorder involving Al-Si is responsible for a significant proportion of the total variation, although other contributions were also deemed important. It is possible that over the next few years, spectroscopic techniques, perhaps in conjunction with molecular dynamics simulations, will yield a basis for establishing quantitative correlations between speciation in the melt and the macroscopic thermodynamic properties as expressed through the activity coefficients of the end-member oxides. In the interim, associated solution models in which specific species are postulated and quasichemical models in which short-range order is explicitly considered are likely to become progressively more sensitized to real constraints arising from liquid structure. Such models are already commonly employed for systems of interest to the metallurgical and materials sciences (e.g., Nagata et al., 1977; Bergman et al., 1982; Schmid and Chang, 1985; Egner et al., 1997; Kress, 2000; Pelton et al., 2000) and have also found limited utility for silicate liquids of geological interest (e.g., Wen and Nekvasil, 1994; Zeng and Nekvasil, 1996). There are some theoretical drawbacks to associated models (e.g., Luck et al., 1989; Pelton et al., 2000) but their practical ability to handle sharp changes in activities with composition is a big plus. On the basis of the above analysis, modeling that includes associates of the type $MgAl_2O_4$ and $CaAl_2O_4$ may be productive.

The fact that optical basicity can be correlated to Pauling's electronegativity suggests a sensitivity to local bonding environments and a relative insensitivity to variations in configurational contributions. The value of Λ (Eqn. 3) is the same independent of whether or not Al is 4, 5, or 6 coordinated. It is the same independent of whether or not Al avoidance is obeyed and it is nominally independent of whether the tetrahedra are isolated, completely polymerized or distributed among collections of chains, sheets and rings. Although $\ln(\gamma_{CaO}^{Liq})$ and $\ln(\gamma_{MgO}^{Liq}/\gamma_{SiO_2}^{Liq})$ are correlated to optical basicity (Figs. 1a, 3a), there are still significant variations at constant Λ that may at least in part capture variations in relative magnitudes of the configurational contributions (see also discussion of Fig. 1d above). The present results suggest that it may be profitable to evaluate spectroscopic, rheological, and calorimetric properties of CMAS liquids, glasses, or both as a function of composition and temperature at constant Λ.
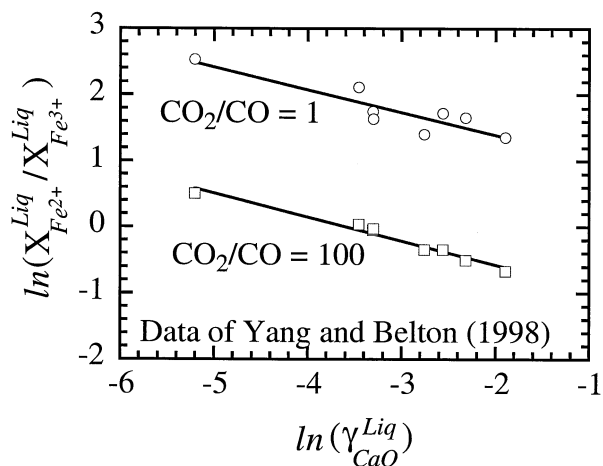

Fig. 8. Relationship between $\ln(\gamma_{CaO}^{Liq})$ and $\ln(X_{Fe^{2+}}^{Liq}/X_{Fe^{3+}}^{Liq})$ for data of Yang and Belton (1998) at 1500°C.

2.6. Implications for the Solubility and Speciation of Other Elements Added to a CMAS Liquid

If a small amount of an element such as iron or sulfur is added to a solvent such as a CMAS liquid, the response of the element must be at least in part dictated by the nature of the solvent. It is therefore a reasonable expectation that there may be correlations between properties such as Fe^{2+}/Fe^{3+} ratios or sulfide solubility and the optical basicity or activity-composition relations of the CMAS liquid. This section provides a brief overview of predictive correlations that have been developed primarily through optical basicity and examines how these may play out through the activity coefficients.

Duffy and Ingram (1976), Sumita et al. (1982), and Baucke and Duffy (1991), among others, have noted that the ratio of reduced to oxidized cations of a multivalent element (e.g., Fe^{2+}/Fe^{3+}) tends to decrease with increasing optical basicity (i.e., increasing Λ favors the higher oxidation state). Baucke and Duffy (1993) extended this approach to include pairs of elements (e.g., Fe to Cr). Yang and Belton (1998) have, however, pointed out that although Fe^{2+}/Fe^{3+} data for their suite of slags can be related to a curve in optical basicity under oxidizing conditions, the correlation degrades dramatically under more reducing conditions. They also noted that previous correlations involving optical basicity were generally constructed from the results of experiments conducted in air and suggested that this might not be a sound approach to determining relationships under other conditions.

Figure 8 shows the relationship between Fe^{2+}/Fe^{3+} for the data of Yang and Belton (1998) and $\ln(\gamma_{CaO}^{Liq})$. There is a good linear correlation for both oxidizing and reducing conditions although the correlation for the latter is significantly poorer. Interestingly, Yang and Belton's data for $CO_2/CO = 1$ plot along a single-valued curve in $\ln(\gamma_{CaO}^{Liq}/\gamma_{Al_2O_3}^{Liq})$, suggesting that the activity coefficients of Fe^{2+} and Fe^{3+} in the liquid may be affected by different aspects of the CMAS liquid into which they are inserted. This would be consistent with Fe^{3+} acting predominately as a network former and Fe^{2+} mostly taking on a network modifying role (Brown et al., 1995). It is likely that useful predictive relationships for redox ratios of multivalent

cations, when present in small amounts, can be obtained from activity coefficients in the base CMAS liquid.

The greatest practical success for optical basicity is a strong linear correlation between Λ and the logarithm of the sulfide capacity C_S, defined as the weight percentage sulfur times the square root of P_{O_2}/P_{S_2} (e.g., Sommerville and Sosinsky, 1984; Sosinsky and Sommerville, 1986). The sulfide capacity is an important parameter in steelmaking because of the need to control and, generally, minimize sulfur concentrations in the metal. The concept was originally developed by Fincham and Richardson (1954) in considering the reaction

$$CaS_{(Liq)} + \frac{1}{2}O_2 = CaO_{(Liq)} + \frac{1}{2}S_2,$$
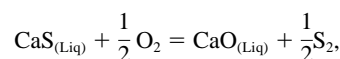
for which there is an equilibrium constant

$$K \cong \frac{a_{CaO}^{Liq}\, P_{S_2}^{1/2}}{a_{CaS}^{Liq}\, P_{O_2}^{1/2}}$$

or

$$C_s = K' \frac{a_{CaO}^{Liq}}{\gamma_{CaS}^{Liq}}.$$

Figure 9a shows that there is an excellent linear correlation between the optical basicity and $\ln(C_S)$ for literature data on ternary and quaternary compositions in CMAS at 1600°C. On the basis of the data of Fincham and Richardson (1954) as corrected by Abraham and Richardson (1960), Abraham et al. (1960), Kalyanram et al. (1960), Kalyanram and Bell (1961), Brown et al. (1982), Hino et al. (1993), Görnerup and Wijk (1996), Drakaliysky et al. (1997), Nzotta (1997), Nzotta et al. (1997, 1998), and Seo and Kim (1999), linear relationships are also observed for other temperatures in the range 1450 to 1650°C, although the errors are much larger. It is possible that more complex expressions may be needed for $\Lambda > {\sim}0.8$ (Young et al., 1992), but this is not relevant to stable CMAS liquids at temperatures $\leq$1600°C. Figure 9b shows that $\ln(C_S)$ is also linearly correlated with $\ln(a_{CaO}^{Liq})$. From Eqn. 4, this implies that γ_{CaS}^{Liq} is a weak function of composition. The assumption that γ_{CaS}^{Liq} is approximately constant has in fact been used previously in attempts to evaluate CaO activities in CMAS liquids (e.g., Carter and Macfarlane, 1957; Kalyanram et al., 1960; Cameron et al., 1966). When $\ln(C_S)$ is plotted against $\ln(\gamma_{CaO}^{Liq})$ for CMAS liquids at 1600°C (Fig. 9c), there is a linear correlation except for one point from Drakaliysky et al. (1997), which plots well below the regression line. If the aberrant point is correct, then on the basis of Figure 1a, γ_{CaS}^{Liq} increases with decreasing Λ for $\Lambda < 0.54$ in concert with γ_{CaO}^{Liq}. Correlations involving optical basicity extend to systems with transition elements (Sommerville and Sosinsky, 1984; Young et al., 1992), which suggests that the correlations involving activity coefficients described in this work may also extend to other systems.
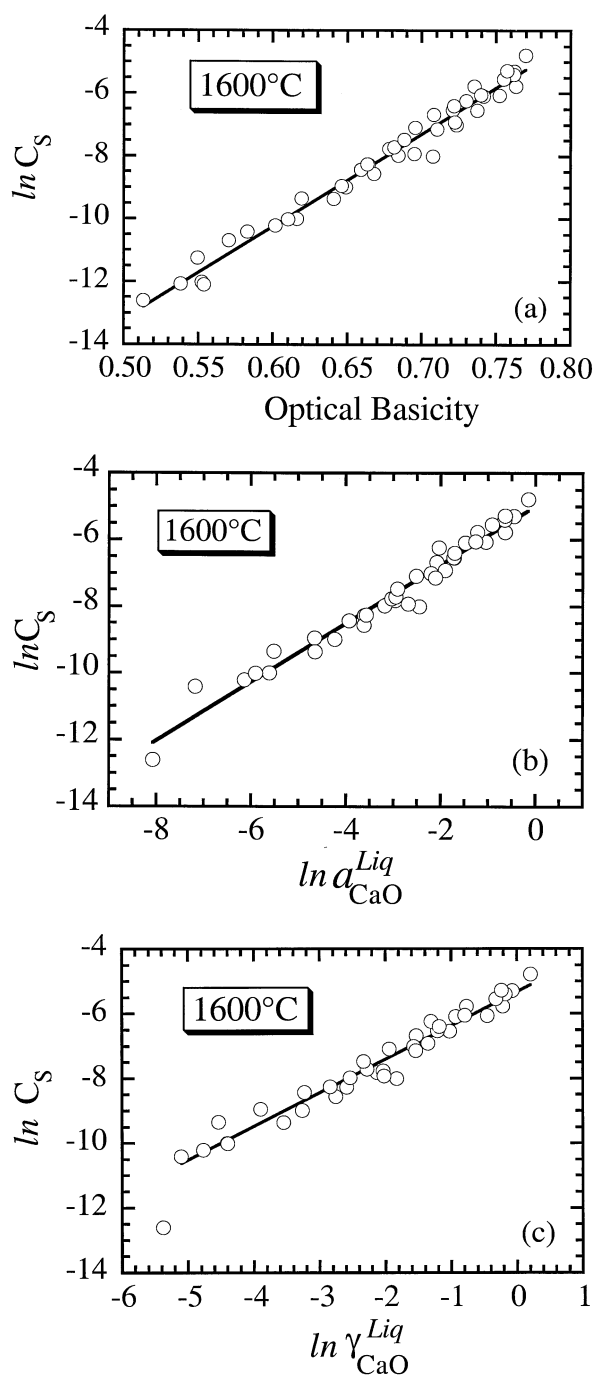
Fig. 9. Sulfide capacities of CMAS liquids at 1600°C. Data are from Drakaliysky et al. (1997), Görnerup and Wijk (1996), Hino et al. (1993), Nzotta (1997), and Nzotta et al. (1997, 1998). Selected studies were restricted to those for which oxygen and sulfur fugacities were fixed through gas mixing and to ternary or quaternary compositions. Data for which the model of Berman (1983) predicted supersaturation with respect to a crystalline phase were rejected, and activities of oxide components were calculated assuming that the effect of S on them is negligible. (a) Optical basicity vs. $\ln(C_S)$. An unweighted regression line through the data is also shown. (b) $\ln(a_{CaO}^{Liq})$ vs. $\ln(C_S)$ with an unweighted regression line for all data. (c) $\ln(\gamma_{CaO}^{Liq})$ vs. $\ln(C_S)$. An unweighted regression line for all data except for the single point that falls well off the linear trend is also given. Note that there are fewer points in (b) and (c) than in (a) because some of the data plotted in (a) refer to the system MgO-Al_2O_3-SiO_2.

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