Statistical Thermodynamic Model for Si/Al Ordering in Amorphous Aluminosilicates

John L. Provis, Peter Duxson, Grant C. Lukey, and Jannie S. J. van Deventer*

Department of Chemical and Biomolecular Engineering, University of Melbourne, Victoria 3010, Australia

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A statistical thermodynamic model for the ordering of aluminum- and silicon-centered tetrahedra in fully condensed X-ray amorphous aluminosilicate network structures is presented. In particular, the model is applied to metakaolin-based geopolymers in the presence of different charge-balancing cations and mixtures of cations. The model uses Gibbs energy minimization techniques based on the energetic preference for Si−O−Al linkages over Si−O−Si and Al−O−Al to calculate the concentrations of each of the types of bonds. A random bond distribution is then applied to calculate the concentration of each possible tetrahedron coordination. The model output is compared with experimental ^{29}Si MAS NMR results, and is found to predict the observed behavior satisfactorily. A correction to account for the presence of unreacted metakaolin in geopolymers is found to significantly improve the model fit at low silica content. The calculated energy penalty parameters closely match those obtained from the literature, and the trends in the parameters allow discussion and analysis of the effects of the different cations on geopolymerization of metakaolin. The applicability of this model to geopolymeric systems indicates the potential for wider utilization in description of other amorphous aluminosilicate systems.

Introduction

"Geopolymer" is the term applied to a class of high-performance mineral binders obtained by activation of solid aluminosilicate materials with alkali metal hydroxide or silicate solutions at ambient or slightly elevated temperature.[1] While it is believed that, when cured under certain sets of conditions, these materials are largely composed of nanometer-sized crystallites,[2] geopolymers are essentially X-ray amorphous and thus have no clearly defined network topology. With a view toward potential applications in radioactive waste treatment,[3−5] understanding of the degree of chemical ordering in geopolymers, which will play a significant role in determining long-term chemical stability of these systems, is critical.

Recently, high-resolution ^{29}Si MAS NMR spectra of geopolymers spanning a range of silicate content and Na/(Na + K) ratios have been presented.[6] Deconvolution of these spectra by curve-fitting of Gaussian line shapes was found to provide meaningful information regarding the distribution of silicon and aluminum tetrahedra within the geopolymeric binder, as has been observed in aluminosilicate glasses[7] and minerals.[8,9] The aim of this paper is to provide a quantitative, fundamentally based model describing these observed trends, and allowing analysis of the effects of different compositions and synthesis parameters on chemical ordering in these materials.

The notation introduced by Engelhardt et al.[10,11] will be followed in this work, with $Q^n(m\text{Al})$ ($0 \leq m \leq n \leq 4$) representing a silicate center coordinated to n other tetrahedral centers, of which m are aluminum and $(n - m)$ are silicon. Similarly, $q^{n'}(m'\text{Al})$ ($0 \leq m' \leq n' \leq 4$) will be used to represent an aluminum center coordinated to n' other tetrahedral centers, of which m' are aluminum and $(n' - m')$ are silicon. The presence of nonbridging oxygens in geopolymeric systems is considered negligible, with all tetrahedral sites being observed by NMR to have cross-link density $n = 4$.[6,12,13] This observation will be utilized throughout model development and analysis to simplify the discussion of bond distribution, with $n = 4$ taken to be constant throughout this investigation.

The distribution and short-range (chemical) ordering of silicon and aluminum within tetrahedral framework structures have been the subject of significant work, and often controversy, for over 50 years.[14] However, such calculations have never before been applied to geopolymeric materials, with the amorphicity of these materials and the lack of

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* To whom correspondence should be addressed. E-mail: jannie@unimelb.edu.au.

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reliable data regarding atomic configurations within the binder phase combining to make such analysis very difficult. However, the recent publication[6] of a set of data relating composition to the distribution of $Q^4(m\mathrm{Al})$ centers now enables the development of such a model. The partially reacted raw materials present in geopolymers also cause some difficulties as will be discussed later in this paper.

The standard starting point in short-range structural analysis of aluminosilicates is Loewenstein's rule,[14] which states that no two aluminum ions can occupy the centers of tetrahedra linked by one oxygen. This "rule" was initially based on the Pauling radius ratio rule,[15] and is often assumed—either explicitly or implicitly—to be obeyed strictly in aluminosilicate structures.[1,16−18] However, there is no theoretical basis for strict application of aluminum avoidance, but rather a thermodynamic preference giving a strong tendency toward avoidance of Al−O−Al bonds. Lattice energy[19,20] and combined ab initio/molecular mechanics calculations[21] have shown that this tendency is primarily due to the exothermicity of the reaction depicted by eq 1 both in solution and in the solid state.

$$[\equiv\mathrm{Si{-}O{-}Si}\equiv] + [\equiv\mathrm{Al{-}O{-}Al}\equiv] \leftrightarrow 2[\equiv\mathrm{Si{-}O{-}Al}\equiv] \tag{1}$$

Free energy minimization considerations may therefore be used to interpret the observed tendency toward Al−O−Al avoidance in aluminosilicate structures. The unfavorable formation of Al−O−Al bonds in solution is believed to be largely responsible for the short-range ordering of silicon and aluminum centers in hydrothermally synthesized aluminosilicates.[21] Significant degrees of Si/Al disorder have been observed in melt-quenched glasses,[7,22] synthetic feldspars,[8] and natural minerals.[23−25] A Monte Carlo simulation of Si/Al ordering in ultramarines over a wide range of synthesis temperatures[26] showed a sudden decrease in ordering at approximately 500 °C, with the high-temperature regime producing essentially random ordering. Similar temperature effects were incorporated into the simple statistical model of Lee and Stebbins[7] via a Boltzmann-type exponential term.

This investigation utilizes the Si/Al distribution data obtained previously.[6] The free-energy model for chemical ordering of tetrahedral sites in alloys,[27] based on Gibbs energy minimization with explicit consideration of both enthalpic and entropic effects, is adapted and applied to the description of aluminosilicates in general, using geopolymers as a model system. The validity of the application of this model, originally presented in the description of Si−C−H ordering in amorphous hydrogenated silicon carbide alloys, to the inorganic polymer network structure will be discussed. The implication of this applicability is that the model is suitable for use in the study of bond ordering in other amorphous aluminosilicate materials, as the model does not require prior knowledge of the framework structure of the material.

Experimental Section

A full description of experimental and spectral deconvolution procedures is given in ref 6. These procedures may be summarized as follows.

Geopolymer samples were prepared by mechanically mixing stoichiometric amounts of metakaolin (effective composition $2.3\mathrm{SiO_2}\cdot\mathrm{Al_2O_3}$ from XRF analysis) and alkaline silicate solutions to give products with $\mathrm{Al_2O_3/M_2O} = 1$ and various ratios of $\mathrm{Na/(Na + K)}$ and $\mathrm{SiO_2/M_2O}$. Samples were tightly sealed, cured in a laboratory oven at 40 °C and ambient pressure for 20 h, and then cured in sealed storage vessels at ambient temperature and pressure for 2 weeks.

^{29}Si MAS NMR spectra were obtained at a Larmor frequency of 59.616 MHz with a Varian (Palo Alto, CA) Inova 300 NMR spectrometer (7.05 T), using 5-mm zirconia rotors and a Chemmagnetics broadband MAS probe. A spinning speed of 5 kHz was used, and peak positions were referenced to an external standard of tetramethylsilane. A total of 1024 transients were acquired using a single $\pi/2$ (4.8 μs) pulse and recycle delays of at least 5 times T_1.[6] Line broadening of 50 Hz was applied to all spectra prior to deconvolution.

The $Q^4(m\mathrm{Al})$ distribution of each sample was determined by deconvolution of the ^{29}Si MAS NMR spectra into 5 component peaks corresponding to $m = 0, 1, 2, 3$, and 4. Intensity of the five $Q^4(m\mathrm{Al})$ peaks was allowed to vary freely. Peak positions and widths were allowed to vary subject to matching the nominal composition of each sample while falling within the range of chemical shift and peak width parameters previously observed for amorphous aluminosilicate materials.[6,7,11] Compositions were calculated from NMR data using the procedure outlined by Engelhardt and Michel.[11] This procedure assumes full Loewensteinian behavior, which is not strictly true in the systems of interest, but provides a composition that is at least approximately correct. All deconvoluted compositions were within ±1.5% of nominal values.[6]

Statistical Thermodynamic Model

The basis of the model used in the current work was originally developed by Efstathiadis et al.[27] for application to a 3-component Si−C−H alloy, with the specific case of the 2-component Si−C system discussed in detail. In this work, the model and its derivation will be presented solely on a 2-component basis, replacing Si and C tetrahedra with the tetrahedral $\mathrm{SiO_{4/2}}$ and $\mathrm{AlO_{4/2}}^-$ centers of aluminosilicate network structures. The notation and reasoning of Efstathiadis et al. will be followed where possible, with some steps of the derivation expanded from the earlier discussion to provide greater clarity in application to aluminosilicate materials. The choice of this particular model was largely determined by the fact that the models commonly used in description of

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Al−Si ordering in minerals, particularly the cluster variation method[28] and Monte Carlo simulations on lattices,[26,29] rely on a knowledge of the network topology that is currently unavailable for geopolymeric materials due largely to their X-ray amorphous nature. This also provides the potential for its applicability in largely unmodified form to other amorphous aluminosilicate systems including glasses.

The composition of the geopolymeric binder is represented for the purpose of the thermodynamic model as $(SiO_2)_x(MAlO_2)_{1-x}$, where M is an alkali metal cation and $0.52 < x < 0.70$ for the samples under investigation. Geopolymer compositions are often described in the form $M_2O{\cdot}Al_2O_3{\cdot}rSiO_2$. This latter form is more appropriate in the general description of a geopolymeric binder, but is less convenient for modeling purposes. The effect of the nature of charge-balancing cations on the energetics of ordering in aluminosilicates is incorporated into the model by consideration of the variation of bond energies with cation charge density.

As was noted previously, the energetic basis of chemical ordering in geopolymers is primarily due to the exothermicity of eq 1. The enthalpy of this reaction is dependent on several factors including the cations present and the positions of the centers within the network structure.[7,19,30] This energy is therefore treated as a model parameter denoted Ω, equivalent to the parameters J_1 of Bosenick et al.[31] and W_1 of Herrero.[32] Ω is defined by eq 2, where $E(\text{I}-\text{O}-\text{J})$ represents the energy of a bond linking tetrahedral centers I and J.

$$\Omega = 2E(\text{Si}-\text{O}-\text{Al}) - E(\text{Si}-\text{O}-\text{Si}) - E(\text{Al}-\text{O}-\text{Al}) \quad (2)$$

It is generally understood that bond ordering energies in minerals are insensitive to composition provided that the variation is only in the ratio of the ordering cations, in this case Si and Al,[31] and so any possible dependence of Ω on x will not be considered. However, it is entirely possible that Ω will change in the presence of different charge-balancing cations, and this will be considered in the application of the model to the different geopolymeric systems under investigation. Framework cation substitution in the second coordination sphere of a particular tetrahedral site has been calculated to contribute approximately ±20% to the value of Ω.[33] However, this effect causes highly significant complications in modeling, and is therefore often neglected in simulations.[28,34] For the sake of simplicity, this effect will not be considered explicitly in this model, but rather will be discussed later as a potential source of error.

The Gibbs free energy of mixing (network formation), G_M, may then be expressed in terms of the entropy and enthalpy of mixing:

$$G_M = H_M - TS_M \quad (3)$$

The entropy of mixing is given by the Boltzmann equation, eq 4:

$$S_M = k_B \ln \Gamma \quad (4)$$

where k_B is Boltzmann's constant and Γ is the number of distinct states the system may occupy. Γ is then given by the product $h(x)\Gamma_{Si}\Gamma_{Al}$, where Γ_I is the number of possible configurations of tetrahedral sites containing framework cation I.[27] The factor $h(x)$, $0 < h(x) < 1$, occurs because the product $\Gamma_{Si}\Gamma_{Al}$ necessarily includes many unphysical configurations due to the method of separately counting the configurations of Si and Al centers. A means of estimating $h(x)$ for a multicomponent solid solution is given by Onabe,[35] whereby it may be seen to be dependent only on composition for a system of given size. The primary intention of this calculation is to minimize G_M as given by eq 3 with respect to the degree of ordering rather than to calculate the most accurate possible expression for G_M. Therefore, the term $k_B \ln(h(x))$ obtained by substitution of the expression for Γ into eq 4, being both negligible in magnitude compared to the other terms in the expression for G_M and unimportant to the energy minimization procedure, will be omitted entirely from calculations in the current work.

The assumption that the free energy of a geopolymeric binder is minimized, upon which this model is fundamentally based, requires that chemical ordering within the system is at or very close to its thermodynamic equilibrium value. Several previous studies[36−39] have found that the rates of silicate and aluminate exchange in aluminosilicate solutions are sufficiently fast that the solution phase present in a geopolymeric synthesis may be considered to be very close to thermodynamic equilibrium throughout the setting process. The highly stable cage-like silicate anions which are the commonly cited exception to this principle of very rapid exchange[40] are not expected to be present to a significant degree in these systems due to the absence of the large organic cations by which they are selectively stabilized. Therefore, the assumption of thermodynamic equilibrium, and consequently the validity of the free energy minimization approach, is justified.

Following the arguments of Yin and Smith[41] and Efstathiadis et al.[27] and due to the equivalency of each of the 4 bonds linked to a given tetrahedral site, eqs 5 and 6 for Γ_{Si} and Γ_{Al}, respectively, may be obtained. These expressions relate to a system containing N tetrahedral centers, $N(\text{Si}) = xN$ of which are silicon and $N(\text{Al}) = (1 - x)N$ are aluminum, with $N_{I,J}$ defined[27] as the concentration of centers of type I bonded via I−O−J bonds to sites of type J. It must also be noted that $N_{Al,Si} = N_{Si,Al}$.

$$\Gamma_{Si} = \left(\frac{N(\text{Si})!}{N_{Si,Si}!N_{Si,Al}!}\right)^4 \quad (5)$$

$$\Gamma_{Al} = \left(\frac{N(\text{Al})!}{N_{Al,Al}!N_{Si,Al}!}\right)^4 \quad (6)$$

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The entropy of mixing may then be expressed, following substitution of eqs 5 and 6 into eq 4 and removal of the $h(x)$ term, by eq 7.

$$S_M = k_B \ln\left(\left(\frac{N(\mathrm{Si})!}{N_{\mathrm{Si,Si}}!N_{\mathrm{Si,Al}}!}\right)^4\left(\frac{N(\mathrm{Al})!}{N_{\mathrm{Al,Al}}!N_{\mathrm{Si,Al}}!}\right)^4\right) \tag{7}$$

By application of Stirling's approximation to simplify the factorials of large argument eq 8 may be obtained. This expression is given in terms of the "normalized bond concentrations" $n_{\mathrm{I,J}}$ of each type of bond,[27] where $n_{\mathrm{I,J}} = N_{\mathrm{I,J}}/N(\mathrm{Si})$, and is asymptotically correct in the limit of large $N(\mathrm{Si})$. Details of the derivation of eq 8 are supplied in Appendix A.

$$S_M = -4k_B N(\mathrm{Si})\left[n_{\mathrm{Si,Si}}\ln(n_{\mathrm{Si,Si}}) + n_{\mathrm{Al,Al}}\ln(n_{\mathrm{Al,Al}}) + 2n_{\mathrm{Si,Al}}\ln(n_{\mathrm{Si,Al}}) + \frac{1-x}{x}\ln\left(\frac{x}{1-x}\right)\right] \tag{8}$$

The enthalpy of mixing for a system of N atoms may be simply expressed in terms of heats of formation of free tetrahedra $H_0(\mathrm{I})$ and bond energies $E(\mathrm{I{-}O{-}J})$ by eq 9.[27] The expression for the bond energy contribution to this equation is developed by considering each tetrahedral site in turn, and summing the enthalpy contribution of the bonds from it to its neighbors. There are 4 bonds from each atom. Because every bond is therefore counted twice, once at each end of the bond, each time a bond I−O-J is counted must contribute $^1/_2E(\mathrm{I{-}O{-}J})$ to the total system energy. Counting all bonds from all atoms in the system then gives a total bond energy of $4x \times (^1/_2)(n_{\mathrm{Si,Si}} + n_{\mathrm{Si,Al}} + n_{\mathrm{Al,Si}} + n_{\mathrm{Al,Al}})$. Recognizing that $n_{\mathrm{Al,Si}} = n_{\mathrm{Si,Al}}$ then gives eq 9 in its final form.

$$H_M = N(\mathrm{Si})\left[H_0(\mathrm{SiO_{4/2}}) + \frac{1-x}{x}H_0(\mathrm{MAlO_{4/2}}) - 2n_{\mathrm{Si,Si}}E(\mathrm{Si{-}O{-}Si}) - 4n_{\mathrm{Si,Al}}E(\mathrm{Si{-}O{-}Al}) - 2n_{\mathrm{Al,Al}}E(\mathrm{Al{-}O{-}Al})\right] \tag{9}$$

Equations 3, 8, and 9 may then be readily combined to give an expression for the Gibbs energy of mixing for a system of N tetrahedral centers in terms of normalized bond concentrations. Differentiation of this expression with respect to $n_{\mathrm{Si,Si}}$, with the observation that $\partial n_{\mathrm{Al,Al}}/\partial n_{\mathrm{Si,Si}} = 1$ and $\partial n_{\mathrm{Si,Al}}/\partial n_{\mathrm{Si,Si}} = -1$ from the definitions of the normalized bond concentrations, allows the use of eq 2 to replace the combination of $E(\mathrm{I - O - J})$ terms by Ω. Setting $\partial G_M/\partial n_{\mathrm{Si,Si}} = 0$ gives eq 10, comparable to eq 13 of Efstathiadis et al.[27] Full details of the derivation of this equation are provided in Appendix B.

$$\frac{n_{\mathrm{Si,Al}}^2}{n_{\mathrm{Si,Si}}n_{\mathrm{Al,Al}}} = \exp\left(\frac{\Omega}{2k_BT}\right) \tag{10}$$

Combining eq 10 with the fundamental bond concentration relationships for a binary system (eqs 11 and 12) and solving algebraically, eq 13 is obtained. This is then an analytical expression for the degree of Si−O−Al bonding in terms of the concentration, bond energy penalty, and the temperature of formation. A synthesis temperature of 40 °C is used throughout this work.[6]

$$n_{\mathrm{Si,Si}} + n_{\mathrm{Si,Al}} = 1 \tag{11}$$

$$n_{\mathrm{Si,Al}} + n_{\mathrm{Al,Al}} = \frac{1-x}{x} \tag{12}$$

$$n_{\mathrm{Si,Al}} = \frac{\frac{1}{x}\exp\left(\frac{\Omega}{2k_BT}\right) - \sqrt{\left(\left(\frac{1}{x} - 2\right)\exp\left(\frac{\Omega}{2k_BT}\right) + 2\right)^2 + 4\left(\exp\left(\frac{\Omega}{2k_BT}\right) - 1\right)}}{2\left(\exp\left(\frac{\Omega}{2k_BT}\right) - 1\right)} \tag{13}$$

Equation 13 may then be used in conjunction with eqs 11 and 12 to calculate the total number of each type of bond present in the system for a given composition x and energy penalty Ω. Next, the relative fraction of each type of tetrahedral center, $Q^4(m\mathrm{Al})$ and $q^4(m\mathrm{Al})$, present must be calculated.

The distribution of the bonds among the tetrahedra is assumed to be essentially random, neglecting next-nearest neighbor effects. This appears to contradict the often-cited principle known as Dempsey's rule which suggests that, specifically for zeolitic framework structures but also for aluminosilicates in general, linkages of the form Al−O−Si−O−Al are unfavorable.[42] Justification of this "rule" was based on electrostatic considerations, stating that the negatively charged aluminum centers will be located as far from each other as possible. A number of analyses of lattice ordering in faujasites by ^{29}Si MAS NMR via nearest-neighbor (T−O−T, where T represents Si or Al) and/or next-nearest-neighbor (T−O−T−O−T) interactions[32,43,44] showed preferential but not exclusive obedience to Dempsey's rule. However, lattice energy calculations on high-silica (Si/Al > 5) zeolites have shown a tendency toward Al−O−Si−O−Al linkage formation,[45] contrary to Dempsey's rule. This suggests that any invocation of Dempsey's rule in description of aluminosilicate ordering must be undertaken with a significant degree of caution. Next-nearest-neighbor interactions are not included explicitly in this model, but will be discussed as a possible source of error in the application of the model to a geopolymeric material.

Application of a random bond distribution model then allows the calculation of $F_{\mathrm{Si}}(m)$ and $F_{\mathrm{Al}}(m)$, the fraction of all tetrahedra present that are $Q^4(m\mathrm{Al})$ and $q^4(m\mathrm{Al})$ respectively, as presented in Table 1. The factors of $x^4/(1-x)^3$

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Table 1. Tetrahedron Fractions Calculated from Random Bond Distribution

Si sites	$F_{Si}(m)$	Al sites	$F_{Al}(m)$
Q^4(0Al)	$xn^4_{Si,Si}$	q^4(0Al)	$\frac{x^4}{(1-x)^3}n^4_{Si,Al}$
Q^4(1Al)	$4xn^3_{Si,Si}n_{Si,Al}$	q^4(1Al)	$4\frac{x^4}{(1-x)^3}n^3_{Si,Al}n_{Al,Al}$
Q^4(2Al)	$6xn^2_{Si,Si}\ n^2_{Si,Al}$	q^4(2Al)	$6\frac{x^4}{(1-x)^3}n^2_{Si,Al}\ n^2_{Al,Al}$
Q^4(3Al)	$4xn_{Si,Si}n^3_{Si,Al}$	q^4(3Al)	$4\frac{x^4}{(1-x)^3}n_{Si,Al}n^3_{Al,Al}$
Q^4(4Al)	$xn^4_{Si,Al}$	q^4(4Al)	$\frac{x^4}{(1-x)^3}n^4_{Al,Al}$

observed in the aluminum site fractions are introduced through the definition of $n_{I,J} = N_{I,J}/N(\mathrm{Si})$. The coefficients 1,4,6,4,1 are generated by the equivalence of the different arrangements of mAl and $(4 - m)$Si centers around a given tetrahedral site, thereby providing each value of m with a degeneracy factor calculated from the binomial distribution.[41]

Only silicon sites are directly observable by ^{29}Si MAS NMR, so the calculated quantity available for comparison to experimental data will be $F_{Si}(m)/x$, the fraction of the silicon present that is coordinated to m aluminum sites. Recent work has shown that, in some cases, it is possible to use ^{27}Al MAS NMR to obtain quantitative information regarding q^4(mAl) distribution in certain minerals.[46] However, analysis of these data requires knowledge of the framework topology, which is not available for geopolymers due to their largely amorphous nature.

Application of the Model to Experimental Data

Fitting of the statistical thermodynamic model to the experimental data requires the estimation of the energy penalty Ω for each set of data. Selected literature values for this parameter in a range of aluminosilicate systems and in the presence of a variety of charge-balancing cations are given in Table 2. These values are divided into those determined experimentally and those calculated by a variety of simulation methods. Bosenick et al.[31] reviewed computational studies of cation ordering, and compiled a set of literature data for aluminosilicates which may be used to supplement those given here. Error values are presented where given in the original work.

A number of authors over the past 25 years have carried out ab initio calculations on aluminosilicate clusters with the aim of calculating Ω. In 1989, Sauer[52] reviewed the then-current literature relating to ab initio calculations on aluminosilicate ordering, citing a number of calculated values in the range of 400−500 kJ/mol for Ω in dimeric clusters and values exceeding 120 kJ/mol in four- and five-membered rings. More recent calculations shown in Table 2 have given values more closely resembling those observed experimentally, suggesting that these early higher values must be treated with a significant degree of caution. However, it remains obvious that, in general, calculated and simulated values of Ω are higher than those obtained experimentally. Tossell[53] noted a decrease in Ω of approximately 22 kJ/mol with addition of Na^+ cations to each of the bridging oxygens of a noncharge-balanced 4-ring. Incorporation of an effect of this magnitude into the noncharge-balanced ab initio calculations outlined in Table 2 gives values of Ω in the order of 53−55 kJ/mol, which agree more closely with the results of other simulations and experiments than if charge-balancing were neglected. The effects of different cations on ab initio calculations of Ω have not been fully quantified, with McConnell et al.[50] finding no significant difference in the calculated energies of kalsilite structures either with localized K^+ ions or with a uniform background charge referred to as "jellium".

Other than to note that calculations and simulations generally seem to be overestimating experimental data for comparable materials, it is very difficult to discern a clear trend in Ω with regard to either the charge or radius of the charge-balancing cations present from the data in Table 2. Myers[54] observed that energy penalties calculated from empirical potentials are generally too high by approximately 10 kJ/mol due to difficulties in treatment of covalent bonding. The graphical presentation of Bosenick et al.[31] presents similar difficulties in trend identification with respect to charge-balancing cations. However, the work of Myers does

Table 2. Selected Literature Data for Energy Penalty Parameter Ω

experimental source	Ω (kJ/mol)	comment
Phillips et al. (2000)[9]	26 ± 3	β-eucryptite, NMR/calorimetry
Lee & Stebbins (1999)[7]	31 ± 8	Na-aluminosilicate glass, NMR
	16 ± 2	Ca-aluminosilicate glass, NMR
Phillips et al. (1992)[8]	39 ± 12	synthetic anorthite, NMR/calorimetry
Carpenter (1991)[47]	14 ± 4	anorthite (minimum value), calorimetry
Navrotsky et al. (1985)[30]	22.6	Na-aluminosilicate glass, calorimetry
	9.2	Ca-aluminosilicate glass, calorimetry
Putnis & Angel (1985)[48]	25	albite, NMR/calorimetry
	34	cordierite, NMR/calorimetry

simulated/calculated source	Ω (kJ/mol)	comment
Tossell (2002)[49]	73 ± 2	$Al_2Si_2O_4(OH,H)_8^{2-}$ ring, ab initio, various basis sets
Myers et al. (1998)[34]	32	anorthite, Monte Carlo simulation
McConnell et al. (1997)[50]	34 ± 5	kalsilite, ab initio total energy calculation
Catlow et al. (1996)[21]	75	$Al_2Si_2O_4(OH)_8^{2-}$ ring, ab initio
	162	hydrated $Al_2Si_2O_4(OH)_8^{2-}$ ring, ab initio/MM
Dove & Heine (1996)[29]	40	cordierite, Monte Carlo simulation
Bell et al. (1992)[20]	40	zeolite NaA, lattice energy calculation
Earley (1992)[51]	43	aluminosilicate cubic octamer $(Q^3,q^3)_8$, semiempirical AM1 Hamiltonian
Cohen & Burnham (1985)[19]	24	Ca-Tschermak's pyroxene, exchange across chains, lattice energy calculation

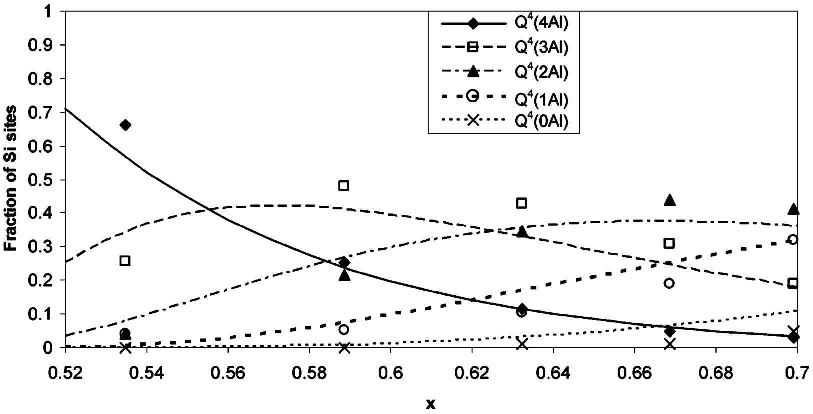

Figure 1. Comparison of model predictions to the deconvoluted experimental NMR data of Duxson et al.[6] for Na geopolymers, $\Omega = 40$ kJ/mol. Lines represent model predictions and points are experimental data.

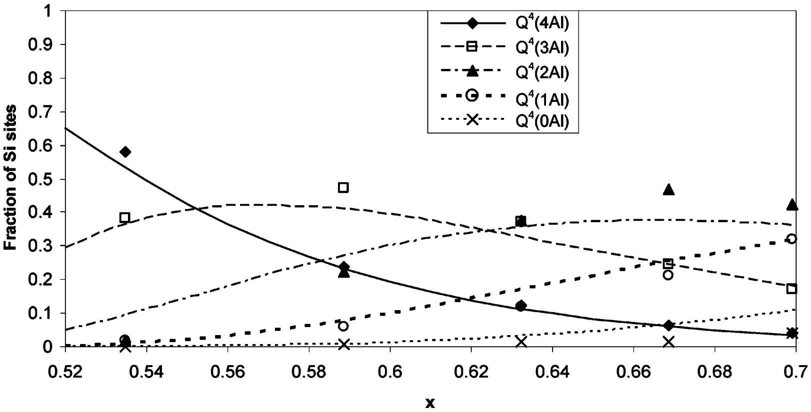

Figure 2. Comparison of model predictions to the deconvoluted experimental NMR data of Duxson et al.[6] for K geopolymers, $\Omega = 30$ kJ/mol. Lines represent model predictions and points are experimental data.

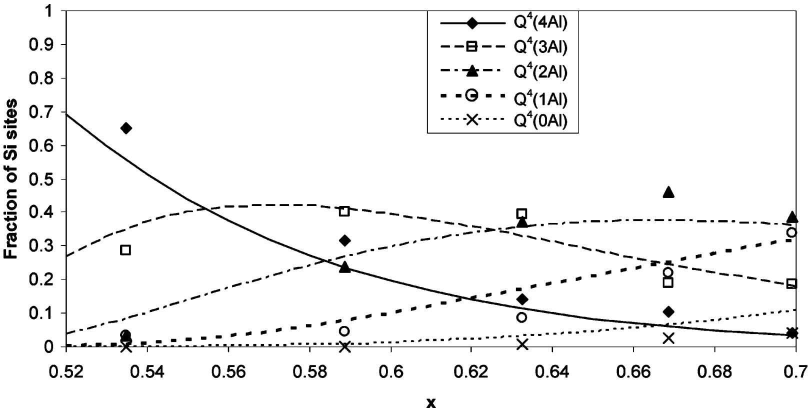

Figure 3. Comparison of model predictions to the deconvoluted experimental NMR data of Duxson et al.[6] for mixed (1:1) Na/K geopolymers, $\Omega = 35$ kJ/mol. Lines represent model predictions and points are experimental data.

provide potentially valuable information regarding the application of energy penalty data obtained from pure systems to systems of intermediate composition. In investigating feldspar structures of compositions corresponding to albite, anorthite, and an intermediate composition midway between the two endmembers, it was found that the nearest-neighbor energy penalty in the mixed system was generally equal to or very slightly less than the arithmetic mean of the endmember energy penalties.[54] This fact will be used in the analysis of the mixed Na/K geopolymeric system, meaning that the energy penalty of this system will be taken to be the mean of the parameters for the pure Na and K systems. These parameters must themselves be estimated by the simple expedient of choosing the value of Ω that gives the best fit to the experimental data for each pure system. This fitting

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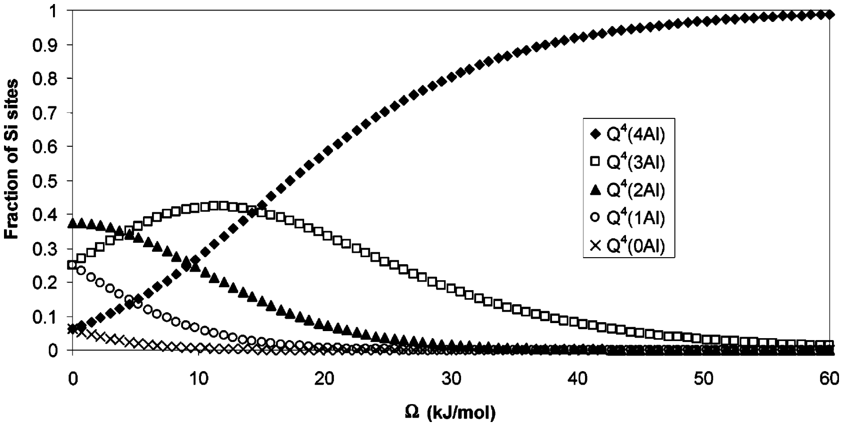

Figure 4. Variation of silicate center speciation with changes in Ω, $x = 0.500$.

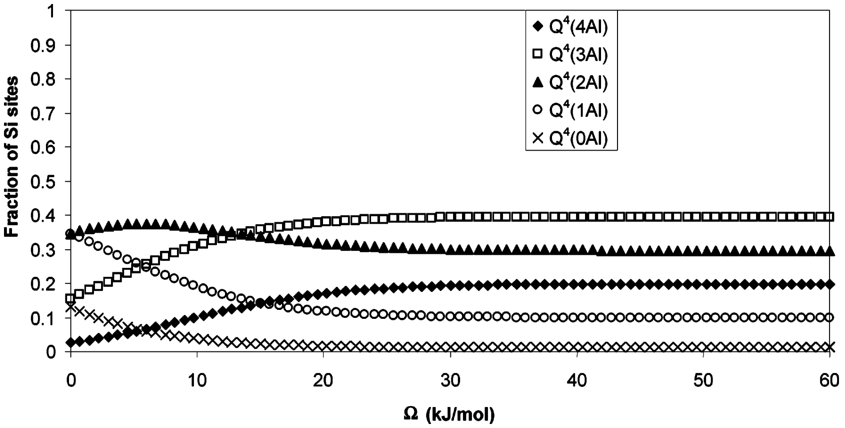

Figure 5. Variation of silicate center speciation with changes in Ω, $x = 0.600$.

procedure will be discussed further in the next section of this paper.

Results and Discussion

Figures 1−3 show the application of the statistical thermodynamic model developed in the previous section of this paper to the experimental ^{29}Si MAS NMR data[6] for Na, K, and mixed Na−K metakaolin-based geopolymers, respectively. Appropriate values of Ω were found to be 40 kJ/mol for Na geopolymers and 30 kJ/mol for K geopolymers, comparable to the values given in Table 2. Taking an arithmetic mean of the values for pure Na and K systems gives $\Omega = 35$ kJ/mol for the mixed Na/K system.

From these graphs, it may be seen that the proposed model is generally applicable to description of the Si/Al ordering behavior of geopolymers. Next-nearest-neighbor interactions have been estimated, as discussed previously, to be approximately 20% of the magnitude of the nearest-neighbor interactions upon which this model is exclusively based.[33] Therefore, the fact that this simplified model matches all trends in the experimental data across a wide range of geopolymer compositions for two different charge-balancing cations and also for mixed-cation systems with the use of only two empirically determined parameters—one for each charge-balancing cation—is highly noteworthy. The fact that these parameters are found to fall in exactly the same range (30−40 kJ/mol) as the majority of the experimental and calculated energy penalty parameter values obtained from the literature is also significant, further validating the model and providing a means of comparison on an atomic scale between geopolymeric materials and other aluminosilicate compounds including zeolites, other minerals, and glasses.

The application of a model initially developed for investigation of ordering behavior in Si−C−H alloys to the very different chemistry of an aluminosilicate geopolymer is therefore justified, and provides a means of studying the balance between enthalpic and entropic considerations in the formation of geopolymers. If the energy penalty was infinitely high, enthalpy would dominate the Gibbs energy minimization, and full ordering would occur. For a zero energy penalty, entropic effects would dominate, and a random cation distribution would be produced. The finite values of Ω found to apply in geopolymeric materials show that the actual situation falls between these two extremes.

The effect of variations in the energy penalty parameter on the calculated distribution of tetrahedral sites at different compositions is depicted in Figures 4 and 5. For a composition of $x = 0.500$, the effect of variations in the energy penalty may be seen from Figure 4 to decrease significantly as the energy penalty increases. The energy penalties used in this model may be seen to fall in the region just below where changes in energy penalty have negligible effect on speciation at this concentration. However, Figure 5 shows that the effect of changing Ω at higher silica content is much lower. This matches the observed trend in the experimental data where, as was noted previously,[6] the effect of the different charge-balancing cations decreases with increasing silica content. However, the primary consequence of this decrease in sensitivity is that the model predictions are only significantly affected by the choice of Ω at the lower-silica compositions, and so it is these data that are most useful in the estimation of the value of Ω for each different charge-balancing cation. Therefore, the values of Ω used in this model for the Na and mixed Na/K geopolymers, 40 and 35 kJ/mol, respectively, should generally be considered accurate only to within approximately ±5 kJ/mol. The value used for the K geopolymers, 30 kJ/mol, may be considered to be more accurate as it falls within the region in which the speciation is still significantly sensitive to Ω, and therefore is estimated to be accurate to within ±2 kJ/mol.

A probable source of some error in the application of this model to geopolymers is the presence of unreacted metakaolin in the samples. All previously published microscopic and/or spectroscopic studies of geopolymers have shown a significant but largely unquantifiable degree of unreacted raw material within the binder phase, particularly when low levels of soluble silica are present in the activating solution.[55] In this case, using metakaolin as a solid aluminosilicate source, the presence of unreacted raw material is likely to be evidenced by increased levels of Q^4(1Al) silicon centers, with three bonds to other silicon centers within the silica layers of the metakaolin structure, and a single bond to a tetrahedral aluminum center in the neighboring aluminate layer.[56] This is observed in each of Figures 1−3, where all sets of experimental data display the presence of the Q^4(1Al) species at $x = 0.535$ while the model predicts that it will be negligible. However, the fact that in each case the observed abundance of Q^4(1Al) equals or exceeds that of Q^4(2Al) shows that this is genuinely due to the presence of unreacted metakaolin rather than a deficiency in the model.

The presence of unreacted metakaolin in the low-silica samples may also be used to account for the significant underestimation by the model of the Q^4(4Al) content of the Na and Na/K geopolymers at low silica content. It has been observed that the initial stage of dissolution of many aluminosilicate minerals and clays in alkaline solution displays preferential release of aluminum above that which would be expected from the mineral stoichiometry, leading to silica-rich undissolved material.[57−60] A previous study investigating a wide range of aluminosilicate minerals to evaluate their suitability for use as raw materials in geopolymerization[61] also found that the partial dissolution of most of these minerals in highly alkaline solutions left a slightly aluminum-depleted remnant solid phase.

Therefore, it is reasonable to expect that the portion of a geopolymeric binder formed by reprecipitation of the dissolved components of the initial metakaolin will be slightly aluminum-rich when compared to the superficial composition of the system. This means that the values of x used to plot Figures 1−3 may be slightly higher than the actual binder composition, with increasing error at lower silica content. This is not shown as horizontal error bars on these graphs due to the difficulties in quantifying both the degree of unreacted material present and also the degree to which its aluminum content is depleted. However, to illustrate this point, if it is estimated that 10% of the metakaolin remains unreacted but aluminum-depleted to $x = 0.600$ in a sample of superficial composition $x = 0.535$, subtraction of the unreacted material gives an actual binder composition of $x_{corr} = 0.528$. This corresponds to only 3% additional Al dissolution above that which would be observed if dissolution were congruent, in a sample that is 90% reacted. Applying this estimated sample composition correction to all data, Figures 6−8 are obtained.

From Figures 6−8 it may be observed that the effect of the sample composition correction on the fit of the model to the data for the samples with little or no added soluble silicate is significant, with accuracy of the model predictions improved dramatically. It must be noted that this correction is simply an estimate of the degree of unreacted material and the degree to which its aluminum content is depleted. The isolation and analysis of unreacted metakaolin from within geopolymeric materials has to date proved impossible, although work in developing methods of quantifying the degree of reaction in geopolymeric materials is ongoing.[55] However, the remarkable improvements in the fit of the model through the application of such a simple correction justify its use in this instance.

The other possible source of error in the application of this model to geopolymerization could be the next-nearest-neighbor (Dempsey's rule) effects mentioned previously. At the higher silica contents, the model slightly underestimates the level of Q^4(2Al) present, while overestimating Q^4(0Al). Exact quantification of the Q^4(0Al) peak in the deconvolution procedure was not always straightforward, as this peak is often very small and hence difficult to distinguish from the background level of the spectra, so no great significance should be drawn from the difficulties in model fitting to this peak. In the moderate silica content region, the level of Q^4(3Al) is slightly overestimated at the expense of both Q^4(2Al) and Q^4(4Al).

Dempsey's rule[42] predicts that Al−O−Si−O−Al bonds will be relatively unfavorable. However, while this appears to be true in the high-silica region, the observed behavior in the moderate-silica region appears to run contrary to this principle. In this region, the formation of Q^4(3Al) is expected to be favorable but in fact appears from experimental data to be unfavorable relative to model predictions. This suggests that there are energetic and/or electrostatic effects competing with Dempsey's rule in these systems, possibly with regard to the distribution of charge-balancing cations. As the stoichiometry of a geopolymeric material is such that there is one charge-balancing cation for every negatively charged tetrahedral aluminum site, the moderate-silica samples will also contain significantly more alkali cations than those with the highest silica content. These samples with high cation

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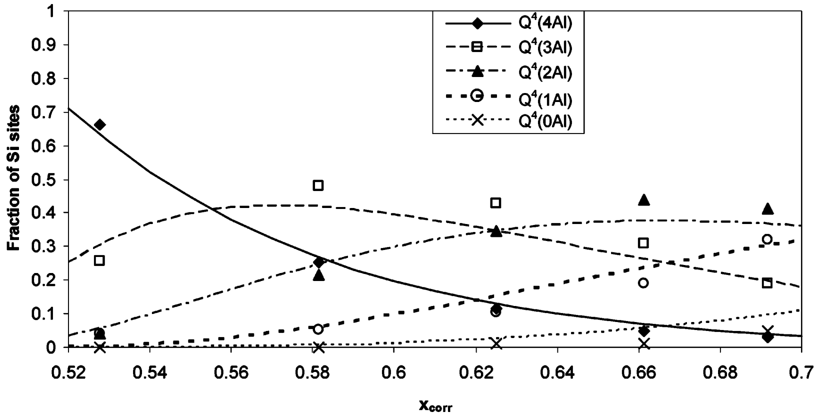

Figure 6. Comparison of model predictions to experimental data with composition corrected for the presence of 10% unreacted, alumina-depleted metakaolin. Na geopolymers, $\Omega = 40$ kJ/mol. Lines represent model predictions and points are experimental data.

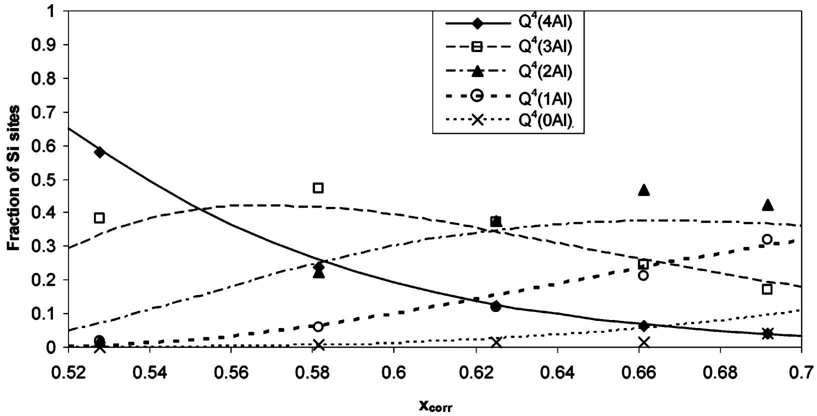

Figure 7. Comparison of model predictions to experimental data with composition corrected for the presence of 10% unreacted, alumina-depleted metakaolin. K geopolymers, $\Omega = 30$ kJ/mol. Lines represent model predictions and points are experimental data.

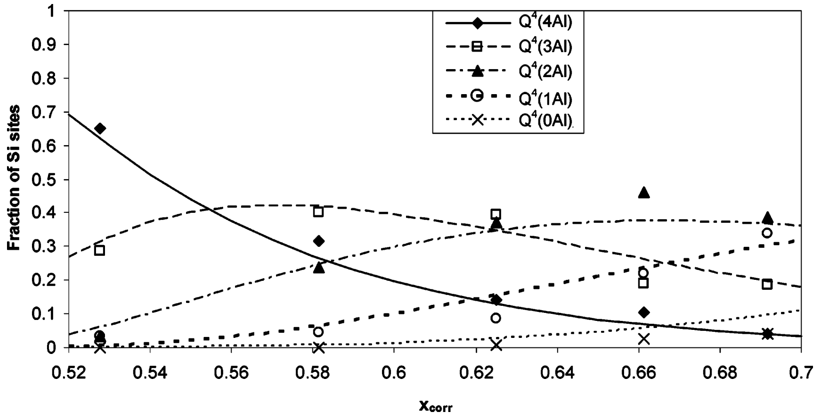

Figure 8. Comparison of model predictions to experimental data with composition corrected for the presence of 10% unreacted, alumina-depleted metakaolin. Mixed Na/K geopolymers, $\Omega = 35$ kJ/mol. Lines represent model predictions and points are experimental data.

density are expected to show deviation from Dempsey's rule behavior, as the positive charges localized on the cations allow negatively charged aluminum sites to be located more closely than would be favorable in the absence of the cations. Some ab initio calculations on aluminosilicate chemistry under geopolymerization conditions have previously been carried out, focused primarily on characterization of mineral dissolution reactions,[62,63] but significant further work applying these techniques to the rearrangement and reprecipitation reactions will be required to determine the validity or otherwise of Dempsey's rule in these systems.

Determination of the degree of Al−O−Al avoidance in geopolymers may prove to be important in the analysis of variations in durability and chemical resistance of these materials. It has been noted previously that high-alumina zeolites become structurally weakened by certain cation-exchange processes, a fact which has been attributed on the atomic scale to breakage of the relatively unstable Al−O−Al bonds.[64] If this is also the case in geopolymeric structures, any attempts to maximize durability of these materials or to tailor chemical resistance to particular environments must

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take into account the degree of Al−O−Al bonding present. By controlling this through manipulation of composition, charge-balancing cations, and synthesis temperature, geopolymers optimized for desired applications may be produced. The results of this investigation suggest that Na geopolymers will inherently have a lesser extent of Al−O−Al formation than K geopolymers at low silica content, and may therefore provide greater durability or chemical resistance in this composition range. Also, lower synthesis temperatures give a lesser extent of Al−O−Al formation, and should therefore be considered if such properties are desired. These suggestions are yet to be tested experimentally, and the effects of variation in the degree of reaction across different cations and temperatures may be found to swamp the effects of Al−O−Al bond instability. However, considering the significant interest in the use of geopolymers as durable, chemically resistant binders in high-risk applications including immobilization of toxic and/or radioactive wastes,[4,65] such effects must be taken into consideration.

The different energy penalty parameters for sodium and potassium charge-balancing cations in geopolymers may also be correlated with the observed differences in the behavior of these cations in geopolymerization. It has previously been both observed[66] and calculated[62] that Na^+ affects the geopolymerization process by accelerating the initial dissolution rate, while K^+ has been observed to accelerate the polycondensation reactions involved in setting.[36,67] A greater extent of crystallinity is also observed in Na-containing systems than in the presence of K.[68] The trend in Ω across the two cations may be used to explain these observations. Na-containing systems, with a higher dissolution rate and slower setting, will have more time and freedom to find a minimum-energy state, and so will be more highly ordered, more crystalline, and display a greater effective energy penalty for bond disordering. K-containing systems, on the other hand, will not have the same freedom to rearrange into lower-energy states due to the faster polycondensation and therefore increased presence and stability of larger silicate and aluminosilicate species, and so will display less crystallinity and a lower energy penalty corresponding to the greater influence of entropic effects.

Conclusion

A statistical thermodynamic model for the investigation of Si/Al ordering within metakaolin-based geopolymers has been presented, and applied via ^{29}Si MAS NMR data to the prediction of silicate speciation within the geopolymeric network structure. Without knowledge of network topology it is only possible to include nearest-neighbor interactions explicitly into the model, and so the model applies Gibbs energy minimization based on the energy penalty incurred when exchanging two Si−O−Al linkages for Si−O−Si and Al−O−Al linkages. This energy penalty is treated as a model parameter, but comparison of the values taken by this parameter in the implementation of the model to literature data for systems containing different charge-balancing cations shows that the calculated parameter values are physically realistic and meaningful. The model uses this energy penalty in calculating the concentrations of Si−O−Si, Si−O−Al, and Al−O−Al bonds in the system to minimize the Gibbs energy. The random distribution of these bonds among tetrahedra then provides a binomial-type expression for calculation of tetrahedron speciation for comparison to ^{29}Si MAS NMR data. Because knowledge of network topology is not required for implementation of this model, application to other amorphous aluminosilicate materials will also be possible.

Possible sources of error in the model are next-nearest-neighbor interactions and the presence of unreacted metakaolin. Implementation of a simple correction to account for the extent of reaction significantly improves the fit of the model to the experimental data at low silica content. Next-nearest-neighbor interactions cannot be explicitly accounted for without knowledge of the network topology of geopolymers, which to date has proven somewhat elusive due to the X-ray amorphous nature of these materials. These interactions are believed to be significant in determining Si/Al ordering in relatively higher-silica geopolymeric materials, but are complicated by the presence of varying degrees of charge-balancing cations associated with the negatively charged tetrahedral aluminum centers.

The trends in the energy penalty parameter across different charge-balancing cations and mixtures of cations may be correlated with the observed differences in the behavior of these cations in geopolymerization. Behavior that has previously been noted, but never explicitly explained from a fundamental level, has been reevaluated and an energetic basis for observed macroscopic behavior has been proposed.

Acknowledgment. This work was funded through the Particulate Fluids Processing Centre (PFPC), a Special Research Centre of the Australian Research Council.

Appendix A. Calculation of the Entropy of Mixing

Equation A1 reproduces eq 7, an expression for the entropy of mixing in terms of the system composition and number of each type of bonds present:

$$S_M = k_B \ln\left(\left(\frac{N(\mathrm{Si})!}{N_{\mathrm{Si,Si}}!N_{\mathrm{Si,Al}}!}\right)^4\left(\frac{N(\mathrm{Al})!}{N_{\mathrm{Al,Al}}!N_{\mathrm{Si,Al}}!}\right)^4\right) \qquad (A1)$$

Simplifying:

$$S_M = 4k_B \ln\left(\frac{N(\mathrm{Si})!N(\mathrm{Al})!}{N_{\mathrm{Si,Si}}!N_{\mathrm{Al,Al}}!(N_{\mathrm{Si,Al}}!)^2}\right) \qquad (A2)$$

Equation A3 is Stirling's approximation for factorials of large argument (Abramowitz and Stegun, Handbook of Mathematical Functions, 1964):

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$$N! \approx \sqrt{2\pi N}e^{-N}N^{N} \tag{A3}$$

Applying this approximation to the factorials in eq A2 gives eq A4.

$$S_{\mathrm{M}} = 4k_{\mathrm{B}}\ln\left(\frac{1}{4\pi^{2}}\sqrt{\frac{N(\mathrm{Si})N(\mathrm{Al})}{N_{\mathrm{Si,Si}}N_{\mathrm{Al,Al}}N_{\mathrm{Si,Al}}{}^{2}}}\cdot e^{N_{\mathrm{Si,Si}}+2N_{\mathrm{Si,Al}}+N_{\mathrm{Al,Al}}-N(\mathrm{Si})-N(\mathrm{Al})}\cdot\frac{N(\mathrm{Si})^{N(\mathrm{Si})}N(\mathrm{Al})^{N(\mathrm{Al})}}{N_{\mathrm{Si,Si}}{}^{N_{\mathrm{Si,Si}}}N_{\mathrm{Al,Al}}{}^{N_{\mathrm{Al,Al}}}N_{\mathrm{Si,Al}}{}^{2N_{\mathrm{Si,Al}}}}\right) \tag{A4}$$

In the application of Stirling's approximation, it is assumed that the number of atoms in the system is very large. Therefore, the square root term in eq A4 is negligible in magnitude compared to the terms of the form N^{N}, and the exponential term may be seen by comparison with the mole balances of eqs 11 and 12 to evaluate to unity. Discarding these terms and simplifying gives eq A5.

$$S_{\mathrm{M}} = 4k_{\mathrm{B}}\{N(\mathrm{Si})\ln(N(\mathrm{Si})) + N(\mathrm{Al})\ln(N(\mathrm{Al})) - N_{\mathrm{Si,Si}}\ln(N_{\mathrm{Si,Si}}) - N_{\mathrm{Al,Al}}\ln(N_{\mathrm{Al,Al}}) - 2N_{\mathrm{Si,Al}}\ln(N_{\mathrm{Si,Al}})\} \tag{A5}$$

Expressing eq A5 in terms of normalized bond concentrations $n_{\mathrm{I,J}} = N_{\mathrm{I,J}}/N(\mathrm{Si})$ and $x = N(\mathrm{Si})/N_{\mathrm{total}}$ yields eq A6:

$$S_{\mathrm{M}} = 4k_{\mathrm{B}}N(\mathrm{Si})\left[\ln(N(\mathrm{Si})) + \frac{1-x}{x}\ln\left(\frac{1-x}{x}N(\mathrm{Si})\right) - n_{\mathrm{Si,Si}}\ln(N(\mathrm{Si})n_{\mathrm{Si,Si}}) - n_{\mathrm{Al,Al}}\ln(N(\mathrm{Si})n_{\mathrm{Al,Al}}) - 2n_{\mathrm{Si,Al}}\ln(N(\mathrm{Si})n_{\mathrm{Si,Al}})\right] \tag{A6}$$

Collecting terms:

$$S_{\mathrm{M}} = 4k_{\mathrm{B}}N(\mathrm{Si})\left\{\left[1 + \frac{1-x}{x} - n_{\mathrm{Si,Si}} - n_{\mathrm{Al,Al}} - 2n_{\mathrm{Si,Al}}\right]\ln(N(\mathrm{Si})) + \frac{1-x}{x}\ln\left(\frac{1-x}{x}\right) - n_{\mathrm{Si,Si}}\ln(n_{\mathrm{Si,Si}}) - n_{\mathrm{Al,Al}}\ln(n_{\mathrm{Al,Al}}) - 2n_{\mathrm{Si,Al}}\ln(n_{\mathrm{Si,Al}})\right\} \tag{A7}$$

The term inside the square brackets may be seen from eqs 11 and 12 to be zero. Rearranging and taking a negative sign outside the curly braces then gives eq A8, which is identical to eq 8.

$$S_{\mathrm{M}} = -4k_{\mathrm{B}}N(\mathrm{Si})\left[n_{\mathrm{Si,Si}}\ln(n_{\mathrm{Si,Si}}) + n_{\mathrm{Al,Al}}\ln(n_{\mathrm{Al,Al}}) + 2n_{\mathrm{Si,Al}}\ln(n_{\mathrm{Si,Al}}) + \frac{1-x}{x}\ln\left(\frac{x}{1-x}\right)\right] \tag{A8}$$

Appendix B. Minimization of Gibbs Free Energy

Combining eqs 3, 8, and 9 gives eq B1, a detailed expression for the Gibbs energy of the system:

$$G_{\mathrm{M}} = N(\mathrm{Si})\left[\mathrm{H}_0(\mathrm{SiO}_{4/2}) + \frac{1-x}{x}\mathrm{H}_0(\mathrm{MAlO}_{4/2}) - 2n_{\mathrm{Si,Si}}E(\mathrm{Si{-}O{-}Si}) - 4n_{\mathrm{Si,Al}}E(\mathrm{Si{-}O{-}Al}) - 2n_{\mathrm{Al,Al}}E(\mathrm{Al{-}O{-}Al})\right] - 4Tk_{\mathrm{B}}N(\mathrm{Si})\left[n_{\mathrm{Si,Si}}\ln(n_{\mathrm{Si,Si}}) + n_{\mathrm{Al,Al}}\ln(n_{\mathrm{Al,Al}}) + 2n_{\mathrm{Si,Al}}\ln(n_{\mathrm{Si,Al}}) + \frac{1-x}{x}\ln\left(\frac{x}{1-x}\right)\right] \tag{B1}$$

Differentiating with respect to $n_{\mathrm{Si,Si}}$ then yields eq B2:

$$\frac{\partial \mathrm{G}_{\mathrm{M}}}{\partial n_{\mathrm{Si,Si}}} = N(\mathrm{Si})\left[-2E(\mathrm{Si{-}O{-}Si}) - 4\frac{\partial n_{\mathrm{Si,Al}}}{\partial n_{\mathrm{Si,Si}}}E(\mathrm{Si{-}O{-}Al}) - 2\frac{\partial n_{\mathrm{Al,Al}}}{\partial n_{\mathrm{Si,Si}}}E(\mathrm{Al{-}O{-}Al})\right] - 4Tk_{\mathrm{B}}N(\mathrm{Si})\left[\ln(n_{\mathrm{Si,Si}}) + 1 + \frac{\partial n_{\mathrm{Al,Al}}}{\partial n_{\mathrm{Si,Si}}}\ln(n_{\mathrm{Al,Al}}) + \frac{\partial n_{\mathrm{Al,Al}}}{\partial n_{\mathrm{Si,Si}}} + 2\frac{\partial n_{\mathrm{Si,Al}}}{\partial n_{\mathrm{Si,Si}}}\ln(n_{\mathrm{Si,Al}}) + 2\frac{\partial n_{\mathrm{Si,Al}}}{\partial n_{\mathrm{Si,Si}}}\right] \tag{B2}$$

Using the relationships $\partial n_{\mathrm{Al,Al}}/\partial n_{\mathrm{Si,Si}} = 1$ and $\partial n_{\mathrm{Si,Al}}/\partial n_{\mathrm{Si,Si}} = -1$ as well as the definition of Ω in eq 2 yields eq B3.

$$\frac{\partial G_{\mathrm{M}}}{\partial n_{\mathrm{Si,Si}}} = -2\Omega N(\mathrm{Si}) - 4Tk_{\mathrm{B}}N(\mathrm{Si})\,[\ln(n_{\mathrm{Si,Si}}) + \ln(n_{\mathrm{Al,Al}}) - 2\ln(n_{\mathrm{Si,Al}})] \tag{B3}$$

Setting $\partial G_{\mathrm{M}}/\partial n_{\mathrm{Si,Si}} = 0$ and rearranging:

$$\ln\left(\frac{n_{\mathrm{Si,Si}}n_{\mathrm{Al,Al}}}{n_{\mathrm{Si,Al}}^{2}}\right) = -\frac{\Omega}{2k_{\mathrm{B}}T} \tag{B4}$$

This is then readily rearranged to give eq 10.

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