

Science Paper

Thermal Expansion of Metal Oxides in Silicate Melts: A Simple Theoretical Analysis

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The isobaric, isochemical coefficient of thermal expansion (α) is the proportionality constant relating $\partial V/V$ and ∂T . Noting that $\partial V/V$ equals $\partial \ln V$ at constant pressure and composition (i.e., P and X):

$$\alpha = \left(\frac{\partial V}{V \partial T} \right)_{P,X} = \left(\frac{\partial \ln V}{\partial T} \right)_{P,X}$$

A polynomial expression for the temperature dependence of $\ln V$ yields direct and accurate calculation of α of melts and glasses. Using the approach, α_G of Na-silicate glasses is shown to be constant between 300 and ~650 K (P and X constant), but it increases linearly with Na₂O content, indicating that α is controlled mostly by Na behaviour. Values of α for a melt or glass are necessarily (thermodynamically) related to the coefficients of thermal expansion of its 'N' melt components (α_N) by:

$$\alpha = \alpha_1 \theta_1 + \alpha_2 \theta_2 + \alpha_3 \theta_3 + \dots + \alpha_N \theta_N$$

where θ represents volume fraction of a component. Calculated $\alpha_{\text{Na}_2\text{O}}$ and α_{SiO_2} values compare satisfactorily with reported values for melts containing ~40–60 mole% Na₂O but are less satisfactory for highly siliceous melts, implying need for refinement of α values.

The Coulombic force of attraction between cation and anion is the primary determinant of the magnitude of α values of alkali and alkaline earths oxides. Their values represent a lower bound on α of 3d and 4f modifier oxides. Values larger than this lower bound likely result from a change in coordination number (CN) from higher to lower CN values of modifier cations. Experimental and molecular dynamics studies indicate that partial charges on NBO (O of Si-O-M moieties) and BO (O of Si-O-Si moieties) are about -0.96 and -0.64 respectively, thus NBOs should be incorporated into the first coordination spheres of modifier cations in preference to BOs. A simple mechanism is proposed whereby NBO-BO exchange occurs and CN of the modifier cation decreases with minimal topological adjustment or energetic cost to the melt.

1. INTRODUCTION

The volumetric properties of silicate melts and glasses are critically important to the glass industry, to igneous petrology, and to the prediction of natural hazards. To give a single example, these properties must be known to determine the buoyancy of magma from mantle to the surface of the Earth, which makes them particularly relevant to the prediction or forecasting of volcanic activity. Explosive volcanism represents a continual and immediate environmental hazard to life. It is also a hazard to the stability of climatic conditions on the short term (a few years), due primarily to contamination of the upper atmosphere and stratos-

phere with volcanic gases and particulate matter. There is, therefore, good reason to expand our understanding of the processes that affect volumetric properties. This study focusses on the isobaric coefficients of thermal expansion of melts and glasses and on the coefficients of thermal expansion of their constituent oxides (α_N , N = metal oxide). Although α values of numerous melts were documented over 60 years ago (Bockris et al., 1956; Tomlinson et al., 1958), there seems to be no discussion of the basic physical-chemical factors that affect the magnitudes and signs of α for glasses or melts. The situation exists because the relationships among α , isothermal compressibility (β) and heat capacities ($C_p - C_v = TV\alpha^2/\beta$) does not provide general,

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fundamental insights into aspects affecting α owing to the specificity of the atomic interactions involved in different systems. Lange and Carmichael (1990) however, offer insight by noting a systematic, inverse relationship between thermal expansion and cationic field strength of the alkali oxides. To understand better the physical chemical aspects contributing to α , the relationship between temperature and the molar volumes of melts and glasses is addressed followed by an investigation into the relationship between α of a melt (or glass) and α of its 'N' component oxides (α_N). We then address the effects that Coulombic interactions have on α_N , followed by aspects affecting coordination numbers (CNs) of modifier cations, including discussion of a mechanism by which CNs are altered.

2. MOLAR VOLUMES AND THERMAL EXPANSION

2.1. Functional relationships

Coefficients of thermal expansion (α) cannot be measured directly. The densities of melts or glasses first must be determined as a function of temperature at a *constant pressure (P) and composition (X)*. With densities known, molar volumes (V), then α , can be calculated. Values of α traditionally were determined using a finite difference approach ($\alpha \sim [\Delta V/\Delta T]/V_{Av}$) derived from the partial differential expression of equation (1), given below. Volumes may be determined, for example, at two temperatures, T_1 and T_2 , from which an average volume ($V_{Av} = [V_{T2} - V_{T1}]/2$) is obtained. Similarly, $\Delta V/\Delta T$ can be evaluated ($[V_{T2} - V_{T1}]/[T_2 - T_1]$) and taken as an approximation to $\partial V/\partial T$, which then may be used to estimate α . A numerical methods approach, using a Taylor series expansion would provide both accurate evaluation of α over a specified temperature range and of its uncertainty over the same range. This, however, should be the focus of a separate study.

Ottonello (1997, p. 254, table 5.22), in his summary of thermal expansion of some crystalline silicates, used the following expression to evaluate the coefficient of thermal expansion, α , as a function of temperature:

$$\alpha = \left(\frac{\partial V}{V \partial T} \right)_{P,X} = a_1 + a_2 T + a_3 T^2 \quad (1)$$

T is temperature, $\partial V/\partial T$ is the partial derivative of volume with respect to temperature of a phase held at constant pressure (P) and composition (X). Values for a_1 , a_2 , a_3 are obtained by fitting volumetric-temperature data. Where temperature alone is varied (P and X are constant), equation (1) can be rewritten as an ordinary differential equation:

$$\alpha = (1/V)dV/dT = a_1 + a_2 T + a_3 T^2 \quad (2)$$

With respect to the differentials:

$$\alpha = (dV/V) = (a_1 + a_2 T + a_3 T^2)dT \quad (3)$$

Integrating both sides of equation (3) (at constant P and X), then combining the constants of integration yields:

$$\ln V_{P,X} = a_1 T + (a_2/2)T^2 + (a_3/3)T^3 + C \quad (4)$$

where C is the constant of integration. It may be eliminated by integrating between two temperature limits. The sub-

scripts indicate that the equation holds only where P and X are constant. Fits of $\ln V_{P,X}$ versus T yield the a_1 , a_2 , a_3 , and C coefficients, from which $V_{P,X}$ and α may be evaluated using respectively, equations (4) and (2). Because the same coefficients are used in evaluations of both $\ln V_{P,X}$ and α , their uncertainties are commensurate.

Not all coefficients may be required to fit volumetric data over limited temperature ranges. Employing only the first polynomial term (a_1) of equation (4) yields:

$$\ln V_{P,X} = a_1 T + C \quad (5)$$

The constant of integration, C, equals $\ln V_{P,X}$ at $T = 0$ K. Integration between two temperature limits eliminates C. Fitting experimental $\ln V_{P,X}$ -T data yields a value for the a_1 fit coefficient, which is the coefficient of thermal expansion for the phase ($\alpha = a_1$; $a_2 = a_3 = 0$). The coefficient of thermal expansion thus is determined directly from the fit to the $\ln V_{P,X}$ -T experimental data. Importantly, a separate fit or calculation is not required to obtain α . The equation pertains to sodic glasses.

Over large temperature ranges volume is likely to be a function of T requiring at least the first two terms on the right side of equation (4) to be used. If so then:

$$\ln V_{P,X} = a_1 T + (a_2/2)T^2 + C \quad (6)$$

A fit to experimental data ($\ln V_{P,X}$ versus T) permits determination of a_1 and a_2 , ($a_3 = 0$) which can be substituted into equation (3) to obtain the value of α for the phase at T. Substitution of the coefficients into equation (3) yields the temperature dependence of α with accuracy commensurate with the fits to the experimental volumes. The fits and fit coefficients, however, are accurate only between the temperature limits of the fits. Where volume follows a *quadratic* expression in temperature (eq 4), a fit of $\ln V_{P,X}$ -T experimental data yields the a_1 , a_2 , a_3 fit coefficients which can be substituted into equations (1) or (2) to obtain α at T. The fit coefficients obtained from equation (4) permit evaluation of both α and $V_{P,X}$ as a function of temperature. By fitting a polynomial of order 'n' to $\ln V_{P,X}$ vs T data to obtain the fit coefficients, the derivative (a polynomial of order 'n-1'), and its coefficients, are immediately obtained which yields α as a function of temperature. The uncertainty in α is commensurate with that of V. A numerical methods approach utilizing a Taylor series rather than an arbitrary polynomial such as equation (4) would be a better approach in that the uncertainty in V and α would be obtained.

2.2. An example: diopsidic melts

The logarithms of the molar volumes of diopsidic melts (V_M) are plotted against T in [figure 1A](#) using the same data as Toplis and Richet (2000, their fig. 7c). The dashed curve represents a least-squares, quadratic fit to the data using equation (6). The derivative of the fit yields the expression for α as a function of temperature. It is linear in T, as shown in [figure 1B](#). The coefficients required to determine α of equation (3) are obtained from the fit coefficients shown in [figure 1A](#). Noting the constant, $a_2/2$ of equation (6), α becomes:

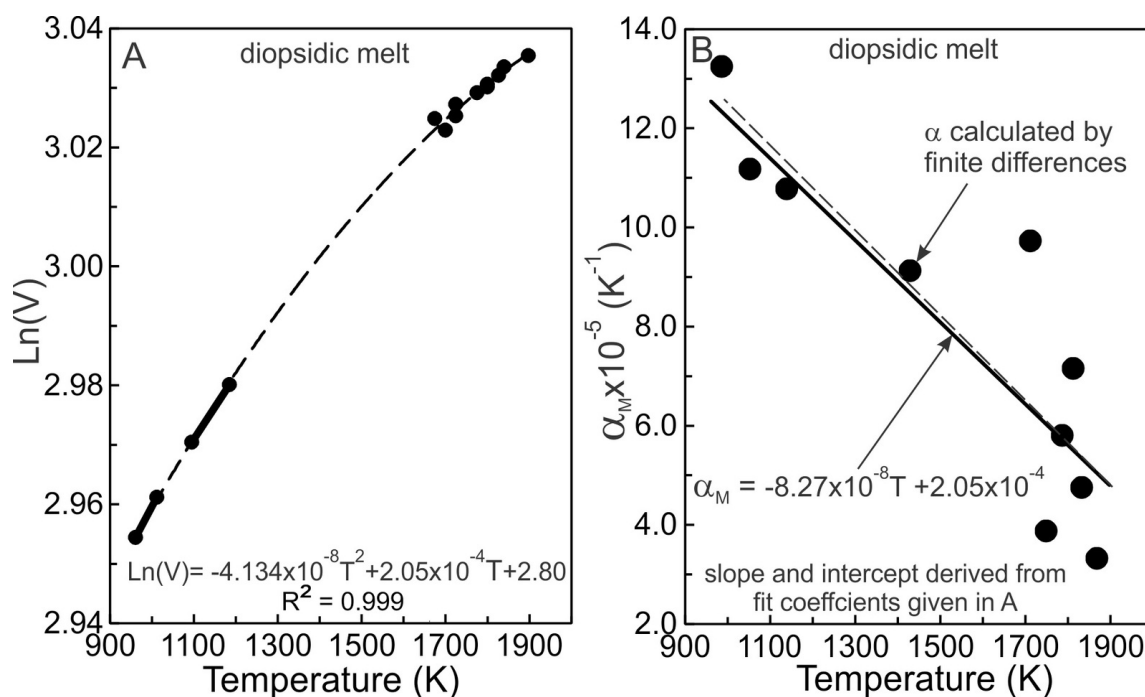


Figure 1. The temperature variation of $\ln V$ and α of diopsidic melts employing the same data as Toplis and Richet (2000, their fig. 7c). (A) A quadratic fit to $\ln V$ – temperature data is illustrated by the dashed line. The thick lines terminated by dots represent data of Toplis and Richet (2000) near and beyond the fictive temperature (~ 966 K). Separate dots are from Gottsmann and Dingwell (2000), Knoche et al. (1992), Lange and Carmichael (1987) and Taniguchi (1989). (B) α values calculated by finite differences ($\alpha = (\Delta V/\Delta T)/V$), are shown as large dots. The dashed line is a least-squares best fit to the dots. Additional, and different, values of α may be obtained using different ΔT step sizes. The α values determined from the fit shown in figure 1A are represented by the solid line. Its slope and intercept were *calculated* from the fit coefficients of figure 1A ($m = 2 \times [-4.134 \times 10^{-8}]$ and $b = 2.05 \times 10^{-4}$). Both approaches use the same molar volume temperature data.

$$\begin{aligned} (d \ln V / dT)_{P,X} &= \alpha \\ &= 2(-4.134 \times 10^{-8})T + 2.05 \times 10^{-4} \quad (7) \\ &= -8.268 \times 10^{-8} + 2.05 \times 10^{-4} \end{aligned}$$

It is shown as the straight line in [figure 1B](#). The straight line *is not a fit*. Its slope and intercept were determined entirely from the coefficients of the fit to the $\ln V_M$ versus T data ([fig. 1A](#)) so that the uncertainty in α is commensurate that of the experimental volume of the melt. The finite difference calculations ($\alpha = (\Delta V/\Delta T)/V$) of α are illustrated as large dots and the uncertainty associated with the technique is apparent. The dashed line is the best fit to the dots. Additional volumetric measurements may demonstrate that $\ln V_{P,X}$ vs T is better described by a cubic or quartic expression in temperature, and re-evaluation of α then would be required.

2.3. Na-silicate glasses

Knoche et al. (1994) determined the temperature dependence of molar volumes of Na-silicate glasses containing 1.9, 4.9, 10.6, 16.0, 20.2, 25.7, 30.4, 35.3, 40.2 and 45.0 mole% Na_2O . Four results are illustrated in [figure 2](#). $\ln V_{P,X}$ values between 300 and 650 K ([fig. 2](#), dots) were fit using equation (5). Fits to the other glass compositions are similar, all yielding effectively linear trends. The values of the slopes of the fits (a_1) equal α_G and they are constant be-

tween 300 and 650 K for each glass composition and at ambient pressure. With glass transition temperatures (T_g) between ~ 710 and 780 K, configurational changes do not contribute to the molar volumes of the glasses at $T < 650$ K, although Si-O and Na-O vibrational contributions do (Lange, 1997; Richet, 2001b, 2001a; Richet & Neuville, 1992).

2.3.1. VIBRATIONAL CONTRIBUTIONS

An anharmonic potential energy (PE) surface of a diatomic molecule ([fig. 3A](#)) is used as an analogue for Si-O and Na-O potential energy (PE) wells of Na-silicate glasses (Huheey et al., 1993, pp. 99–104), recognizing that PE wells vary appreciably for lack of long range order. Na-O and Si-O dissociation energies (D_e) are 257 and 798 kJ/mol respectively (Speight, 2005), thus Na-O bonds are much weaker than Si-O bonds. The energy levels separating the ground and excited vibrational states of a PE well are dependent on D_e , so less energy is required to promote a Na-O than a Si-O vibration from its ground state to its first excited state, which results in increased M-O bond distances ([fig. 3A](#)) and molar volumes (Bayram & Freamat, 2012; Moelwyn-Hughes, 1961, pp. 416–418). The increase in volume of Na-silicate glasses between 300 and 650 K ([fig. 2](#)) thus should derive from the Na_2O component of these glasses. As evidence,

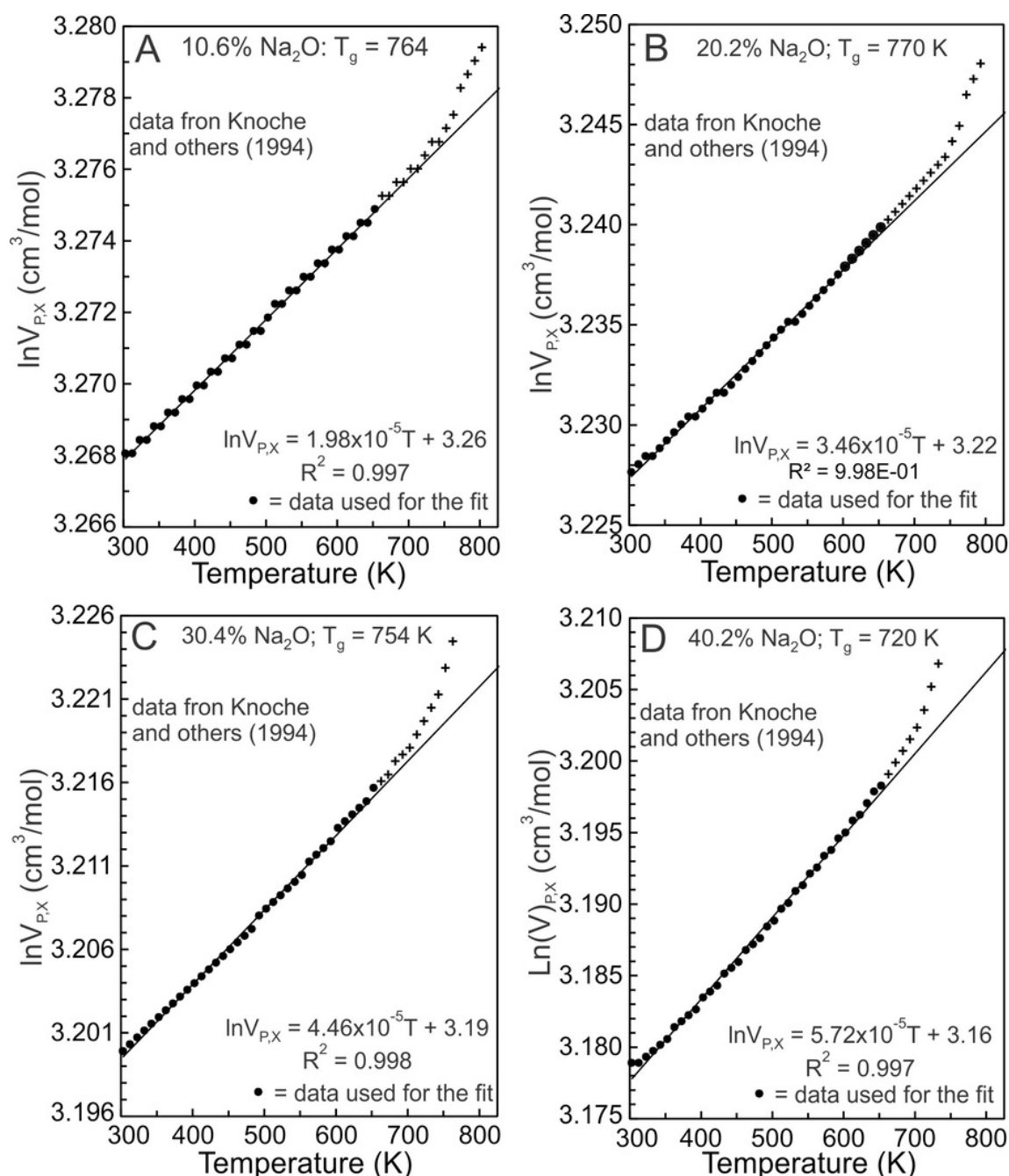


Figure 2. Plots are shown of $\ln V$ versus temperature for Na-silicate glasses at four different glass compositions. Least-squares fits to the dots, using equation (2), are illustrated by straight lines. The temperature interval for all fits is 300 K to 650 K. The data represented by the crosses were not included in the fits. All measurements were at ambient pressure. Data are from Knoche et al. (1994).

the slopes of the fits of $\ln V_{P,X}$ versus T (fig. 2), which represent α_G values, are plotted against $X_{\text{Na}_2\text{O}}$ in figure 4. The α_G values increase linearly with Na_2O content. The linear relationship is that expected if α_G were controlled by Na-O vibrational excitation in asymmetric potential energy wells. The increased $\ln V$ values result primarily from promotion of Na^+ to excited vibrational states. Si-O vibrations remain mostly ground state vibrations.

Si-O vibrational excitation apparently contributes negligibly to α_G of the glasses, an indication being the very small value of the intercept of the fit ($6.77 \times 10^{-6} \text{ K}^{-1}$) shown in fig-

ure 4. The intercept represents α of a glass devoid of Na_2O (but containing 0.03–0.1 wt.% H_2O as measured by Knoche et al., 1994, their table 1). The value is greater than quoted by Deng et al. (2020) for bulk fused silica, but as they and Oishi and Kimura (1969) emphasize, variation in the value is expected and may be related to H_2O or other contaminants (Knoche et al., 1994). There is an effectively constant α value for fused silica applicable to the sodic glasses for $T < T_g$.

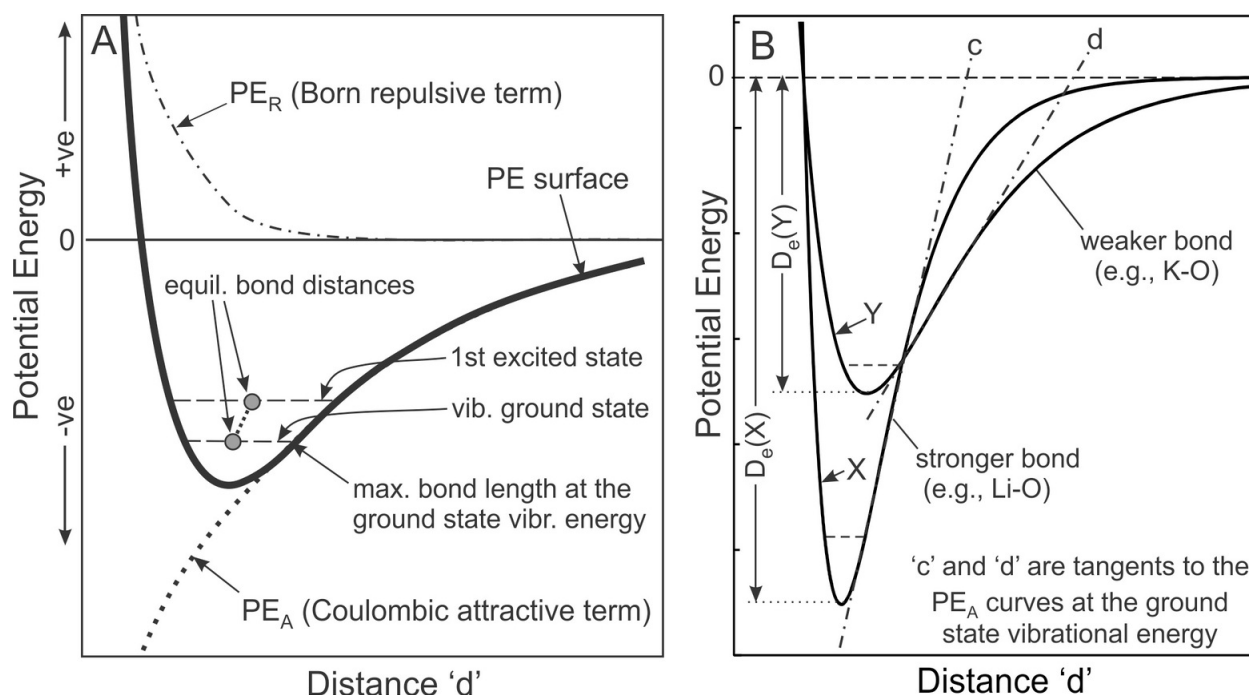


Figure 3. Hypothetical potential energy (PE) surfaces are plotted as functions of distance separating a cation and an anion. (A) PE surface constructed from a Coulombic attractive potential (PE_A) and a Born (electron cloud) repulsive potential (PE_R) following Huheey et al. (1993). Hypothetical ground and first excited states are shown as dashed lines. Shaded circles are located at the equilibrium bond distance for the ground and first excited states. (B) PE surfaces for a strong cation-anion interaction (PE surface of X) and a weak cation-anion interaction (PE surface of Y). Dissociation energies (D_e) for each are shown. Dash-dot lines are slopes to each PE surface at their respective ground state energy and are determined primarily by the tangent to the PE_A contribution to the PE surface.

2.3.2. CONFIGURATIONAL CONTRIBUTIONS

$\ln V$ increases non-linearly with T beginning at ~ 650 – 750 K (fig. 2, crosses) indicating an additional contribution to α (hence V). Na-O potential energy (PE) wells are shallower than Si-O PE wells, so that with increased temperature, Na should become mobile in advance of Si, with Na^+ migrating (hopping) from one site to another, resulting in new topologies (Cormack et al., 2002; Habasaki, 2021). Thus, with thermal agitation, Na-O bonds are ruptured by Na^+ ‘topping’ PE barriers, allowing new, more energetic arrangements (topologies) to be accessed (Richet, 2001a, his fig. 5). As evidence, Lei et al. (2015) classify $Na_2Si_2O_5$ glass as a fast Na-ion conductor at temperatures above ~ 600 – 700 K and they emphasize that Si and O contribute negligibly to conduction at these temperatures. At ~ 600 – 700 K, some Na-O bonds rupture with some reforming to produce more energetic arrangements (topologies), which affect V and α . As evidence, Na^+ mobility results in an abnormal increase in heat capacity of $NaSiO_3$ crystals above ~ 700 K (Nesbitt, Cormack, et al., 2017; Richet et al., 1996) followed by production of some Q^3 species (Si tetrahedra with 3 apical BOs and a NBO) in $NaSiO_3$ crystals commencing at 750 – 800 K (Nesbitt, Bancroft, et al., 2017; Nesbitt, Cormack, et al., 2017). The Q^3 species form cross-chain linkages which stabilize the chains. Importantly, upon removal of Na^+ from its PE well, the original Coulombic force

of attraction between Na^+ and O atoms of its first coordination sphere is replaced by Coulombic *repulsion* among the same O atoms. Net repulsive forces build within the glass as the fraction of mobile Na^+ increases. These repulsive forces likely promote relaxation of glasses at temperatures somewhat greater than that at which Na becomes mobile. The repulsive forces can be minimized only by rearrangement of Si tetrahedra, which contributes to changes in V and α (Richet, 2001a).

3. MOLAR AND PARTIAL MOLAR COEFFICIENTS OF THERMAL EXPANSION

The volume of a crystal, glass, liquid, aqueous solution or gas, is the sum of the partial molar volumes ($\bar{V}$) its ‘N’ components multiplied its mole fraction. The molar volume of a melt or glass (V_M or V_G) thus may be expressed as:

$$V_M = \bar{V}_1 X_1 + \bar{V}_2 X_2 + \bar{V}_3 X_3 + \dots + \bar{V}_N X_N \quad (8)$$

where $\bar{V}_N$ is the partial molar volume and $\bar{V}_N$ is the mole fraction of the N^{th} component. The relationship between molar and partial molar volumes is illustrated in figure 5A for Na_2O - SiO_2 glasses at 703 K. The quadratic fit to the glass molar volumes reproduces the data within experimental uncertainty and to obtain $\bar{V}_{SiO_2}$ and $\bar{V}_{Na_2O}$ of the glass at $X_{Na_2O} = 0.311$, the derivative of the quadratic equation at this composition may be taken (dashed line of fig. 5A).

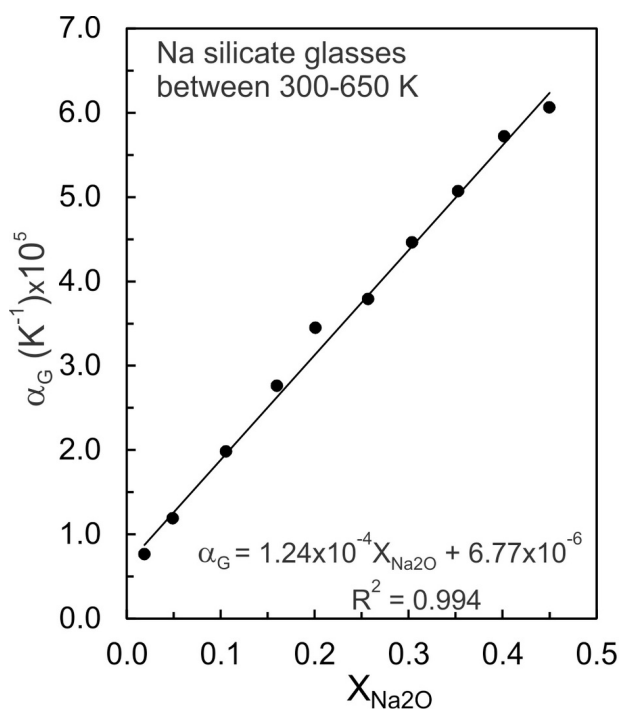


Figure 4. Illustrates the coefficients of thermal expansion of sodic glasses (α_G) at specific Na_2O contents. The α_G values were obtained by fitting equation (2) ($\ln V$ vs. T) to the experimental data for a glass of specific Na_2O content over, the range ~300-650 K, as shown in figure 2. The dots represent α_G for each glass composition. All data are from Knoche et al. (1994).

Its extension to the compositional boundaries yields $\bar{V}_{SiO_2}$ and $\bar{V}_{Na_2O}$ at 703 K ($X_{Na_2O} = 0.311$; $P = 101.3$ kPa). The procedure may be repeated for any composition.

Where two components mix ideally, the molar volumes of a melt (or glass) adhere to a straight line with respect to composition, where the intercepts at the compositional boundaries are $V^{\circ}_{SiO_2}$ and $V^{\circ}_{Na_2O}$, (the molar volumes of pure liquid SiO_2 and Na_2O). Where glasses or melts display linear mixing trends over a *limited compositional range* (fig. 5B), the linear mixing trend cannot be taken as evidence for ideal mixing unless it is shown that the partial molar volumes, $\bar{V}_{SiO_2}$ and $\bar{V}_{Na_2O}$ equal respectively, $V^{\circ}_{SiO_2}$ and $V^{\circ}_{Na_2O}$.

Following Moelwyn-Hughes (1961, p. 815), and differentiating equation (8) with respect to temperature, at constant pressure and composition, yields:

$$\left(\frac{\partial V_M}{\partial T}\right)_{P,X} = \left(\frac{\partial \bar{V}_1}{\partial T}\right)X_1 + \left(\frac{\partial \bar{V}_2}{\partial T}\right)X_2 + \dots + \left(\frac{\partial \bar{V}_N}{\partial T}\right)X_N \quad (9)$$

Rearranging equation (1) to $(\partial V/\partial T)_{P,X} = \alpha V$ and noting that $\partial V_M/\partial T = \alpha_M V_M$ and $\partial \bar{V}_N/\partial T = \alpha_N \bar{V}_N$, then substitution of the last two equations into equation (9) gives:

$$\begin{aligned} \left(\frac{\partial V_M}{\partial T}\right)_{P,X} &= \alpha_M V_M \\ &= \alpha_1 \bar{V}_1 X_1 + \alpha_2 \bar{V}_2 X_2 \\ &\quad + \dots + \alpha_N \bar{V}_N X_N \end{aligned} \quad (10)$$

The symbols α_M and α_N refer respectively to the molar coefficient of thermal expansion of the melt and the coefficient of thermal expansion attributable to the N^{th} component of the melt (or glass) at constant composition and pressure. Division of both sides of equation (10) by the melt molar volume (V_M) yields:

$$\alpha_M = \alpha_1 \theta_1 + \alpha_2 \theta_2 + \alpha_3 \theta_3 + \dots + \alpha_N \theta_N \quad (11)$$

where θ_N is the *volume fraction* of the N^{th} component ($\theta_N = \bar{V}_N X_N / V_M$) and $\sum \theta_N = 1.0$. For binary systems:

$$\alpha_M = \alpha_1 + (\alpha_2 - \alpha_1) \theta_2 \quad (12)$$

Bockris et al. (1956) report molar volumes and α_M for silicate melts containing 11–60 mole% Na_2O . Bottinga et al. (1983) report α_{SiO_2} , α_{Na_2O} , $V^{\circ}_{SiO_2}$ and $V^{\circ}_{Na_2O}$ to be respectively $1.0 \times 10^{-6} K^{-1}$ and $25.9 \times 10^{-5} K^{-1}$, $26.75 \text{ cm}^3/\text{mole}$ and $29.03 \text{ cm}^3/\text{mole}$. These values were substituted into equations (8) and (12) to calculate V_M and α_M of the melt at each composition reported by Bockris et al. (1956). The same procedure was performed using the results of Lange and Carmichael (1987) and Ghiorso and Kress (2004). These *calculated* V_M values are compared with the *experimental* values in figure 6A and the three studies yield remarkably good approximations to experimental V_M values. Only at the extremes of composition do they differ appreciably from experiment.

Equation (12) provides a rigorous test of the accuracy of α_N values in that α_M can be evaluated from α_N values via equation (12) and compared directly to experimental α_M values. Equation (12) has been used to calculate α_M of sodic melts from the component α_N values listed by Bottinga et al. (1983), Lange and Carmichael (1987), and Ghiorso and Kress (2004). The calculated values are compared with the experimental values of Bockris et al. (1956) in figure 6B. Calculated α_M values from these studies agree with experiment between ~30 and 53 mole% Na_2O , but those of Ghiorso and Kress (2004) reproduce best the experimental values within the above-noted compositional range. None of the studies reproduces accurately the experimental α_M values of highly siliceous melts ($SiO_2 > 75$ mole%). The deviations from experimental values observed in figure 6B arise from inaccuracies in α_{Na_2O} and α_{SiO_2} values. Additional studies are required to re-evaluate these coefficients and perhaps the other alkali and alkaline earths α values in highly siliceous melts.

4. POTENTIAL ENERGY, COULOMBIC INTERACTIONS AND α

Coulombic interactions account for ~90% of bond energies of ionic crystals. Dispersion, zero-point energy and other aspects account for the remainder (Huheey et al., 1993, Chapter 3; Moelwyn-Hughes, 1961). Navrotsky et al. (1985) emphasized that equilibrium M-O bond distances were similar in ionic crystals, glasses and melts from which we surmise that these same forces affect alkali-O and alkaline

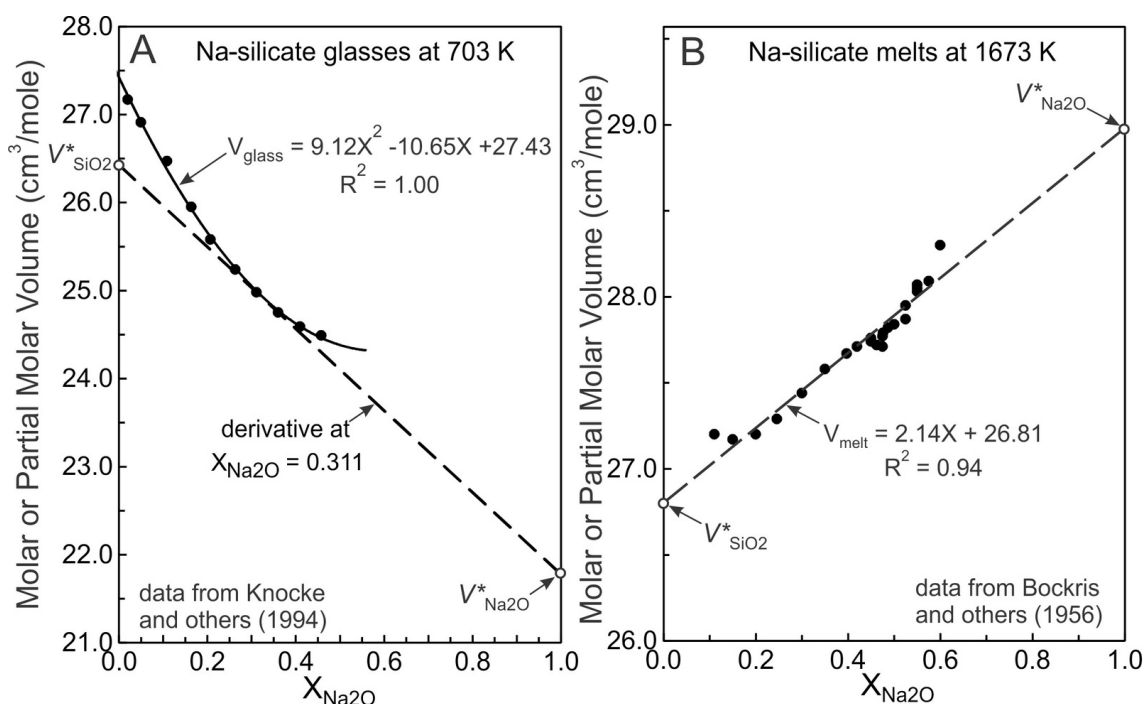


Figure 5. Illustrates the relationship between the molar volume (V) and partial molar volumes ($\bar{V}$) of components, of sodic glasses and melts. (A) Illustrates the relationship between V_{glass} containing 31.1 mole% Na_2O ($X_{\text{Na}_2\text{O}} = 0.311$) and the partial molar volumes of the two components, $\bar{V}_{\text{SiO}_2}$ and $\bar{V}_{\text{Na}_2\text{O}}$, of the glass. Mixing is of a non-linear nature. (B) Illustrates the relationship between V_{melt} and $\bar{V}_{\text{SiO}_2}$ and $\bar{V}_{\text{Na}_2\text{O}}$ of Na-silicate melt where linear mixing is assumed to occur over the compositional interval $X_{\text{Na}_2\text{O}} = 0.2$ to 0.6 . Determination of $\bar{V}$ values is explained in the text.

earth-O interactions in the three states of matter. In support, Nesbitt et al. (2022) demonstrate that ionic M-O bond distances derived from ionic crystals (Huheey et al., 1993; Ottonello, 1997; Shannon, 1976) can be utilized to calculate partial molar volumes of modifier oxides in melts and glasses.

Following Huheey et al. (1993; p. 99–104), the derivative (with respect to distance) of the Coulombic force of attraction yields the attractive potential energy (PE_A) of a diatomic molecule composed of a cation (M) and an anion (O), as shown qualitatively in [fig. 3A](#):

$$PE_A = \left[\frac{(z^+)(z^-)}{4\pi} \right] / d \quad (13)$$

where d is the M-O bond distance. The derivative of the Born repulsive force yields the repulsive potential energy (PE_R , [fig. 3A](#), dash-dot line).

$$PE_R = \left(\frac{B}{n} \right) / d^{n-1} \quad (14)$$

B is a constant and ‘ n ’ is the ‘Born exponent’, which is typically ~ 9 (Huheey et al., 1993, pp. 99–104). The sum of equations (13) and (14) yield a potential energy curve (a PE ‘well’ in 3 dimensions) as shown in [figure 3A](#) (thick curve). Its minimum occurs at the equilibrium M-O bond distance.

Potential energy wells resulting from the above interactions are asymmetric due to the differing nature of the attractive and repulsive forces. The asymmetry leads to anharmonicity, and as noted in a previous section, heating increases M-O bond distances, volumes and α through population of excited vibrational states ([fig. 3A](#)). The energy

separating the ground and first excited state is related to the slope of the PE_A curve in that the shallower the slope the smaller the energy separating the vibrational levels, primarily because the slopes are mostly determined by the M-O dissociation energy (D_e) and the force constant (k) associated with M-O vibrations (Bayram & Freamat, 2012; Moelwyn-Hughes, 1961, p. 485). The stronger each is, the steeper the slope of the attractive portion (PE_A) of the PE well near the vibrational ground state energy ([fig. 3B](#)). The slope of the PE_A curve at a specified M-O distance is the derivative of equation (13) and yields equation (15) which is Coulomb’s Law. With heating, time-averaged M-O bond distances, molar volumes and α should increase in proportion to the inverse of Coulomb’s force of attraction.

To emphasize the relationship between D_e and the slope of the PE_A curve, two PE wells labelled X and Y are shown in [figure 3B](#). The cation-anion bond is stronger for ‘X’ than for ‘Y’, as required by the different values of D_e . The slopes of the PE_A portions of the two curves at the vibrational ground state are labelled ‘c’ and ‘d’ respectively. The smaller is D_e the weaker is the bond, and the shallower is the slope of the attractive part of the PE curve (PE_A) near the ground state energy. With an equivalent amount of heating, the time-averaged equilibrium bond distance should increase more for ‘Y’ than for ‘X’. From this we argue that α_N , should correlate the inverse of Coulomb’s force of attraction ($1/F_C$). The relationship between α and $1/F_C$ is thus explored.

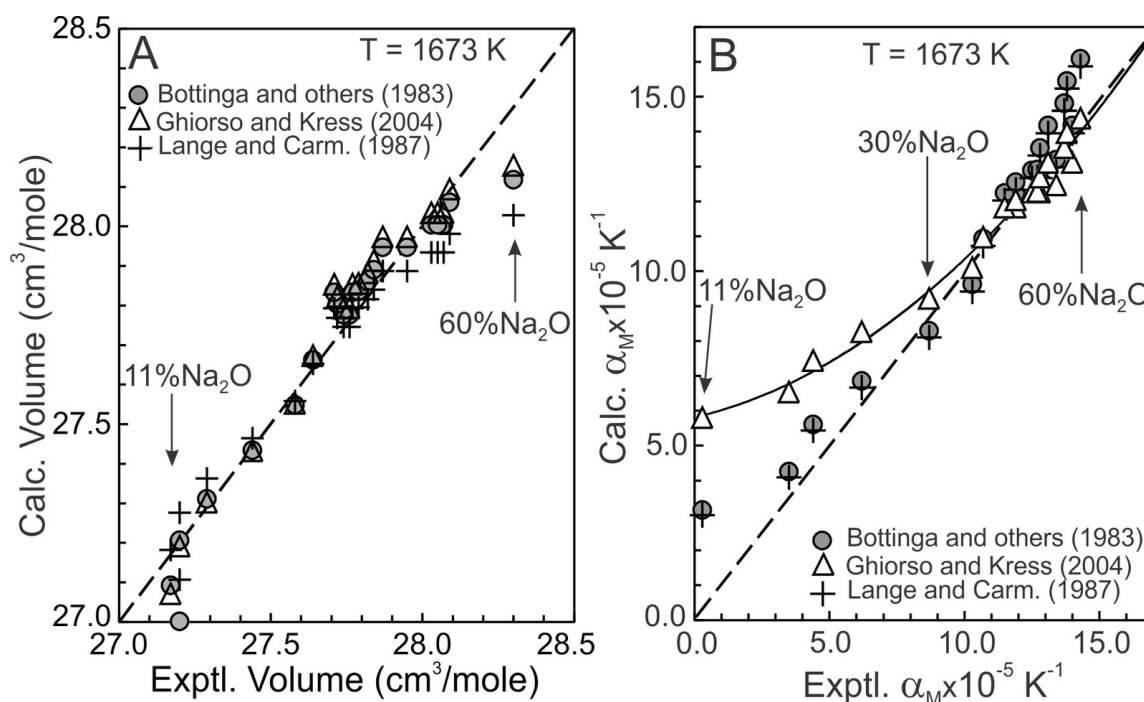


Figure 6. Illustrates the differences between (consistency of) calculated and experimental volumetric properties, V_{melt} and α_M , in Na-silicate melts of different Na_2O content. (A) Experimental molar volumes of melts of Bockris et al. (1956) are compared with molar volumes calculated using equation (8), $\bar{V}_{\text{Na}_2\text{O}}$ and $\bar{V}_{\text{SiO}_2}$ values quoted by the three studies listed. (B) Experimental melt molar coefficients of thermal expansion (α_M) of Bockris et al. (1956) are compared with melt molar coefficients of thermal expansion calculated using equation (11) and partial molar coefficients of thermal expansion ($\alpha_{\text{Na}_2\text{O}}$ and α_{SiO_2}) reported by the three studies. Carm. indicates Carmichael.

4.1. Alkali and Alkaline earth oxides

Coulomb's force of attraction (F_C) is:

$$F_C = k(z^+z^-)/d^2 \quad (15)$$

where k is a proportionality constant, z^+ and z^- are the charges on the cation (M) and anion (O) and d is the equilibrium distance separating them. Equilibrium bond distances ' d ' were calculated using the ionic radii of alkali and alkaline earths cations and O^{2-} ($= 1.21\text{\AA}$) listed in [table 1](#) (Huheey et al., table 4.4, 1993). Alkali and alkaline earth oxide α_N values of [table 1](#) are plotted against $1/F_C$ on [figure 7](#). There is a correlation, even though maximum bond distances are greater than equilibrium bond distances. The α_N values describe an arcuate trend referred to and labelled as the 'Coulombic trend'. The trend is arcuate owing to the values of Rb_2O and Cs_2O . The seven other oxides conform to an effectively linear trend regardless of the charge or radius of the cation ([fig. 7](#)). Clearly, the stronger the Coulombic force of attraction, the smaller the coefficient of thermal expansion (α_N) of Groups I and II metal oxides. The conclusion is that α_N varies as $1/F_C$ for the Group I and II oxides.

The α_N values of Rb_2O and Cs_2O plot above the dotted linear trend of the others, indicating an additional contribution that enhances their α values. This contribution may relate to the previous approximation that the repulsive force makes the same contribution to PE wells of all alkali and alkaline earth oxides. The approximation probably is overly simple in that the weaker the Coulombic force of

attraction the greater the proportional contribution of the repulsive force to the cation-anion interaction. Rb_2O and Cs_2O are the most likely of all Group I and II oxides to include a greater repulsive contribution and greater than expected α_N values.

4.2. 3d and 4f oxides

The α_N values of the 3d- and 4f-metal oxides ([tables 2, 3](#)) plotted on [figures 8A and 8B](#) describe near-vertical trends with the largest values being greater than $\alpha_{\text{K}_2\text{O}}$. The smallest α_N values of the 3d metal oxides plot close to the Coulombic trend. The α_N values of MnO , one ZnO and one NiO are similar to those of MgO and CaO , and Coulombic interactions likely determine their α_N values. The α_N values of 4f metal oxide describe a similar trend ([fig. 8B](#)) in that they span a large range in α with two values being greater than $\alpha_{\text{K}_2\text{O}}$. Four values plot close to the Coulombic trend and near α_N of MgO and CaO . The low α_N values of these 4f metal oxides are consistent with control by Coulombic interactions. Apparently, Coulombic interactions set a lower bound on α_N values of the 3d, 4f, alkali and alkaline earths oxides.

Other α_N values are greater than expected from Coulombic interactions. Guo et al. (2013), for example, observed an increase in $\bar{V}_{\text{FeO}}$ as CaO was added to Fe silicate melts at constant temperature. Addition of CaO resulted in a decrease in the proportion of VI FeO and an increase in IV FeO

Table 1. $\bar{V}$ and α of alkali and alkaline earths at 1673K

Oxide	$\bar{V}$ per O cm ³ /mol	$\alpha \times 10^5$ K ⁻¹	C.N.	r(ion) Å	$1/[(z^+z^-)/d^2]$ -Å ² /e ²
Oxide Ion			2	1.21	
Bottinga et al. (1983); T = 1673K					
Li ₂ O	17.31	22.0	4	0.73	1.88
Na ₂ O	29.03	25.9	5	1.14	2.76
K ₂ O	46.30	35.9	7	1.52	3.73
Rb ₂ O	54.22	61.3	9	1.77	4.44
Cs ₂ O	68.33	71.4	10	1.95	4.99
MgO	12.32	12.2	5	0.80	1.01
CaO	16.59	16.7	8	1.26	1.53
SrO	20.45	15.4	10	1.50	1.84
BaO	26.20	17.4	12	1.75	2.19
Lange and Carmichael (1987) at 1673K					
Li ₂ O	16.85	31.2	4	0.73	1.88
Na ₂ O	28.78	25.7	5	1.14	2.76
K ₂ O	45.84	26.0	7	1.52	3.73
MgO	11.45	22.9	5	0.80	1.01
CaO	16.57	17.6	8	1.26	1.53
Lange (1997, table 4); $\bar{V}$ and α are evaluated at 1673K					
Na ₂ O	28.88	26.6	5	1.14	2.76
K ₂ O	46.07	26.2	7	1.52	3.73
MgO	11.69	28.0	5	0.80	1.01
CaO	16.53	22.6	8	1.26	1.53
Courtial and Dingwell (1999, table 4) evaluated at 1673K					
MgO	12.45	30.0	5	0.80	1.01
CaO	19.91	18.8	8	1.26	1.53

(Guo et al., 2013, their fig. 5), demonstrating a relationship between $\bar{V}_{FeO}$ and CN of FeO. The change in volume at constant temperature necessitates, by equation (2), an increase in α_{FeO} , thus a change to CN leads to a change in α_N . The α_N values of 3d and 4f oxides plotting above the Coulombic trend of [figure 8](#) thus may reflect CNs differing from those plotting on the trend. The question to answer then becomes; why do cations of similar size have different CNs. Changes to CN change packing. Corner-shared tetrahedra pack less efficiently than octahedra (Chaikin, 2007; Hoyleman, 1970; Song et al., 2008), especially where the latter share edges (Rossano et al., 2000). Similarly, different α_{ZnO} , α_{NiO} values ([table 2](#)) may result from the same cation being differently coordinated in different melts or glasses (Calas et al., 2014; Rosenthal & Garofalini, 1987).

4.3. Network-former oxides

The α_N values of [table 3](#) describe a near-vertical trend on [figure 8C](#) extending from negative values (Ga₂O₃ = -9.1×10^{-5} K⁻¹; Al₂O₃ = -3.2×10^{-5} K⁻¹) to 37.1×10^{-5} K⁻¹ for TiO₂ ([table 3](#)). An apparently unique aspect of the network-former oxides is that some have very small or negative α_N values. If controlled solely by Coulombic interactions, the

lower limit of α values would be $\sim 8 \times 10^{-5}$ K⁻¹ ([fig. 8C](#)) for these oxides. Clearly, other interactions affect α values of the network former oxides. CN transitions cannot explain the small positive to negative α values of α_{SiO_2} and α_{GeO_2} because they do not change CN in melts at ambient pressure. Electrostriction may provide a partial explanation. Nesbitt et al. (2022) demonstrate that tetrahedra collapse around *all* modifier cations in melts, decreasing somewhat melt molar volumes. Collapse around modifier cations thus may contribute to small or negative α values of Si and Ge tetrahedra. Although Coulombic interactions causes such collapse, these interactions are largely insensitive to temperature, the major effect being on Si-O and M-O bond distances and are unlikely to cause additional changes to $\bar{V}_{SiO_2}$ or $\bar{V}_{GeO_2}$. This aspect combined with the effects of electrostriction should result in small α_{SiO_2} values. Electrostriction does not affect vitreous silica and cannot explain its small α_{SiO_2} values. Topological aspects clearly are important (Deng et al., 2020).

With respect to other network former oxides, Courtial and Dingwell (1999) provided a concise summary of aspects related to $\bar{V}_{Al_2O_3}$ and $\alpha_{Al_2O_3}$ values. $\bar{V}_{TiO_2}$, α_{TiO_2} , $\bar{V}_{Fe_2O_3}$, $\alpha_{Fe_2O_3}$, $\bar{V}_{FeO}$ and α_{FeO} vary due in part to changes to CN and to the presence of different counter oxides in the melts

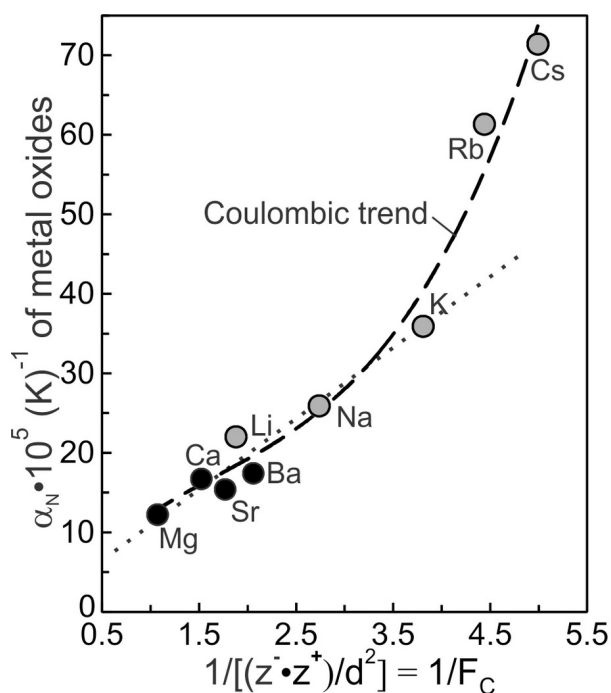


Figure 7. Coefficients of thermal expansion of Groups I and II metal oxides (α_N) plotted against $1/F_C$ ($1/F_C = 1/[k \cdot z^+ \cdot z^- / d^2]$). The dashed curve represents a least squares cubic polynomial fit to the data and for convenience it is referred to as the ‘Coulombic trend’. The straight dotted line represents the trend of α_N for the metal oxides excluding Rb_2O and Cs_2O .

(Courtial & Dingwell, 1995; Guo et al., 2013; Henderson et al., 2003, 2006; Henderson & Fleet, 1995; Liu & Lange, 2001, 2006; Toplis, 2001). Changes to CN and different melt

compositions also may be relevant to Ni, Co and Zn oxides (Allwardt et al., 2005; Calas et al., 2014; Farges et al., 2001, 2004; Galois et al., 2001; Galois & Calas, 1993a, 1993b; Hunault et al., 2014; Jackson et al., 1993, 2005; Stebbins, 1995). The above-quoted studies point to changes in CN as (partial?) explanations for the different $\bar{V}$ and α values of various network former oxides. The effects of cluster formation and complexes are not considered here, although they may contribute significantly to nonlinear volumetric-compositional relations (for example, Bockris et al., 1956; Nesbitt & Fleet, 1981; Toplis, 2001).

The large positive α_N values of TiO_2 and Fe_2O_3 (fig. 8C) may be related to change from higher to lower CN (Guo et al., 2013; Henderson et al., 2003; Liu & Lange, 2006). As previously noted, changes to CN affect packing, as apparent from lattice packing of corner-linked tetrahedra compared with edge-shared octahedra (Rossano et al., 2000). Theoretical considerations have considered packing efficiencies in disordered materials, yielding tetrahedral and octahedral packing efficiencies of ~39% and ~92% respectively (Chaikin, 2007; Hoylman, 1970; Song et al., 2008). Two aspects concerning changes to CN are now addressed.

5. COORDINATION CHANGES IN MELTS

Some 3d and 4f metal oxide components display more than one CN and α_N value (tables 2 and 3), examples being ZnO, FeO, Fe_2O_3 and TiO_2 (figs. 8B, 8C). Questions thus arise concerning why and how CNs of oxide components change in melts and glasses, and what effect the changes have on α_N . Noting that the lower limit of α_N for 3d and 4f oxides coincides with the Coulombic trend defined by the alkali and alkaline earths (Fig. 8A, 8B), we focus on properties of the first coordination sphere (FCS) of the alkalis in

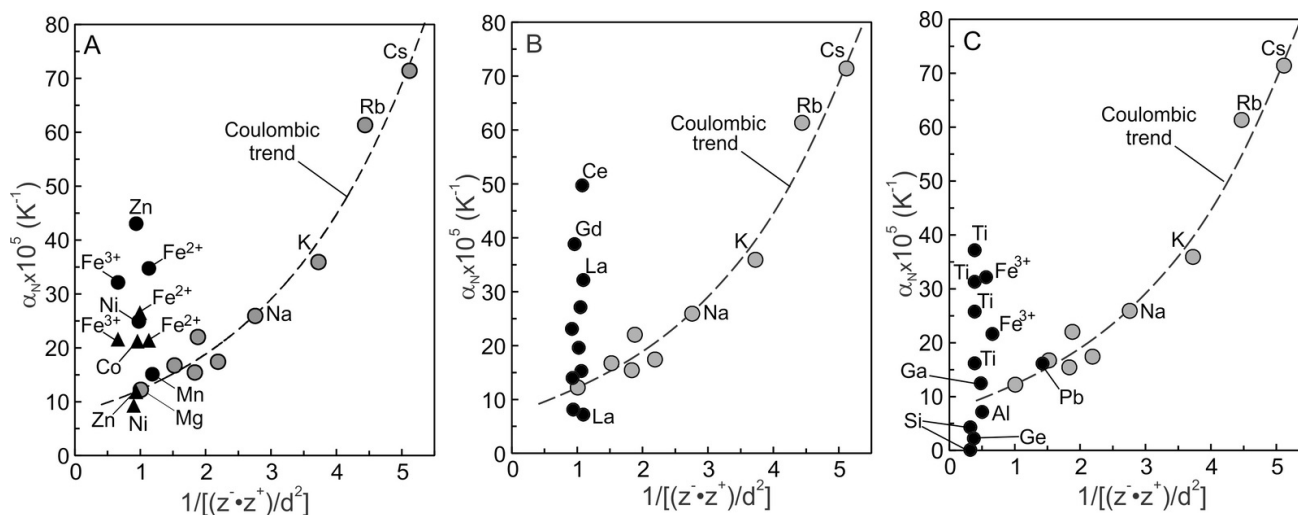


Figure 8. Illustrates the relationships between α_N and $1/F_C$ ($F_C = k \cdot z^+ \cdot z^- / d^2$). Groups I and II metal oxides from table 1 are plotted as shaded circles on all figures and the Coulombic trend of figure 7 is also shown. (A) Triangles represent α_N values from Bottinga et al. (1983) and R. A. Lange and Carmichael (1987). Solid circles represent more recent data for 3d metal oxides listed in table 2 (see references in table 2 for dates). (B) solid circles represent α_N values of the 4f metal oxides (see table 2). (C) Solid circles represent α values of the network former metal oxides from table 3. Negative values are not plotted to maintain scale with figures 8A and 8B.

Table 2. $\bar{V}$ and α of 3d and 4f metal oxides at 1673K

Oxide	$\bar{V}$ per O ^a cm ³ /mol	$\alpha \times 10^5$ K ⁻¹	C.N. estimated	r(ion) ^b Å	$1/[(z^+z^-)/d^2]$ -Å ² /e ²
Oxide ion				1.21	
$\bar{V}$ and α of 3d metal oxides: Bottinga et al. (1983) et al.					
MnO	14.13	15.1	6	0.97	1.19
ZnO	13.46	43.0	4	0.73	0.94
FeO	13.94	34.7	6	0.92	1.13
NiO	12.48	24.9	5	0.77	0.98
Fe ₂ O ₃	14.80	32.1	6	0.785	0.66
FeO ^b	13.65	21.4	6	0.92	1.13
Fe ₂ O ₃ ^b	14.04	21.6	6	0.785	0.66
NiO ^c	16.14	9.3	4	0.69	0.90
CoO ^c	13.85	21.2	6	0.75	0.96
ZnO ^d	14.10	11.8	4	0.73	0.94
FeO ^e	12.11		6	0.92	1.13
FeO ^e	17.10		4	0.77	0.98
Fe ₂ O ₃ ^g	15.17	26.5	4	0.785	1.00
Fe ₂ O ₃ ^g	11.37		6	0.63	0.56
$\bar{V}$ and α from Courtial and Dingwell (2005) at 1673K					
La ₂ O ₃ ^f	15.10	7.2	9	1.356	1.10
La ₂ O ₃ ^f	14.04	32.1	9	1.356	1.10
Ce ₂ O ₃	15.46	49.7	9	1.336	1.08
Pr ₂ O ₃	18.20	15.3	9	1.319	1.07
Nd ₂ O ₃	14.15	27.1	9	1.303	1.05
Sm ₂ O ₃	14.08	19.5	9	1.272	1.03
Eu ₂ O ₃	14.08		8	1.206	0.97
Gd ₂ O ₃	13.27	38.8	8	1.193	0.96
Tb ₂ O ₃	13.44		8	1.18	0.95
Dy ₂ O ₃	15.92	8.1	8	1.167	0.94
Ho ₂ O ₃	13.75	14.0	8	1.155	0.93
Er ₂ O ₃	11.58	23.1	8	1.144	0.92
Tm ₂ O ₃	11.94		8	1.134	0.92
Yb ₂ O ₃	12.30		8	1.125	0.91

a - Partial molar volume per mole of O.

b - Lange and Carmichael (1987).

c - Courtial et al. (1999)

d - Potuzak et al. (2006) for Na-disilicate melt

e - Guo et al. (2013), $\bar{V}$ and α quoted for 1723 K

f - Courtial and Dingwell (2006) for Na and K silicate melts

g - Liu and Lange (2006); Table 5, α for Fe₂O₃ is very small.

an attempt to understand better, aspects affecting CN and α_N of modifier cations, including 3d and 4f cations. Hess (1996) emphasized that “cations are coordinated not only to NBOs, but to BOs as well”. This becomes apparent by considering a trace amount of a mono or divalent modifier oxide dissolved and well dispersed in SiO₂ melt. Each monovalent cation produces one NBO⁻ upon dissolution. If the cation were tetrahedrally coordinated, then three BOs would be incorporated into its FCS to achieve 4-fold coordination. Divalent cations produce two NBO⁻ in a siliceous melt. If the CN of the cation were 6, then as many as 4

BOs would be incorporated into its FCS. Molecular dynamics calculations on siliceous Li, Na and K glasses are illuminating (Du & Cormack, 2004; Du & Corrales, 2006). Results of the 2006 study are plotted on [figure 9](#). Each alkali is coordinated to both NBO and BO, and the ratio changes as a function of melt composition. [Figure 9](#) also shows that the greater the CN of the cation the greater the fraction of BO contributing to the FCS. Modifier cations of crystals are also coordinated to both NBO and BO, as in α -Na₂Si₂O₅, β -Na₂Si₂O₅ and Na₂SiO₃ (Ching et al., 1983 and references therein), and Li₂Si₂O₅ and Li₂SiO₃ crystals (Ching et al.,

Table 3. $\bar{V}$ and α of network-former oxides at 1673K

Oxide	$\bar{V}$ per O ^a cm ³ /mol	$\alpha \times 10^5$ K ⁻¹	C.N. ^b	r(ion) ^b Å	$1/\left[(z^+z^-)/d^2\right]$ -Å ² /e ²
SiO ₂ ^a	13.38	0.10	4	0.40	0.32
SiO ₂ ^b	13.44	-1.23	4	0.40	0.32
SiO ₂ ^c	13.43		4	0.40	0.32
SiO ₂ ^d	13.53	4.26	4	0.40	0.32
GeO ₂ ^e	14.87	2.18	4	0.53	0.38
Ga ₂ O ₃ ^e	12.20	12.4	6?	0.76	0.49
Ga ₂ O ₃ ^e	16.46	-9.1	4?	0.61	0.41
Al ₂ O ₃ ^b	12.37	7.12	4	0.53	0.50
Al ₂ O ₃ ^c	12.47		4	0.53	0.50
Al ₂ O ₃ ^d	12.30	-3.22	4	0.53	0.50
TiO ₂ ^a	11.23	37.10	4	0.56	0.39
TiO ₂ ^b	11.58	31.26	4	0.56	0.39
TiO ₂ ^f	13.94	25.75	4	0.56	0.39
TiO ₂ ^g	15.20	16.15	4	0.56	0.39
PbO ^a	25.71	16.10	4	1.18	1.43
Fe ₂ O ₃ ^h	15.17	32.10	4	0.63	0.56
Fe ₂ O ₃ ^h	11.33	21.58	6	0.79	0.66

a - Bottinga et al. (1983)

b - Lange and Carmichael (1987) – see their table 6.

c - Lange (1997)

d - Courtial and Dingwell (1999)

e - Holzapfel et al. (2001), Na

f - Liu and Lange (2001), NTS-1 sample

g - Liu and Lange (2001), KTS-2 sample

h - Liu and Lange (2006)

1985). In the sodic crystals, and in melts and glasses, Na bonded to BO (at equilibrium bond distances) results in the BO being 3-fold coordinated (two Si-BO bonds and one Na-BO bond). The 3d and 4f cations likewise should incorporate both types of oxygen into their FCS at least in highly *siliceous* glasses because there are insufficient NBOs to fully coordinate the modifier cations (Hess, 1996). From these observations we conclude that most, if not all, modifier cations incorporate both BO and NBO into their FCSs in siliceous melts and glasses. Electron densities on bridging and nonbridging oxygens are different (Brückner et al., 1980; Ching et al., 1983; Nesbitt et al., 2015; Nesbitt, Henderson, et al., 2017), which requires the partial charges on each to be different. We here investigate the consequences of differing partial charges on BO and NBO of modifier cation polyhedra and their effect on CN. We then introduce a mechanism by which CNs of these cations may be altered.

5.1. Effects of NBO and BO partial charges

XPS studies demonstrated that the partial charges on BO and NBO differed, with the greater negative charge resident on NBO (Brückner et al., 1980; Ching et al., 1983, 1985; Hsieh et al., 1994; Nesbitt et al., 2015; Nesbitt, Henderson, et al., 2017). They also demonstrated that the charges on NBO and BO become more negative with increased alkali oxide content. With this information as guide, we propose

a means by which CNs of modifier cations may change as a function of NBO and BO content of melts and glasses.

Guo et al. (2013) demonstrate that $\bar{V}_{FeO}$ increases and α_{FeO} decreases in Fe-silicate melts to which CaO is added. They attribute these to topological changes associated with production of Q³ species at the expense of Q⁴ species, or alternatively, production of NBO at the expense of BO. We focus on NBO and BO. Two moles of NBO are produced per mole of Fe²⁺ dissolved in a melt. The CN of Fe²⁺, however, ranges from ~6 to ~4 (Guo et al., 2013) thus in siliceous melts or glasses, and as previously argued, both NBO and BO likely are present in the first coordination sphere of Fe²⁺. Progressive addition of FeO to a silicate melt decreases the ratio of O:Fe from, for example, 5:1 in FeSi₂O₅ to 2:1 in Fe₂SiO₄ melt, due primarily to the decrease of BO contributed by SiO₂. Addition of CaO to a Fe-silicate melt causes the O:Fe ratio to decrease still more, resulting in competition between Fe and Ca for O atoms required to establish their coordination spheres. One response to the competition is to share O atoms by establishing shared edges of Fe and Ca polyhedra, such as observed by Rossano et al. (2000).

Where both BO and NBO are present in FCSs of modifier cations, there is another means by which Fe²⁺ polyhedra may adjust to competition for O atoms. The partial charges on NBO and BO atoms are about -0.96 and -0.64 respectively in Na disilicate glass (Hsieh et al., 1994). The greater

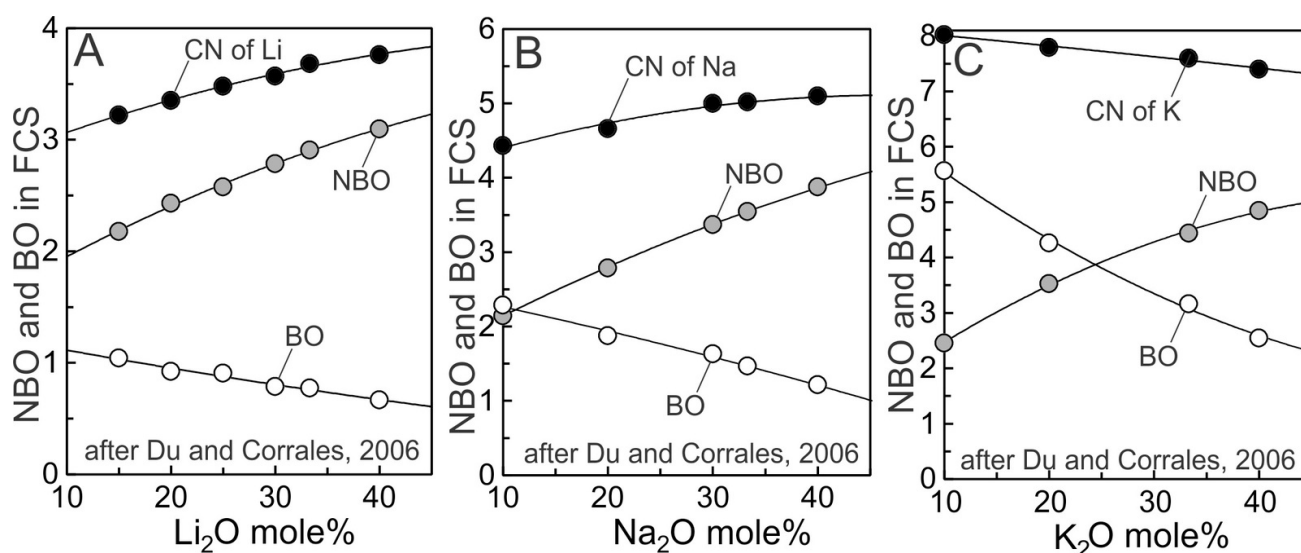


Figure 9. Illustrates the changes to coordination number (CN) and number of BO and NBO atoms in the first coordination sphere (FCS) of: (A) Li, (B) Na, and (C) K modifier cations. All data are taken from Du and Corrales (2006, their table 6).

charge density on NBO has been confirmed by others (Brückner et al., 1980; Ching et al., 1983, 1985; Nesbitt et al., 2015; Nesbitt, Henderson, et al., 2017). Also, the charge on BO is supported by MD simulations of Demiralp et al. (1999). The greater negative charge on NBO favors its incorporation (over BO) into the first coordination sphere (FCS) of cations. The ionic radius of Fe²⁺ is ~0.92 Å in 6-fold coordination and ~0.77 Å in 4-fold coordination whereas the radius of Ca²⁺ is ~1.26 Å (Huheey et al., 1993). Fe²⁺-NBO Coulombic attraction consequently is stronger than Ca²⁺-NBO attraction at equilibrium bond distances. NBOs produced upon dissolution of CaO in Fe-silicate melts thus will be attracted more to the FCS of the smaller Fe²⁺ than to that of the larger Ca²⁺. There is an important implication. Consider a Fe²⁺ coordination sphere consisting of 2 NBOs and 4 BOs. Its total charge is -4.48 (2[-0.96]+4[-0.64]). Replacement of three BOs by two NBOs leaves the total charge of the FCS unchanged at -4.48. Its CN has decreased from 6 to 5, as observed by Guo et al. (2013). Competition between Fe²⁺ and Ca²⁺ for O atoms thus may be resolved by Fe²⁺ shedding BOs while incorporating additional NBOs into its coordination sphere, thereby decreasing by one its CN. The BO lost may be incorporated into the FCS of a Ca²⁺. Competition for O atoms by modifier cations, coupled with the difference in charges on NBOs and BOs provides an explanation for changed CNs of Fe²⁺ in response to CaO dissolution in Fe-silicate melts. Uchino and Yoko (1999, p. 1857, last paragraph) came to the same conclusion from their ab-initio molecular orbital calculations on Li- and Na-silicate clusters. Their calculations indicated that the smaller Li atom bonded preferentially to NBOs for energetic reasons. Na (the larger cation) by contrast was coordinated to proportionally fewer NBOs and to proportionally more BOs. Shimoda et al. (2007) provide an example where Mg coordination decreases from 6 in MgSiO₃ glass to 5 in Mg₂SiO₄ glass. We suggest that destabilization of Mg sites by a de-

crease in CN is compensated for by an increased proportion of NBO in its first coordination sphere.

The change in CN (^{VI}Fe to ^VFe) results in less efficient packing (Hoylman, 1970; Song et al., 2008) and a greater $\bar{V}_{FeO}$ (table 2). Where the change occurs at constant temperature, α_{FeO} must increase (eq 2), all changes being driven by progressive dissolution of CaO in the Fe silicate melt. The process should affect preferentially CNs and α_N of small cations in melts containing large cations. Al³⁺, Fe³⁺ and Ti⁴⁺ are likely candidates to undergo CN reduction. MD calculations can be used to test the process by checking NBO:BO ratios in FCS of cations and correlating them with CNs of the cations. The MD code must, however, allow charges to be readjusted with change in melt topology, as did Demiralp et al. (1999).

5.2. A mechanism to change CN of cations

To decrease a CN by one, a M-O bond must be ruptured to extract an O atom from the FCS of M. An obvious mechanism would be for a tetrahedron to migrate away from the modifier cation, thereby removing an O from the FCS. The energetic cost likely would be similar to that associated with viscous flow. There is an energetically more favorable mechanism where no tetrahedra need to be 'displaced' beyond the second coordination sphere of the modifier cation.

A triangular section through a Si tetrahedron with an idealized O-Si-O angle of 109.45° and a Si-O ionic bond length of 1.61 Å is illustrated in figure 10A. Its solution yields an O-O distance of 2.63 Å, as obtained by Du and Corrales (2006, their table 7). Consider a K⁺ bonded to the two O atoms separated with the equilibrium K-O bond length. Accepting a ^{VIII}K-O ionic bond distance of 2.86 Å (Huheey et al., 1993, table 4.4), the O-K-O bond angle of figure 9A is calculated to be 54.7°. Du and Corrales (2006) documented the bond angle frequencies from their MD simulations and they obtain the greatest frequency at ~50° (fig. 10B, aster-

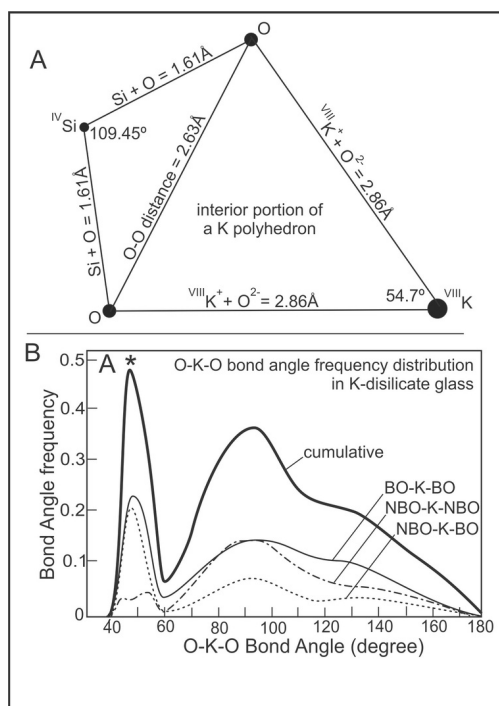


Figure 10. (A) Illustrates the geometric relationships between the O-Si-O angle of a tetrahedron and the O-M-O angle with a shared O-O side. The Si-O-Si triangle shown is a portion of a tetrahedron with an ideal tetrahedral angle of 109.45° and a typical Si-O bond length of 1.61 Å. The O-M-O triangle represents a portion of the K⁺ cation polyhedron with a K-O bond length equal to K-O values obtained by Du and Corrales (2006). The O-O bond distance, 2.63 Å is calculated from the O-Si-O triangle and the O-K-O angle is calculated by solving the triangle using the O-O and K-O bond lengths. (B) Illustrates the frequency distribution of O-K-O bond angles in K disilicate glass derived from molecular dynamics simulations of Du and Corrales (2006). The asterisk indicates the bond angle to be compared with the calculated O-K-O bond angle shown in (A).

isk). The ~50° bond angle is expected where two O atoms of the same Si tetrahedron are bonded to one K⁺ as shown in [figure 10A](#). The arrangement should be stable in that the O-Si-O tetrahedral angle is little strained and all bond distances are equilibrium values. The same calculation is performed on sodic glasses. Du and Corrales (2006) reported Na to be ~5-fold coordinated in Na-disilicate glass. The ^VNa⁺-O ionic bond length is 2.35 Å (Huheey et al., 1993). With this Na-O bond length and an O-O bond distance of 2.63 Å ([fig. 10A](#)), an O-Na-O bond angle of 68.1° is obtained by solving the O-Na-O triangle. The MD simulations of Du and Corrales (2006, their [fig. 10b](#)) yielded a strong bond angle frequency at ~60°. It is the angle expected where one tetrahedron contributes two O atoms to the first coordination sphere of Na⁺. In support, Du and Cormack (2004) had already noted that the small angle peaks in *Na-silicate crystals* arise from the arrangement. The O-M-O bond angle agreement is reasonable for K, and somewhat less so for

Na. The results demonstrate that individual tetrahedra may contribute two O atoms to the first coordination sphere of modifier oxides of size similar to or greater than Na⁺.

[Figure 11A](#) is a schematic diagram of a modifier cation (M) coordinated to 'n' O atoms, of which four O atoms are illustrated. The Q³ species contributes a NBO and BO to the first coordination sphere of M ([fig. 11A](#)). With the partial charge on BO being less than that on NBO, the BO-M bond is weaker than, and is more likely to dissociate than the NBO-M bond. With rupture of the BO-M bond, BO may rotate away from M ([fig. 11B](#), dashed arrow) thereby decreasing the CN of M by one with no change to the Si content of the second coordination sphere of M. Repeated rupture and re-formation of the BO-M bond results in a non-integer CN value of M averaged over time. Where a NBO approaches M, it may form a NBO-M bond displacing a BO-M bond. As NBO accumulates in the first coordination sphere of the modifier cation its CN may decrease by preferential loss of BOs, as argued in the previous section.

6. CONCLUSIONS

Integration of the differential form for the coefficient of thermal expansion (eq 1) to obtain a logarithmic expression in volume and temperature (eqs 2, 4, 6) simplifies quantification of α values and should provide more accurate α values of melts (and their components) than do traditional methods. A thermodynamically rigorous equation is developed (eq 11) by which to check α values of components of melts or glasses against experimentally determined α values of a bulk melt or glass. The equation provides a severe test of the accuracy of partial α values of the constituent components of melts and glasses.

The coefficients of thermal expansion of alkali and alkaline earths oxides in siliceous melts are determined primarily by the strength of the Coulombic force of attraction between the cation and oxygen ion. The oxide with the weakest attraction (Cs₂O) has the greatest expansivity of the Group 1 and 2 metal oxides whereas that with the strongest Coulombic interactions has the smallest expansivity (MgO). The coefficients of thermal expansion of a few 3d (MnO for example) and 4f metal oxides (Dy₂O₃ and Ho₂O₃) also seem to be controlled by the Coulombic force of attraction, but α_N for the majority of both groups likely are determined by changes to CN. The α_N values of network formers apparently are determined by changes to CN yielding both large positive and negative α values and to electrostriction.

The partial charges on NBO (-0.96) and BO (-0.64) affect their ratio in the first coordination sphere of Na⁺ (and other modifier cations) as well as affecting the CN of a modifier cation. The greater the number of NBOs in the coordination sphere of a modifier cation, the lower its CN may be. These partial charges also influence, indirectly, the mechanism by which CNs of cations are altered. By the mechanism proposed, changes to the CN of a modifier cation involve only rotation or tilting of Si tetrahedra contributing O atoms to the first coordination sphere of a cation. No disruption to the second coordination sphere (Si atoms) of the modifier

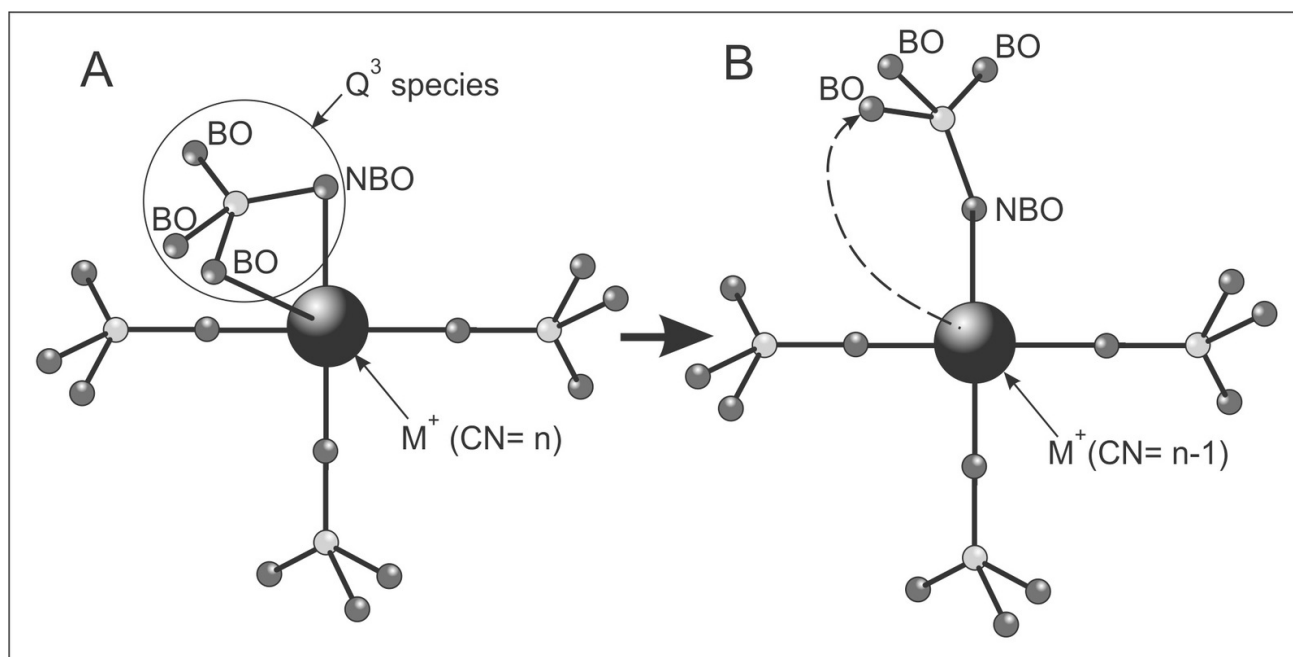


Figure 11. Illustrates the manner in which the coordination number of a modifier cation decrease without involvement of the second coordination sphere (Si atoms) of the modifier cation. (A) Highly schematic representation of a modifier cation (K^+) bonded to four Si tetrahedra, one of which contributes two O atoms to the first coordination sphere (FCS) of K^+ . For simplicity, only 5 O atoms of the FCS are shown. One tetrahedron contributes a NBO and a BO thus to the FCS of K^+ . (B) With thermal agitation, the weaker BO- K^+ bond may rupture while the NBO- K^+ is maintained, thus reducing by one the CN of K^+ . In response the partial molar volume of the modifier oxide should increase in response to a decrease in CN (as should expansivity if the change to CN occurs at constant (or very small change to) temperature. There is, however, no change to the second coordination sphere of the modifier cation.

cation need occur during changes to CN of the modifier cation.

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