[American Journal of Science, Vol. 304, October/November, 2004, P. 637–678]

American Journal of Science

OCTOBER/NOVEMBER 2004

AN EQUATION OF STATE FOR SILICATE MELTS.
I. FORMULATION OF A GENERAL MODEL

MARK S. GHIORSO

Department of Geophysical Sciences, The University of Chicago, 5734 S Ellis Avenue,
Chicago, Illinois 60637; ghiorso@geosci.uchicago.edu

ABSTRACT. A simple, empirical, volume-explicit equation of state (EOS) is developed for use in describing the volumetric properties of materials that exhibit large thermal expansivities and strongly non-linear, pressure-dependent compressibilities. Existing and commonly used EOS expressions, like the Universal and Birch-Murnaghan equations, develop singularities at critical values of temperature and pressure that prevent the calculation of derived thermodynamic properties for this class of substances. The proposed EOS reduces to a simple polynomial form at low-pressure; this form is utilized in the literature to describe the properties of silicate melts at 10^5 Pa. At high-pressures, the proposed EOS can be parameterized to yield a finite, non-zero volume limit, unlike other formulations. Thermodynamic properties can be calculated using the proposed EOS without the need for iterative solutions and all derivative and integral representations of the equation are analytic.

A detailed example is developed demonstrating how the proposed EOS can be utilized in modeling the Gibbs free energy of amorphous silica at elevated temperature and pressure. The thermodynamic model described in the example accounts for *vibrational* contributions to the energy of the system as well as *configurational* effects arising from increases in the coordination number of Si with temperature and pressure. Vibrational contributions are modeled at elevated pressure by the proposed EOS. Configurational contributions are described by a simple associated solution model for the entropy of mixing. Parameters are calibrated from molecular dynamical simulations of the configurational and volumetric properties of amorphous silica. The calibration is used to calculate the phase diagram of silica to 3000 K and 15 GPa, which compares quite favorably with experimental data on melting.

INTRODUCTION

An equation of state (EOS) embodies a quantitative functional relationship between the volumetric properties of a phase and its specified composition, temperature (T) and pressure (P). Such a relation allows for estimates of density to be made at elevated T and P as well as all derivative and integral properties of the volume. In conjunction with measurements or model values of the zero-pressure heat capacity, an EOS permits calculation of all thermodynamic state functions at elevated temperatures and pressures. The ability to quantify the thermodynamic properties of silicate melts at elevated pressure is essential for a detailed understanding of the generation of magmas. Estimates of melt-productivity and melt-buoyancy as functions of T, P and bulk composition are critical quantities that constrain geophysical models of melting and melt-transport. Consequently, an accurate, robust and comprehensive EOS is fundamental to any quantitative analysis of magma production in the Earth and related planetary bodies.

In this paper, a new functional form for an EOS of molten silicate liquids is developed. The proposed EOS is designed for application over a wide range of melt compositions and for use at pressures from reference conditions (P_r, that is 10^5 Pa) to approximately 100 GPa. In subsequent contributions, the parameters of this EOS will be calibrated from extensive data available on reference pressure properties (Ghiorso and Kress, 2004, hereafter Part II), fusion curves of silicate minerals (Ghiorso, 2004a, hereafter, Part III), molecular dynamical simulations of liquid properties [this paper; Ghiorso 2004a, 2004b (hereafter Part IV)], and experimental data on melt densities at high P derived from both static and dynamic (shock wave) measurements (Ghiorso, 2004a, 2004 b). In a subsequent contribution, the proposed EOS will be utilized in the construction of a thermodynamic model suitable for the description of melting relations in the Earth's mantle at pressures up to those corresponding to the base of the transition zone.

In formulating an EOS for a phase of variable composition and structure, like a multicomponent silicate liquid, consideration must be given to a number of factors that are not a concern in the development and calibration of an EOS for isostructural stoichiometric solids. First and foremost is the issue of mixing relations. How will the parameters of the EOS be specified as a function of composition? In the case of silicate liquids, the development of mixing relations is thwarted by an inadequacy of experimental data, especially at elevated pressure. If progress is to be made in developing an EOS that may be used to describe natural composition liquids, some simplification must be adopted that both captures the first order features of existing experimental observations and lends itself to extrapolation to chemical systems and physical conditions not represented by measurement. Whatever EOS is adopted for describing the volumetric properties of silicate liquids, the parameters of that EOS must vary smoothly and *consistently* from one composition to the next, and to be practical, this compositional variation must be predictable by a suitably simple algorithm. Most importantly, whatever algorithm is chosen to specify the mixing relations, the model parameters must satisfy the thermodynamic constraints embodied in the Gibbs-Duhem relation, that is, the cross-partial derivatives of the chemical potentials of components in the liquid with respect to composition must be equivalent – a requirement derived from the fact that the Gibbs free energy is a function of state (Prigogene and Defay, 1954). Arbitrary and independent mixing relations applied to EOS parameters that are meant to describe a thermodynamic quantity (for example, bulk modulus or its derivatives) may not satisfy the Gibbs-Duhem requirement unless particular care is taken in specifying the functional form of these relations.

A second consideration that is not a principal concern for solids but enters into the formulation of an EOS for condensed fluids is the issue of variation in the structural state of the material. At issue in silicate melts is the change in melt structure with T, P and composition, which develops in liquids mainly from the absence of long-range order. It is well known that volume, thermal expansion, bulk modulus, *et cetera*, differ across polymorphic transitions in minerals and that compositional variation in mineral solid solutions can induce structural phase transitions. Although equivalent structural transformations in liquids are generally not first order (Tanaka, 2000), nevertheless the variation in thermodynamic properties that derives from the transformation must be accounted for. Generally, these contributions are considered to be *configurational* in origin, while the changes in thermodynamic properties that take place in isostructural materials are termed *vibrational*. Dominance of either contribution to the thermodynamic quantity of interest depends largely on the "narrowness" of the structural transition, that is, the temperature, pressure or compositional interval over which the transformation occurs. An EOS can be formulated to account for both configurational and vibrational contributions to the volume, but such formulations are necessarily complex, and there are more intuitive thermodynamical methods, which account explicitly for configurational entropy, that are better suited for modeling the non-vibrational contribution. One such method, based upon associated solution theory, will be developed later in this paper as an example for utilizing the proposed EOS on a silicate liquid that undergoes change in coordination of silicon with respect to oxygen as a function of T and P. In this paper a functional form for a liquid EOS will be derived on the assumption that it accounts solely for vibrational contributions to the volumetric properties of the system. This assumption permits the adoption of a number of simplifying features without necessarily compromising the utility of the resulting model. In Part IV it will be shown how this assumption permits EOS-parameter-mixing relations to be developed that are both simple and that satisfy the Gibbs-Duhem requirement on the Gibbs free energy of the multicomponent liquid.

This paper deals with the following topics. Existing EOS models for silicate melts are reviewed and their deficiencies noted. Requirements of a silicate liquid EOS are stated and a suitable expression is derived. Characteristics of the proposed EOS are examined in (1) a simple application of the T and P dependence of the thermodynamic properties of an "isostructural" liquid, and (2) a more complex and realistic application of the EOS to a liquid undergoing coordination changes as a function of both T and P. In the course of development of the second example, it is demonstrated how to combine the proposed EOS with an associated solution model for the melt in order to account for configurational contributions to the volumetric properties. An appendix is provided with expressions for all the derivative and integral thermodynamic functions of state that may be needed to apply the proposed EOS in practice.

Current Models and Calibrations for the Liquid State

Two EOS formulations are commonly applied to silicate melts. The first involves a polynomial or Taylor expansion of the volume (V) in pressure, usually truncated at second order, for example,

$$V = V_0(n_i, T) + V_1(n_i, T) \times (P - P_r) + V_2(n_i, T) \times (P - P_r)^2 \tag{1}$$

where the coefficients of the expansion are taken to be simple functions of composition (n_i) and temperature. This EOS has been utilized for parameterization of experimental data on melting curves (Ghiorso and Sack, 1995), for the analysis of ferric-ferrous equilibria in melts at 10^5 Pa (Kress and Carmichael, 1991), and for calculation of phase equilibria involving multicomponent silicate melts at pressures less than 2 GPa (Ghiorso and Sack, 1995).

The second most commonly applied EOS for silicate melts is the Birch-Murnaghan equation, which has had enormous success as a means of systematizing and extrapolating the P-V-T relations of minerals and the bulk properties of many other substances of geophysical interest. Application of this EOS to silicate liquids has been popularized by researchers focused on the analysis of fusion curves of simple silicate minerals (for example, Herzberg, 1987a, 1987b; Lange and Carmichael, 1987; Lange, 2003). The Birch-Murnaghan EOS has also been utilized to interpret experimental constraints on liquid density at high pressure (for example, Rigden and others, 1984; Stixrude and Bukowinski, 1990; Saxena and others, 1993; Agee, 1998; Fabrichnaya and others, 2004) and Ghiorso and others (2002) applied this EOS to the calculation of thermodynamic properties of multicomponent silicate liquids at pressures up to 3 GPa. The functional form of the Birch-Murnaghan EOS is derived from the Eulerian finite-strain theory of solids (Birch, 1939, 1952; Anderson, 1989). The equation most commonly used corresponds to a particular case of the general pressure-strain expansion that is truncated to third order:

$$P = \frac{3}{2} K\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]\left\{1 - \frac{3}{4}(4 - K')\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\} \tag{2}$$

where V_0 is the volume at zero pressure, K is the isothermal bulk modulus,[1] and K' is dK/dP. As will be shown below, both equations (1) and (2) can be problematic when applied as an EOS for silicate melts.

Use of the Taylor expansion form of the liquid EOS (eq 1) is motivated mainly by its success in describing low-pressure experimental results. Generally, temperature dependence of the volume is accommodated by assuming linear behavior in the low-order coefficients, as

$$V = V_{0,T_r}(n_i) + \frac{dV_0}{dT}(n_i) \times (T - T_r) + \left[V_{1,T_r}(n_i) + \frac{dV_1}{dT}(n_i) \times (T - T_r) \right] \times (P - P_r) + V_2(n_i) \times (P - P_r)^2 \tag{3}$$

The mixing relations are usually described by linear functions, for example, $V_{m,T_r}(n_i) = \Sigma n_i \bar{v}_{m,i,T_r}$, where n_i denotes the moles of component i and $\bar{v}_{m,i,T_r}$ are constants parameterized from experimental data. The observation that linear mixing relations are sufficient to describe the vast majority of experimental measurements of melt density and sound speed at 10^5 Pa is both remarkable and convenient, and although important exceptions to the linear mixing "rule" occur in alkali-rich, Ti-bearing melts (Liu and Lange, 2001) and CaO-rich liquids in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system (Courtial and Dingwell, 1995), linear mixing accounts for experimental observations on multicomponent "magmatic" composition melts to within the accuracy of measurement (Lange and Carmichael, 1990). The simplicity that this approximation brings to the implementation of equation (3) for magmatic composition liquids is enormously compelling and would motivate its use as a liquid EOS were it not for the poor manner in which the expression extrapolates at elevated pressure. As P becomes very large V becomes unbounded and the only way to dampen this behavior is to modify equation (3) with additional higher order terms in P. The polynomial expansion is simply not suited to the exercise of extrapolating measurements made at low pressure to higher P conditions when there is a dearth of experimental data at elevated pressure. This drawback essentially precludes the use of equation (3) (or variants of it) as an EOS for silicate melts at $P > 2$ GPa (Ghiorso and Sack, 1995).

Use of the Birch-Murnaghan EOS (eq 2) for silicate liquids is aimed directly at addressing this deficiency. It is apparent from examination of equation (2) that as P trends to very high pressure, the volume must trend asymptotically to zero. Consequently, $V(P)$ curves may be extrapolated meaningfully in P with estimates of only three parameters, V_0, K, and K'. The principal question in utilizing the Birch-Murnaghan EOS is how to parameterize temperature-dependence in the model equation. One approach commonly utilized (for example, Saxena and others, 1993; Ghiorso and others, 2002; Fabrichnaya and others, 2004) is to incorporate the temperature-dependence by making the model parameters V_0 and K functions of T. Two problems with this approach emerge in practice. First, if K' is treated as a constant, then it is easy to show that[2]

$$2V_0 \frac{\partial K}{\partial T} = K \frac{\partial V_0}{\partial T} \tag{4}$$

must hold. By replacing $\partial K/\partial T$ with the thermodynamic identity

---

[1] The isentropic bulk modulus may be utilized in other applications of the Birch-Murnaghan equation, as for example in the analysis of shock compression data.

[2] Start with $(\partial/\partial T)(\partial V/\partial P) = (\partial/\partial P)(\partial V/\partial T)$ and insert the definition of $K\,[\equiv -V/(\partial V/\partial P)]$

$$\frac{\partial K}{\partial T} = \frac{K}{V}\frac{\partial V}{\partial T} + \frac{K^2}{V}\frac{\partial^2 V}{\partial T \partial P}$$

a required relation is obtained that must be supported by experimental observation

$$\frac{\partial^2 V_0}{\partial T \partial P} = \frac{1}{2V_0}\frac{\partial V_0}{\partial T}\frac{\partial V_0}{\partial P} \tag{5}$$

Equation (5) in fact does not hold for silicate melts (Kress and Carmichael, 1991), and if K' is treated as constant, this violation introduces an inconsistency which ultimately leads to a violation of Maxwell's relations (exactness criteria) involving the second partial derivatives of the Gibbs free energy.

The second problem alluded to in the previous paragraph relates again to the issue of constant K', but here the focus is on the value of K' required to describe the pressure dependence of the compressibility in molten silicate liquids. Analysis of silicate fusion curves and high-P density data (for example, Herzberg, 1987a, 1987b; Agee, 1998) reveal that values of K' on the order of 10 to 12 are necessary to account for the rapid increase in K (or equivalently a decrease in melt compressibility) with increasing pressure above 10^5 Pa. Unfortunately, such large values of K' exceed the theoretically valid range over which the 3rd order Birch-Murnaghan EOS may be applied ($3.8 < K' < \sim 8$, Hofmeister, 1993). Poirer and Tarantola (1998) attempt to address this deficiency by re-deriving Birch's expression utilizing the Hencky or logarithmic strain. Their resulting isothermal EOS is valid for a much wider numerical range of K'.

One possible approach to using the Birch-Murnaghan EOS on silicate melts of moderate K', is to avoid the inconsistencies generated by treating V_0 and K (or possibly even K') as functions of T, and take these parameters to be constants for a particular reference temperature (T_r). The model-derived pressure (P_{T_r}) *from equation (2) is then corrected using the relation*

$$P = P_{T_r} + \alpha K(T - T_r) \tag{6}$$

where α is the thermal coefficient of expansion. Equation (6) embodies the "so-called" thermal pressure correction (Anderson, 1984, 1995), which has been shown to work reasonably well for a variety of solids and is incorporated into a number of EOS formulations. In particular, Stixrude and Bukowinski (1990) utilize the thermal pressure correction to the third-order Birch-Murnaghan EOS to parameterize the thermodynamic properties of silicate melting phase diagrams to pressures up to 100 GPa. Schlosser and others (1989) develop a similar method and apply it to the pressure dependence of the melting of metals. Despite these successes, there remains a difficulty with using equation (6) in conjunction with Birch-Murnaghan in that the combination leads to singularities in derivative thermodynamic functions of state for moderate degrees of expansion. The analysis supporting this claim proceeds as follows. Rewriting equations (2) and (6) as

$$P = 3Kf(1 + 2f)^{5/2}\left[1 - \frac{3}{2}f(4 - K')\right] + \alpha K(T - T_r) \tag{7}$$

where $f = \frac{1}{2}[(V_0/V)^{2/3} - 1]$, and forming the isothermal pressure derivative of f, results in the relation

$$\frac{\partial f}{\partial P} = \frac{\beta}{2}\left(\frac{V_0}{V}\right)^{2/3} = \frac{2}{3K(1 + 2f)^{3/2}[2 - 2(5 - 3K')f + 27(K' - 4)f^2]} \tag{8}$$

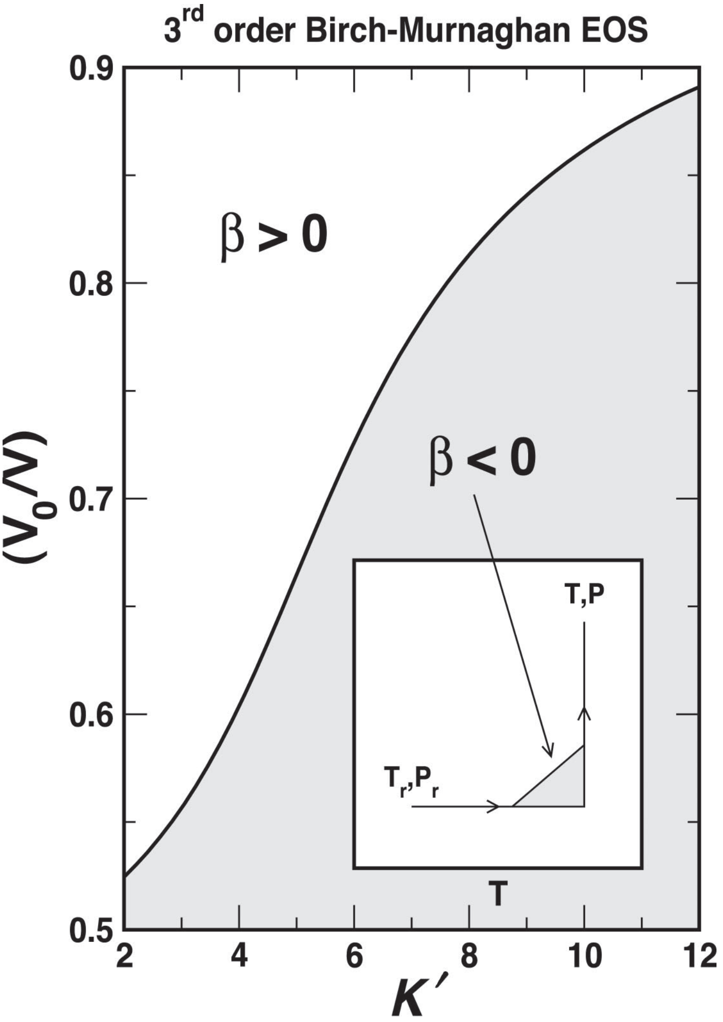

Fig. 1. Feasible solution region for the 3rd order Birch-Murnaghan EOS modified for the "thermal pressure" correction. The curve separating the fields of inferred positive and negative compressibility (β) denotes a locus of singular solutions given by equation (9) where β approaches +∞ as K' increases and β approaches −∞ as K' decreases. Note that ordinal values less than unity imply expansion, and consequently this singular condition is only realized in practice when the EOS is utilized to calculate Gibbs free energies at high T and low P (see inset and discussion in the text).

where β is the isothermal compressibility $[-(1/V)(\partial V/\partial P)]$. The right-hand-side of equation (8) is singular (and consequently β becomes infinite) at the roots of the polynomial enclosed by the square brackets. These roots are given by

$$f = \frac{1}{2}\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right] = \frac{(5 - 3K') \pm \sqrt{241 - 84K' + 9K'^2}}{27(K' - 4)} \tag{9}$$

A plot of this relation between expansion and K' is provided in figure 1, where for example it can be seen that for a K' of 8, an expansion of roughly 17 percent leads to a singularity in the compressibility (which is preceded by a rapid rise in β). An argument could be made that the EOS would never be used for the case of $V > V_0$, but that argument is spurious. For the purposes of thermodynamic calculations, the volume and all of its derivatives must be defined over the entire T-, P-rectangular region bounded by the coordinates (T_r, P_r), (T, P_r), (T_r, P), and (T, P) (see inset in fig. 1). This procedure is necessary in order that the line integral of the differential of the Gibbs free energy,

$$G_{T,P} - G_{T_r,P_r} = \int_{\xi_r}^{\xi} \left(-S\frac{dT}{d\xi} + V\frac{dP}{d\xi} \right) d\xi$$

be defined for *an arbitrary integration path* $[T(\xi), P(\xi)]$. As the Gibbs free energy is an exact function, any arbitrary path of integration from (T_r, P_r) to (T, P) must yield the same result, so if the integral is undefined because the integrand becomes singular along some particular path through T-P space, the integral must be undefined for all paths through T-P space. Consequently, the singular behavior exhibited by the "thermal pressure" modification of the Birch-Murnaghan equation (for example, fig. 1) renders it unsuitable as a *thermodynamic* EOS although it remains a legitimate means of calculating volumetric quantities *within the feasible portion* of T-P space. For temperatures considerably above the reference state, and for liquids with large thermal coefficients of expansion, it is not unusual to encounter volume expansions that approach the thermodynamically invalid region of figure 1. Apparently, Stixrude and Bukowinski (1990) never tested a parameter combination of K' and thermal expansion that fell outside the feasible region. They probably never tested this combination because they did not have the opportunity to analyze data for alkali silicate liquids or for stoichiometric orthosilicate liquids (for example, Mg_2SiO_4 or Fe_2SiO_4), where infeasible parameter combinations are more likely to occur (Ghiorso, 2004a).

From the above discussion of the limitations and difficulties of applying both a simple Taylor expansion EOS and the Birch-Murnaghan EOS, it is worth exploring the applicability of other EOS formalisms to the silicate melts problem before embarking on an entirely new approach. Because of its enormous success in describing the properties of many condensed phases to very high pressure (Hama and Suito, 1996) and because its application requires values of only four parameters, all of which can be obtained from low-pressure experimental measurements, the Universal EOS of Vinet and coworkers (Vinet and others, 1986, 1987) is worth serious consideration.

The Universal EOS has the form

$$P = \frac{3K(1 - x)e^{\eta(1-x)}}{x^2} + \alpha K(T - T_r) \tag{10}$$

where η and x are defined as

$$\eta = \frac{3}{2}(K' - 1) \tag{11}$$

and

$$x = \left(\frac{V}{V_0}\right)^{1/3} \tag{12}$$

Model parameters of the Universal EOS (V_0, α, K, K') are treated as constants with values obtained from low-pressure experiments. The first term in the Universal EOS is derived from a generalized bonding potential function. The second term is simply the thermal pressure correction (eq 6) to the reference temperature potential. Equation

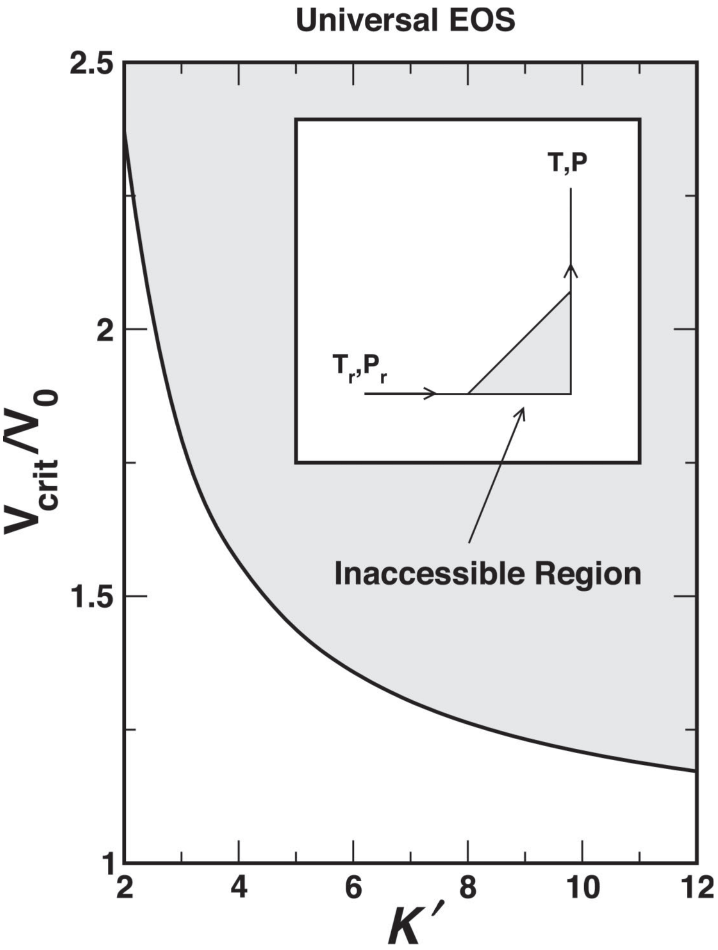

Fig. 2. Feasible solution region for the Universal EOS. The curve separating the accessible from the inaccessible region denotes a locus of singular solutions given by equation (14) where $\alpha_{T,P}$ approaches $\pm\infty$. Ordinal values greater than unity imply expansion, and as in the EOS evaluated in figure 1, this singular condition is only realized in practice when the EOS is utilized to calculate Gibbs free energies at high T and low P (see inset and discussion in the text).

(10) is valid under T, P conditions corresponding to compression but like the Birch-Murnaghan EOS, fails for critical values of expansion. This failure is easy to demonstrate by differentiating equations (10) and (12) to examine the functional form of $\partial V/\partial T$,

$$\frac{\partial V}{\partial T} = 3V_0x^2\frac{\partial x}{\partial T} = -\frac{3V_0\alpha x^5}{3e^{\eta(1-x)}[\eta x^2 + (1-\eta)x - 2]} \tag{13}$$

which has a singularity at the root of the polynomial $\eta x^2 + (1-\eta)x - 2$, given by

$$\left(\frac{V_{crit}}{V_0}\right)^{1/3} = x_{crit} = \frac{\eta - 1 \pm \sqrt{\eta^2 + 6\eta + 1}}{2\eta} \tag{14}$$

Solutions to equation (14) are plotted in figure 2 where it can be seen that, like the

Birch-Murnaghan EOS, the singular behavior in the Universal EOS precludes evaluation of the volume at temperatures corresponding to moderate values of expansion (at high values of K'). This behavior in turn prevents evaluation of the pressure integral of the Gibbs free energy, which requires that the volume function be defined everywhere along the path $(T, P_r) \rightarrow (T, P)$. Although this behavior is seldom a difficulty in application to solids (where α values are small and K values are large), for silicate liquids, which characteristically have α about an order of magnitude greater (at P_r) than for solids, the infeasible region is more often encountered. Consequently, as a generally applicable functional form for silicate liquids, the Universal EOS falls deficit.

A survey of a variety of alternate EOS formulations developed for solids and simple liquids point to similar deficiencies. The models of Stacy and others (1981), Kumari and Dass, (1986, 1990a, 1990b, 1991, 1993), Schlosser (1990; Schlosser and Ferrante, 1988a, 1988b, 1989; Schlosser and others, 1989), Parsafar and Mason (1994), Baonza and others (1995), Kaufman and Schlosser (1995), Hama and Suito (1996), Taravillo and others (1996), Kuchhal and others (1997), and Poirier and Tarantola (1998) all involve a thermal pressure correction of some kind or are formulated to deal only with the isothermal case.

Given the failure of the polynomial expression (eq 1) in extrapolation, and the potential pitfalls associated with adding temperature dependence in the Birch-Murnaghan and Vinet models, there is clearly incentive to develop an EOS formulation better suited to the particular P-V-T behavior of silicate liquids.

REQUIREMENTS OF A GENERAL LIQUID EOS

The objective is to develop an EOS for silicate melts with the following characteristics and constraints:

- The EOS must embody a relation between V, T and P that permits calculation of V under any T, P conditions, including expansion.
- The EOS must provide a flexible enough functional form to capture the rapid decrease in β with increasing P at low pressures.
- The EOS must exhibit limiting behavior at high pressure in order to (1) account for experimental results observed in shock compression studies (for example, Rigden and others, 1984) and (2) facilitate the extrapolation of low-P measurements to high-P conditions.
- The EOS must reduce in the low-pressure limit to the simple "polynomial-like" functions that have been used to successfully model experimental data at 10^5 Pa.
- The EOS should have simple mixing relations because silicate melts seem to exhibit this behavior at low-pressure and because of the desire to minimize the number of adjustable parameters needed to describe the V-T-P relations of complex melts at elevated pressure.
- The EOS should have analytic integrals and derivatives so that closed form expressions for thermodynamic state functions may be derived from it.
- The EOS should attempt to account only for the T and P dependence of the volumetric properties of liquids of constant structural configuration. In other words, the EOS should correspond to a standard state of *unit activity of a hypothetical silicate liquid of specified composition and structure at any T and P.*

Pressure Dependence

A procedure to construct an EOS that meets these requirements is followed by generalizing the low-P polynomial EOS (eq 1) as a 4th-order Taylor expansion of the volume about the reference pressure (hereafter, 10^5 Pa):

$$V = V_0 + V_1(P - P_r) + \frac{V_2}{2}(P - P_r)^2 + \frac{V_3}{6}(P - P_r)^3 + \frac{V_4}{24}(P - P_r)^4 \qquad (15)$$

The coefficients of equation (15) correspond to the 0th to the 4th order pressure derivatives of the volume at P_r. Although convenient from the standpoint of physical interpretation and ease of manipulation, as an EOS, equation (15) is unacceptable because it extrapolates poorly in pressure (see above). This situation can be rectified however, by constructing an approximation to equation (15) that has the functional form of the ratio of two polynomials. If both of these polynomials are of the same order, then the limit of the transformed function at high P will be bounded. A suitable transformation is the Padé Approximant (Baker and Graves-Morris, 1996) of equation (15), which is given by

$$V = \frac{V_0 + (V_1 + V_0 a)(P - P_r) + \left(\frac{V_2}{2} + V_1 a + V_0 b\right)(P - P_r)^2}{1 + a(P - P_r) + b(P - P_r)^2} \tag{16}$$

where the parameters a and b are defined as

$$a = \frac{V_2 V_3 - \frac{1}{2} V_1 V_4}{2 V_1 V_3 - 3 V_2^2} \tag{17}$$

$$b = \frac{\frac{1}{4} V_2 V_4 - \frac{1}{3} V_3^2}{2 V_1 V_3 - 3 V_2^2} \tag{18}$$

The parameters of equation (16) can be directly related back to the original physically meaningful Taylor expansion coefficients, for example,

$$V_3 = -3(2bV_1 + aV_2) \tag{19}$$

$$V_4 = 12(a^2 V_2 + 2abV_1 - bV_2) \tag{20}$$

but the functional form of equation (16) allows for smooth and bounded extrapolation to high-pressure; the volume behaves as a quadratic polynomial in pressure that is dampened by the denominator so that at high-P the ratio of the two polynomials approaches an asymptotic limit. To this end, the order of truncation of the Taylor expansion of V in equation (15) was chosen to give the Padé Approximant the desired characteristics, namely quadratic pressure-dependence in both the numerator and the denominator, as the sum of the order of both polynomials of this rational function must be the order of the original polynomial expansion.

Temperature Dependence

Development of the proposed liquid EOS is completed by generalizing equation (16) to include temperature dependence. The most direct approach is to make each of the Taylor expansion coefficients, V_0, V_1, V_2, V_3, and V_4 functions of T, and therefore also the derived parameters a and b. The major difficulty with this approach is that experimental data are only available on the temperature dependence of V_0 and V_1 (see Part II) while that for the other Taylor expansion coefficients must be inferred. In an effort to minimize the number of parameters that must be fitted or estimated in order to utilize the proposed EOS, the following assumptions regarding temperature dependence will be made. The parameter $V_2 \left(\left.\frac{\partial^2 V}{\partial P^2}\right|_{P_r}\right)$ will be assumed to be independent of T as will the parameters a and b. The latter assumption requires that V_3 and V_4 exhibit a temperature-dependence related to that of V_1 via the relations (19) and (20).

The functional form of the temperature dependence of V_0 and V_1 should be simple; experimental observations suggest that a straightforward linear dependence on T is justified. However, an expression of the form

$$V_{0,T} = c + d(T - T_r) \tag{21}$$

implies that the thermal coefficient of expansion,

$$\alpha_T = \frac{1}{V_{0,T}} \frac{\partial V_{0,T}}{\partial T} \tag{22}$$

has a temperature dependence

$$\frac{\partial \alpha_T}{\partial T} = -\left[\frac{d}{c + d(T - T_r)}\right]^2 \tag{23}$$

that requires a decrease with increasing T. Although there is no thermodynamic requirement that is violated by this condition, the behavior is unusual in solids (Anderson, 1995) and is generally associated with some structural transformation. Generalizing equation (21) to include a term like $e(T - T_r)^2$ will allow for both positive and negative $\partial\alpha/\partial T$, but this term introduces an additional parameter that is poorly constrained from available experimental data.

In order to avoid these difficulties and in order to keep the number of parameters at an absolute minimum, the following temperature dependence is adopted for V_0 in the proposed EOS

$$V_{0,T} = V_{0,T_r} e^{\alpha(T - T_r)} \tag{24}$$

where V_{0,T_r} is the melt volume and α is the thermal expansion coefficient, both evaluated at T_r and P_r. The form for the temperature-dependence of V_1 will be motivated by the experimental calibration of this quantity in Part II. At this point it should be noted that a temperature-dependence to V_1 is required, but for now its functional form is left unspecified.

PROPOSED EOS

Summarizing the arguments and assumptions of the previous paragraphs, equation (16) may be rewritten to provide an expression for $V(T, P)$

$$V = \frac{V_{0,T} + (V_{1,T} + V_{0,T}a)(P - P_r) + \left(\frac{V_2}{2} + V_{1,T}a + V_{0,T}b\right)(P - P_r)^2}{1 + a(P - P_r) + b(P - P_r)^2} \tag{25}$$

Various thermodynamic state functions are developed from this expression in the Appendix. Below, some comments are made regarding general features of this EOS and limiting behavior. Following that, a detailed example using equation (25) to describe the volumetric properties of a real liquid is developed. The issue of developing mixing algorithms for parameter values in the proposed EOS will be taken up in Parts II and IV.

DISCUSSION AND APPLICATION TO SIMPLE LIQUIDS

In figure 3A comparison is drawn between the pressure dependence of V, K and K' along a 1400 °C-isotherm for four different EOS forms: the 3rd order Birch-Murnaghan EOS, the Universal EOS, the EOS proposed in this paper, and the equivalent 4th order polynomial representation of the volume. All four are evaluated for the case of $CaMgSi_2O_6$ liquid (parameters listed in table 1). A K' of 4.6 is chosen for

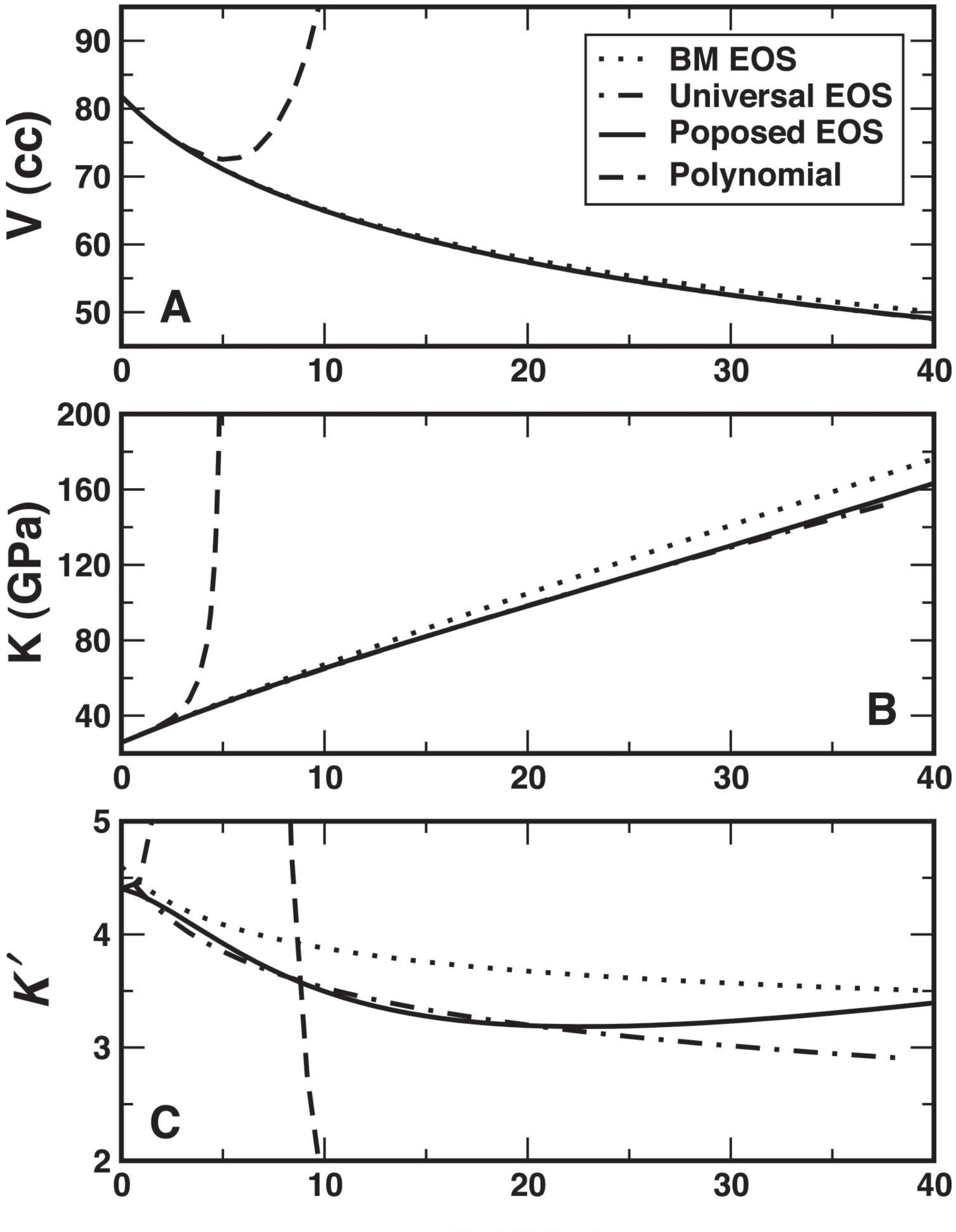

Fig. 3. Comparison of $V(P)$, $K(P)$ and $K'(P)$ relations for four EOS forms discussed in this paper: the 3rd order Birch-Murnaghan EOS (BM), the Universal EOS, the EOS proposed in this paper, and the equivalent polynomial Taylor expansion expression. Parameters correspond to $CaMgSi_2O_6$ composition liquid and are tabulated in table 1. The proposed EOS is calibrated to mimic the Universal EOS over the pressure range shown. Note that above the singularity in K for the polynomial equation (at about 5 GPa), values of K are negative and are not plotted.

TABLE 1

Parameter values for EOS comparison

Parameter	Value	Units	Source
V_0	81.82	cc	Lange and Carmichael (1987)
$\frac{\partial V_0}{\partial T}$	5.54×10^{-3}	cc/K	
α	6.77×10^{-5}	1/K	
$\frac{\partial V_0}{\partial P}$	-3.17	cc/GPa	Kress and Carmichael (1991)
β	3.87×10^{-2}	1/GPa	
K	25.8	GPa	
K'	4.6		Estimated
$\frac{\partial^2 V_0}{\partial T \partial P}$	-1.60×10^{-3}	cc/K-GPa	Kress and Carmichael (1991)
ε	5.05×10^{-4}	1/K	
a	1.58×10^{-1}	1/GPa	Estimated from fit to Universal EOS over the range 0-40 GPa
b	3.00×10^{-3}	$1/(\text{GPa})^2$	
V_2	6.64×10^{-1}	$1/(\text{GPa})^2$	

illustration, and unspecified parameters for equation (25), that is V_2, a, and b, are estimated by non-linear regression of volumes calculated from the Universal EOS over the range 0 to 40 GPa. Figure 3A demonstrates that the proposed EOS can be made to exactly mimic $V(P)$ of the Universal EOS, but the functional form of the proposed EOS is not limited to this pressure dependence. The relative sizes of the a, b and V_2 parameters govern the curvature of $V(P)$ at pressures close to P_r and the asymptotic behavior of the EOS at high pressure. Close to P_r, the curvature is dominated by the parameter V_2; at intermediate P, where $|a(P-P_r)| >> |b(P-P_r)^2|$, the a parameter has principal influence on the shape of the $V(P)$ curve; while at higher pressure the curvature is largely controlled by the b parameter. All three parameters can be varied independently to achieve considerable flexibility with the functional form of the $V(P)$ curve. At high P, the volume limit is given by

$$\frac{\lim}{P \rightarrow \infty} V = V_{0,T} + \frac{V_{1,T}a + V_2}{b} \tag{26}$$

and this limit may be used as a dependency amongst the high-P EOS parameters, especially when experimental data for calibration are only available at low pressures. Note that unlike the Birch-Murnaghan or Vinet equations, the high-pressure volume limit of the proposed EOS is not necessarily zero. This characteristic is shared with other well-known formulations for fluids including the van der Waals and the Redlich-Kwong equation (Prausnitz, 1969). The physical interpretation of this limit is that practically, compression can only proceed until it asymptotically approaches an intrinsic volume of the system, bearing in mind that the structural state of the material may be metastable under such extreme levels of compression.

The curves graphed in figure 3A highlight the advantage of the rational approximation form of the EOS when compared directly against the polynomial Taylor expansion curve. The Taylor expansion form is acceptable only at pressures below about 4 GPa. Figures 3B and 3C illustrate the pressure dependence of derivatives of the volume. Note that whereas the constrained fit to the Universal EOS generates nearly an identical estimate of the bulk modulus over the whole pressure interval, the pressure dependence of K' exhibits more variation. For the proposed EOS form plotted in figure 3, both K and K' will tend towards infinite values as pressure approaches infinity unless the parameter values chosen cause the limit in equation (26) to be zero. This behavior is a natural consequence of an EOS with a finite volume limit.

One additional complication that arises in choosing parameter values for the proposed EOS is that because the functional form is that of a rational approximation, the volume can become unbounded for some P_{crit} if $1 + a(P_{crit} - P_r) + b(P_{crit} - P_r)^2 = 0$. These pressure values are given by

$$P_{crit} = \frac{2bP_r - a \pm \sqrt{a^2 - 4b}}{2b} \tag{27}$$

Procedures for parameter calibration of the proposed EOS should avoid values that render positive roots for equation (27). One such method is outlined in the Appendix to Part IV of this series of papers. In practice infeasible parameter combinations that generate volume singularities are easy to avoid and do not compromise the ability to represent the range of melt properties found in experiments.

APPLICATION OF THE EOS TO REAL LIQUIDS: A DETAILED EXAMPLE

If the proposed EOS (eq 25) is to be applied to a silicate melt that undergoes some structural rearrangement as a function of T or P, than explicit provision must be made for the configurational contributions to the volumetric properties. These contributions are not meant to be accounted for by any of the simple EOS formulations described above, be it Birch-Murnaghan, Vinet, or equation (25). Changes in melt configuration can take the form of the creation or destruction of short- to medium-range ordered structures in the melt, akin to complexes in aqueous solution, or the change in anionic coordination of cations accompanying variation in T, P. The latter is especially relevant to analysis of the volumetric properties of melts at elevated pressure and will be the subject of this last section.

Molecular dynamical (MD) simulations of amorphous silica (SiO_2) demonstrate that silicon exhibits systematic changes in coordination with respect to oxygen as a function of T and P. Rustad and others (1990, 1991a, 1991b) have produced a data set on amorphous SiO_2 that unambiguously documents the correlation between bulk macroscopic properties and the coordination number (CN) of silicon with respect to oxygen. This data set consists of estimated percentages of Si in IV-, V-, VI-, VII-, and VIII-fold coordination with respect to oxygen along a 900 K isotherm over the pressure range 0 to 135 GPa (Rustad and others, 1991a), and along a 4000 K isotherm over the pressure range 0 to 20 GPa (Rustad and others, 1990). These data are plotted in figure 4. In addition, Rustad and others (1991b) provide estimates of the density (ρ), bulk modulus (K), thermal coefficient of expansion (α) and isochoric heat capacity (C_V) of amorphous SiO_2 along a 1200 K isotherm over the pressure range 0 to 120 GPa. Their data on ρ, K, and α are plotted in figures 5, 6 and 7, respectively. While alternate MD estimates of Si CN in amorphous SiO_2 are available (for example, Trave and others, 2002), Rustad and others present the only self-consistent data set that include CN and bulk properties calculated over a wide range of pressure. For the purposes of this example, which is aimed more at the issue of how to model configurational contributions to the volumetric properties with the proposed EOS, rather than results of the parameterization, the amorphous phase will be assumed to be representative of the liquid state over the whole range of T and P studied.

Thermodynamic Model

A model expression for the molar Gibbs free energy (G) of amorphous SiO_2 may be written in terms of configurational (*conf*) and vibrational (*vib*) contributions

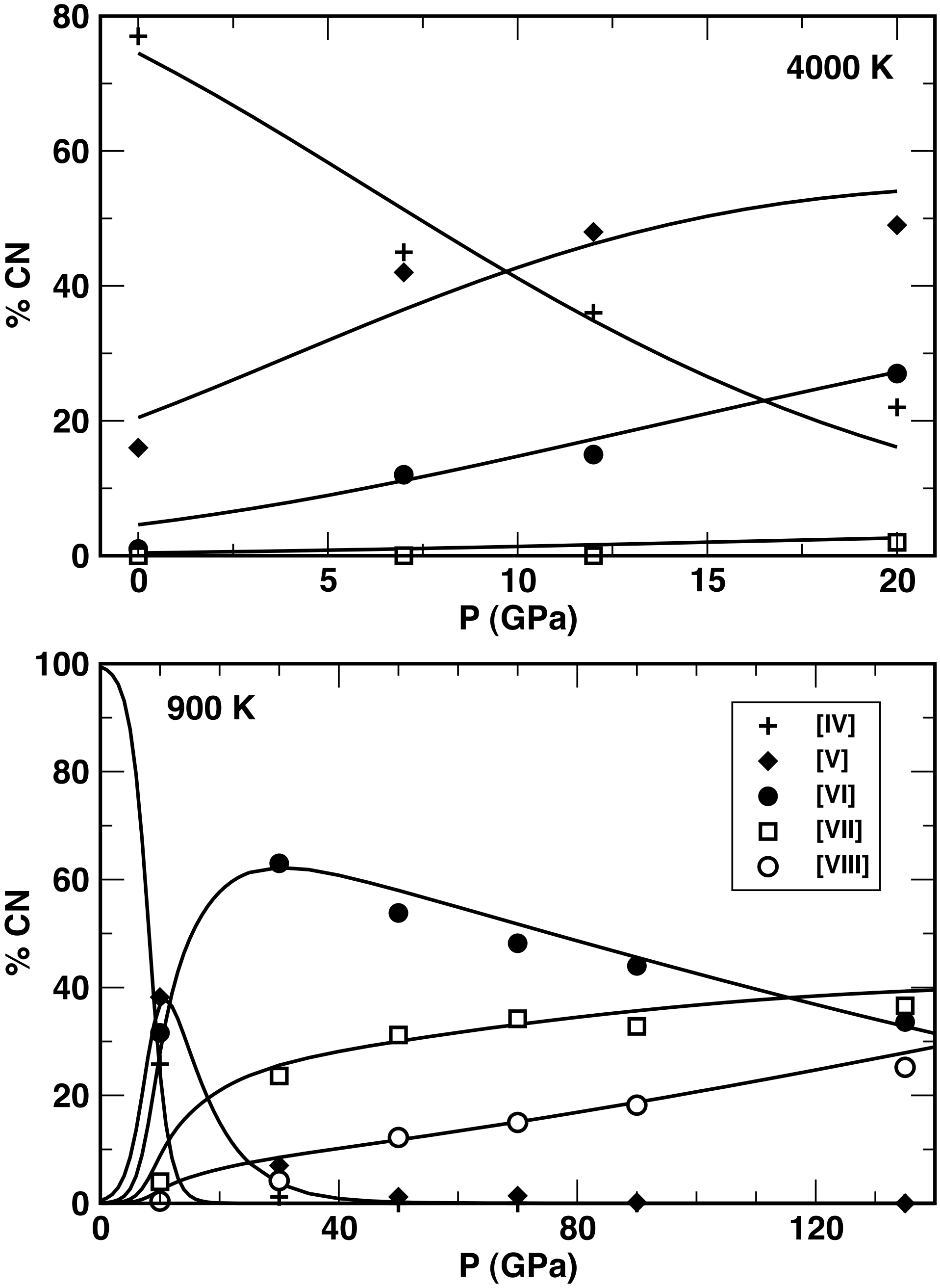

Fig. 4. Estimates of the distribution of Si in IV-, V-, VI-, VII-, and VIII-fold coordination in amorphous SiO_2. Data points are derived from molecular dynamical simulations at 900 K (lower panel, Rustad and others, 1991b) and 4000 K (Rustad and others, 1990). The curves are calculated from the model discussed in the text and parameters reported in table 2.

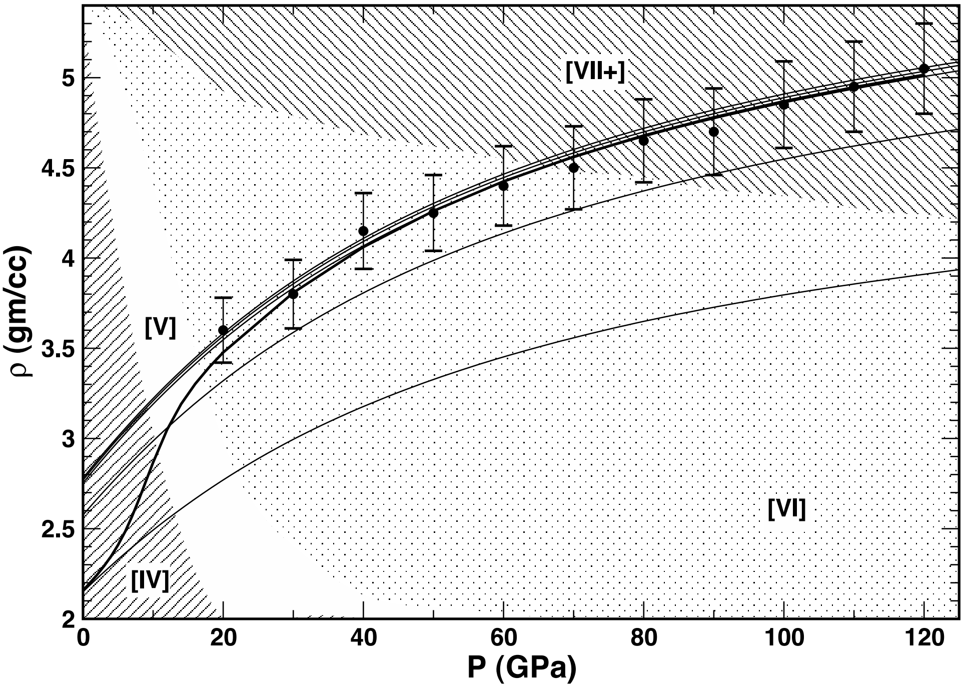

Fig. 5. Density of amorphous silica at 1200 K. Data points are taken from the molecular dynamical simulations of Rustad and others (1991a). Relative amounts of Si in IV-, V-, VI, and VII+ coordination are displayed with shading. The light curves refer to density variation of $Si^{IV}O_2$ (bottom), $Si^{V}O_2$, $Si^{VI}O_2$, $Si^{VII}O_2$, and $Si^{VIII}O_2$ (top), respectively. The heavy curve is the variation of density with pressure for silica with an equilibrium distribution of coordination states. The curves are calculated from the model discussed in the text and parameters reported in table 2.

$$G = G^{conf} + G^{vib} \tag{28}$$

where the configurational term is given by

$$G^{conf} = RT[X^{IV}\ln X^{IV} + X^{V}\ln X^{V} + X^{VI}\ln X^{VI} + X^{VII}\ln X^{VII} + X^{VIII}\ln X^{VIII}] \tag{29}$$

and where the vibrational contribution is given by

$$G^{vib} = X^{IV}G^{IV} + X^{V}G^{V} + X^{VI}G^{VI} + X^{VII}G^{VII} + X^{VIII}G^{VIII} + G^{excess} \tag{30}$$

The X^{IV}, X^{V}, X^{VI}, X^{VII}, and X^{VIII} are mole fractions of IV, V, VI, VII, and VIII coordinated Si in one mole of SiO_2 and these quantities are multiplied by the standard state molar Gibbs free energies of amorphous $Si^{IV}O_2$, $Si^{V}O_2$, $Si^{VI}O_2$, $Si^{VII}O_2$, and $Si^{VIII}O_2$. The mole fractions in equation (30) are dependent on T and P as are the standard state properties. G^{excess} refers to a molar excess Gibbs free energy and the inclusion of this term allows for non-ideal mixing between Si in its various coordination states. The model embodied by equations (28) to (30) is a form of non-ideal *associated* solution. Tanaka (2000) has utilized such a model to develop a theory for critical phenomena and first and second order phase transitions in liquids and glasses.

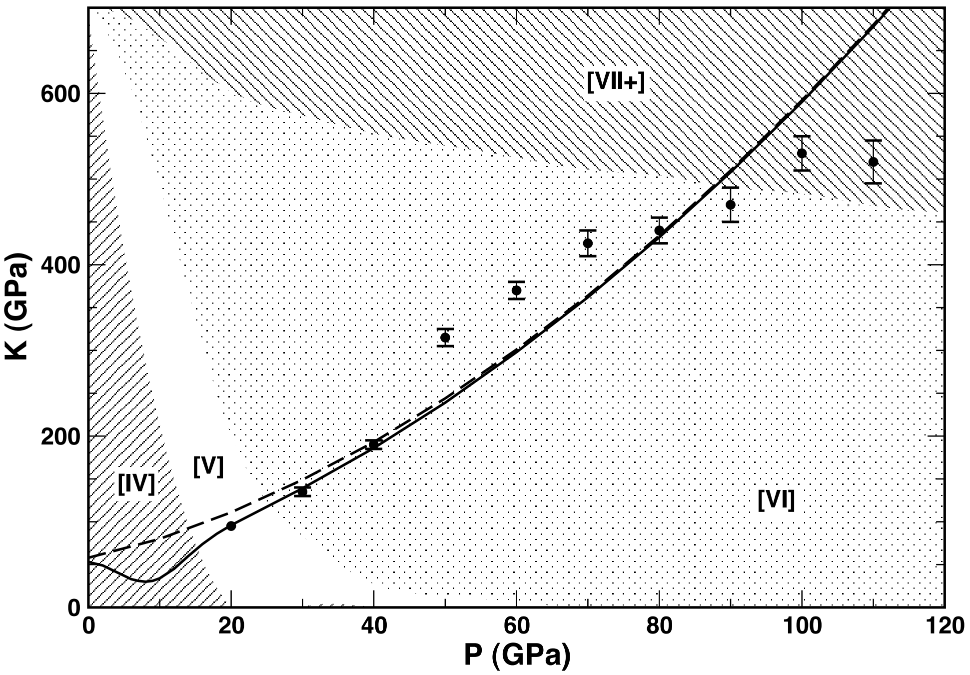

Fig. 6. Bulk modulus of amorphous silica at 1200 K. Data points are taken from the molecular dynamical simulations of Rustad and others (1991a). Relative amounts of Si in IV-, V-, VI, and VII+ coordination are displayed with shading. The dashed curve refers to variation of the vibrational contribution to the bulk modulus. The heavy curve is the variation of bulk modulus with pressure for silica with an equilibrium distribution of coordination states. The curves are calculated from the model discussed in the text and parameters reported in table 2.

The standard state terms in equation (30) may be expanded as

$$G^{IV} = G^{IV}_{P_r} + \int_{P_r}^{P} V^{IV}\, dP \tag{31a}$$

$$G^{V} = G^{V}_{P_r} + \int_{P_r}^{P} V^{V}\, dP \tag{31b}$$

$$G^{VI} = G^{VI}_{P_r} + \int_{P_r}^{P} V^{VI}\, dP \tag{31c}$$

$$G^{VII} = G^{VII}_{P_r} + \int_{P_r}^{P} V^{VII}\, dP \tag{31d}$$

$$G^{VIII} = G^{VIII}_{P_r} + \int_{P_r}^{P} V^{VIII}\, dP \tag{31e}$$

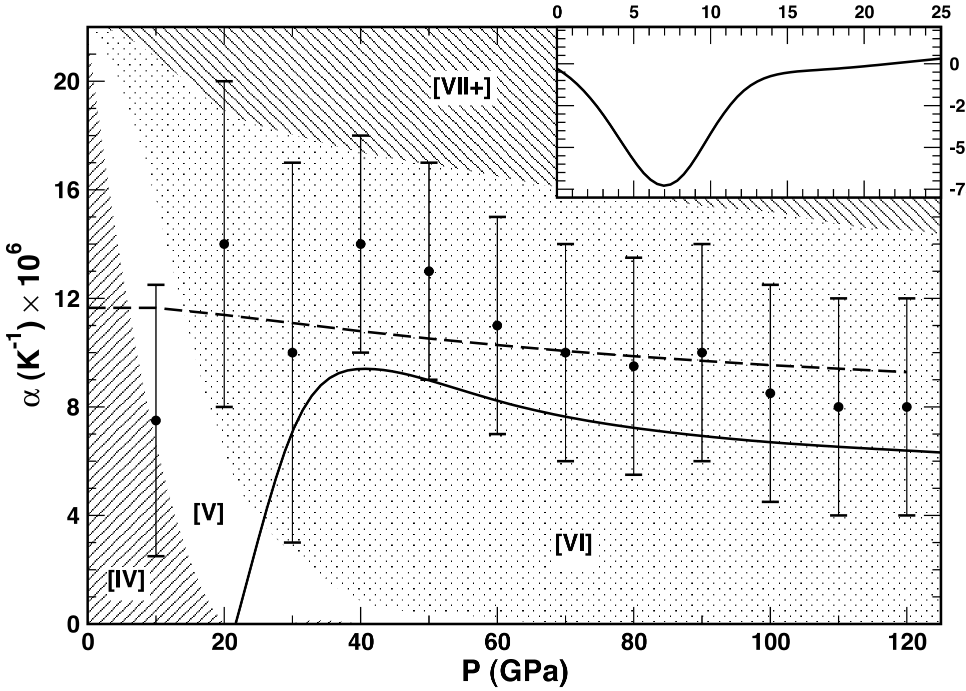

Fig. 7. Thermal coefficient of expansion of amorphous silica at 1200 K. Data points are taken from the molecular dynamical simulations of Rustad and others (1991a). Relative amounts of Si in IV-, V-, VI, and VII+ coordination are displayed with shading. The dashed curve refers to variation of vibrational contribution to the thermal expansion. The heavy curve is the variation of thermal expansion with pressure for silica with an equilibrium distribution of coordination states. The curves are calculated from the model discussed in the text and parameters reported in table 2.

where the integrals are over an EOS parameterization of the volume of SiO_2 *for each* CN. Adopting equation (25) as the model EOS, it can be seen that evaluation of equation (30) would require a large number of parameter values (at least five parameters for each EOS description in each coordination state) that would probably exceed the number of data points available for calibration. Adopting alternate EOS formalisms would meet with the same difficulty; the issue is not intrinsic to equation (25). Some simplification is therefore warranted to make the problem tractable.

The simplest approach is to assume that the relation

$$V^{CN} = f^{CN} V^{IV} \tag{32}$$

holds for all T and P and $CN >$ IV, where the f^{CN} are constants. Assuming that volumes decrease as cations enter higher states of coordination, the f^{CN} should obey the inequality relation

$$0 \leq f^{VIII} \leq f^{VII} \leq f^{VI} \leq f^{V} \leq 1 \tag{33}$$

Equation (32) implies that the Taylor expansion coefficients of the volume (eq 15) scale as f^{CN}, and consequently that the a and b parameters (eqs 17 and 18) of the proposed EOS are identical in each coordination state. A further implication of equation (32) is that both the thermal coefficient of expansion (eq 22) and the compressibility ($-V_1/V_0$) or its inverse, the bulk modulus (K), remains the same in each coordination state. Jeanloz (1982) has shown that CN shifts associated with polymorphic phase transitions may induce an increase or a decrease in K, so the implication of no variation is consistent with theoretical analysis. Importantly, since K is related to the sound speed (c) as

$$\frac{1}{K} = -\left(\frac{V}{Mc^2} + \frac{VT\alpha^2}{C_P}\right) \tag{34}$$

(Part II; where M is the molar mass and C_P is the isobaric heat capacity), then if equation (32) holds it follows that

$$C_P^{CN} = f^{CN} C_P^{IV} \tag{35}$$

and

$$c^{CN} = (f^{CN})^{1/2} c^{IV} \tag{36}$$

for CN > IV. Equation (36) is consistent with known deviations from Birch's law (Jeanloz, 1982); the sound speed is expected to decrease in polymorphic phase transitions to a higher coordination state. Whether the approximations resulting from adoption of equation (32) are valid can in part be judged by the ability of the resulting model to account for observations in the data set.

Using equation (32), the model expression for the vibrational Gibbs free energy (eq 30) may be simplified to

$$\begin{aligned} G^{vib} = {} & X^{IV}\left(G^{IV}_{P_r} + \int_{P_r}^{P} V^{IV}\,dP\right) + X^{V}\left(G^{V}_{P_r} + f^{V}\int_{P_r}^{P} V^{IV}\,dP\right) + X^{VI}\left(G^{VI}_{P_r} + f^{VI}\int_{P_r}^{P} V^{IV}\,dP\right) \\ & + X^{VII}\left(G^{VII}_{P_r} + f^{VII}\int_{P_r}^{P} V^{IV}\,dP\right) + X^{VIII}\left(G^{VIII}_{P_r} + f^{VIII}\int_{P_r}^{P} V^{IV}\,dP\right) + G^{excess} \end{aligned} \tag{37}$$

and further reduced to

$$\begin{aligned} G^{vib} = {} & X^{IV}G^{IV}_{P_r} + X^{V}G^{V}_{P_r} + X^{VI}G^{VI}_{P_r} + X^{VII}G^{VII}_{P_r} + X^{VIII}G^{VIII}_{P_r} \\ & + (X^{IV} + f^{V}X^{V} + f^{VI}X^{VI} + f^{VII}X^{VII} + f^{VIII}X^{VIII}) \int_{P_r}^{P} V^{IV}\,dP + G^{excess} \end{aligned} \tag{38}$$

Though not required for this analysis, the assumption will be made that the excess free energy is zero (activities are equal to mole fractions), which will allow analytical expressions for derivative thermodynamic properties to be obtained. Combining equations (38) with (28) and (29) provides a simplified model expression for the Gibbs energy of one mole of amorphous SiO_2

$$\begin{aligned} G = {} & RT[X^{IV}\ln X^{IV} + X^{V}\ln X^{V} + X^{VI}\ln X^{VI} + X^{VII}\ln X^{VII} + X^{VIII}\ln X^{VIII}] + X^{IV}G^{IV}_{P_r} \\ & + X^{V}G^{V}_{P_r} + X^{VI}G^{VI}_{P_r} + X^{VII}G^{VII}_{P_r} + X^{VIII}G^{VIII}_{P_r} + (X^{IV} + f^{V}X^{V} + f^{VI}X^{VI} + f^{VII}X^{VII} \\ & + f^{VIII}X^{VIII}) \int_{P_r}^{P} V^{IV}\,dP \end{aligned} \tag{39}$$

From equation (39) it is straightforward to derive expressions for homogeneous equilibrium between "species" of SiO_2 in various states of cation coordination. The easiest way to derive this expression is to introduce four independent variables, s_V, s_{VI}, s_{VII}, s_{VIII}, defined so that

$$X^{IV} = 1 - s_V - s_{VI} - s_{VII} - s_{VIII}, \tag{40a}$$

$$X^{V} = s_V, \tag{40b}$$

$$X^{VI} = s_{VI}, \tag{40c}$$

$$X^{VII} = s_{VII}, \tag{40d}$$

$$X^{VIII} = s_{VIII} \tag{40e}$$

which are analogous to *ordering* variables in mineral solid solutions. With equations (40a-e) equation (39) becomes

$$\begin{aligned} G = {} & RT[(1 - s_V - s_{VI} - s_{VII} - s_{VIII})\ln(1 - s_V - s_{VI} - s_{VII} - s_{VIII})] \\ & + RT[s_V \ln s_V + s_{VI} \ln s_{VI} + s_{VII} \ln s_{VII} + s_{VIII} \ln s_{VIII}] + G_{P_r}^{IV} \\ & + s_V\, \Delta G_{P_r}^{V,IV} + s_{VI}\, \Delta G_{P_r}^{VI,IV} + s_{VII}\, \Delta G_{P_r}^{VII,IV} + s_{VIII}\, \Delta G_{P_r}^{VIII,IV} + [1 + (f^{V} - 1)s_V \\ & + (f^{VI} - 1)s_{VI} + (f^{VII} - 1)s_{VII} + (f^{VIII} - 1)s_{VIII}] \int_{P_r}^{P} V^{IV}\, dP \end{aligned} \tag{41}$$

where $\Delta G_{P_r}^{V,IV}$, $\Delta G_{P_r}^{VI,IV}$, $\Delta G_{P_r}^{VII,IV}$, $\Delta G_{P_r}^{VIII,IV}$ are standard state Gibbs free energy changes at reference pressure associated with the homogeneous equilibria

$$\mathrm{Si^{IV}O_2} \Leftrightarrow \mathrm{Si^{V}O_2}$$
$$\mathrm{Si^{IV}O_2} \Leftrightarrow \mathrm{Si^{VI}O_2}$$
$$\mathrm{Si^{IV}O_2} \Leftrightarrow \mathrm{Si^{VII}O_2}$$
$$\mathrm{Si^{IV}O_2} \Leftrightarrow \mathrm{Si^{VIII}O_2}$$

respectively. The equilibrium distribution of cation coordination states is given by the thermodynamic condition that homogeneous equilibrium corresponds to a minimum in the Gibbs free energy with respect to variation of the ordering variables

$$\frac{\partial G}{\partial s_V} = 0 = RT \ln \frac{s_V}{1 - s_V - s_{VI} - s_{VII} - s_{VIII}} + \Delta G_{P_r}^{V,IV} + (f^{V} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{42a}$$

$$\frac{\partial G}{\partial s_{VI}} = 0 = RT \ln \frac{s_{VI}}{1 - s_{VI} - s_{VI} - s_{VII} - s_{VIII}} + \Delta G_{P_r}^{VI,IV} + (f^{VI} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{42b}$$

$$\frac{\partial G}{\partial s_{VII}} = 0 = RT \ln \frac{s_{VII}}{1 - s_V - s_{VI} - s_{VII} - s_{VIII}} + \Delta G_{P_r}^{VII,IV} + (f^{VII} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{42c}$$

$$\frac{\partial G}{\partial s_{VIII}} = 0 = RT \ln \frac{s_{VIII}}{1 - s_V - s_{VI} - s_{VII} - s_{VIII}} + \Delta G_{P_r}^{VIII,IV} + (f^{VIII} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{42d}$$

With the aid of equations (40a-e), equations (42a-d) are easily shown to be the usual statements of the law of mass action

$$RT \ln K^{V,IV} \equiv RT \ln \frac{X^{V}}{X^{IV}} = -\Delta G_{P_r}^{V,IV} - (f^{V} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{43a}$$

$$RT \ln K^{VI,IV} \equiv RT \ln \frac{X^{VI}}{X^{IV}} = -\Delta G_{P_r}^{VI,IV} - (f^{VI} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{43b}$$

$$RT \ln K^{VII,IV} \equiv RT \ln \frac{X^{VII}}{X^{IV}} = -\Delta G_{P_r}^{VII,IV} - (f^{VII} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{43c}$$

$$RT \ln K^{VIII,IV} \equiv RT \ln \frac{X^{VIII}}{X^{IV}} = -\Delta G_{P_r}^{VIII,IV} - (f^{VIII} - 1) \int_{P_r}^{P} V^{IV}\, dP \tag{43d}$$

where the equilibrium constants, $K^{V,IV}$, $K^{VI,IV}$, $K^{VII,IV}$, $K^{VIII,IV}$, are introduced for expedience. A solution to the set of equations (43a-d) for CN mole fractions is conveniently analytic, as non-ideal interactions that would result in activity coefficients have been neglected. This solution is

$$X^{IV} = \frac{1}{1 + K^{V,IV} + K^{VI,IV} + K^{VII,IV} + K^{VIII,IV}} \tag{44a}$$

$$X^{V} = \frac{K^{V,IV}}{1 + K^{V,IV} + K^{VI,IV} + K^{VII,IV} + K^{VIII,IV}} \tag{44b}$$

$$X^{VI} = \frac{K^{VI,IV}}{1 + K^{V,IV} + K^{VI,IV} + K^{VII,IV} + K^{VIII,IV}} \tag{44c}$$

$$X^{VII} = \frac{K^{VII,IV}}{1 + K^{V,IV} + K^{VI,IV} + K^{VII,IV} + K^{VIII,IV}} \tag{44d}$$

$$X^{VIII} = \frac{K^{VIII,IV}}{1 + K^{V,IV} + K^{VI,IV} + K^{VII,IV} + K^{VIII,IV}} \tag{44e}$$

The equilibrium constants are functions only of temperature, pressure and the adopted EOS parameters for $Si^{IV}O_2$.

Model Expressions for Volumetric Properties

Because pressure does not appear explicitly in any but the last term in equation (39), it is tempting to derive an expression for the molar volume of amorphous SiO_2 by simply taking the pressure derivative of G at constant temperature, to obtain

$$V = (X^{IV} + X^{V} f^{V} + X^{VI} f^{VI} + X^{VII} f^{VII} + X^{VIII} f^{VIII}) V^{IV} \tag{45}$$

But, as the results of the previous paragraph clearly demonstrate, the mole fraction terms in equation (39) are implicitly functions of pressure. The correct derivation of the molar volume is as follows (see Ghiorso, 1990). Write the total derivative of G in terms of the four ordering variables, temperature and pressure

$$dG = \frac{\partial G}{\partial s_V} ds_V + \frac{\partial G}{\partial s_{VI}} ds_{VI} + \frac{\partial G}{\partial s_{VII}} ds_{VII} + \frac{\partial G}{\partial s_{VIII}} ds_{VIII} + \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP \tag{46}$$

where the partial derivatives are taken holding all other independent variables constant (that is, in the case of $\partial G/\partial P$, T, s_V, s_{VI}, s_{VII}, and s_{VIII} are held constant). Next, transform equation (46) to the gradient in the Gibbs free energy with respect to pressure

$$\frac{dG}{dP} = \frac{\partial G}{\partial s_V}\frac{ds_V}{dP} + \frac{\partial G}{\partial s_{VI}}\frac{ds_{VI}}{dP} + \frac{\partial G}{\partial s_{VII}}\frac{ds_{VII}}{dP} + \frac{\partial G}{\partial s_{VIII}}\frac{ds_{VIII}}{dP} + \frac{\partial G}{\partial T}\frac{dT}{dP} + \frac{\partial G}{\partial P} \tag{47}$$

Finally, specify that the gradient be evaluated along a path corresponding to no variation in T and that an equilibrium distribution of coordination states is maintained during evaluation

$$\left.\frac{\partial G}{\partial P}\right|_{T,eq} = \frac{\partial G}{\partial s_V}\left.\frac{\partial s_V}{\partial P}\right|_{T,eq} + \frac{\partial G}{\partial s_{VI}}\left.\frac{\partial s_{VI}}{\partial P}\right|_{T,eq} + \frac{\partial G}{\partial s_{VII}}\left.\frac{\partial s_{VII}}{\partial P}\right|_{T,eq} + \frac{\partial G}{\partial s_{VIII}}\left.\frac{\partial s_{VIII}}{\partial P}\right|_{T,eq} + \frac{\partial G}{\partial P} \tag{48}$$

Equation (48) gives the correct expression for the molar volume of amorphous SiO_2 in an equilibrium distribution of coordination states, whereas equation (45) corresponds only to the last of the five terms in equation (48). But, as luck would have it, the first four terms in equation (48) are zero because in a state of homogeneous equilibrium equations (42a-d) must hold and the partial derivatives of the Gibbs free energy with respect to ordering variable vanish. Therefore, equation (45) is a valid expression for the molar volume of the system as long as an equilibrium distribution of coordination states is maintained. In a metastable configuration (that is, a rapidly quenched glass) this approximation would no longer be valid.

In order to analyze the Rustad and others (1990, 1991a, 1991b) data set two more model expressions are required beyond equations (44a-d) and (45). These are expressions for the bulk modulus and the thermal coefficient of expansion. Unfortunately, the simplifications that led to the model expression for volume do not apply to these quantities. The bulk modulus is defined as

$$K = -V\Big/\frac{\partial V}{\partial P} \tag{49}$$

and the thermal coefficient of expansion as

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T} \tag{50}$$

Model expressions are therefore required for $\left.\frac{\partial V}{\partial P}\right|_{T,eq}$ and $\left.\frac{\partial V}{\partial T}\right|_{P,eq}$ both in a state of equilibrium CN distribution.

Starting from the total derivative of the volume

$$dV = d\frac{\partial G}{\partial P} = \frac{\partial^2 G}{\partial s_V \partial P}ds_V + \frac{\partial^2 G}{\partial s_{VI}\partial P}ds_{VI} + \frac{\partial^2 G}{\partial s_{VII}\partial P}ds_{VII} + \frac{\partial^2 G}{\partial s_{VIII}\partial P}ds_{VIII} + \frac{\partial^2 G}{\partial T\partial P}dT + \frac{\partial^2 G}{\partial P^2}dP$$

the temperature and pressure gradients can be obtained

$$\frac{dV}{dP} = \frac{\partial^2 G}{\partial s_V \partial P}\frac{ds_V}{dP} + \frac{\partial^2 G}{\partial s_{VI}\partial P}\frac{ds_{VI}}{dP} + \frac{\partial^2 G}{\partial s_{VII}\partial P}\frac{ds_{VII}}{dP} + \frac{\partial^2 G}{\partial s_{VIII}\partial P}\frac{ds_{VIII}}{dP} + \frac{\partial^2 G}{\partial T\partial P}\frac{dT}{dP} + \frac{\partial^2 G}{\partial P^2} \tag{51}$$

$$\frac{dV}{dT} = \frac{\partial^2 G}{\partial s_V \partial P}\frac{ds_V}{dT} + \frac{\partial^2 G}{\partial s_{VI}\partial P}\frac{ds_{VI}}{dT} + \frac{\partial^2 G}{\partial s_{VII}\partial P}\frac{ds_{VII}}{dT} + \frac{\partial^2 G}{\partial s_{VIII}\partial P}\frac{ds_{VIII}}{dT} + \frac{\partial^2 G}{\partial T\partial P} + \frac{\partial^2 G}{\partial P^2}\frac{dP}{dT} \tag{52}$$

that produce expressions for the desired quantities

$$\left.\frac{\partial V}{\partial P}\right|_{eq,T} = \frac{\partial^2 G}{\partial s_V \partial P}\left.\frac{\partial s_V}{\partial P}\right|_{eq,T} + \frac{\partial^2 G}{\partial s_{VI} \partial P}\left.\frac{\partial s_{VI}}{\partial P}\right|_{eq,T} + \frac{\partial^2 G}{\partial s_{VII} \partial P}\left.\frac{\partial s_{VII}}{\partial P}\right|_{eq,T} + \frac{\partial^2 G}{\partial s_{VIII} \partial P}\left.\frac{\partial s_{VIII}}{\partial P}\right|_{eq,T} + \frac{\partial^2 G}{\partial P^2} \quad (53)$$

$$\left.\frac{\partial V}{\partial T}\right|_{eq,P} = \frac{\partial^2 G}{\partial s_V \partial P}\left.\frac{\partial s_V}{\partial T}\right|_{eq,P} + \frac{\partial^2 G}{\partial s_{VI} \partial P}\left.\frac{\partial s_{VI}}{\partial T}\right|_{eq,P} + \frac{\partial^2 G}{\partial s_{VII} \partial P}\left.\frac{\partial s_{VII}}{\partial T}\right|_{eq,P} + \frac{\partial^2 G}{\partial s_{VIII} \partial P}\left.\frac{\partial s_{VIII}}{\partial T}\right|_{eq,P} + \frac{\partial^2 G}{\partial T \partial P} \quad (54)$$

The trailing terms in equations (53) and (54) are given by differentiating equation (41)

$$\frac{\partial^2 G}{\partial P^2} = [1 + (f^V - 1)s_V + (f^{VI} - 1)s_{VI} + (f^{VII} - 1)s_{VII} + (f^{VIII} - 1)s_{VIII}]\frac{\partial V^{IV}}{\partial P} \quad (55)$$

and

$$\frac{\partial^2 G}{\partial T \partial P} = [1 + (f^V - 1)s_V + (f^{VI} - 1)s_{VI} + (f^{VII} - 1)s_{VII} + (f^{VIII} - 1)s_{VIII}]\frac{\partial V^{IV}}{\partial T} \quad (56)$$

Unfortunately, the remaining terms in equations (53) and (54) are not zero. They represent the contribution to the thermal expansion and compressibility of the system arising from *changes* in CN as a function of temperature and pressure. These contributions could very well be of the order of the vibrational contribution embodied in the last term of each expression. The Gibbs free energy derivatives in the configurational terms of equations (53) and (54) are obtained from (41)

$$\frac{\partial^2 G}{\partial s_V \partial P} = (f^V - 1)V^{IV} \quad (57a)$$

$$\frac{\partial^2 G}{\partial s_{VI} \partial P} = (f^{VI} - 1)V^{IV} \quad (57b)$$

$$\frac{\partial^2 G}{\partial s_{VII} \partial P} = (f^{VII} - 1)V^{IV} \quad (57c)$$

$$\frac{\partial^2 G}{\partial s_{VIII} \partial P} = (f^{VIII} - 1)V^{IV} \quad (57d)$$

and

$$\frac{\partial^2 G}{\partial s_V \partial T} = R \ln K^{V,IV} - \Delta S_{P_r}^{V,IV} + (f^V - 1)\int_{P_r}^{P} \frac{\partial V^{IV}}{\partial T}\, dP \quad (58a)$$

$$\frac{\partial^2 G}{\partial s_{VI} \partial T} = R \ln K^{VI,IV} - \Delta S_{P_r}^{VI,IV} + (f^{VI} - 1)\int_{P_r}^{P} \frac{\partial V^{IV}}{\partial T}\, dP \quad (58b)$$

$$\frac{\partial^2 G}{\partial s_{VII}\partial T} = R\ln K^{VII,IV} - \Delta S_{P_r}^{VII,IV} + (f^{VII} - 1)\int_{P_r}^{P}\frac{\partial V^{IV}}{\partial T}\,dP \tag{58c}$$

$$\frac{\partial^2 G}{\partial s_{VIII}\partial T} = R\ln K^{VIII,IV} - \Delta S_{P_r}^{VIII,IV} + (f^{VIII} - 1)\int_{P_r}^{P}\frac{\partial V^{IV}}{\partial T}\,dP \tag{58d}$$

with the aid of the identities in (43a-d).[3] The variation of ordering variable with changes in T and P requires a bit more manipulation. First, each of the four conditions of homogeneous equilibrium is formally expanded as a total derivative

$$d\frac{\partial G}{\partial s_V} = \frac{\partial^2 G}{\partial s_V^2}ds_V + \frac{\partial^2 G}{\partial s_V\partial s_{VI}}ds_{VI} + \frac{\partial^2 G}{\partial s_V\partial s_{VII}}ds_{VII} + \frac{\partial^2 G}{\partial s_V\partial s_{VIII}}ds_{VIII} + \frac{\partial^2 G}{\partial s_V\partial T}dT + \frac{\partial^2 G}{\partial s_V\partial P}dP \tag{59a}$$

$$d\frac{\partial G}{\partial s_{VI}} = \frac{\partial^2 G}{\partial s_V\partial s_{VI}}ds_V + \frac{\partial^2 G}{\partial s_{VI}^2}ds_{VI} + \frac{\partial^2 G}{\partial s_{VI}\partial s_{VII}}ds_{VII} + \frac{\partial^2 G}{\partial s_{VI}\partial s_{VIII}}ds_{VIII} + \frac{\partial^2 G}{\partial s_{VI}\partial T}dT + \frac{\partial^2 G}{\partial s_{VI}\partial P}dP \tag{59b}$$

$$d\frac{\partial G}{\partial s_{VII}} = \frac{\partial^2 G}{\partial s_V\partial s_{VII}}ds_V + \frac{\partial^2 G}{\partial s_{VI}\partial s_{VII}}ds_{VI} + \frac{\partial^2 G}{\partial s_{VII}^2}ds_{VII} + \frac{\partial^2 G}{\partial s_{VII}\partial s_{VIII}}ds_{VIII} + \frac{\partial^2 G}{\partial s_{VII}\partial T}dT + \frac{\partial^2 G}{\partial s_{VII}\partial P}dP \tag{59c}$$

$$\begin{aligned} d\frac{\partial G}{\partial s_{VIII}} = {} & \frac{\partial^2 G}{\partial s_V\partial s_{VIII}}ds_V + \frac{\partial^2 G}{\partial s_{VI}\partial s_{VIII}}ds_{VI} + \frac{\partial^2 G}{\partial s_{VII}\partial s_{VIII}}ds_{VII} + \frac{\partial^2 G}{\partial s_{VIII}^2}ds_{VIII} + \frac{\partial^2 G}{\partial s_{VIII}\partial T}dT \\ & + \frac{\partial^2 G}{\partial s_{VIII}\partial P}dP \end{aligned} \tag{59d}$$

Next, a pressure gradient is constructed from this system of equations along a path corresponding to an equilibrium coordination state at constant temperature

$$0 = \frac{\partial^2 G}{\partial s_V^2}\left.\frac{\partial s_V}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_V\partial s_{VI}}\left.\frac{\partial s_{VI}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_V\partial s_{VII}}\left.\frac{\partial s_{VII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_V\partial s_{VIII}}\left.\frac{\partial s_{VIII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_V\partial P} \tag{60a}$$

---

[3] Note that alternately equations (58a-e) may be written

$$\frac{\partial^2 G}{\partial S_V\partial T} = -\frac{\Delta H_{P_r}^{V,IV}}{T} + (f^{V} - 1)\int_{P_r}^{P}\left(\frac{\partial V^{IV}}{\partial T} - \frac{V^{IV}}{T}\right)dP,$$

$$\frac{\partial^2 G}{\partial S_{VI}\partial T} = -\frac{\Delta H_{P_r}^{VI,IV}}{T} + (f^{VI} - 1)\int_{P_r}^{P}\left(\frac{\partial V^{IV}}{\partial T} - \frac{V^{IV}}{T}\right)dP,$$

$$\frac{\partial^2 G}{\partial S_{VII}\partial T} = -\frac{\Delta H_{P_r}^{VII,IV}}{T} + (f^{VII} - 1)\int_{P_r}^{P}\left(\frac{\partial V^{IV}}{\partial T} - \frac{V^{IV}}{T}\right)dP,$$

and

$$\frac{\partial^2 G}{\partial S_{VIII}\partial T} = -\frac{\Delta H_{P_r}^{VIII,IV}}{T} + (f^{VIII} - 1)\int_{P_r}^{P}\left(\frac{\partial V^{IV}}{\partial T} - \frac{V^{IV}}{T}\right)dP$$

$$0 = \frac{\partial^2 G}{\partial s_V \partial s_{VI}} \left.\frac{\partial s_V}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VI}^2} \left.\frac{\partial s_{VI}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VI} \partial s_{VII}} \left.\frac{\partial s_{VII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VI} \partial s_{VIII}} \left.\frac{\partial s_{VIII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VI} \partial P} \tag{60b}$$

$$0 = \frac{\partial^2 G}{\partial s_V \partial S_{VII}} \left.\frac{\partial s_V}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VI} \partial s_{VII}} \left.\frac{\partial s_{VI}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VII}^2} \left.\frac{\partial s_{VII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VII} \partial s_{VIII}} \left.\frac{\partial s_{VIII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VII} \partial P} \tag{60c}$$

$$0 = \frac{\partial^2 G}{\partial s_V \partial s_{VIII}} \left.\frac{\partial s_V}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VI} \partial s_{VIII}} \left.\frac{\partial s_{VI}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VII} \partial s_{VIII}} \left.\frac{\partial s_{VII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VIII}^2} \left.\frac{\partial s_{VIII}}{\partial P}\right|_{T,eq} + \frac{\partial^2 G}{\partial s_{VIII} \partial P} \tag{60d}$$

The critical observation in developing equations (60a-d) from (59a-d) is that in an equilibrium coordination state the partial derivatives $\partial G/\partial s_V$, $\partial G/\partial s_{VI}$, $\partial G/\partial s_{VII}$, and $\partial G/\partial s_{VIII}$ are zero, and since they remain zero if pressure is changed *while homogeneous equilibrium is maintained*, the total derivative of these quantities must itself be zero. That is why the left hand sides of equations (60a-d) vanish. The system of equations (60a-d) can be arranged as a vector-matrix expression to give

$$-\begin{bmatrix} \dfrac{\partial^2 G}{\partial s_V \partial P} \\ \dfrac{\partial^2 G}{\partial s_{VI} \partial P} \\ \dfrac{\partial^2 G}{\partial s_{VII} \partial P} \\ \dfrac{\partial^2 G}{\partial s_{VIII} \partial P} \end{bmatrix} = \begin{bmatrix} \dfrac{\partial^2 G}{\partial s_V^2} & \dfrac{\partial^2 G}{\partial s_V \partial s_{VI}} & \dfrac{\partial^2 G}{\partial s_V \partial s_{VII}} & \dfrac{\partial^2 G}{\partial s_V \partial s_{VIII}} \\ \dfrac{\partial^2 G}{\partial s_V \partial s_{VI}} & \dfrac{\partial^2 G}{\partial s_{VI}^2} & \dfrac{\partial^2 G}{\partial s_{VI} \partial s_{VII}} & \dfrac{\partial^2 G}{\partial s_{VI} \partial s_{VIII}} \\ \dfrac{\partial^2 G}{\partial s_V \partial s_{VII}} & \dfrac{\partial^2 G}{\partial s_{VI} \partial s_{VII}} & \dfrac{\partial^2 G}{\partial s_{VII}^2} & \dfrac{\partial^2 G}{\partial s_{VII} \partial s_{VIII}} \\ \dfrac{\partial^2 G}{\partial s_V \partial s_{VIII}} & \dfrac{\partial^2 G}{\partial s_{VI} \partial s_{VIII}} & \dfrac{\partial^2 G}{\partial s_{VII} \partial s_{VIII}} & \dfrac{\partial^2 G}{\partial s_{VIII}^2} \end{bmatrix} \begin{bmatrix} \left.\dfrac{\partial s_V}{\partial P}\right|_{T,eq} \\ \left.\dfrac{\partial s_{VI}}{\partial P}\right|_{T,eq} \\ \left.\dfrac{\partial s_{VII}}{\partial P}\right|_{T,eq} \\ \left.\dfrac{\partial s_{VIII}}{\partial P}\right|_{T,eq} \end{bmatrix} \tag{61}$$

The Gibbs free energy partial derivatives in equation (61) are obtained by differentiation of equation (41). Using the definitions for CN-mole fractions and equilibrium constants from equations (40a-e) and (43a-d), equation (61) becomes

$$-V^{IV}\begin{bmatrix} f^{V} - 1 \\ f^{VI} - 1 \\ f^{VII} - 1 \\ f^{VIII} - 1 \end{bmatrix} = \frac{RT}{X^{IV}} \begin{bmatrix} 1 + \dfrac{1}{K^{V,IV}} & 1 & 1 & 1 \\ 1 & 1 + \dfrac{1}{K^{VI,IV}} & 1 & 1 \\ 1 & 1 & 1 + \dfrac{1}{K^{VII,IV}} & 1 \\ 1 & 1 & 1 & 1 + \dfrac{1}{K^{VIII,IV}} \end{bmatrix} \begin{bmatrix} \left.\dfrac{\partial s_V}{\partial P}\right|_{T,eq} \\ \left.\dfrac{\partial s_{VI}}{\partial P}\right|_{T,eq} \\ \left.\dfrac{\partial s_{VII}}{\partial P}\right|_{T,eq} \\ \left.\dfrac{\partial s_{VIII}}{\partial P}\right|_{T,eq} \end{bmatrix} \tag{62}$$

Matrix inversion and some manipulation provides a solution for the unknown vector of partial derivatives

$$\begin{bmatrix} \left.\frac{\partial s_V}{\partial P}\right|_{T,eq} \\ \left.\frac{\partial s_{VI}}{\partial P}\right|_{T,eq} \\ \left.\frac{\partial s_{VII}}{\partial P}\right|_{T,eq} \\ \left.\frac{\partial s_{VIII}}{\partial P}\right|_{T,eq} \end{bmatrix} = \frac{-V^{IV}}{RT} \begin{bmatrix} X^V f^V - X^V(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII}) \\ X^{VI} f^{VI} - X^{VI}(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII}) \\ X^{VII} f^{VII} - X^{VII}(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII}) \\ X^{VIII} f^{VIII} - X^{VIII}(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII}) \end{bmatrix} \tag{63}$$

Finally, the quantity $\left.\frac{\partial V}{\partial P}\right|_{eq,T}$ can be obtained by substituting the result above along with that given in equation (55) into equation (53). These substitutions give

$$\begin{aligned} \left.\frac{\partial V}{\partial P}\right|_{eq,T} = {} & -(f^V - 1)[X^V f^V - X^V(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII})]\frac{(V^{IV})^2}{RT} \\ & - (f^{VI} - 1)[X^{VI} f^{VI} - X^{VI}(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII})]\frac{(V^{IV})^2}{RT} \\ & - (f^{VII} - 1)[X^{VII} f^{VII} - X^{VII}(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII})]\frac{(V^{IV})^2}{RT} \\ & - (f^{VIII} - 1)[X^{VIII} f^{VIII} - X^{VIII}(X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII})]\frac{(V^{IV})^2}{RT} \\ & + (X^{IV} + f^V X^V + f^{VI} X^{VI} + f^{VII} X^{VII} + f^{VIII} X^{VIII})\frac{\partial V^{IV}}{\partial P} \end{aligned} \tag{64}$$

The first four terms in equation (64) are the configurational contributions to the volume pressure derivative. The last term is vibrational in origin. The bulk modulus is obtained by combing equations (64) and (45) via equation (49).

Analogous to the procedure developed above, the equivalent to equation (63) may be derived from equations (59a-d) for the quantities $\left.\frac{\partial s_V}{\partial T}\right|_{P,eq}$, $\left.\frac{\partial s_{VI}}{\partial T}\right|_{P,eq}$, $\left.\frac{\partial s_{VII}}{\partial T}\right|_{P,eq}$, $\left.\frac{\partial s_{VIII}}{\partial T}\right|_{P,eq}$, and these definitions along with equations (56) and (58a-d) may be inserted into equation (54) to give a model expression for $\left.\frac{\partial V}{\partial T}\right|_{eq,P}$. The reader is spared the details and the result will be simply stated

$$\begin{aligned} \left.\frac{\partial V}{\partial T}\right|_{eq,P} = {} & X^V(f^V - X^{IV} - f^V X^V - f^{VI} X^{VI} - f^{VII} X^{VII} - f^{VIII} X^{VIII}) \\ & \times \left[-R \ln K^{V,IV} + \Delta S^{V,IV}_{P_r} - (f^V - 1)\int_{\mathrm{P_r}}^{\mathrm{P}} \frac{\partial V^{IV}}{\partial T}\, dP \right]\frac{V^{IV}}{RT} \\ & + X^{VI}(f^{VI} - X^{IV} - f^V X^V - f^{VI} X^{VI} - f^{VII} X^{VII} - f^{VIII} X^{VIII}) \end{aligned}$$

$$
\begin{aligned}
&\times \left[-R \ln K^{VI,IV} + \Delta S_{P_r}^{VI,IV} - (f^{VI} - 1) \int_{P_r}^{P} \frac{\partial V^{IV}}{\partial T}\, dP \right] \frac{V^{IV}}{RT} \\
&+ X^{VII}(f^{VII} - X^{IV} - f^{V}X^{V} - f^{VI}X^{VI} - f^{VII}X^{VII} - f^{VIII}X^{VIII}) \\
&\times \left[-R \ln K^{VII,IV} + \Delta S_{P_r}^{VII,IV} - (f^{VII} - 1) \int_{P_r}^{P} \frac{\partial V^{IV}}{\partial T}\, dP \right] \frac{V^{IV}}{RT} \\
&+ X^{VIII}(f^{VIII} - X^{IV} - f^{V}X^{V} - f^{VI}X^{VI} - f^{VII}X^{VII} - f^{VIII}X^{VIII}) \\
&\times \left[-R \ln K^{VIII,IV} + \Delta S_{P_r}^{VIII,IV} - (f^{VIII} - 1) \int_{P_r}^{P} \frac{\partial V^{IV}}{\partial T}\, dP \right] \frac{V^{IV}}{RT} \\
&- X^{IV}(1 - X^{IV} - f^{V}X^{V} - f^{VI}X^{VI} - f^{VII}X^{VII} - f^{VIII}X^{VIII}) \frac{V^{IV}}{RT} \int_{P_r}^{P} \frac{\partial V^{IV}}{\partial T}\, dP \\
&+ (X^{IV} + f^{V}X^{V} + f^{VI}X^{VI} + f^{VII}X^{VII} + f^{VIII}X^{VIII}) \frac{\partial V^{IV}}{\partial T} \qquad (65)
\end{aligned}
$$

The thermal coefficient of expansion is obtained by combing equations (65) and (45) via equation (50).

Application of the Model

The data set of Rustad and others (1990, 1991a, 1991b) may now be evaluated by optimizing values of model parameters against reported X^{IV}, X^{V}, X^{VI}, X^{VII}, X^{VIII}, ρ, α, *and K.* The unkown parameters of the optimization are $\Delta G_{P_r,900K}^{V,IV}$, $\Delta G_{P_r,900K}^{VI,IV}$, $\Delta G_{P_r,900K}^{VII,IV}$, $\Delta G_{P_r,900K}^{VIII,IV}$, $\Delta G_{P_r,4500K}^{V,IV}$, $\Delta G_{P_r,4500K}^{VI,IV}$, $\Delta G_{P_r,4500K}^{VII,IV}$, $\Delta G_{P_r,4500K}^{VIII,IV}$, f^{V}, f^{VI}, f^{VII}, f^{VIII}, $V_{0,1673K}^{IV}$, α, V_2^{IV}, V_3^{IV}, V_4^{IV}, and V_1^{IV}. The V_1^{IV} parameter (recall that this is the Taylor expansion coefficient describing the first pressure derivative of the volume) will be treated in a special manner, following an analysis developed in Part II. V_1^{IV} is expressed in terms of the sound speed (c) and its temperature derivative as

$$
V_1^{IV} = -V_0^{IV} \left(\frac{V_0^{IV}}{M\left(c^{IV} + \dfrac{dc^{IV}}{dT}\right)^2} + \frac{V_0^{IV} T \alpha^2}{C_P^{IV}} \right) \qquad (66)
$$

where M is the molecular weight of SiO_2 and C_P^{IV} is its isobaric heat capacity. c^{IV} and dc^{IV}/dT are optimized in lieu of V_1^{IV} in this analysis.

A weighted non-linear least squares model is constructed from the Rustad and others data set using appropriate model expressions for CN percentages, density, bulk modulus and thermal expansion developed above. The optimization is carried out in Microsoft™ Excel using the Solver function. The EOS parameter $V_{0,1673K}^{IV}$ is further constrained to match the initial slope of the quartz fusion curve (see discussion below) and non-linear equality constraints are imposed on the fitting procedure to insure that the numerator and the denominator of equation (25) are bounded *strictly* positive.[4] These paramter bound constraints guarantee an absence of singularities in the

---

[4] These constraints are $a^2 - 4b < 0$ and $(V_1^{IV} + V_0^{IV}a)^2 - 4V_0^{IV}\left(\frac{V_2^{IV}}{2} + V_1^{IV}a + V_0^{IV}b\right) < 0$

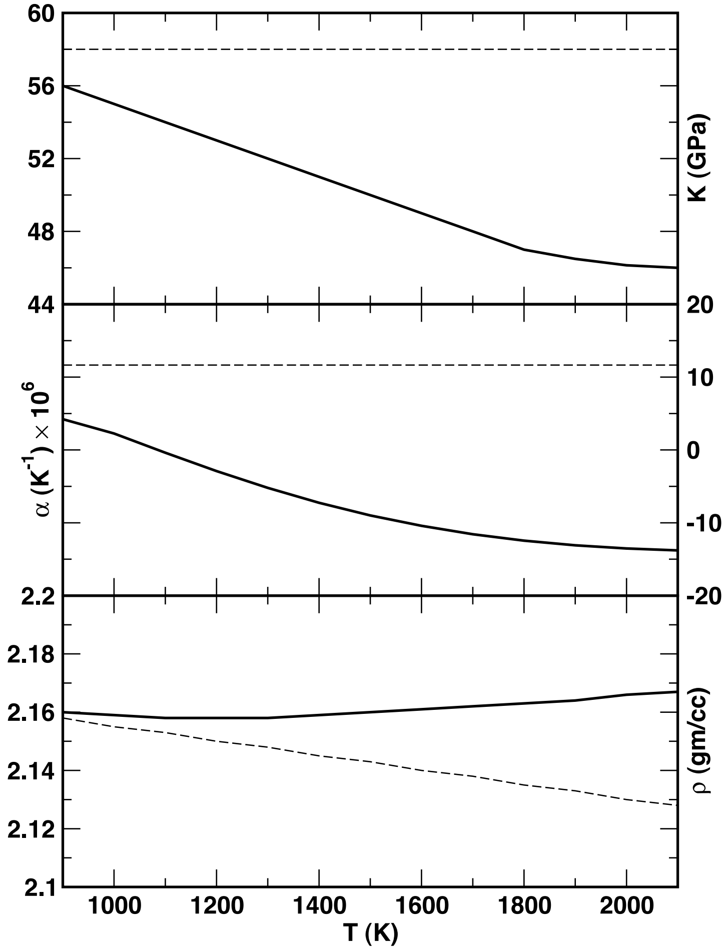

Fig. 8. Temperature dependence of the density, thermal coefficient of expansion and the bulk modulus of amorphous silica at reference pressure (10^5). The dashed curves describe the properties of $Si^{IV}O_2$. The heavy curve is the variation of these same properties for silica with an equilibrium distribution of coordination states. The curves are calculated from the model discussed in the text and parameters reported in table 2.

vibrational component of the fitted EOS. Curves predicted from the fit parameters are provided in figures 4, 5, 6, 7, and 8. Model parameters are reported in table 2.

The model reference volume at 1673 K and 10^5 Pa can be calculated from equation (45) and the constants reported in table 2 to give a value of 27.70 cc/mol. This number is larger than that typically found for the partial molar volume of SiO_2 in multicomponent liquids (Lange and Carmichael, 1987; Gaetani and others, 1998; Part II) and it is smaller than the value obtained for pure silica by Bacon and others (1960), though likely within the uncertainty of these measurements. The model reference pressure thermal expansion is negative, on the order of 10^{-5} (see fig. 8 and discussion below), and is inconsistent with the estimate of 1.03×10^{-4} K^{-1} from Bacon and others (1960). As noted by Richet and others (1982), Bacon's number is almost certainly in error by at least an order of magnitude because it leads to unrealistic values of C_V. The model sound speed is calculated to be ~5250 m/sec in the temperature range 2060 to

TABLE 2

Model parameter values for amorphous silica

Parameter	Value	Units	Notes/Source
$\Delta G^{V,IV}_{P_r,900K}$	39.566	kJ/mol	
$\Delta G^{VI,IV}_{P_r,900K}$	55.446	kJ/mol	
$\Delta G^{VII,IV}_{P_r,900K}$	65.262	kJ/mol	
$\Delta G^{VIII,IV}_{P_r,900K}$	75.746	kJ/mol	
$\Delta G^{V,IV}_{P_r,4500K}$	42.961	kJ/mol	
$\Delta G^{VI,IV}_{P_r,4500K}$	92.648	kJ/mol	
$\Delta G^{VII,IV}_{P_r,4500K}$	172.653	kJ/mol	
$\Delta G^{VIII,IV}_{P_r,4500K}$	1467.733	kJ/mol	
f^{V}	0.8346		
f^{VI}	0.7811		
f^{VII}	0.7765		
f^{VIII}	0.7732		
$V^{IV}_{0,1673K}$	28.10	cc/mol	
α	1.165×10^{-5}	K^{-1}	
V_2^{IV}	2.220×10^{-2}	cc/GPa^2-mol	
V_3^{IV}	-5.021×10^{-4}	cc/GPa^3-mol	
V_4^{IV}	-2.267×10^{-4}	cc/GPa^4-mol	
c^{IV}	5227	m/sec-mol	@ 1673.15 K
$\frac{dc^{IV}}{dT}$	4.157×10^{-4}	m/sec-K-mol	
T_{fusion} (quartz)	1700	K	Richet and others (1982)
$\Delta S_{fus,T_f}$ (quartz)	5.53	J/K-mol	Richet and others (1982)
C_P	82.6	J/K-mol	Lange and Navrotsky (1992)

2160 K where Baidov and Kunin (1968) measure a value of 6000 m/sec. This difference leads to a somewhat smaller model compressibility than the measurements would indicate, but Richet and others (1982) argue that the Baidov and Kunin number could be too high and it is found to be inconsistent with the analysis of sound speeds on multicomponent silicate liquids performed in Part II. It is worth noting that the model temperature derivative of the sound speed is determined largely by the pressure dependence of the thermal expansion.[5]

Values of f^V, f^{VI}, f^{VII}, and f^{VIII} reported in table 2 indicate a volume reduction of about 17 percent associated with a change in Si CN of IV to V, and an additional 5 percent reduction from V to VI. Curiously, higher coordination state transformations do not have a significant effect on the volume. The entropic consequences however are

---

[5] A first order Taylor expansion of Appendix equation (A-3) gives

$$\alpha_{T_r,P} \approx \alpha_{T_r,P_r} + \left(\frac{V_1\alpha}{V_0} + \frac{V_0 \; dc}{Mc^3 dT} - \frac{V_0\alpha^2}{C_P} \right)\Bigg|_{T_r,P_r} (P - P_r)$$

dramatic. As can be seen from examination of figure 4, the effect of temperature is to stabilize the presence of V-fold coordinated Si at the expense of higher CN species. The MD simulations and model calculations indicate that V- and higher-fold coordinated Si should be present in significant concentrations even at reference pressure which is consistent with the experimental observations of Stebbins (1991) and Mortuza and others (2000). Stebbins (1991) estimates an enthalpy for the reaction $Si^{IV}O_2 \Leftrightarrow Si^{V}O_2$ of ~20 ± 10 kJ/mol. Extrapolating $\Delta G_{P_r}^{V,IV}$ to zero K gives a model estimate of 38.6 kJ/mol; the difference may suggest some overestimation of the abundance of Si^{V} in the MD simulations (Trave and others, 2002). A model enthalpy for the V- to VI-fold transformation is smaller at ~ 6 kJ/mol. Model entropies for the IV to V and V to IV reactions are ~1 J/K and ~ 12 J/K, respectively. The absence of MD data along the 4000 K isotherm at pressures above 20 GPa precludes placing any confidence in model values of $\Delta G_{P_r,4500K}^{VII,IV}$, $\Delta G_{P_r,4500K}^{VIII,IV}$ other than that they are expectedly more positive than corresponding quantities at 900 K.

An interesting consequence of the results presented in figure 4 concerns the impact of CN transformation on the calculated activity of silica. Adopting a standard state of unit activity of $Si^{IV}O_2$ at any T and P, the activity of silica varies from 0.99 at 1000 K and 10^5 Pa to 0.90 at 2000 K. More dramatic is the effect of pressure. Along a 1200 K isotherm, the activity drops to 0.30 at 10 GPa, 0.005 at 20 GPa and $\sim 10^{-16}$ at 100 GPa. Now, of course, this variation in the activity of silica is entirely a consequence of the choice of the standard state, but these calculations highlight that if the low pressure volumetric properties of silica are utilized to estimate the Clapyron slope of a solid-liquid melting reaction (for example, the fusion of quartz), then the activity of silica in pure SiO_2 liquid, *referenced to the low pressure structural state of the liquid*, will not be unity, but some smaller value reflecting the changed average CN indicative of the higher pressure conditions. Consequently, great care must be taken in the analysis of fusion curves involving liquids that undergo CN transformations over the range of experimental measurements.

The MD data of Rustad and others (1991b) showing density as a function of pressure along a 1200 K isotherm are plotted in figure 5. Model calculated densities are also plotted as well as relative abundances of SiO_2 in its various coordination states. Reference state free energies for the coordination transformation reactions at 1200 K are interpolated from the constants reported in table 2. Several features should be noted. The model density of amorphous silica in a state of homogenous equilibrium is given by the heavy solid curve. The lighter solid curves are plotted as reference and describe the density of $Si^{IV}O_2$, $Si^{V}O_2$, $Si^{VI}O_2$, $Si^{VII}O_2$, and $Si^{VIII}O_2$ respectively. Within the first 20 GPa of compression, the equilibrium density curve transforms to reflect the change in dominant CN. The effect of the CN transformation over this initial 20 GPa is to enhance the compressibility of the phase, or alternately, lower the bulk modulus. This feature is plotted in figure 6 along with MD data on the bulk modulus at various pressures along a 1200 K isotherm. Notice that the bulk modulus initially decreases and subsequently increases with pressure. This effect is entirely configurational in origin. The "vibrational" bulk modulus, given by the dashed line in figure 6, is *assumed identical* for every CN species of SiO_2. The equilibrium value of the bulk modulus departs significantly from the purely vibrational value when the configurations or CN transformations are changing most rapidly with increase in pressure. In terms of the model expression for K derived above (eqs 45, 49 and 64) the configurational terms involving the $\left.\frac{\partial s_i}{\partial P}\right|_{T,eq}$ dominate in the 0 to 20 GPa range, and essentially vanish much above 50 GPa. There are still CN transformations above 50 GPa, as is obvious in figure 4, but the volumetric consequences of these transformations are trivial which in turn leads to a trivial effect on the bulk modulus. Of further interest are the systematic deviations of the MD values of K from the calculated curve above 50 GPa. These deviations support the notion that there may be a significant vibrational contribution to the bulk modulus associated with CN transformations involving VI- to VII- and VII- to VIII-fold coordinated Si. The Gibbs free energy model developed in this example could be modified to account for this possibility, but these modifications will not be pursued here. Alternatively, the MD bulk modulus values at higher pressure may represent disequilibrium configurations corresponding to a quenched glass state. Further MD studies at similar pressures but much higher temperatures would illuminate this issue.

In contrast to the effect of configurational contributions to the pressure dependence of the bulk modulus, the thermal coefficient of expansion shows significant non-vibrational effects over the entire pressure range (fig. 7). The reason for these effects is that the configurational contribution to α is dominated by the Gibbs free energy changes of the homogenous reactions (eq 65) and these changes do not vanish at elevated pressure. The dashed line in figure 7 corresponds to the "vibrational" thermal expansion, calculated from equation (A-3). The solid line corresponds to an equilibrium CN distribution. From the figure inset, it can be seen that the thermal expansion plunges to negative values, reaching a minimum where the average CN exhibits its most rapid change with pressure, rising to positive values at pressures greater than 20 GPa. The fit to the MD data in figure 7 appears poorer than the fits displayed in figures 5 and 6 because these data with their attendant larger uncertainties were down weighted in the overall optimization.

In order to illustrate the effect of CN transformations on the macroscopic volumetric properties at reference pressure, model densities, thermal coefficients of expansion and bulk moduli are plotted as a function of T in figure 8. The dashed lines correspond to the vibrational properties of $Si^{IV}O_2$. The solid lines are properties calculated in a state of homogeneous equilibrium. Both the bulk modulus and thermal coefficient of expansion decrease because the percentage of $Si^{V}O_2$ increases with temperature and the smaller molar volume of $Si^{V}O_2$ leads to an overall reduction in volume and increase in density. The net negative $\Delta V/\Delta T$ due to the $Si^{IV}O_2$ to $Si^{V}O_2$ transformation contributes to the decrease in both thermal expansion and bulk modulus. The calculations presented in figure 8 are a sobering reminder of the power a thermodynamic model has in providing a self-consistent picture of the T and P dependence of functions of state in a chemical system. Although calibrated almost exclusively from MD simulations of volumetric properties at elevated pressure, the systematics of these observations filtered through a self-consistent thermodynamic model, require variation in volumetric properties at reference pressure where measurements are lacking. Details of these predictions may change with alternate MD data or model EOS expressions, but the principle trends demonstrated by this analysis are unlikely to be substantially in error.

The configurational and vibrational Gibbs free energy model for amorphous silica calibrated from the MD data can be combined with thermodynamic properties for solid phases of silica in order to calculate the liquid-solid phase diagram. Properties of β-cristobalite, β-quartz, and coesite are taken from the internally consistent thermodynamic data set of Hudon and others (2002) with the addition of data on stishovite from Swamy and Saxena (1994). The entropy of fusion of β-quartz is from Richet and others (1982). The liquid heat capacity is taken from Lange and Navrotsky (1992), who report a value slightly smaller than that suggested by Richet and others (1982). Piston cylinder experimental data on the fusion curve of β-cristobalite and β-quartz are reported by Jackson (1976). The fusion curve of β-quartz has been recently redetermined by Hudon and others (2002), who obtain melting at systematically higher temperatures than Jackson (1976) and argue that their measurements more accurately reflect the

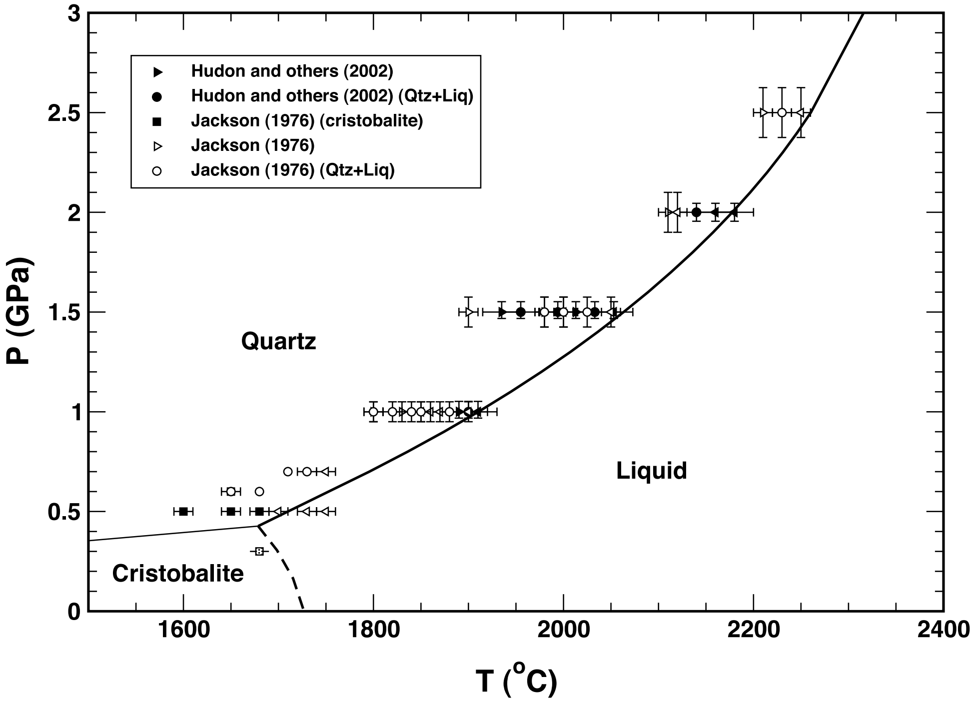

Fig. 9. Phase diagram for silica at low pressure. Experimental melting data and solid phase thermodynamic properties are discussed in the text. The heavy solid line is calculated using the model developed here with parameters reported in table 2.

dry melting curve of β-quartz. Melting experiments in multianvil apparatus have been performed by Kanzaki (1990) on β-quartz and coesite, and by Zhang and others (1993) on both coesite and stishovite. In figures 9 and 10 the experimental fusion curve data are plotted along with a calculated phase diagram. Liquid properties are calculated via equation (28) and its dependencies, where the volume integral of the liquid EOS is given by equation (A-28) of the appendix. It should be emphasized that the only EOS parameter influenced by data plotted in these figures is $V_{0,1673K}^{IV}$ which was chosen so that the initial slope of the fusion curve of β-quartz would pass through the lowest pressure reversal of Hudon and others (2002). Consequently, agreement of the experimental reversals and calculated liquid-solid phase boundaries much above 2 GPa is entirely coincidental.

The model developed above does a remarkable job in describing the liquid-solid phase relations of silica. At pressures below the stishovite stability field the calculated phase diagram in figure 10 is comparable to the diagrams fitted from the experimental reversals by Mao and others (2001), Hudon and others (2002) and Fabrichnaya and others (2004). Above the coesite to stishovite transition the model phase diagram of figure 10 deviates from that published by Fabrichnaya and others (2004) in that these authors show an almost isothermal melting curve for stishovite that starts at the transition pressure and rises to 40 GPa. The data that Fabrichnaya and others (2004) utilize to constrain liquid properties to produce such a melting curve are from Shen and Lazor (1995) and represent laser heating experiments on stishovite in diamond cells. If the data of Shen and Lazor (1995) reflect equilibrium melting conditions, then either the liquid densities inferred from the MD simulations are grossly in error, or the

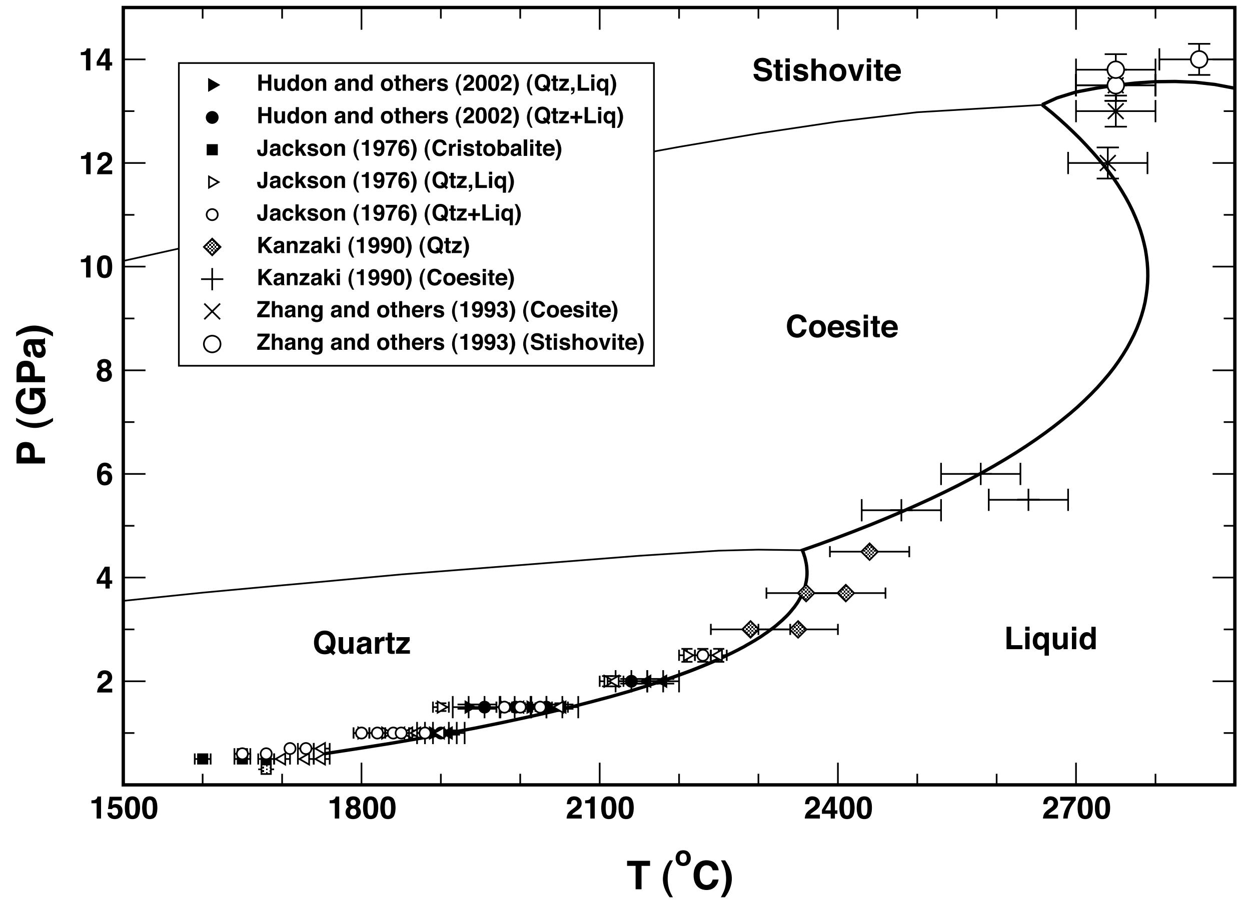

Fig. 10. Phase diagram for silica at high pressure. See legend for figure 9.

thermodyamic properties of stishovite change abruptly above 14 GPa, or some important energetic feature of SiO_2 liquid that develops above 15 GPa is not captured by the simple thermodynamic treatment developed here. However, the calculated melting curve for stishovite shown in figure 10 is consistent with estimates of stishovite melting determined in shock wave studies (Schmitt and Ahrens, 1989).

The volume of fusion of β-quartz at its metastable melting point of 1700 K and 10^5 Pa is calculated to be 3.74 cc/mol and should be compared to the hypothetical volume of fusion to $Si^{IV}O_2$ liquid of 4.06 cc/mol. The volume of fusion of β-cristobalite at its melting point of 1996 K (10^5 Pa) is –2.26 cc/mol (–1.79 cc/mol to $Si^{IV}O_2$ liquid). Solid volumetric properties from Hudon and others (2002) are utilized in both estimates. The suggested entropies of fusion of β-quartz and β-cristobalite, 5.53 J/K-mol and 4.46 J/K-mol, respectively (Richet and others, 1982), may be adjusted for the configurational entropy of the liquid. Model values are 2.04 J/K-mol at 1700 K and 2.70 J/K-mol at 1996 K. The latter should be compared to the estimate of 3.15 J/K-mol derived by Stebbins and others (1984) and the much higher estimate of 7.5 J/K-mol from Richet and Bottinga (1986), both from calorimetric data. The calorimetric estimates include all aspects of material disorder developed above the glass transition, so an unknown percentage of each value is attributable to disruption of long-range order and rotational degrees of freedom in liquid $Si^{IV}O_2$, effects which are not included in the model developed here. The model values for the configurational entropy may be used to estimate the hypothetical fusion entropy of β-quartz and β-cristobalite to $Si^{IV}O_2$ liquid, giving 3.49 J/K-mol and 1.76 J/K-mol respectively. The importance of these calculations is the implication that a significant fraction of the entropy and volume of fusion of low-pressure silica minerals is configurational in origin, which has previously been suggested by Stebbins and others (1984) and Richet and Bottinga (1986).

The "cusps" in the calculated phase diagram displayed in figure 10 are the result of the melt becoming denser than its coexisting solid, which induces a turnover in the fusion curve. The liquid densification is driven in part by a volume reduction associated with an increase in average CN. The liquid densification effect is mitigated by the stabilization of a denser solid. Above each solid-solid phase transition, the Clapyron slope changes back to a positive value, and remains positive until CN transformations in the liquid render it once again more dense than the coexisting solid phase. Structural transformations in the solids lag behind those in the liquid largely because long-range order in the solid induces a first-order phase transition whereas the lack of long-range order in the liquid smears the structural transition over a finite pressure interval. Broadly speaking, the energetic consequences of compression results in similar structural rearrangements in both phases, but the liquid is free to exhibit these changes first. The melting relations calculated for stishovite reflect the emergence of highly coordinated Si (VI, VII, VIII) in the melt at these pressures, and the maximum in the fusion curve indicates that the entropy of the solid approaches and exceeds that of the liquid. This unusual phase diagram geometry is both contradicted and supported by experimental evidence (see above), but the overturn is not in violation of any fundamental thermodynamic constraint.

One final observation regarding the phase diagram of figure 10 is that agreement with experimental observations and the MD volumetric data can only be achieved with a coupled configurational/vibrational description of the Gibbs energy of the amorphous phase. The MD data alone can be fitted to a single set of EOS parameters in an attempt to incorporate CN changes implicitly, but the resulting model fails to reproduce all but the lowest pressure features of the phase diagram. Silica serves as a case example of the need to completely and carefully characterize the various thermodynamic contributions to the amorphous phase and illustrates why treating such a phase as if it were an isostructural solid is insufficient when configurational and vibrational contributions to thermodynamic properties are comparable.

SUMMARY

The liquid EOS developed in this paper is designed with three features in mind. Firstly, to avoid the pitfalls inherent to commonly used formulations created for solid phases, where the thermal coefficient of expansion and the bulk modulus are sufficiently well behaved that a constant "thermal pressure" correction may be used to describe the temperature dependence of the EOS. Secondly, to facilitate the creation of simple, thermodynamically consistent mixing relations that permit generalization of the parameters of the EOS to fluids of variable composition. And, thirdly, to minimize the number of adjustable parameters required to utilize the EOS at elevated pressure.

The EOS developed here is intended to account for the volumetric properties of liquids whose structural configurations do not vary with pressure and temperature. In the world of silicate melts, such liquids are hypothetical, as configurational changes in the form of shifting coordination number of cations are an important consideration, especially at elevated pressure. For real liquids that exhibit configurational changes, utilization of the proposed EOS is facilitated by incorporating it into a thermodynamic model for the Gibbs free energy of the liquid that explicitly accounts for the entropic effects of the configuration. This approach is more theoretically sound and certainly less cumbersome than an attempt to incorporate configurational effects into the EOS directly. Although it may be argued that EOS parameters can be fitted for any given bulk liquid composition to experimental volumetric data that implicitly incorporates the effects of configurational variation, the difficulty arises when this approach is to be utilized in a general parameterization that includes compositional variation. For example, if the EOS parameters are taken to vary as a function of average coordination number, which is itself a function of composition, then the parameters themselves can not be calculated until after the equilibrium value of the average coordination number is known. But this average coordination number cannot be known *a priori*. The coordination number distribution can only be determined by computing homogeneous equilibrium for the system as a whole, and this calculation requires some expression for the energy of the system that is minimal at the equilibrium configuration. Any algorithm that establishes an *ad hoc* dependence of EOS parameters on coordination number distribution will in general not be consistent with the equilibrium distribution resulting in the minimum of the configurational energy of the system. The method illustrated in this paper, which decouples the EOS from the configuration state, provides a simple and internally consistent way of modeling the energetic features of the liquid.

ACKNOWLEDGMENTS

Thoughtful discussions with Marc Hirschmann, Victor Kress, Raymond Pierrehumbert, and Frank Spera were pivotal in developing the arguments presented in this paper. Material support for this investigation was generously provided by the National Science Foundation (OCE-9977416 and EAR-9980518) and by The University of Chicago.

Appendix

The EOS form proposed in the body of the text is given by the expression

$$V = \frac{V_{0,T} + (V_{1,T} + V_{0,T}\,a)(P - P_r) + \left(\frac{V_2}{2} + V_{1,T}\,a + V_{0,T}\,b\right)(P - P_r)^2}{1 + a(P - P_r) + b(P - P_r)^2} \tag{A-1}$$

where the parameters $V_{0,T}$ and $V_{1,T}$ are functions of temperature and composition, and a, b and V_2 are functions only of composition. The V computed in equation (A-1) is an extensive quantity, as are the parameters $V_{0,T}$, $V_{1,T}$, and V_2. Thermodynamic state functions are derived from equation (A-1) below.

Derived Derivative Quantities

Equation (A-1) may be differentiated with respect to temperature to give

$$\frac{\partial V}{\partial T} = \frac{\alpha V_{0,T} + \left(\frac{\partial V_{1,T}}{\partial T} + \alpha V_{0,T}\, a\right)(P - P_r) + \left(\frac{\partial V_{1,T}}{\partial T}\, a + \alpha V_{0,T}\, b\right)(P - P_r)^2}{1 + a(P - P_r) + b(P - P_r)^2} \tag{A-2}$$

and utilizing the definition of the thermal coefficient of expansion,

$$\alpha_{T,P} = \frac{1}{V}\frac{\partial V}{\partial T}$$

equation (A-2) yields the model expression

$$\alpha_{T,P} = \frac{\alpha V_{0,T} + \left(\frac{\partial V_{1,T}}{\partial T} + \alpha V_{0,T}\, a\right)(P - P_r) + \left(\frac{\partial V_{1,T}}{\partial T}\, a + \alpha V_{0,T}\, b\right)(P - P_r)^2}{V_{0,T} + (V_{1,T} + V_{0,T}\, a)(P - P_r) + \left(\frac{V_2}{2} + V_{1,T}\, a + V_{0,T}\, b\right)(P - P_r)^2} \tag{A-3}$$

The limit of the right-hand-side of equations (A-2) and (A-3) as pressure tends toward infinity is

$$\lim_{P \to \infty} \frac{\partial V}{\partial T} = \alpha V_{0,T} + \frac{\partial V_{1,T}}{\partial T}\frac{a}{b} \tag{A-4}$$

and

$$\lim_{P \to \infty} \alpha_{T,P} = \frac{\alpha V_{0,T}\, b + \frac{\partial V_{1,T}}{\partial T}\, a}{V_{0,T}\, b + V_{1,T}\, a + V_2} \tag{A-5}$$

respectively. The temperature dependence of $\alpha_{T,P}$ is obtained from the definition by differentiation

$$\frac{\partial \alpha_{T,P}}{\partial T} = \frac{1}{V}\frac{\partial^2 V}{\partial T^2} - \alpha^2_{T,P}$$

where the second volume derivative is given by

$$\frac{\partial^2 V}{\partial T^2} = \frac{\alpha^2 V_{0,T} + \left(\frac{\partial^2 V_{1,T}}{\partial T^2} + \alpha^2 V_{0,T}\, a\right)(P - P_r) + \left(\frac{\partial^2 V_{1,T}}{\partial T^2}\, a + \alpha^2 V_{0,T}\, b\right)(P - P_r)^2}{1 + a(P - P_r) + b(P - P_r)^2} \tag{A-6}$$

that can be shown to have the following low and high-pressure limits

$$\lim_{P \to P_r} \frac{\partial^2 V}{\partial T^2} = \alpha^2 V_{0,T} > 0 \tag{A-7}$$

$$\lim_{P \to \infty} \frac{\partial^2 V}{\partial T^2} = \alpha^2 V_{0,T} + \frac{\partial^2 V_{1,T}}{\partial T^2}\frac{a}{b} \tag{A-8}$$

The pressure derivative of equation (A-1) is given by

$$\frac{\partial V}{\partial P} = \frac{\left[V_{1,T} + V_{0,T}\, a + 2\left(\frac{V_2}{2} + V_{1,T}\, a + V_{0,T}\, b\right)(P - P_r)\right] - V[a + 2b(P - P_r)]}{1 + a(P - P_r) + b(P - P_r)^2} \tag{A-9}$$

and, from the definition of the compressibility and the bulk modulus,

$$\beta = -\frac{1}{V}\frac{\partial V}{\partial P}, \quad K = \frac{1}{\beta}$$

K is given by

$$K = -\frac{V_{0,T} + (V_{1,T} + V_{0,T}a)(P - P_r) + \left(\frac{V_2}{2} + V_{1,T}a + V_{0,T}b\right)(P - P_r)^2}{\left[V_{1,T} + V_{0,T}a + 2\left(\frac{V_2}{2} + V_{1,T}a + V_{0,T}b\right)(P - P_r)\right] - V[a + 2b(P - P_r)]} \tag{A-10}$$

The following limits result from equation (A-10)

$$\lim_{P \to \infty} K = \infty \tag{A-11}$$

$$\lim_{P \to P_r} K = -\frac{V_{0,T}}{V_{1,T}} \tag{A-12}$$

The pressure derivative of the bulk modulus is given by

$$K' = \frac{\partial K}{\partial P} = \frac{V\frac{\partial^2 V}{\partial P^2}}{\left(\frac{\partial V}{\partial P}\right)^2} - 1 = \frac{1}{V}K^2\frac{\partial^2 V}{\partial P^2} - 1 \tag{A-13}$$

which requires evaluation of the derivative

$$\frac{\partial^2 V}{\partial P^2} = \frac{(V_2 + 2V_{1,T}a + 2V_{0,T}b) - 2\frac{\partial V}{\partial P}[a + 2b(P - P_r)] - 2Vb}{1 + a(P - P_r) + b(P - P_r)^2} \tag{A-14}$$

The value of K' at the reference pressure,

$$\lim_{P \to P_r} K' = \frac{V_{0,T}V_2}{(V_{1,T})^2} - 1 \tag{A-15}$$

serves to provide a means of obtaining a numerical value of the parameter V_2 given an estimate of K'

$$V_2 = \frac{(1 + K'_{P_r})(V_{1,T})^2}{V_{0,T}} \tag{A-16}$$

The derivative,

$$\frac{\partial^2 V}{\partial T \partial P} = \frac{\left[\frac{\partial V_{1,T}}{\partial T} + \alpha V_{0,T}a + 2\left(\frac{\partial V_{1,T}}{\partial T}a + \alpha V_{0,T}b\right)(P - P_r)\right] - \frac{\partial V}{\partial T}[a + 2b(P - P_r)]}{1 + a(P - P_r) + b(P - P_r)^2} \tag{A-17}$$

may be used to estimate the effect of temperature on the bulk modulus

$$\frac{\partial K}{\partial T} = K\alpha_{T,P} + \frac{K^2}{V}\frac{\partial^2 V}{\partial T \partial P} \tag{A-18}$$

or alternatively, the effect of temperature on the compressibility

$$\frac{\partial \beta}{\partial T} = -\alpha_{T,P}\beta - \frac{1}{V}\frac{\partial^2 V}{\partial T \partial P} \tag{A-19}$$

or, the effect or pressure on the thermal coefficient of expansion

$$\frac{\partial \alpha_{T,P}}{\partial P} = \frac{\partial \beta}{\partial T}$$

The first term on the right-hand-side of equation (A-18) is the "thermal pressure term" and is given by

$$K\alpha_{T,P} = -\frac{\alpha V_{0,T} + \left(\frac{\partial V_{1,T}}{\partial T} + \alpha V_{0,T}\, a\right)(P-P_r) + \left(\frac{\partial V_{1,T}}{\partial T}\, a + \alpha V_{0,T}\, b\right)(P-P_r)^2}{\left[V_{1,T} + V_{0,T}\, a + 2\left(\frac{V_2}{2} + V_{1,T}\, a + V_{0,T}\, b\right)(P-P_r)\right] - V[a+2b(P-P_r)]} \tag{A-20}$$

Note that equation (A-17) has the following high-pressure limit

$$\lim_{P \to \infty} \frac{\partial^2 V}{\partial T \partial P} = 0 \tag{A-21}$$

and that

$$\lim_{P \to \infty} \frac{\partial \beta}{\partial P} = \lim_{P \to \infty} \frac{\partial \alpha_{T,P}}{\partial T} = 0 \tag{A-22}$$

Derived Integral Quantities

The pressure contribution to the Gibbs free energy of a substance is given by the thermodynamic relation

$$G_{T,P} = H_{T,P_r} - TS_{T,P_r} + \int_{P_r}^{P} V_T\, dP \tag{A-23}$$

The pressure integral in equation (A-23) can be evaluated analytically after substitution of equation (A-1). Five cases may be developed.

Case: $a = b = 0$

$$\int_{P_r}^{P} V\, dP = V_{0,T}(P-P_r) + \frac{V_{1,T}}{2}(P-P_r)^2 + \frac{V_2}{3}(P-P_r)^3 \tag{A-24}$$

Case: $a = 0$

$$\int_{P_r}^{P} V\, dP = \left(V_{0,T} + \frac{V_2}{2b}\right)(P-P_r) + \frac{1}{2b} V_{1,T} \ln[1 + b(P-P_r)^2] - \frac{V_2}{2b^{3/2}} \tan^{-1}[\sqrt{b}\,(P-P_r)] \tag{A-25}$$

Case: $b = 0$

$$\int_{P_r}^{P} V\, dP = \left(V_{0,T} - \frac{V_2}{2a^2}\right)(P-P_r) + \frac{1}{2}\left(V_{1,T} + \frac{V_2}{2a}\right)(P-P_r)^2 + \frac{V_2}{2a^3} \ln[1 + a(P-P_r)] \tag{A-26}$$

Case: $a^2 - 4b = 0$

$$\int_{P_r}^{P} V\, dP = \left[V_{0,T} + \frac{2}{a}\left(2V_{1,T} + \frac{V_2}{a}\right)\right](P-P_r) + \frac{4\left(V_{1,T} + \frac{V_2}{a}\right)(P-P_r)}{a[2 + a(P-P_r)]} - \frac{4}{a^2}\left[3V_{1,T} + \frac{2V_2}{a}\right]\ln\left[1 + \frac{a}{2}(P-P_r)\right] \tag{A-27}$$

Case: $a^2 - 4b \neq 0$

$$\int_{P_r}^{P} V\,dP = \left(V_{0,T} + \frac{a}{b}V_{1,T} + \frac{V_2}{2b}\right)(P - P_r) + \frac{1}{2b}\left[V_{1,T}\left(1 - \frac{a^2}{b}\right) - \frac{V_2 a}{2b}\right]\ln[1 + a(P - P_r) + b(P - P_r)^2]$$
$$- \frac{1}{b}\left[V_{1,T}\,a\left(3 - \frac{a^2}{b}\right) + V_2\left(1 - \frac{a^2}{2b}\right)\right]\begin{cases} \dfrac{1}{\sqrt{a^2 - 4b}}\tanh^{-1}\left[\dfrac{\sqrt{a^2 - 4b}\,(P - P_r)}{2 + a(P - P_r)}\right] & a^2 - 4b > 0 \\ \dfrac{1}{\sqrt{4b - a^2}}\tan^{-1}\left[\dfrac{\sqrt{4b - a^2}\,(P - P_r)}{2 + a(P - P_r)}\right] & a^2 - 4b < 0 \end{cases} \tag{A-28}$$

Note that in the last, most general case, the integral has two branches that depend on the sign of the quantity $a^2 - 4b$.

The pressure contribution to the entropy, enthalpy and heat capacity are given by differentiation of equation (A-23) and substitution of appropriate thermodynamic identities. The following definitions

$$S_{T,P} = -\frac{\partial G_{T,P}}{\partial T} = S_{T,P_r} - \frac{\partial}{\partial T}\int_{P_r}^{P} V_T\,dP \tag{A-29}$$

$$H_{T,P} = G_{T,P} + TS_{T,P} = H_{T,P_r} + \int_{P_r}^{P} V_T\,dP - T\frac{\partial}{\partial T}\int_{P_r}^{P} V_T\,dP \tag{A-30}$$

$$Cp_{T,P} = T\frac{\partial S_{T,P}}{\partial T} = Cp_{T,P_r} - T\frac{\partial^2}{\partial T^2}\int_{P_r}^{P} V_T\,dP \tag{A-31}$$

$$Cv_{T,P} = Cp_{T,P} - T\alpha_{T,P}^2 KV \tag{A-32}$$

$$\frac{\partial Cp_{T,P}}{\partial T} = \frac{\partial Cp_{T,P_r}}{\partial T} - \frac{\partial^2}{\partial T^2}\int_{P_r}^{P} V_T\,dP - T\frac{\partial^3}{\partial T^3}\int_{P_r}^{P} V_T\,dP \tag{A-33}$$

all depend on first and higher-order temperature derivatives of the volume integral. Taking the general case (eq 28) as a model, the i^{th} such derivative may be written

$$\frac{\partial^i}{\partial T^i}\int_{P_r}^{P} V\,dP = \left(\alpha^i V_{0,T} + \frac{a}{b}\frac{\partial^i V_{1,T}}{\partial T^i}\right)(P - P_r) + \frac{\partial^i V_{1,T}}{\partial T^i}\frac{1}{2b}\left(1 - \frac{a^2}{b}\right)\ln[1 + a(P - P_r) + b(P - P_r)^2]$$
$$- \frac{\partial^i V_{1,T}}{\partial T^i}\frac{a}{b}\left(3 - \frac{a^2}{b}\right)\begin{cases} \dfrac{1}{\sqrt{a^2 - 4b}}\tanh^{-1}\left[\dfrac{\sqrt{a^2 - 4b}\,(P - P_r)}{2 + a(P - P_r)}\right] & a^2 - 4b > 0 \\ \dfrac{1}{\sqrt{4b - a^2}}\tan^{-1}\left[\dfrac{\sqrt{4b - a^2}\,(P - P_r)}{2 + a(P - P_r)}\right] & a^2 - 4b < 0 \end{cases} \tag{A-34}$$

Dependent Quantities

A number of thermodynamic relations and dependent quantities can be constructed from the above relations. For comparison with other EOS formulations it might be instructive to examine the Grüneisen parameter, defined as

$$\gamma = \frac{\alpha_{T,P}KV}{Cv} \tag{A-35}$$

or alternatively

$$\gamma = \frac{\alpha_{T,P}KV}{Cp - T\alpha_{T,P}^2 KV} \tag{A-36}$$

Substitution of definitions appropriate to the proposed EOS into equations (A-35) or (A-36) reveals that the high pressure limit of the Grüneisen parameter is finite and is given by

$$\lim_{P \to \infty} \gamma = -\frac{2V_{1,T}\,a + 2V_{0,T}\,b + V_2}{2T\left(\dfrac{\partial V_{1,T}}{\partial T}\,a + \alpha V_{0,T}\,b\right)} \tag{A-37}$$

It should be possible to use equation (A-37) as a constraint on EOS model parameters if independent experimental evidence is available that provides estimates of the Grüneisen parameter at elevated pressure.

References

Agee, C. B., 1998, Crystal-liquid density inversions in terrestrial and lunar magmas: Physics of the Earth and Planetary Interiors, v. 107, p. 63–74.

Anderson, D. L., 1989, Theory of the Earth: Blackwell Scientific Publications, 366 p.

Anderson, O. L., 1984, A universal thermal equation of state: Journal of Geodynamics, v. 1, p. 185–214.

—— 1995, Equations of state for solids in geophysics and ceramic science: Oxford Monographs on Geology and Geophysics, v. 31, 405 p.

Bacon, J. F., Hasapis, A. A., and Wholley, J. W., Jr., 1960, Viscosity and density of molten silica and high silica content glasses: Physics and Chemistry of Glasses, v. 1, p. 90–98.

Baidov, V. V., and Kunin L. L., 1968, Speed of ultrasound and compressibility of molten silica: Soviet Physics Doklady, v. 13, p. 64–65.

Baker, G. A., Jr., and Graves-Morris, P., 1996, Padé Approximants: New York, Cambridge University Press, Encyclopedia of Mathematics, v. 59, 2^{nd} edition.

Baonza, V. G., Cáceres, M., and Núñez, J., 1995, Universal compressibility behavior of dense phases: Physical Review B, v. 51, p. 28–37.

Birch, F., 1939, The variation of seismic velocities within a simplified Earth model in accordance with the theory of finite strain: Bulletin of the Seismological Society of America, v. 29, p. 463.

—— 1952, Elasticity and constitution of the Earth's interior: Journal of Geophysical Research, v. 57, p. 227–286.

—— 1968, Thermal expansion at high pressure: Journal of Geophysical Research, v. 73, p. 817–819.

Courtial, P., and Dingwell, D. B., 1995, Nonlinear composition dependence of molar volume of melts in the CaO-Al_2O_3-SiO_2 system: Geochimica et Cosmochimica Acta, v. 59, p. 3685–3695.

Fabrichnaya, O., Saxena, S. K., Richet, P., Westrum, E. F., Jr., 2004, Thermodynamic data, models, and phase diagrams in multicomponent oxide systems: New York, Springer-Verlag, 198 p.

Gaetani, G. A., Asimow, P. D., Stolper, E. M., 1998, Determination of the partial molar volume of SiO_2 in silicate liquids at elevated pressures and temperatures: A new experimental approach: Geochimica et Cosmochimica Acta, v. 62, p. 2499–2508.

Ghiorso, M. S., 1990, Application of the Darken equation to mineral solid-solutions with variable degrees of order-disorder: American Mineralogist, v. 75, p. 539–543.

—— 2004a, An Equation of State for Silicate Melts. III. Analysis of stoichiometric liquids at elevated pressure: shock compression data, molecular dynamics simulations and mineral fusion curves: American Journal of Science, v. 304, p. 752–810.

—— 2004b, An Equation of State for Silicate Melts. IV. Calibration of a multicomponent mixing model to 40 GPa: American Journal of Science, v. 304, p. 811–838.

Ghiorso, M. S., and Kress, V. C., 2004, An Equation of State for Silicate Melts. II. Calibration of volumetric properties at 10^5 Pa: American Journal of Science, v. 304, p. 679–751.

Ghiorso, M. S., and Sack, R. O., 1995, Chemical Mass Transfer in Magmatic Processes IV. A revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and pressures: Contributions to Mineralogy and Petrology, v. 119, p. 197–212.

Ghiorso, M. S., Hirschmann, M. M., Reiners, P. W., and Kress, V. C., 2002, The pMELTS: A revision of MELTS aimed at improving calculation of phase relations and major element partitioning involved in partial melting of the mantle at pressures up to 3 GPa: Geochemistry, Geophysics, Geosystems, v. 3, 10.1029/2001GC000217.

Hama, J., and Suito, K., 1996, The search for a universal equation of state correct up to very high pressures: Journal of Physics: Condensed Matter, v. 8, p. 67–81.

Herzberg, C. T., 1987a, Magma density at high pressure Part 1: The effect of composition on the elastic properties of silicate melts, *in* Mysen, B. O., editor, Magmatic Processes: Physiochemical Principles: University Park, Pennsylvania, Geochemical Society Special Publication, v. 1, p. 25–46.

—— 1987b, Magma density at high pressure Part 2: A test of the olivine floatation hypothesis, *in* Mysen, B. O., editor, Magmatic Processes: Physiochemical Principles: University Park, Pennsylvania, Geochemical Society Special Publication, v. 1, p. 47–58.

Hofmeister, A. M., 1993, Interatomic potentials calculated from equations of state: Limitation of finite strain to moderate K': Geophysical Research Letters, v. 20, p. 635–638.

Hudon, P., Jung, I. H., and Baker, D. R., 2002, Melting of β-quartz up to 2.0 GPa and thermodynamic optimization of the silica liquidus up to 6.0 Gpa: Physics of the Earth and Planetary Interiors, v. 130, p. 159–174.

Jackson, I., 1976, Melting of the silica isotypes SiO_2, BeF_2 and GeO_2 at elevated pressures: Physics of the Earth and Planetary Interiors, v. 13, p. 218–231.

Jeanloz, R., 1982, Effect of coordination change on thermodynamic properties, *in* Akimoto, S., and Manghnani, M. H., editors, High-Pressure Research in Geophysics: Advances in Earth and Planetary Sciences, v. 12, p. 479–498

—— 1988, Universal equation of state: Physical Review B, v. 38, p. 805–807.

Kanzaki, M., 1990, Melting of silica up to 7 GPa: Journal of the American Ceramic Society, v. 73, p. 3706–3707.

Kaufman M., and Schlosser H., 1995, A thermodynamic model for pressurized solids: Journal of Physics: Condensed Matter, v. 7, p. 2259–2264.

Kress, V. C., and Carmichael, I. S. E., 1991, The compressibility of silicate liquids containing Fe_2O_3 and the effect of composition, temperature, oxygen fugacity and pressure on their redox states: Contributions to Mineralogy and Petrology, v. 108, p. 82–92.

Kuchhal, P., Kumar R., and Dass, N., 1997, Temperature-dependent equation of state of condensed matter: Journal of Physics: Condensed Matter, v. 9, p. 2987–2998.

Kumari, M., and Dass, N., 1986, On the pressure dependence of Grüneisen parameter in solids: Physica Status Solidi (b), v. 133, p. 101–110.

—— 1990a, An equation of state applied to 50 solids: II, Journal of Physics: Condensed Matter, v. 2, p. 7891–7895.

—— 1990b, An equation of state applied to sodium chloride and cesium chloride at high pressures and high temperatures: Journal of Physics: Condensed Matter, v. 2, p. 3219–3229.

—— 1991, An equation of state applied to liquids: Journal of Physics: Condensed Matter, v. 3, p. 4099–4103.

—— 1993, Temperature dependence of density and thermal expansion in some liquid metals: Journal of Non-Crystalline Solids, v. 156–158, p. 417–420.

Lange, R. A., 2003, The fusion curve of albite revisited and the compressibility of $NaAlSi_3O_8$ liquid with pressure: American Mineralogist, v. 88, p. 109–120.

Lange, R. A., and Carmichael, I. S. E., 1987, Densities of Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2 liquids: New measurements and derived partial molar properties: Geochimica et Cosmochimica Acta, v. 51, p. 2931–2946.

—— 1990, Thermodynamic properties of silicate liquids with emphasis on density, thermal expansion and compressibility, *in* Modern Methods of Igneous Petrology: Understanding Magmatic Processes: Reviews in Mineralogy, v. 24, p. 25–64.

Lange, R. A., and Navrotsky, A., 1992, Heat capacities of Fe_2O_3-bearing silicate liquids: Contributions to Mineralogy and Petrology, v. 110, p. 311–320.

Liu Q., and Lange, R. A., 2001, The partial molar volume and thermal expansivity of TiO_2 in alkali silicate melts: Systematic variation with Ti coordination: Geochimica et Cosmochimica Acta, v. 65, p. 2379–2393.

Mao, H., Sundman B., Wang Z., and Saxena, S. K., 2001, Volumetric properties and phase relations of silica – thermodynamic assessment: Journal of Alloys and Compounds, v. 327, p. 253–262.

Mortuza, M. G., Absan, M. R., Chudek, J. A., and Hunter, G., 2000, First evidence for the coexistence of four-, five-, and six-coordinated silicon in glasses prepared at ambient pressure: Chemical Communications, p. 2055–2056.

Parsafar, G., and Mason, E. A., 1994, Universal equation of state for compressed solids: Physical Review B, v. 49, p. 3049–3060.

Poirier, J. P., and Tarantola A., 1998, A logarithmic equation of state: Physics of the Earth and Planetary Interiors, v. 109, p. 1–8.

Prausnitz, J. M., 1969, Molecular Thermodynamics of Fluid-phase Equilibria: Englewood Cliffs, New Jersey, Prentice-Hall Inc., 523 p.

Prigogene, I., and Defay, R., 1954, Chemical Thermodynamics: New York, Longmans Green and Co., 543 p.

Richet, P., and Bottinga, Y., 1986, Thermochemical properties of silicate glasses and liquids: A review: Reviews of Geophysics, v. 24, p. 1–25.

Richet, P., Bottinga, Y., Denielou, L., Petitet, J. P., and Tequi, C., 1982, Thermodynamic properties of quartz, cristobalite and amorphous SiO_2: drop calorimettry measurements between 1000 and 2000 K and a review from 0 to 2000 K: Geochimica et Cosmochimica Acta, v. 46, p. 2639–2658

Rigden, S. M., Ahrens, T. J., and Stolper, E. M., 1984, Densities of liquid silicates at high pressures: Science, v. 226, p. 1071–1074.

Rustad, J. R., Yuen, D. A., and Spera, F. J., 1990, Molecular dynamics of liquid SiO_2 under high pressure: Physical Review A, v. 42, p. 2081–2089.

—— 1991a, Molecular dynamics of amorphous silica at very high pressures (135 GPa): Thermodynamics and extraction of structures through analysis of Voronoi polyhedra: Physical Review B, v. 44, p. 2108–2121.

—— 1991b, The sensitivity of physical and spectral properties of silica glass to variations of interatomic potentials under high pressure: Physics of the Earth and Planetary Interiors, v. 65, p. 210–230.

Saxena, S. K., Chatterjee, N., Fei, Y., and Shen, G., 1993, Thermodynamic Data on Oxides and Silicates. An assessed data set based on thermochemistry and high pressure phase equilibrium: New York, Springer-Verlag, 428 p.

Schlosser, H., 1990, Rare-gas liquids: Equation of state and reduced-pressure, reduced-bulk-modulus, and reduced-sound-velocity functions: Physical Review B, v. 41, p. 1173–1175.

Schlosser, H., and Ferrante, J., 1988a, Universality relationships in condensed matter: Bulk modulus and sound velocity: Physical Review B, v. 37, p. 4351–4357.

—— 1988b, Erratum: Universality relationships in condensed matter: Bulk modulus and sound velocity: Physical Review B, v. 38, p. 2187.

—— 1989, Liquid alkali metals: Equation of state and reduced-pressure, bulk-modulus, sound-velocity, and specific-heat functions: Physical Review B, v. 40, p. 6405–6408.

Schlosser, H., Vinet, P., and Ferrante, J., 1989, Pressure dependence of the melting temperature of metals: Physical Review B, v. 40, p. 5929–5935.

Schmitt, D. R., and Ahrens, T. J., Shock temperatures in silica glass: implications for modes of shock induced deformation, phase transformation, and melting with pressure: Journal of Geophysical Research, v. 94, p. 5851–5871.

Shen, G., and Lazor, P., 1995, Measurement of melting temperatures of some minerals under lower mantle pressures: Journal of Geophysical Research, v. 100, p. 17699–17713.

Stacey, F. D., Brennan, B. J., and Irvine, R. D., 1981, Finite strain theories and comparisons with seismological data: Geophysical Surveys, v. 4, p. 189–232.

Stebbins, J. F., 1991, NMR evidence for five-coordinated silicon in a silicate glass at atmosphere pressure: Nature, v. 351, p. 638–639.

Stebbins, J. F., Carmichael, I. S. E., and Moret, L. K., 1984, Heat capacities and entropies of silicate liquids and glasses: Contributions to Mineralogy and Petrology, v. 86, p. 131–148.

Stixrude, L., and Bukowinski, M. S. T., 1990, Fundamental thermodynamic relations and silicate melting with implications for the constitution of D": Journal of Geophysical Research, v. 95, p. 19311–19325.

Swamy, V., and Saxena, S. K., 1994, A thermodynamic assessment of silica phase diagram: Journal of Geophysical Research, v. 99, p. 11787–11794.

Tanaka, H., 2000, General view of a liquid-liquid phase transition: Physical Review B, v. 62, p. 6968–6976.

Taravillo, M., Baonza, V. G., Núñez, J., and Cáceres, M., 1996, Simple equation of state for solids under compression: Physical Review B, v. 54, p. 7034–7045.

Trave, A., Tangney, P., Scandolo, S., Pasquarello, A., and Car, R., 2002, Pressure-induced structural changes in liquid SiO_2 from Ab Initio simulations: Physical Review Letters, v. 24, p. 245504-1–4.

Vinet, P., Ferrante, J., Smith, J. R., and Rose, J. H., 1986, A universal equation of state for solids: Journal of Physics C: Solid State Physics, v. 19, p. L467–L473.

Vinet P., Smith, J. R., Ferrante, J., and Rose, J. H., 1987, Temperature effects on the universal equation of state of solids: Physical Review B, v. 35, p. 1945–1953.

Zhang, J., Liebermann, R. C., Gasparik, T., Herzberg, C. T., and Fei, Y., 1993, Melting and subsolidus relations of SiO_2 at 9-14 GPa: Journal of Geophysical Research, v. 98, p. 19785–19793.