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A Volume Temperature Relationship for Liquid GeO_2 and some Geophysically Relevant Derived Parameters for Network Liquids

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Abstract. The thermal expansivity of liquid GeO_2 at temperatures just above the glass transition has been obtained using a combination of scanning calorimetry and dilatometry. The calorimetric and dilatometric curves of c_p and dV/dT are normalized to the temperature derivative of fictive temperature versus temperature using the method of Webb et al. (1992). This normalization, based on the equivalence of relaxation parameters for volume and enthalpy, allows the completion of the dilatometric trace across the glass transition to yield liquid expansivity and volume. The values of liquid volume and expansivity obtained in this study are combined with high temperature densitometry determinations of the liquid volume of GeO_2 by Sekiya et al. (1980) to yield a temperature-volume relation for GeO_2 melt from 660 to 1400 °C. Liquid GeO_2 shows a strongly temperature-dependent liquid molar expansivity, decreasing from 20.27×10^{-4} cm^3 mol^{-1} °C^{-1} to 1.97×10^{-4} cm^3 mol^{-1} °C^{-1} with increasing temperature. The coefficient of volume thermal expansion (α_v) decreases from 76.33×10^{-6} °C^{-1} to 2.46×10^{-6} °C^{-1} with increasing temperature. A qualitatively similar volume-temperature relationship, with α_v decreasing from 335×10^{-6} °C^{-1} to 33×10^{-6} °C^{-1} with increasing temperature, has been observed previously in liquid B_2O_3. The determination of the glass transition temperature, liquid volume, liquid and glassy expansivities and heat capacities in this study, combined with compressibility data for glassy and liquid GeO_2 from the literature (Soga 1969; Kurkjian et al. 1972; Scarfe et al. 1987) allows the calculation of the Prigogine-Defay ratio (Π), $c_p - c_v$ and the thermal Grüneisen parameter (γ_{th}) for GeO_2. From available data on liquid SiO_2 it is concluded that liquid GeO_2 is not a good analog for the low pressure properties of liquid SiO_2.

Introduction

GeO_2 is commonly used as an analog of SiO_2 in studies of the structure and properties of glasses, liquids (Richet 1990) and minerals (Ross et al. 1986; Rigden and Jackson 1991). The isomorphous nature of amorphous GeO_2 and SiO_2 has been emphasized in spectroscopic studies (e.g. Konnert et al. 1973). Glassy GeO_2 investigated at high pressure has been shown to undergo a coordination shift (Durben and Wolf 1991; Itie et al. 1989) and the addition of alkalies to GeO_2 glass and liquid also produces a density and bulk modulus maximum that has been interpreted as resulting from a shift to higher coordination (Riebling 1963; Sekiya et al. 1980; Osaka et al. 1985: see, however, Henderson and Fleet 1991). For studies of the liquid state, GeO_2 provides the considerable advantage that the temperature required to achieve the relaxed liquid response of amorphous GeO_2 is 500–600 °C lower than that of SiO_2, at any given frequency. The lower temperature of structural relaxation in GeO_2 (at approx. 580 °C versus 1180 °C for SiO_2 at approx. 10^{-2} Hz) brings studies of the glass transition of this single component network-structure liquid within the temperature range of operation of very precise scanning methods of dilatometry and calorimetry.

In a recent series of studies, the analysis of scanning calorimetric and dilatometric data across the glass transition of silicate melts has been used to obtain liquid thermal expansivity data just above glass transition temperatures (Knoche et al. 1992a, b, c). These low-temperature liquid expansivities have been combined with high temperature densitometry to obtain the first reliable estimates of the temperature-dependence of thermal expansivity in silicate melts. By using these methods, we present an expression for the volume-temperature relationship of GeO_2 liquid from 660 to 1400 °C. The volume and expansivity data point in a consistent manner to a strongly temperature-dependent expansivity for liquid GeO_2.

The new data on the changes in heat capacity and thermal expansivity across the glass transition, the molar volume at the glass transition and the glass transition temperature are combined with literature-derived estimates of the compressibility of GeO_2 glass and liquid to estimate the values of the Prigogine-Defay ratio, $c_p - c_v$ and the thermal Grüneisen parameter for amor-

Table 1. Measured c_p($J g^{-1} °C^{-1}$) data for glass and liquid GeO_2. (heating-rate 5 °C min^{-1})

	Cooling rate			
T(°C)	1 °C min^{-1}	2 °C min^{-1}	5 °C min^{-1}	10 °C min^{-1}
40	0.5257	0.5232	0.5228	0.5264
50	0.5330	0.5313	0.5299	0.5348
60	0.5356	0.5342	0.5325	0.5382
70	0.5463	0.5454	0.5433	0.5489
80	0.5523	0.5536	0.5505	0.5561
90	0.5592	0.5614	0.5557	0.5615
100	0.5647	0.5671	0.5595	0.5668
110	0.5702	0.5731	0.5640	0.5727
120	0.5758	0.5792	0.5689	0.5786
130	0.5808	0.5848	0.5743	0.5840
140	0.5856	0.5900	0.5791	0.5891
150	0.5905	0.5951	0.5833	0.5940
160	0.5952	0.6001	0.5876	0.5988
170	0.5997	0.6044	0.5913	0.6031
180	0.6045	0.6091	0.5979	0.6078
190	0.6091	0.6138	0.6033	0.6122
200	0.6131	0.6176	0.6074	0.6162
210	0.6164	0.6209	0.6111	0.6194
220	0.6197	0.6241	0.6146	0.6226
230	0.6228	0.6268	0.6178	0.6256
240	0.6258	0.6290	0.6207	0.6284
250	0.6286	0.6309	0.6236	0.6309
260	0.6317	0.6329	0.6263	0.6335
270	0.6348	0.6347	0.6289	0.6354
280	0.6377	0.6370	0.6312	0.6377
290	0.6415	0.6404	0.6337	0.6409
300	0.6447	0.6438	0.6370	0.6443
310	0.6483	0.6480	0.6411	0.6487
320	0.6513	0.6511	0.6446	0.6516
330	0.6532	0.6511	0.6471	0.6536
340	0.6540	0.6488	0.6479	0.6543
350	0.6546	0.6501	0.6475	0.6545
360	0.6572	0.6503	0.6481	0.6552
370	0.6583	0.6510	0.6502	0.6570
380	0.6594	0.6534	0.6523	0.6590
390	0.6605	0.6554	0.6540	0.6601
400	0.6614	0.6571	0.6551	0.6614
410	0.6623	0.6584	0.6555	0.6615
420	0.6636	0.6603	0.6564	0.6626
430	0.6648	0.6613	0.6578	0.6645
440	0.6662	0.6628	0.6592	0.6653
450	0.6669	0.6640	0.6602	0.6654
460	0.6677	0.6649	0.6610	0.6658
470	0.6689	0.6663	0.6623	0.6664
480	0.6695	0.6677	0.6634	0.6662
490	0.6708	0.6690	0.6640	0.6662
500	0.6730	0.6711	0.6653	0.6668
510	0.6764	0.6745	0.6676	0.6685
520	0.6810	0.6786	0.6704	0.6711
530	0.6885	0.6848	0.6756	0.6757
540	0.6999	0.6944	0.6831	0.6836
550	0.7148	0.7079	0.6938	0.6946
560	0.7323	0.7246	0.7081	0.7088
570	0.7475	0.7399	0.7242	0.7240
580	0.7541	0.7475	0.7359	0.7343
590	0.7523	0.7463	0.7390	0.7383
600	0.7441	0.7403	0.7358	0.7373
610	0.7357	0.7339	0.7299	0.7339
620	0.7313	0.7309	0.7255	0.7313
630	0.7298	0.7299	0.7239	0.7301
640	0.7293	0.7296	0.7228	0.7293
650	0.7292	0.7297	0.7217	0.7291
660	0.7288	0.7294	0.7210	0.7287
670	0.7287	0.7295	0.7204	0.7285
680	0.7281	0.7292	0.7195	0.7276
690	0.7273	0.7285	0.7191	0.7270
Peak temperature	578 °C	578 °C	584 °C	583 °C

Note: The heat capacities are estimated to have a precision of ±1%; Tg = peak temperature

phous and liquid GeO_2. Using existing data for SiO_2, comparisons are made with the volume-temperature relation and derived parameters.

Calorimetry and Dilatometry

The sample of GeO_2 glass used in the present investigation was made by direct fusion of GeO_2 (ultrapure, Alfa®) powder in a platinum crucible in a vertical tube furnace operating in air at 1400 °C. The sample was stirred with a $Pt_{80}Rh_{20}$ rod for several hours to promote fining. After sufficient time for fining, the spindle was removed from the sample, and the crucible was removed from the furnace to cool in air. A 6.4 mm diameter cylinder was bored from the cooled sample with a diamond coring tool and this cylinder was cut to a length of 1 cm using a diamond saw. The cylinder was stored in a desiccator until use in the dilatometer and calorimeter.

The calorimetry was performed in continuous scanning mode with a Setaram® DSC instrument. The heat flow was recorded during heating runs of 5 °C min^{-1} on glasses that had been previously cooled from ~100 °C above T_g (see Table 1) at cooling rates of 1, 2, 5 and 10 °C min^{-1}. The calorimeter was calibrated regularly against a geometrically identical cylinder of sapphire, using the heat capacity data of Robie et al. (1979). The heat capacity data are presented in Table 1. The heat capacities are estimated to have a precision of ±1% at 1 σ, based on the 4 runs performed for each sample. The measured heat capacities are in excellent agreement with those reported in Robie et al. (1979), but 3% lower than the more recent data of Richet (1990). The reasons for this discrepancy are not clear. A typical calorimetric trace, that obtained for 1 °C min^{-1}/5 °C min^{-1} (cooling-rate/heating-rate) is illustrated in Fig. 1a.

The dilatometry was performed with a Netzsch® TMA 402 quartz-rod dilatometer. The sample, its thermal history and the scanning rates were those used in the calorimetry measurements. This instrument has been calibrated against single crystal sapphire (NBS sheet 732). The molar expansivity of the glass has an accuracy of ±3% at 1 σ, calculated from the errors in

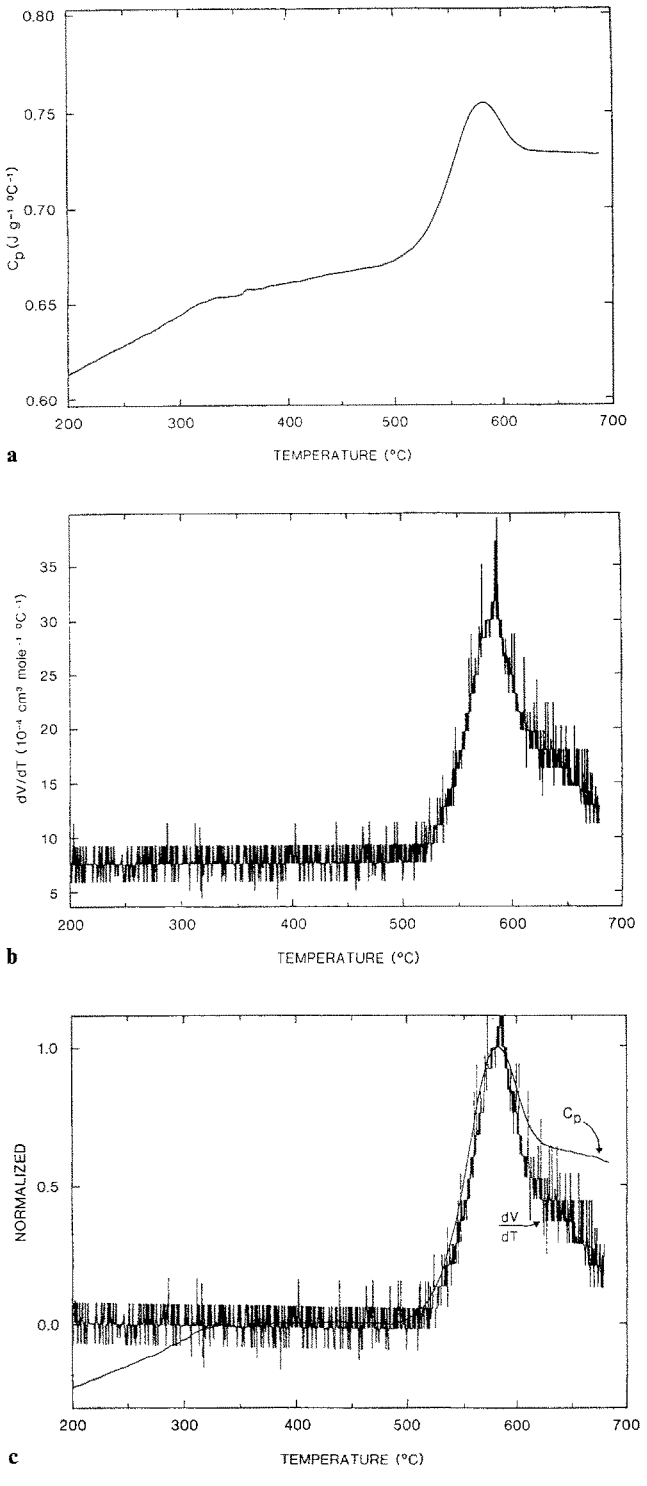

Fig. 1. Calorimetric **a** and dilatometric **b** traces of the glass transition for amorphous GeO_2 **c** normalized comparison of heat capacity and expansivity for liquid GeO_2. (1 °C min^{-1} cooling rate/5 °C min^{-1} heating rate)

the measurements of the thermal expansivity of the standard (±2%) and the sample (±2%). The room temperature density of the glass [ρ(15.5 °C)=3.651 ±0.004 g cm^{-3}] was determined by Archimedean densitometry in toluene. The molar thermal expansion data calculated from the room temperature volume [V(15.5 °C)=28.65±0.03 cm^3 mol^{-1}] combined with the dilatometric data for the glass, are presented in Table 2. The dilatometry trace for GeO_2 (1 °C min^{-1}/5 °C min^{-1}) is illustrated in Fig. 1b.

Derivation of Liquid Expansivity

The derivation of liquid expansivity and volume from calorimetric and dilatometric data is based on the principles of structural relaxation in silicate melts (Narayanaswamy 1971; Moynihan et al. 1976; Scherer 1984). The more general aspects of structural relaxation in silicate melts, their influence on diffusion, viscosity, heat capacity and density, have been discussed previously (e.g. Richet and Bottinga 1986; Dingwell 1990; Dingwell and Webb 1989, 1990). The theory of our procedure for obtaining relaxed liquid molar expansivity data from a combination of scanning calorimetry and dilatometry has been presented in full by Webb et al. (1992). This method of determining the volume and thermal expansivity of relaxed supercooled melts has been successfully tested against the volume and thermal expansivity extrapolated from high temperature double-bob Archimedean density measurements in silicate melts (Knoche et al. 1992a, b, c).

The physical properties of a silicate melt depend upon the configuration or structure of the melt and the ambient temperature T. The configuration of silicate glasses quenched from liquids can be approximated to the equilibrium structure of the liquid at some fictive temperature, T_f. The temperature-derivatives of glass properties can be used to describe the temperature-derivative of the fictive temperature. To do this, the temperature-derivative of any property in the glass transition interval is normalized with respect to the temperature-derivative of the liquid and glassy properties. The temperature-derivative of the fictive temperature T_f at a temperature T' is related to the temperature dependence of a macroscopic property Φ by;

$$\left.\frac{dT_f}{dT}\right|_{T'} = \frac{[(\partial\Phi/\partial T)-(\partial\Phi/\partial T)_g]|_{T'}}{[(\partial\Phi/\partial T)_e-(\partial\Phi/\partial T)_g]|_{T_f}} \quad (1)$$

where the subscripts "e" and "g" are for the liquid (equilibrium) and the glassy values of the property (Moynihan et al. 1976). In order to describe the physical properties of a melt in the glass transition region it is necessary to devise an algorithm for the temperature dependence of the fictive temperature.

In the present study, enthalpy H, and volume V take the place of the general property Φ in [1]. Assuming the equivalence of volume and enthalpy relaxation behavior in the glass transition region (c.f., Webb 1992), Equation 1 can then be rewritten as;

$$\frac{c_p(T')-c_{pg}(T')}{c_{pe}(T_f)-c_{pg}(T_f)} = \left.\frac{dT_f}{dT}\right|_{T'} = \frac{\left[\frac{dV(T)}{dT}-\frac{dV_g(T)}{dT}\right]_{T'}}{\left[\frac{dV_e(T)}{dT}-\frac{dV_g(T)}{dT}\right]_{T_f}}. \quad (2)$$

Table 2. Measured $dV/dT(10^{-4}\ cm^3\ mol^{-1}\ °C^{-1})$ data for glass and liquid GeO_2. (heating-rate 5 °C min^{-1})

	Cooling rate			
T(°C)	1 °C min^{-1}	2 °C min^{-1}	5 °C min^{-1}	10 °C min^{-1}
40	4.18	5.31	5.33	4.95
50	6.15	6.62	6.53	5.46
60	7.40	7.27	5.64	7.21
70	7.08	7.39	7.18	6.92
80	7.20	7.40	6.61	7.67
90	7.32	7.30	7.10	7.10
100	7.32	7.32	6.45	7.20
110	7.21	7.10	7.54	6.72
120	7.61	7.20	7.88	7.51
130	7.35	6.78	8.14	7.45
140	7.27	7.35	7.84	7.11
150	7.19	7.29	7.20	7.27
160	7.21	7.63	7.49	7.50
170	7.78	7.34	7.75	7.46
180	7.74	7.89	8.58	7.48
190	8.04	8.09	6.98	7.92
200	7.93	8.09	7.69	7.91
210	7.44	7.28	8.30	7.60
220	7.61	7.36	7.93	6.91
230	7.73	7.46	7.20	6.39
240	7.58	7.66	7.89	8.41
250	7.20	7.80	6.49	5.84
260	7.50	8.05	7.50	7.45
270	7.78	8.10	7.90	7.68
280	7.78	8.33	8.36	8.10
290	8.04	8.02	7.98	7.24
300	7.86	8.31	7.05	7.11
310	7.86	7.69	8.45	7.62
320	7.77	7.46	8.27	8.75
330	7.99	8.03	6.48	7.13
340	7.95	7.68	7.19	7.50
350	7.67	7.84	7.71	7.37
360	7.98	7.38	6.73	7.29
370	7.81	7.51	7.05	8.20
380	7.69	7.69	7.70	6.96
390	7.61	7.49	8.64	7.66
400	8.55	7.96	7.18	7.59
410	7.88	7.67	7.25	7.55
420	8.00	7.63	7.68	7.17
430	7.47	7.47	7.69	8.20
440	7.90	7.48	7.71	6.66
450	7.97	7.56	7.73	7.86
460	7.94	7.81	7.27	6.66
470	8.29	7.89	7.89	6.50
480	7.97	8.14	8.62	7.26
490	8.42	8.38	5.44	7.00
500	8.10	8.14	5.29	6.58
510	8.73	8.41	7.34	6.70
520	9.57	9.08	7.26	8.91
530	10.68	10.30	8.58	6.69
540	13.01	11.64	10.05	9.24
550	16.68	14.37	12.52	12.44
560	21.43	19.26	14.88	15.53
570	26.47	24.22	19.71	20.57
580	30.06	28.07	23.79	22.19
590	29.97	28.13	26.28	24.38
600	24.62	24.25	22.70	24.24
610	20.82	20.57	19.65	20.48
620	19.07	19.07	17.53	20.16
630	17.75	18.97	16.81	18.42
640	17.44	18.61	15.01	16.64
650	16.09	15.68	13.31	12.30
660	15.27	14.78	11.03	11.10
670	13.86	13.94	8.00	9.33
680	6.63	6.57	3.68	4.75
Peak temperature	583 °C	585 °C	588 °C	586 °C

Note: The thermal expansion is estimated to have a precision of ±3%

In the above equation relating c_p and thermal expansivity dV/dT in the glass transition region, the only unknown parameter is the thermal expansivity of the relaxed liquid at temperature T' above the glass transition temperature. Despite a common origin, various melt properties can, theoretically differ in relaxation behavior. This would imply different relaxation kinetics due to different partitioning of volume and enthalpy amongst the distribution of structures in the melt. Often, however, no such difference can be distinguished (e.g. Rekhson et al. 1971; Sasabe et al. 1977) and the assumption of equivalent relaxation times for different properties can be usefully employed.

Due to the lack of relaxed thermal expansivity data, we recover the liquid molar thermal expansivity from the dilatometric trace by normalizing both the scanning calorimetric and dilatometric data;

$$\Phi'(T)=\frac{\Phi(T)-\Phi_g(T)}{\Phi_p-\Phi_g(T)} \tag{3}$$

where the subscripts "p" and "g" refer to peak and glassy values. The relaxed value of thermal expansivity (dV/dT at $T=T'$) can now be generated from the peak and linearly extrapolated glassy values of normalized heat capacity and thermal expansion curves (see Fig. 1c and [2]). The volume, V, and coefficient of volume thermal expansion $\alpha_v[1/V\cdot(dV/dT)]$ of the melt at $T=T'$ can also be calculated. It should be emphasized that the above method can only be applied to calorimetric and dilatometric data obtained on the same sample using identical experimental conditions and thermal histories. It is only this internal consistency that permits the use of the assumption of the equivalence of the enthalpy and volume relaxation behavior as small changes in composition or fictive temperature of the melt can strongly influence relaxation behavior.

The volume and expansivity of liquid GeO_2 at the glass transition may be compared with liquid GeO_2 density data obtained by Sekiya et al. (1980) using the restrained sphere method. These data at higher temperatures are presented together with our data in Figure 2 and Table 3. The volume-temperature relationship consistent with all the volume data together with the thermal expansion determined at $T=660$ °C is best described by

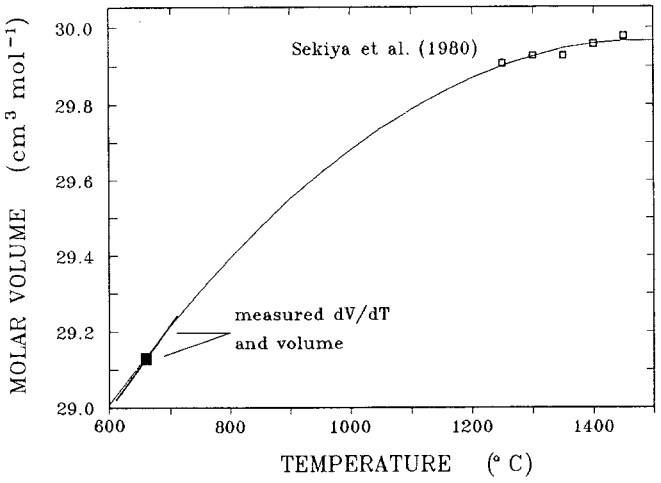

Fig. 2. The volume temperature relationship of liquid GeO_2 from the glass transition to 1400 °C. High temperature data from Sekiya et al. (1980)

Table 3. Molar volume of GeO_2 as a function of temperature. High temperature data from Sekiya et al. (1980)

Temperature (°C)	Volume ($cm^3\ mol^{-1}$)
660	29.1322
1250	29.91
1300	29.93
1350	29.96
1400	29.96
1450	29.98

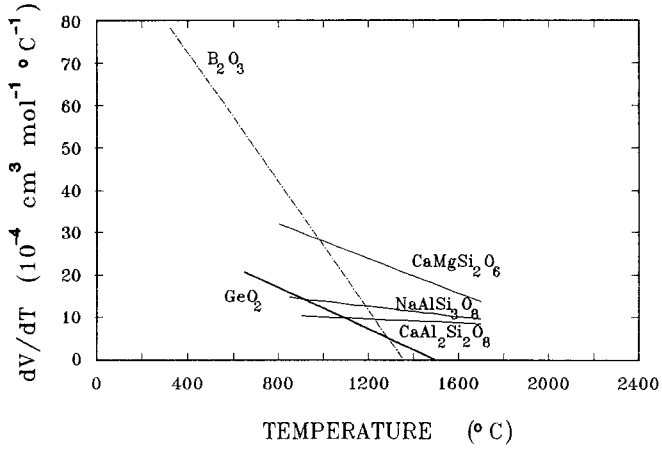

Fig. 3. Thermal expansion of B_2O_3, GeO_2, $NaAlSi_3O_8$, $CaAlSi_2O_6$ and $CaMgSi_2O_6$ liquids as a function of temperature

the polynomial;

$$V(\mathrm{cm^3\ mol^{-1}}) = 27.26(0.06) + 3.67(0.14)\times 10^{-3}\,T - 1.23(0.07)\times 10^{-6}\,T^2 \quad (4)$$

for temperature in °C. The expansivity obtained from [4] for liquid GeO_2 at 660 °C ($20.46 \pm 1.68 \times 10^{-4}$ $cm^3\ mol^{-1}\ °C^{-1}$) is within error of that determined using our dilatometry/calorimetry method ($22.23 \pm 0.96 \times 10^{-4}$ $cm^3\ mol^{-1}\ °C^{-1}$). The expansivity of the liquid decreases strongly (an order of magnitude) as temperature increases from 660 to 1400 °C. Qualitatively similar behavior has been observed for liquid B_2O_3 (Napolitano et al. 1965) and for a wide range of liquids in the anorthite-albite-diopside system (Knoche et al. 1992a, b), as illustrated in Fig. 3.

The Prigogine-Defay Ratio (Π)

For the case in which a single order parameter, along with temperature and pressure conditions, is sufficient to specify the state of a system, the Prigogine-Defay ratio must be unity. Where this is not the case, the question arises as to how many independent parameters of the structure are needed to describe the relaxation of properties across the glass transition. The Prigogine-Defay ratio Π is given by;

$$\Pi = \frac{\Delta\beta\,\Delta c_p}{(\Delta\alpha_v)^2\,T_g\,V} \quad (5)$$

where T_g is the glass transition temperature, $\Delta\beta$ is the difference between the compressibility of the liquid and the glass at T_g, Δc_p is the difference between the heat capacity of the liquid and the glass at T_g, $\Delta\alpha_v$ is the difference between the coefficient of volume thermal expansion of the liquid and the glass at T_g and V is the molar volume at T_g (Lesikar and Moynihan 1980; Gupta and Moynihan 1976; Nemilov et al. 1987).

We can use our data of the glassy and liquid values of heat capacity and expansivity, the glass transition temperature and the volume at this temperature to calculate the Prigogine-Defay ratio for liquid GeO_2. The remaining data required are the compressibility of the glass and the liquid. The compressibility of glassy GeO_2 has been measured at low temperature by Soga (1969) using ultrasonic (20 MHz pulse superposition) methods. The temperature dependence of the glass compressibility has been determined by Kurkjian et al. (1972). The liquid compressibility of GeO_2 has not been measured at 0.1 MPa but density data for the liquid at 1425° C and pressures of 1, 1.5 and 2 GPa are provided by Scarfe et al. (1987) using the falling sphere method. These high pressure densities combined with the 0.1 MPa, 1400 °C density of GeO_2 from Sekiya et al. (1980) can be described by the polynomial volume-pressure relationship;

$$V(\mathrm{cm^3\ mol^{-1}}) = 30.019(0.024) - 3.77(0.11)\,P + 1.86(0.12)\,P^2 \quad (6)$$

for pressure in GPa.

The 0.1 MPa compressibility [$\beta = -(1/V)\cdot(dV/dP)$] calculated from [6] is $12.4(0.4)\times 10^{-11}$ Pa^{-1}. The data used in the calculation of the Prigogine-Defay ratio, their uncertainties and sources are summarized in Table 4. The resultant value of Π is 6.9 ± 1.3. This value compares favorably with the range of values typical for silicate melts (see Table 4) indicating that the relaxation behavior of a pure network component like GeO_2 is qualita-

Table 4. Data used in the calculation of the derived parameters for GeO_2

Property	T(°C)	liquid	glass	$\Phi_l - \Phi_g$
K(GPa)	660	8.08(24)[a,b]	23.87(3)[c,d]	
	1400	8.08		
$\beta(10^{-11}$ Pa$^{-1})$	660	12.4(4)[a,b]	4.19[c,d]	8.19±0.40
	1400	12.4		
$\alpha_v(10^{-6}$ °C$^{-1})$	660	76.3(3.3)[f]	27.1(7)	49.2±3.4
	1400	2.46(11)[f]		
c_p(J mol^{-1} °C^{-1})	660	75.9(4)[f]	70.4(4)	5.5±0.6
	1400	80.7[e]		
$V(10^{-6}$ m^3 mol$^{-1})$	660	29.13(02)[f]		
	1400	29.96(02)[f]		

Note: for ease of calculation, the data are presented in SI units
[a] Scarfe et al. 1987
[b] Sekiya et al. 1980
[c] Soga 1969
[d] Kurkjian et al. 1972
[e] Richet et al. 1982
[f] this study

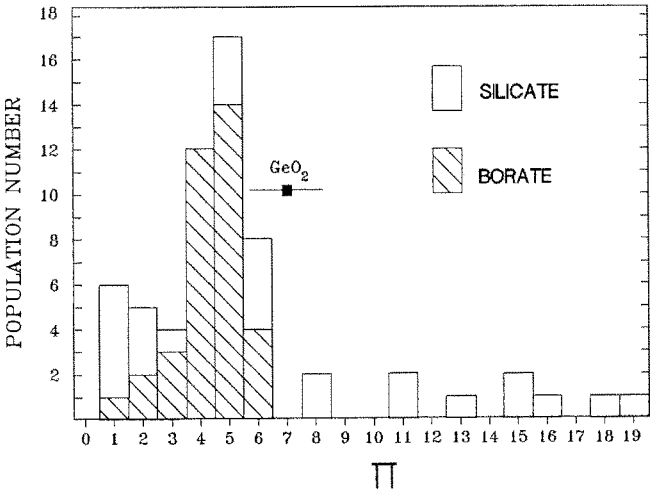

Fig. 4. The Prigogine-Defay ratio for silicate and borate glasses compared with that for GeO_2

tively equivalent to that of more complex silicate and non-silicate compositions. In Fig. 4 we present a histogram of the values of Π that have been derived from literature sources by Nemilov et al. (1987), our value for GeO_2 lies well within the range of values for alkali silicate and borate glasses. Recent data for the ternary system albite-anorthite-diopside (Table 5) result in the determination of $5 < \Pi < 19$ (see Table 6). The Π calculated for B_2O_3 using the data presented in Table 7 is 3.6. Gupta and Moynihan (1976) calculated a Π of 4.7 for B_2O_3 from their data compilation. These two values of Π calculated for B_2O_3 melt are an indication of the range of values of the Prigogine-Defay ratio which can be obtained using different source data. In view of the errors inherent in the calculation of the Prigogine-Defay ratio, a value $1 < \Pi < 10$ cannot, at present, be distinguished from 1.

Table 5. Data used in the calculation of the derived parameters for albite, anorthite and diopside

Property	T(°C)	liquid	glass	$\Phi_l - \Phi_g$
K(GPa)	T_g	15–25[e]	30–50[c]	
	1400	15–25[e]		
$\beta(10^{-11}$ Pa$^{-1})$	T_g	4–7	2–3	1–5
	1400	4–7		
$\alpha_v(10^{-6}$ °C$^{-1})$				
Albite	705	54[a,b]	23[a,b]	31
	1400	3[a,b]		
Anorthite	868	52[a,b]	19[a,b]	33
	1400	22[a,b]		
Diopside	732	125[a,b]	35[a,b]	90
	1400	47[a,b]		
c_p(J mol^{-1} °C^{-1})	705	332[a,b]	300[a,b]	32
Albite	1400	372[f]		
Anorthite	868	417[a,b]	317[a,b]	100
	1400	435[d]		
Diopside	732	364[a,b]	238[a,b]	126
	1400	335[d]		
$V(10^{-6}$ m^3 mol$^{-1})$				
Albite	705	111[a,b]		
	1400	114[a,b]		
Anorthite	868	105[a,b]		
	1400	107[a,b]		
Diopside	732	78[a,b]		
	1400	82[a,b]		

Note: for ease of calculation, the data are presented in SI units
[a] Knoche et al. 1992a
[b] Knoche et al. 1992b
[c] Bansal and Doremus 1986
[d] Richet and Bottinga 1986
[e] Rivers and Carmichael 1987
[f] Richet et al. 1982

Table 6. Prigogine-Defay ratio and Grüneisen parameters for the glasses and liquids

	Π	$\gamma_{th}(T_g)$	$\gamma_{thl}(T_g)$	γ_{th}(1400 °C)
Albite	7.7(3–15)	0.26–0.43	0.27–0.45	0.26–0.43
Anorthite	19(7–38)	0.19–0.31	0.20–0.33	0.08–0.14
Diopside	5.0(2–10)	0.34–0.57	0.40–0.67	0.17–0.29
GeO_2	6.85±1.26	0.27±0.04	0.24±0.05	0.007±0.001
B_2O_3	3.6	0.28	0.20	0.02

The Thermal Grüneisen Parameter (γ_{th})

The thermal Grüneisen parameter, γ_{th}, is given by

$$\gamma_{th} = \frac{\alpha_v K_s V}{c_p} \tag{7}$$

(Anderson 1989) for α_v, the coefficient of volume thermal expansion, K_s, the adiabatic bulk modulus, V, the molar volume, c_p the heat capacity at constant pressure. The thermal Grüneisen parameter is a representation of the thermal energy of a material. It is a measure of the change in pressure on heating at a constant volume. A

Table 7. Data used in the calculation of the derived parameters for B_2O_3

Property	T(°C)	liquid	glass	$\Phi_l - \Phi_g$
K(GPa)	307	~2[a] [2.5][f]	~11[b] [8.3][f]	
	1400	~2		
$\beta(10^{-11}$ Pa$^{-1})$	307	5 [40]	9.1 [12][f]	41 [28][f]
	1400	5		
$\alpha_v(10^{-6}$ °C$^{-1})$	307	335[c] [400][f]	57.9[c] [50][f]	277 [350][f]
	1400	33.4[c]		
c_p(J mol^{-1} °C^{-1})	307	136[d] [134][f]	89[d] [91][f]	47 [43][f]
	1400	147[d]		
$V(10^{-6}$ m^3 mol$^{-1})$	307	41.0[c] [38.8][f]	39.2[e]	
	1400	46.5[c]		

Note: for ease of calculation, the data are presented in SI units
[a] Macedo and Litovitz 1965
[b] Capps et al. 1966
[c] Napolitano et al. 1965
[d] Moynihan et al. 1976
[e] Macedo et al. 1966
[ ][f] data of Gupta and Moynihan 1976

γ_{th} of 0.5–2.8 is observed for crystalline materials (Anderson 1989) and liquids (Boehler and Ramakrishnan 1980) [γ_{th} for water is ~0.1], with $0.8 < \gamma_{th} < 1.4$ being assumed for the Earth (Stacey 1977). For silicate melts, a γ_{th} of 0.1–0.4 is observed (see Table 6). Below their respective glass transition temperatures, $0.19 < \gamma_{th} < 0.57$ for albite, diopside and anorthite composition glasses. Above the glass transition, $0.08 < \gamma_{th} < 0.43$ for these compositions for viscosities of greater than 10^4 Pa s.

In the case of GeO_2, at the glass transition $\gamma_{th}(T_g) \sim 0.27$. With increasing temperature, the coefficient of thermal expansion of liquid GeO_2 decreases by an order of magnitude, resulting in $\gamma_{th}(1200\,°C) = 0.08$ and $\gamma_{th}(1400\,°C) = 0.007$. This behavior is in contrast to the relatively temperature-independent behavior of the Grüneisen parameter for the melts of anorthite, diopside and albite composition over the same temperature range (Knoche et al. 1992a, b; see Table 6). The γ_{th} of B_2O_3 liquid decreases from 0.20 at 400 °C to 0.02 at 1400 °C. As the Grüneisen parameter is a measure of the thermal energy in interatomic bonds in a material, this large deviation of γ_{th} from the "normal" (i.e. $0.1 \leqq \gamma_{th} \leqq 0.4$ and relatively temperature independent) values for melts may be an indication of a coordination change occurring in these melts as a function of temperature.

The Isochoric Heat Capacity (c_v)

The heat capacity at constant volume (c_v) is related to c_p via

$$c_p - c_v = T V \alpha_v^2 K_T \tag{8}$$

where the symbols are the same as in [5] and [7], and K_T is the isothermal bulk modulus of the melt. The calculated value of the difference between c_p and c_v illustrates the heat capacity contribution due to PV work associated with thermal expansion. For GeO_2 at the glass transition temperature $c_p - c_v = 1.3$ J mol^{-1} °C^{-1}. This difference decreases to 0.002 J mol^{-1} °C^{-1} at 1400 °C (see Table 8). For the ternary system albite-anorthite-diopside, $c_p - c_v$ ranges from 1 J mol^{-1} °C^{-1} in the glass, to 5–30 J mol^{-1} °C^{-1} in the liquid at the glass transition, to 1–8 J mol^{-1} °C^{-1} at 1400° C (Knoche et al. 1992a, b; see Table 5). In contrast, for B_2O_3, $c_p - c_v$ is 0.8 J mol^{-1} °C^{-1} for the glass, 5.3 J mol^{-1} °C^{-1} for the liquid at the glass transition temperature and 0.2 J mol^{-1} °C^{-1} at 1400 °C (Macedo and Litovitz 1965; Napolitano et al.1965; Capps et al. 1966; Macedo et al. 1966, Gupta and Moynihan 1976; Moynihan et al. 1976; see Table 7).

Table 8. $c_p - c_v$ for the glasses and liquids

	$c_p - c_v$(glass)	$c_p - c_v$(liquid at T_g)	$c_p - c_v$ (1400 °C)
	J mol^{-1} °C^{-1}	J mol^{-1} °C^{-1}	J mol^{-1} °C^{-1}
Albite	1.7–2.9	4.7–7.9	1.4–2.5
Anorthite	1.3–2.2	4.9–8.1	1.3–2.2
Diopside	2.9–4.8	18.4–30.6	4.5–7.6
GeO_2	1.2	1.3	0.002
B_2O_3	0.8	5.3	0.2

Coefficient of Volume Thermal Expansion of SiO_2 Melt

The geophysical parameters Π, γ_{th} and $c_p - c_v$ for the behavior of melts allow us to estimate the coefficient of volume thermal expansion of SiO_2 melt. Bacon et al. (1960) measured the thermal expansion of liquid SiO_2 to be 108×10^{-6} °C^{-1}. This value, however, is in disagreement with the value of zero, determined from the calculation of the partial molar expansivity of silicate melts (Lange and Carmichael 1990). The partial molar volume of liquid SiO_2 calculated from the systematic treatment of Lange and Carmichael (1990) is not in agreement with the high temperature volume data of Bacon et al. (1960) nor with the low temperature glass volume data of Brückner (1970) (see Fig. 5). Richet et al. (1982) have calculated $\alpha_v(SiO_2)$ at 1727 °C using their own calorimetric data with the sound speed data of Bucaro and Dardy (1974) and the volume and thermal expansivity data of Bacon et al. (1960). Richet et al. (1982) obtained a value of -620 J mol^{-1} °C^{-1} for c_v from [8], concluding that the most likely source of the error in generating this implausible result lay in the expansivity data of Bacon et al. (1960) and that a coefficient of expansivity of $10^{-6} - 10^{-7}$ °C^{-1} (near the glassy value) produces a much more reasonable value for c_v (e.g. $c_v > 79$ J mol^{-1}° C^{-1}). This calculation, however, includes an error in the magnitude of the compressibility. A value of 8.5×10^{-13} Pa^{-1} from Bucaro and Dardy (1974) is quoted, whereas the original reference reports $\beta = 8.5 \times 10^{-11}$ Pa^{-1}. This correct value of the liquid compressibility yields a reasonable value of c_v(90 J mol^{-1}° C^{-1}) via [8], with $c_p - c_v = 5.7$ J mol^{-1} °C^{-1}.

The Bucaro and Dardy (1974) modulus data have been superseded by those of Krol et al. (1986). If we use the Krol et al. (1986) modulus data (12.95 GPa) and the Bacon et al. (1960) expansivity data ($\alpha_v = 108$

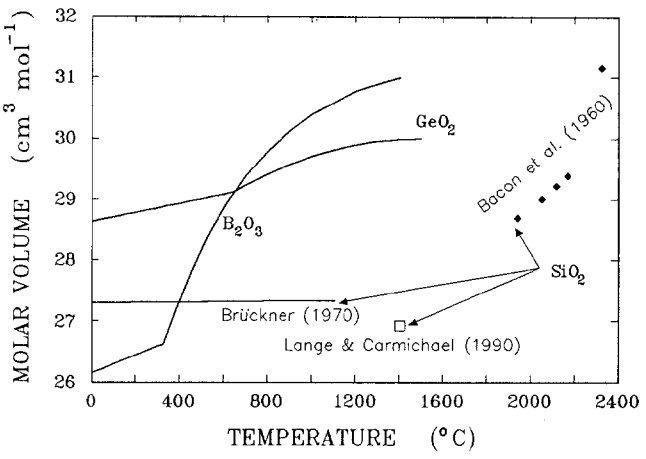

Fig. 5. The molar volume for SiO_2, B_2O_3 and GeO_2 glasses and liquids as a function of temperature

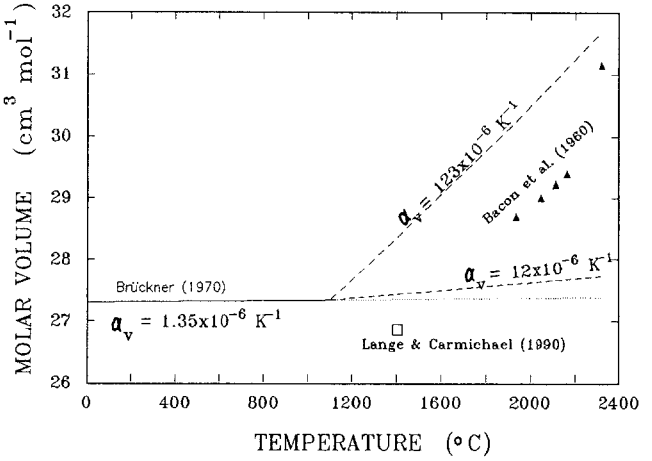

Fig. 6. Measured and calculated molar volume for SiO_2 glass and liquids as a function of temperature together with the estimated α_v for SiO_2 liquid

Table 9. Data used in the calculation of the derived parameters for SiO_2

Property	T(°C)	liquid	glass	$\Phi_l - \Phi_g$
K(GPa)	1100	12.95[a]	49.13[a]	
	1400	12.95[a]	49.13[a]	
$\beta(10^{-11}$ Pa$^{-1})$	1100	7.72[a]	2.04[a]	5.69[a]
	1400	7.72[a]	2.04[a]	5.69[a]
$\alpha_v(10^{-6}$ °C$^{-1})$	500			
	1400			0.25[a]
c_p(J mol^{-1} °C^{-1})	500	69.9[b]		
	1100	71.6[b]		
	1400	81.4[b]		8[a]
$V(10^{-6}$ m^3 mol$^{-1})$	500			
	1100	27.3[a]		
	1400	27.3[a]		

Note: for ease of calculation, the data are presented in SI units
[a] Krol et al. 1986
[b] Richet et al. 1982

$\times 10^{-6}$ °C^{-1}) then we obtain a $c_p - c_v$ of 8.25 J mol^{-1} °C^{-1} for the melt at 1400 °C. Although the expansivity data of Bacon et al. (1960) are relatively poorly constrained it is difficult to discard the volume data. An error of greater than 2% seems unlikely from this method.

Despite uncertainties in the input parameters for the calculation it is difficult to obtain a comparable value of Π for SiO_2 and GeO_2. Krol et al. (1986) have calculated the value of the Prigogine-Defay ratio for pure SiO_2 to be 2×10^5. Their databasc is summarized in Table 9. They point to the uncertainty in Δc_p as a likely cause of the excessively high value of Π and argue that SiO_2 should have a more "normal" value of Π in the range of 1–10, similar to our determination for GeO_2. In part this argument is based upon the similar frequency-domain mechanical relaxation behavior of SiO_2 and other silicate and non-silicate glasses in torsional stress experiments (Mills 1974).

The range of values determined for γ_{th} and Π representative of silicate melts can be used to estimate the coefficient of volume thermal expansion of SiO_2 melt. The "normal" range of γ_{th} values for silicate melts predict, at 500 °C, $5 < \alpha_v(SiO_2) \cdot (10^{-6}$ °C$^{-1}) < 25$ for the glass. At 1400 °C, $23 < \alpha_v(10^{-6}$ °C$^{-1}) < 115$ for $0.1 < \gamma_{th} < 0.5$. This range of α_v agrees with that determined by Bacon et al. (1960) (see Fig. 6). Assuming a similar anomalous behavior of $\gamma_{th}[\gamma(1400$ °C$) = 0.02]$ for both GeO_2 and SiO_2 results in the calculation of $\alpha_v(1400$ °C) of 4.5×10^{-6} °C^{-1} for SiO_2. Taking $1 < \Pi < 10$ to be representative for silicate melts, and $1 < c_p - c_v$ (J mol^{-1} °C$^{-1}) < 10$, results in the calculation of $12.3 < \alpha_v(10^{-6}$ °C$^{-1}) < 123$ for the liquid at the glass transition.

$\alpha - SiO_2$ vs. GeO_2

It is difficult to determine the coefficient of thermal expansion of SiO_2 melt. There has been only one attempt to date. Bacon et al. (1960) determined the density of SiO_2 melt from 1950–2200 °C and found $\alpha_v = 108 \times 10^{-6}$ °C^{-1}. These data have been disputed based on indirect evidence by others (Richet et al. 1982; Bottinga et al. 1983; Lange and Carmichael 1990). The argument posed by Richet et al. (1982) was based on an incorrect value of the compressibility of molten SiO_2; and the coefficient of thermal expansion of Bacon et al. (1960) produces a realistic value of c_v using [8]. Thus the major theoretical objection to Bacon et al.'s data is removed. To the extent that the values of Π and γ_{th} for silicate melts presented here can be taken as representative of silicate melts in general and SiO_2 in particular, the thermal expansion for SiO_2 melt predicted from these parameters is $12–123 \times 10^{-6}$ °C^{-1}. These are "normal" expansivity values. Only anomalous values of γ_{th} at high temperatures as seen for GeO_2 and B_2O_3 result in the calculation of small values of α_v.

Thus it appears with these new data on liquid GeO_2 we are presented with a fundamental dilemma concerning liquid SiO_2. Assumption of a liquid thermal expansivity consistent with the partial molar thermal expansivity of SiO_2 in silicate liquids results in values of Π, γ_{th} and c_v that are qualitatively different to all other silicate

melts and the structural analog GeO_2. This discrepancy is despite very similar results from relaxation spectrometry on these liquids and is inconsistent with the single direct determination of SiO_2 liquid density. Alternatively, a "silicate-like" value of $\Delta\alpha_v$ at T_g that would bring all geophysical parameters into agreement and be consistent with the Bacon et al. (1960) data has eluded experimental investigations to date.

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