

## Dependence of the Glass Transition Temperature on Heating and Cooling Rate

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It is shown that under certain conditions the dependence of the glass transition temperature  $T_g$  on heating or cooling rate  $|q|$  is given to a high degree of approximation by  $d \ln |q| / dT_g = \Delta h^* / RT_g^2$  or alternatively by  $d \ln |q| / d(1/T_g) = -\Delta h^* / R$ , where  $T_r$  is a temperature in the middle of the transition range and  $\Delta h^*$  is the activation enthalpy for the relaxation times controlling the structural enthalpy or volume relaxation. The conditions necessary for the validity of these relations are that the structural relaxation be describable by a temperature-independent distribution of relaxation times and that the glass be cooled from a starting temperature well above the transition region and subsequently reheated at the same rate starting from a temperature well below the transition region. Experimental measurements of  $T_g$  vs.  $|q|$  are presented for  $As_2Se_3$ ,  $B_2O_3$ , potassium silicate, and borosilicate crown glasses.  $\Delta h^*$  is found to be equal within experimental error to the activation enthalpy for the shear viscosity.

### Introduction

Changes in macroscopic properties of liquids, such as the enthalpy or the volume, induced by isobaric changes in temperature are of two types.<sup>1</sup> The first type may be termed a solid- or glass-like response and on ordinary experimental time scales occurs instantaneously. The second type of response arises from changes in the structure or configuration of the liquid. The time scale on which this structural response occurs is highly temperature dependent and at sufficiently low temperatures becomes so long that a rapid temperature change can "freeze in" the liquid structure. It is this last process that is ordinarily understood to be involved in the formation of a glass from a supercooled liquid.

In Figure 1 are shown schematic plots of enthalpy  $H$  and heat capacity  $C_p$  for isobaric cooling and subsequent reheating at a constant rate of a glass-forming liquid.<sup>2</sup> The temperature range during cooling in which the rate of structural relaxation in the liquid starts to become sufficiently slow that the  $H$ - $T$  and  $C_p$ - $T$  curves depart from the equilibrium liquid curves is the beginning of the glass transition or transformation region. The temperature range in which the structural relaxation becomes so slow that it effectively ceases on the experimental time scale marks the end of the transition region and the beginning of glass-like behavior. Irrespective of the direction of temperature change, the direction of the structural relaxation process is always toward equilibrium. Consequently on reheating the glass the  $H$ - $T$  and  $C_p$ - $T$  curves follow paths different from those for the prior cooling, as shown in Figure 1 and explained previously by a number of workers.<sup>3-5</sup>

The glass transition temperature,  $T_g$ , is defined as some characteristic temperature on the  $H$ - $T$  or  $C_p$ - $T$  curve in the transition region during heating or cooling at a constant rate, for example, the temperature of intersection of the extrapolated liquid and glass  $H$ - $T$  curves during cooling, the extrapolated temperature of onset of rapid increase of the  $C_p$ - $T$  curve during heating, or the temperature of inflec-

tion in the region of rapid rise of the  $C_p$ - $T$  curve during heating. Because the "break" in the  $C_p$ - $T$  curve is more pronounced during heating than during cooling and probably because constant heating rate experiments are easier to realize than constant cooling rate experiments, the majority of investigators in the past have reported  $T_g$  values determined from heating curves.

Experimentally, it is found<sup>3,5-14</sup> that  $T_g$  shows a dependence on the heating or cooling rate, higher values of  $T_g$  being observed for faster heating or cooling rates, as shown in Figure 1. The reason for this is not difficult to see if one notes that isobaric heating or cooling at a constant rate is the limit as  $\Delta T \rightarrow 0$  of a series of instantaneous, small temperature changes  $\Delta T$ , each of which is following by an isothermal hold of time duration

$$\Delta t = \Delta T / q \quad (1)$$

where  $q$  is the heating or cooling rate

$$q = dT/dt = \Delta T / \Delta t \quad (2)$$

We may define at any stage of the process a relaxation time  $\tau$  by the equation

$$(\partial H / \partial t)_T = -(H - H_e) / \tau \quad (3)$$

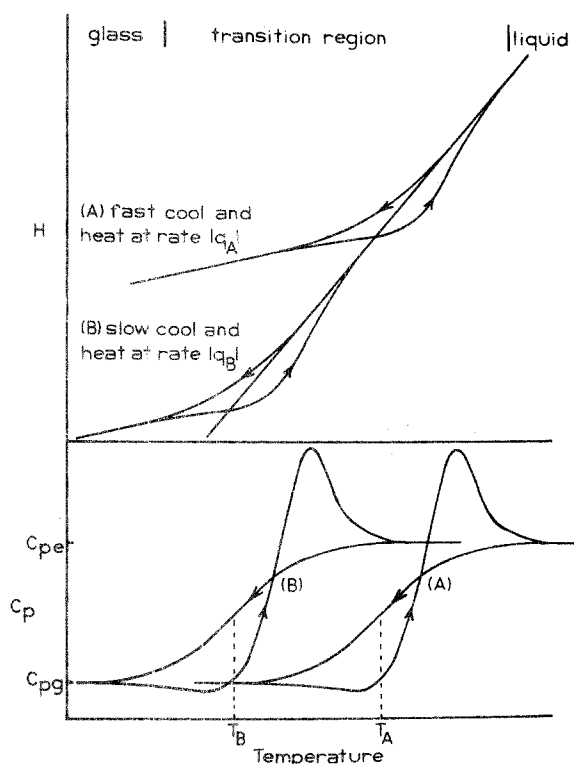
where  $(H - H_e)$  is the departure of the enthalpy  $H$  from the equilibrium liquid value,  $H_e$ , at the temperature of interest.  $\tau$  decreases with increasing temperature. The three temperature regions of Figure 1 then correspond roughly to the conditions

$$\text{liquid} \quad \Delta t \gg \tau \quad (4a)$$

$$\text{transition region} \quad \Delta t \sim \tau \quad (4b)$$

$$\text{glass} \quad \Delta t \ll \tau \quad (4c)$$

From eq 1 it is evident that if the heating or cooling rate  $q$  is increased in magnitude, then the relaxation time  $\tau$  must be correspondingly smaller for eq 4b to hold, and the transition region is shifted to a higher temperature.



**Figure 1.** Enthalpy and heat capacity vs. temperature plots for a glass cooled and then reheated through the transition region at different rates. Temperatures  $T_A$  and  $T_B$  are a pair of corresponding temperatures in eq 15.

From the above discussion it is also evident that the dependence of  $T_g$  on heating or cooling rate  $q$  yields information on the temperature dependence of the kinetic parameter  $\tau$ . The essential features of a treatment which can relate the dependence of  $T_g$  on  $q$  to the temperature dependence of  $\tau$  for  $T_g$ 's determined from cooling curves were presented some years ago by Ritland.<sup>6</sup> More recently McMillan<sup>8</sup> and Rasmussen and MacKenzie<sup>12</sup> attempted to obtain this information from the  $T_g$ 's determined from heating curves. However, it was pointed out in a communication from this laboratory<sup>15</sup> that the temperature dependence of  $\tau$  assessed from heating curve  $T_g$ 's depends on the thermal history received by the glasses during the prior cool through the transition region and is apt to differ from the true temperature dependence. It is the purpose of the present paper to consider the conditions under which the temperature dependence of  $\tau$  can be assessed correctly from the dependence of  $T_g$  on either heating or cooling rate and to present experimental evidence in support of our conclusions.

### Dependence of $T_g$ on Heating or Cooling Rate

We begin with a set of assumptions about the kinetic and thermodynamic parameters controlling the evolution of the enthalpy during the structural relaxation process.

(1) Following an instantaneous, isobaric change in temperature from an initial equilibrium state, the system exhibits at time zero an enthalpy  $H_0$ , but in time the enthalpy relaxes isothermally to a new equilibrium value,  $H_e$ , at the new temperature. We assume that this isothermal relaxation may be described as a sum of  $n$  independent processes<sup>16,17</sup>

$$\left(\frac{\partial H}{\partial t}\right)_T = \sum_{i=1}^n \left(\frac{\partial H_i}{\partial t}\right)_T \quad (5)$$

$H_i$  may be thought of as the enthalpy associated with some order parameter<sup>3,16,17</sup> which changes during the structural relaxation; there are  $n$  distinct order parameters labeled 1, 2, ...,  $i$ , ...,  $n$ . It should be noted, however, that eq 5 is strictly phenomenological and that there need exist no one-to-one correspondence between the order parameters which give an adequate description of the macroscopic process and the elementary or microscopic processes actually taking place on a molecular level. The rate of isothermal change of  $H_i$  is given by a time and temperature dependent relaxation time,  $\tau_i$

$$\left(\frac{\partial H_i}{\partial t}\right)_T = -(H_i - H_{ei})/\tau_i \quad (6)$$

Combination of eq 5 and 6 and integration gives for isothermal relaxation

$$H = H_e + (H_0 - H_e) \sum_{i=1}^n g_i \exp\left(-\int_0^t dt'/\tau_i\right) \quad (7)$$

where  $g_i$  is a weighting coefficient for each order parameter  $i$

$$g_i = (H_{0i} - H_{ei})/(H_0 - H_e)$$

and is subject to the normalization condition  $\sum_{i=1}^n g_i = 1$ .

(2) The difference between the equilibrium liquid and glass heat capacities,  $(C_{pe} - C_{pg})$  (see Figure 1), is assumed to be constant over the experimental range of  $T_g$ . As shown below experimentally, the variation in  $T_g$  produced by changes in  $q$  of, e.g., a factor of  $10^2$ , is comparatively small, and over this range this assumption is valid to a high degree of approximation for most glasses.

(3) At constant pressure the dependence of relaxation time  $\tau_i$  on temperature and structure is assumed to be of the form

$$\tau_i = a_i \exp(-bT) \exp[-c(H - H_e)] \quad (8)$$

$b$  and  $c$  are constants and the relaxation times differ only in their preexponential terms  $a_i$ . Equation 8, along with eq 5-7, corresponds to a condition frequently designated as "thermorheologically simple behavior" or as a "temperature independent distribution of relaxation times."

The relaxation time expression of Sharanov and Vol'kenshtein<sup>9</sup> is identical with that of eq 8, as is the relaxation time expression of Tool<sup>18</sup>

$$\tau_i = a_i \exp(-b'T) \exp(-c'T_f)$$

where  $b'$  and  $c'$  are constants, if one notes that the fictive temperature  $T_f$  is defined by

$$H - H_e = (C_{pe} - C_{pg})(T_f - T)$$

The relaxation time expression of Narayanaswamy<sup>17</sup>

$$\tau_i = a_i'' \exp(x\Delta h^*/RT) \exp[(1-x)\Delta h^*/RT_f]$$

where  $a_i''$ ,  $\Delta h^*$ , and  $x$  ( $0 \leq x \leq 1$ ) are constants, is also of the form of eq 8 in any region centered at a temperature  $T_r$  in which  $1/T$  and  $1/T_f$  may be approximated by the first two terms in their Taylor's series expansions about  $T_r$

$$1/T \approx 1/T_r - (T - T_r)/T_r^2 \quad (9)$$

and similarly for  $1/T_f$ . An activation enthalpy,  $\Delta h^*$ , may be defined which expresses the temperature dependences of the logarithms of the relaxation times of eq 8 both for constant departure from equilibrium (constant  $(H - H_e)$  or constant  $(T_f - T)$ ) and for the linear regime where  $(H - H_e)$  is so small that the second exponential in eq 8 differs negligibly from unity

$$\left[\frac{\partial}{\partial T} (\ln \tau_i)\right]_{(H-H_e)} = \frac{d}{dT} (\lim_{H \rightarrow H_e} \ln \tau_i) = -b \equiv -\Delta h^*/RT^2 \approx -\Delta h^*/RT_r^2 \quad (10)$$

where  $R$  is the ideal gas constant. The approximation in eq 10 is valid in a temperature region around  $T_r$  where eq 9 is valid.

We now note that under isobaric conditions the enthalpy is a function of temperature and time<sup>9</sup>

$$H = H(T, t)$$

and

$$\frac{dH}{dT} = \left( \frac{\partial H}{\partial T} \right)_t + \left( \frac{\partial H}{\partial t} \right)_T \left( \frac{dt}{dT} \right) \quad (11)$$

$dH/dT$  is the total observed heat capacity,  $C_p$ .  $(\partial H/\partial T)_t$  is the heat capacity observed when the temperature is changed instantaneously ( $t$  is constant, so that the system has no time to undergo structural relaxation) and hence is the glass heat capacity,  $C_{pg}$ . Making these notation changes and substituting for the other terms from eq 2, 5, and 6, eq 11 becomes on rearrangement

$$(C_p - C_{pg}) = - \sum_{i=1}^n \frac{(H_i - H_{ei})}{q\tau_i} = \mp \sum_{i=1}^n \frac{(H_i - H_{ei})}{|q|\tau_i} \quad (12)$$

In the last expression of eq 12 the minus sign applies for heating ( $q$  is positive) and the plus sign for cooling ( $q$  is negative).

Let us consider first the case in which the structural enthalpy relaxation (eq 5-7) is controlled by a single order parameter and hence by a single relaxation time  $\tau$  of the form of eq 8. Substituting for  $\tau$  in eq 12 and noting that  $|q|$  may be written  $\exp(\ln|q|)$  we get

$$(C_p - C_{pg}) = \mp \left[ \frac{H - H_e}{a \exp[-c(H - H_e)]} \right] \exp(-\ln|q| + bT) \quad (13)$$

From eq 13 and Figure 1 it is evident that for two heat capacity curves, A and B, produced during cooling at respective rates  $|q_A|$  and  $|q_B|$  the condition will hold that

$$(C_p - C_{pg})_A|_{T_A} = (C_p - C_{pg})_B|_{T_B} \quad (14)$$

at all pairs of corresponding temperatures  $T_A$  and  $T_B$  chosen according to the criterion

$$-\ln|q_A| + bT_A = -\ln|q_B| + bT_B \quad (15)$$

provided that the condition

$$(H - H_e)_A|_{T_A} = (H - H_e)_B|_{T_B} \quad (16)$$

is also satisfied. Since  $C_p$  determines the rate at which the enthalpy changes during the rate cool, it is further evident that eq 16 will be valid for all pairs of corresponding temperatures,  $T_A$  and  $T_B$ , if it can be satisfied for any one pair,  $T_A'$  and  $T_B'$ . Let us choose  $T_A'$  and  $T_B'$  in the range above the transition region where the enthalpy and heat capacity curves A and B of Figure 1 follow the equilibrium liquid  $H$ - $T$  and  $C_p$ - $T$  curves. If we return to the picture of a constant cooling rate corresponding to a series of small instantaneous temperature jumps  $\Delta T$  followed by isothermal holds of duration  $\Delta t = \Delta T/q$ , then immediately following the jumps which bring us respectively to temperatures  $T_A'$  and  $T_B'$  we have

$$(H - H_e)_A|_{T_A'} = (H - H_e)_B|_{T_B'} = -(C_{pe} - C_{pg})\Delta T$$

since just prior to the jumps the system was in equilibrium and  $(H - H_e)$  was zero. From this it follows that eq 14-16 become experimentally self-fulfilling for heat capacity cooling curves which commence at any temperature well above

the transition region. (These arguments are presented in greater detail in Ritland's paper.<sup>6</sup>)

If after cooling at a rate of magnitude  $|q|$  one reverses the direction of temperature change and reheats the glass at the same rate, eq 13 will also describe the subsequent evolution of  $(C_p - C_{pg})$  on reheating if one switches from the plus sign to the minus sign in eq 13 at the temperature at which the reheating commences. Further, eq 14-16 will continue to apply to a pair of heat capacity heating curves such as A and B in Figure 1 if the direction of temperature change is reversed at a pair of respective corresponding temperatures  $T_A''$  and  $T_B''$  chosen according to eq 15. Suppose that these two temperatures  $T_A''$  and  $T_B''$  are chosen to lie below the transition region. Since below the transition region no structural relaxation takes place and the heating and cooling heat capacity curves superimpose, one could cool through temperatures  $T_A''$  or  $T_B''$  at respective rates  $|q_A|$  or  $|q_B|$  to any arbitrary lower temperature and return to them *via* reheating at the same rates without altering the glass structure. Consequently, for eq 14-16 to be valid for heating curves it is necessary only that the direction of temperature change be reversed somewhere below the transition region.

The derivation of eq 13-16 is easily extended to the case for which more than one order parameter and associated relaxation time  $\tau_i$  are required to account for the structural relaxation. If the assumptions listed previously allow for an adequate description of the structural relaxation, then associated with each order parameter will be a corresponding relaxational heat capacity of the form of eq 13

$$(C_{pi} - C_{pgi}) = \mp \left[ \frac{H_i - H_{ei}}{a_i \exp[-c(H - H_e)]} \right] \exp(-\ln|q| + bT) \quad (17)$$

The total relaxational heat capacity at any temperature is merely the sum of these

$$(C_p - C_{pg}) = \sum_{i=1}^n (C_{pi} - C_{pgi}) \quad (18)$$

Equations 14-16 apply to each of the individual  $(C_{pi} - C_{pgi})$  and hence apply also to their sum.

To complete our derivation of the dependence of  $T_g$  on  $|q|$ , we need only note that for a given heating or cooling rate  $T_g$  is defined as the temperature at which some particular value of the relaxational heat capacity,  $(C_p - C_{pg})$ , is observed. Consequently, we may rewrite eq 15 as

$$-\ln|q_A| + bT_{gA} = -\ln|q_B| + bT_{gB}$$

so that we have, using eq 10

$$\frac{d \ln|q|}{dT_g} = b \approx \Delta h^*/RT_r^2 \quad (19)$$

where  $T_r$  is now some temperature in the middle of the transition region. Alternatively, using eq 9 to relate to  $T_g$  to  $T_r$ , we may write eq 19 in the form

$$d \ln|q|/d(1/T_g) \approx -\Delta h^*/R \quad (20)$$

In addition to the assumptions made in eq 5-9, it should be recalled that eq 19 and 20 are valid only for  $T_g$ 's measured from heat capacity cooling curves in which the cooling was started well above the transition region or from heat capacity heating curves obtained by reheating the glass from a temperature well below the transition region after it has been previously cooled through the transition region at a rate  $|q|$  equal to the heating rate.

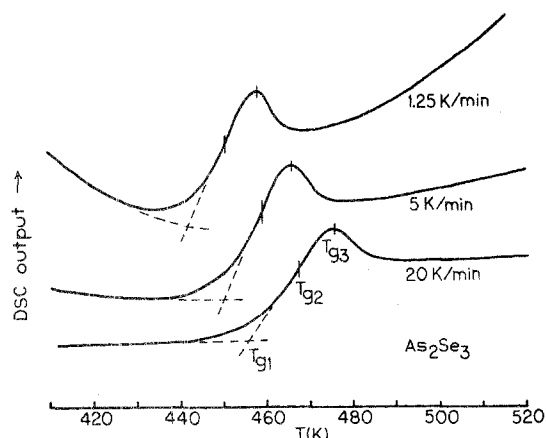


Figure 2. Differential scanning calorimeter traces for heating of  $\text{As}_2\text{Se}_3$  glass through the transition region at various rates after cooling the glass through the transition region at the same respective rates.

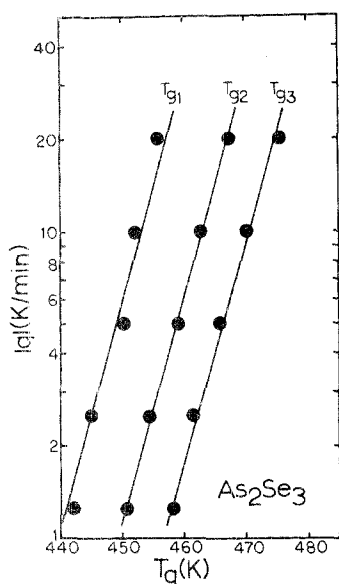


Figure 3.  $\log |q|$  vs.  $T_g$  plots for  $\text{As}_2\text{Se}_3$  glass. Slopes of lines were calculated from eq 19 using  $\Delta h^* = 70$  kcal/mol and  $T_r = 460$  K.

### Experimental Results and Discussion

To test eq 19 and 20 we have carried out measurements of  $T_g$  vs.  $|q|$  for three glasses:  $\text{As}_2\text{Se}_3$ ,  $\text{B}_2\text{O}_3$ , and 23 mol %  $\text{K}_2\text{O}$ -77 mol %  $\text{SiO}_2$ . The  $T_g$  measurements were performed on a Perkin-Elmer DSC-2 differential scanning calorimeter, whose output is proportional to the heat capacity, as a function of heating rate after first cooling the glasses through the transition region at a rate equal to the heating rate. For each glass a temperature calibration was performed at each heating rate using an appropriate melting point standard. Excessive baseline curvature and loss of instrument sensitivity limited the heating rates investigated to 1.25 or 2.5 K/min on the low side; temperature gradients in the sample which prevented accurate temperature determinations limited the heating rates to 20 or 40 K/min on the high side.

A typical set of DSC outputs for different heating rates is shown for  $\text{As}_2\text{Se}_3$  glass in Figure 2.  $T_g$  was determined for three characteristic points on each curve as shown in Figure 2: the extrapolated onset of the heat capacity break

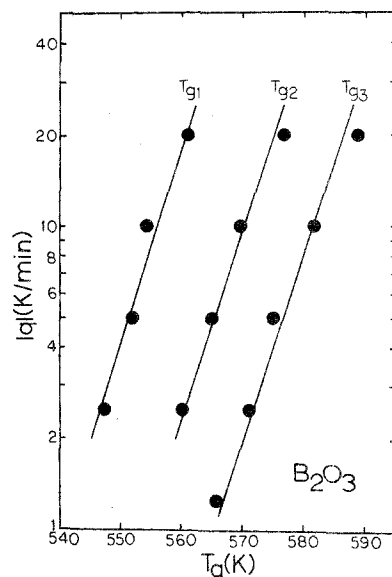


Figure 4.  $\log |q|$  vs.  $T_g$  plots for  $\text{B}_2\text{O}_3$  glass. Slopes of lines were calculated from eq 19 using  $\Delta h^* = 92$  kcal/mol and  $T_r = 570$  K.

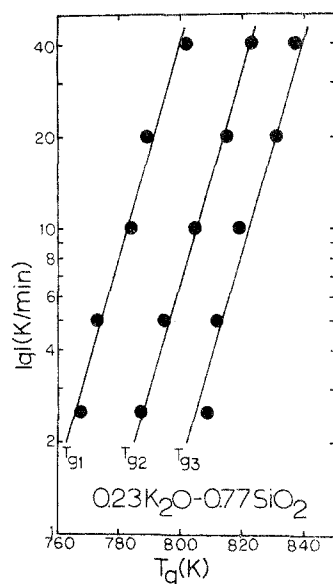
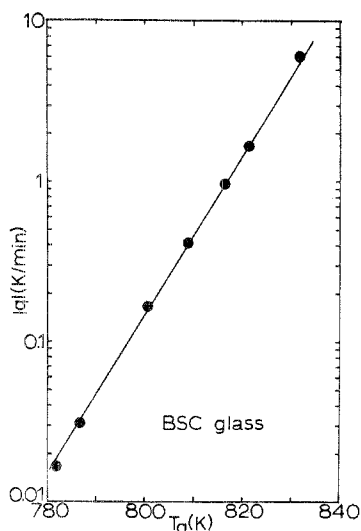


Figure 5.  $\log |q|$  vs.  $T_g$  plots for 23 mol %  $\text{K}_2\text{O}$ -77 mol %  $\text{SiO}_2$  glass. Slopes of lines were calculated from eq 19 using  $\Delta h^* = 101$  kcal/mol and  $T_r = 800$  K.

(designated  $T_{g1}$ ), the inflection point in the rapidly rising part of the heat capacity curve (designated  $T_{g2}$ ), and the heat capacity maximum (designated  $T_{g3}$ ).

In Figures 3-5 are shown semilogarithmic plots of heating rate  $|q|$  vs.  $T_{g1}$ ,  $T_{g2}$ , and  $T_{g3}$  for the three glasses. As expected from eq 19 if the assumptions of eq 5-9 are valid, the three plots for each glass are linear and parallel within the scatter of the data.

It is generally accepted that the molecular motions involved in the structural relaxation are roughly of the same sort as those involved in viscous flow. A number of studies<sup>3,16,17,19,20</sup> of isothermal volume or enthalpy relaxation of glasses in the transition region have shown that the activation enthalpy  $\Delta h^*$  for the volume or enthalpy relaxation is generally the same within experimental error as the activation enthalpy for the shear viscosity,  $\eta_s$ . The shear viscosities of each of the three glasses of Figures 3-5 exhibit Ar-



**Figure 6.**  $\log |q|$  vs.  $T_g$  for borosilicate crown glass. Slope of line was calculated from eq 19 using  $\Delta h^* = 147$  kcal/mol and  $T_r = 805$  K.

Arrhenius behavior (constant  $\Delta h^*$ ) in the glass transition region ( $\eta_s = 10^9$  to  $10^{14}$  P). The lines shown in Figures 3–5 were drawn with slopes calculated from eq 19 using  $\Delta h^*$  values for the shear viscosities in the transition region: 70 kcal/mol for  $\text{As}_2\text{Se}_3$ ,<sup>21–23</sup> 92 kcal/mol for  $\text{B}_2\text{O}_3$ ,<sup>24,25</sup> and 101 kcal/mol for  $0.23\text{K}_2\text{O}-0.77\text{SiO}_2$  glass.<sup>26</sup> Within the scatter of the data the calculated slopes agree with the experimental slopes of the  $\log |q|$  vs.  $T_g$  plots, showing that for the present examples the activation enthalpy controlling the enthalpy structural relaxation is essentially the same as the activation enthalpy for viscous flow.

As a final illustration of the good agreement between  $\Delta h^*$  values for shear viscosity and those assessed from the dependence of  $T_g$  on  $|q|$ , we show in Figure 6 a plot of  $\log |q|$  vs.  $T_g$  for a borosilicate crown glass using the data of Ritland<sup>6</sup> and covering some 2.5 orders of magnitude in  $|q|$ . Here  $T_g$  was taken to be the extrapolated point of intersection of the equilibrium liquid and glass density vs. temperature curves for cooling at various rates. The line through the data was drawn with a slope calculated from the shear viscosity  $\Delta h^*$  value of 147 kcal/mol obtained from Macedo and Napolitano's high-precision viscosity measurements<sup>24</sup>

in the transition region of a glass sample from the same blank. The agreement between the experimental and calculated slopes in Figure 6 is very good.

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