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Estimation of activation energies for structural relaxation and viscous flow from DTA and DSC experiments¹

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Abstract

The activation energy ΔH^* for structural relaxation in the glass transition region can be determined from the heating rate dependence of the glass transition temperature T_g or the cooling rate dependence of the limiting fictive temperature T_f measured using DSC or DTA. ΔH^* values determined this way are in good agreement with the shear viscosity activation energies ΔH_η^* . ΔH_η^* for high T_g inorganic glasses can also be estimated from the width $\Delta(1/T_g)$ of the glass transition region measured by DSC or DTA using an empirical constant $C = (\Delta H_\eta^*/R)\Delta(1/T_g)$. New data for sodium borate glasses yield values of the constant C in agreement with those from earlier studies.

Keywords: Activation energy; Differential scanning calorimetry; Differential thermal analysis; Glass transition; Viscosity

1. Introduction

Differential scanning calorimetry (DSC) or differential thermal analysis (DTA) monitors the heat absorbed or evolved by a material as a function of time, most commonly during rate heating or cooling. If a kinetically impeded process such as crystallization or a chemical reaction which is accompanied by absorption or evolution of heat occurs within the sample, DSC and DTA can be used to characterize the kinetics of the process. In this paper we discuss DSC and DTA determinations of the temperature dependence of the relaxation times controlling the structural relaxation and viscous flow processes associated with the glass transition.

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¹ Dedicated to the Professor Hiroshi Suga.

2. Structural relaxation and the glass transition

Structural relaxation in a glass-forming liquid refers to the kinetically impeded rearrangement of the liquid structure in response to changes in external variables such as temperature T (the variable relevant to DSC and DTA studies), pressure or electric field. Good reviews of the methodology discussed below and used to analyze structural relaxation experiments are given in Refs. [1–8]. Hodge's recent and extensive review [8] is particularly recommended.

Shown schematically in Fig. 1 is the response of the enthalpy H of a glass-forming melt initially in equilibrium to a step change in temperature from T_1 to T_2 imposed at time $t = 0$. The melt initially exhibits a "fast" glass-like change in H associated primarily with the vibrational degrees of freedom. This is followed by a "slow" or kinetically impeded further change in H associated with liquid-like degrees of freedom and generally thought to involve rearrangement of the liquid structure. This structural relaxation progresses until equilibrium is reached at the new temperature T_2 . For computational convenience, results of experiments of this sort are frequently described in terms of the fictive temperature T_f , which is the relaxational part of the measured property (enthalpy H , here) expressed in equivalent temperature units. Fictive temperature is defined so that at equilibrium $T_f = T$. As shown in Fig. 1, during the slow structural relaxation following a step change in temperature from T_1 to T_2 , T_f varies from T_1 to T_2 in parallel with the change in H .

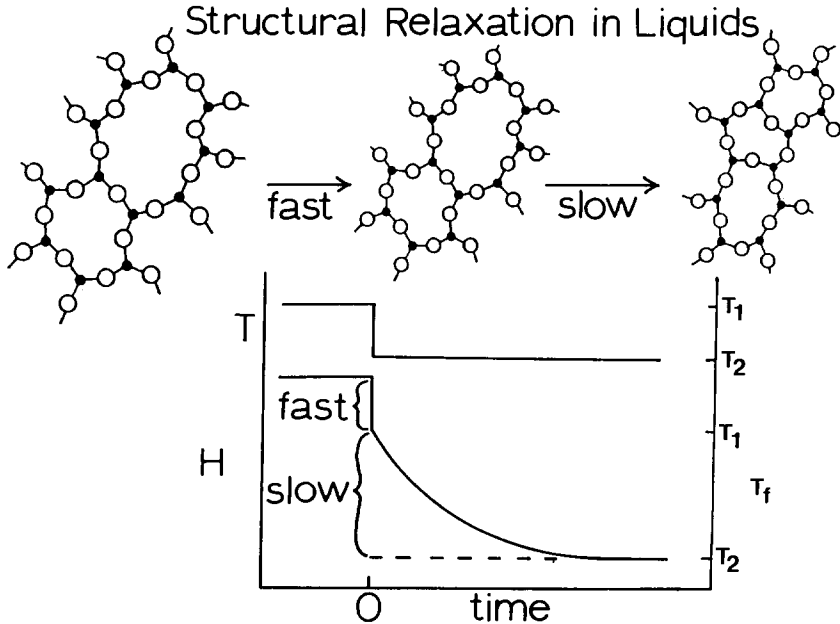


Fig. 1. Schematic plot of enthalpy H and fictive temperature T_f versus time during isothermal structural relaxation following a step change in temperature.

The time dependence of the fictive temperature for the isothermal relaxation in Fig. 1 can be described quite accurately for moderate departures from equilibrium by the relaxation function

$$\phi(t) = \frac{T_f(t) - T_2}{T_1 - T_2} = \sum_i g_i \exp\left(-\int_0^t dt'/\tau_i\right) \quad (1)$$

The relaxation function $\phi(t)$ is, first, *nonexponential* and requires a distribution of relaxation times τ_i with corresponding weighting factors g_i ($\sum_i g_i = 1$). Second, the relaxation function is *nonlinear*, so that the relaxation times τ_i depend both on temperature T and on the instantaneous structure, often parameterized by T_f . Since T_f varies with time, this imparts an implicit time dependence to the τ_i . One expression for the τ_i which works well for moderate departures from equilibrium and over a moderate temperature range in the glass transition region is a modified form of the Arrhenius equation often called the Tool–Narayanaswamy equation

$$\ln \tau_i = \ln \tau_{i0} + \frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f} \quad (2)$$

The τ_{i0} are pre-exponential constants, R the ideal gas constant, ΔH^* the activation energy (more properly, the activation enthalpy) for structural relaxation, and x ($0 \leq x \leq 1$) a nonlinearity parameter which partitions the dependence of the τ_i on T and T_f . Note that both for relaxation close to equilibrium ($1/T_f \approx 1/T$) and for relaxation a moderate but roughly constant distance from equilibrium ($1/T_f = 1/T + \text{const.}$), the temperature dependence of τ_i is given by

$$d \ln \tau_i / d(1/T) = \Delta H^* / R \quad (3)$$

Cooling or heating a liquid or glass at a rate $q = dT/dt$ can be thought of as a series of small temperature steps ΔT followed by isothermal holds of duration $\Delta t = \Delta T/q$. This is illustrated schematically in Fig. 2a [6] for the variation in the experimentally measured enthalpy H and in the equilibrium enthalpy H_e and temperature T (equilibrium fictive temperature) during stepwise cooling and subsequent reheating through the glass transition region. At high temperatures, the τ_i are short enough that the system relaxes completely and hence exhibits liquid-like behavior during the characteristic time interval Δt . At low temperatures the τ_i are very long compared to Δt , so that no relaxation occurs and glass-like behavior is observed in the time interval Δt . The temperature range in between these two extremes is the glass transition region and is delineated in Fig. 2b [6], which shows the variation in H during cooling and reheating and the characteristic hysteresis between the cooling and reheating curves.

A decrease in cooling or heating rate q will increase the characteristic time scale Δt . Since the relaxation times τ_i increase with decreasing temperature, this will shift the glass transition region to lower temperatures. This is shown schematically in Fig. 3 [6, 9] both for the H vs. T cooling and reheating curves and for the corresponding plots of heat capacity $C_p (= dH/dT)$ vs. T . The location of the glass transition is commonly demarcated by some characteristic temperature (the glass transition temperature) on the H or C_p vs. T curves. This might be taken as the temperature T_g for the extrapolated

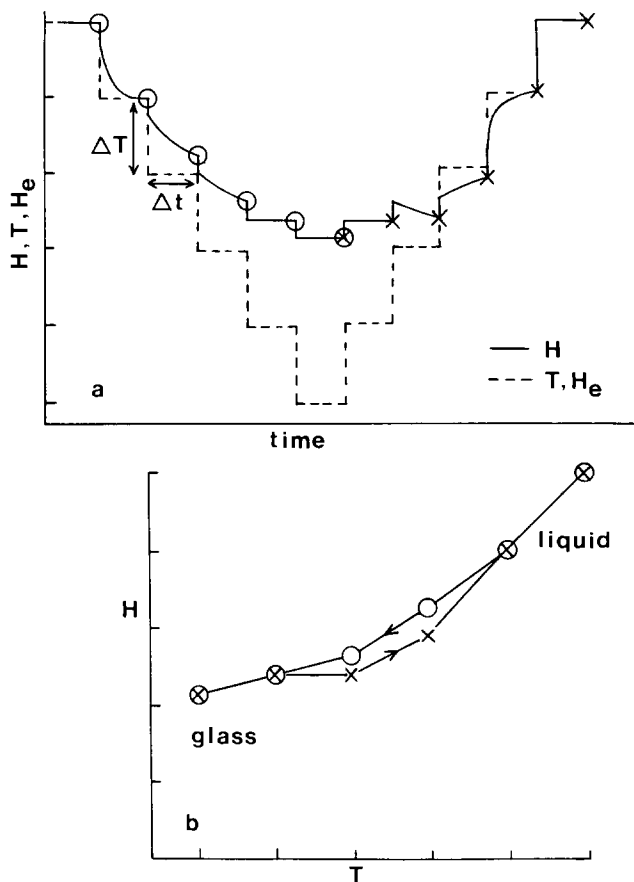


Fig. 2. Schematic plots of (a) variation with time of temperature T , equilibrium enthalpy H_e and experimental enthalpy H , and (b) H versus T during stepwise cooling and reheating in the glass transition region.

onset of rise of the C_p vs. T reheating curve, as shown in the lower part of Fig. 3, or as the extrapolated temperature T'_f of intersection of the equilibrium liquid and glass H vs. T cooling or reheating curves, as shown in the upper part of Fig. 3. T'_f is often referred to as the limiting fictive temperature attained by the glass on cooling. T'_f can be determined by suitable integration of the C_p or heat flow reheating curve as measured by DSC or DTA and illustrated in Fig. 4.

3. Activation energies from the cooling or heating rate dependence of T_g or T'_f

The output of a DSC or DTA during heating is proportional to the heat capacity C_p of the specimen and consequently provides a straightforward way of detecting the glass transition. Moreover, since the characteristic temperatures T_g or T'_f demarking the

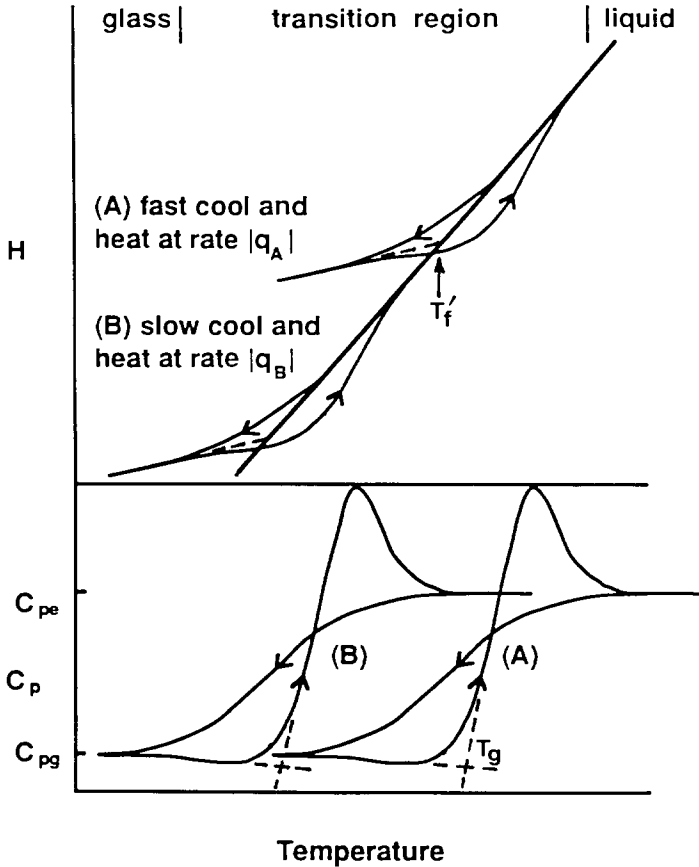


Fig. 3. Schematic plot of enthalpy H and heat capacity C_p during cooling and reheating through the glass transition region at two different rates. From Ref. [9].

glass transition depend on the cooling or reheating rate q , and since this dependence arises from the temperature dependence of the relaxation times τ , DSC or DTA heating data can be used to determine the activation energy ΔH^* of Eq. (3) for the structural relaxation times. Two general techniques for this have gained acceptance over the past twenty years [8].

The first technique involves measurement of the glass transition temperature T_g as a function of heating rate q_h . A necessary constraint is that prior to reheating the glass must be cooled from above to well below the glass transition region at a rate q_c which is either equal to or proportional to the reheating rate q_h . Subject to this constraint, it may be shown [9] that

$$d \ln q_h / d(1/T_g) = - \Delta H^* / R \tag{4}$$

The second technique involves measurement of the limiting fictive temperature T'_f as a function of cooling rate q_c . T'_f may be determined (as in Fig. 4) during subsequent

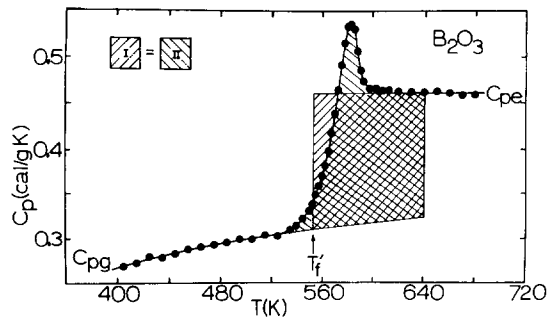


Fig. 4. Heat capacity versus temperature measured during reheating of B_2O_3 glass at 10 K min^{-1} after cooling through the glass transition region at -10 K min^{-1} . T_f is the limiting fictive temperature attained by the glass on cooling to well below T_g at this rate. From Ref. [10].

reheating at any rate (typically $\sim 10\text{ K min}^{-1}$) which gives good precision on the DSC or DTA. The only experimental constraint is that the cooling must commence above and end well below the glass transition region. In this case one obtains [10]

$$d \ln |q_c| / d(1/T_f) = -\Delta H^*/R \quad (5)$$

As noted by Hodge [8], this second technique is considerably more practicable than the first technique. Fig. 5 shows a plot of $\log |q_c|$ vs. $10^3/T_f$ for As_2Se_3 glass [11] from which ΔH^* may be obtained via Eq. (5).

Shown in Table 1 for a number of glass-forming liquids are values of the activation energy ΔH^* for structural relaxation in the glass transition region determined via Eqs. (4) or (5), along with values of T_g measured during heating at a rate between 5 and 20 K min^{-1} following cooling at a comparable rate. Also shown are experimental

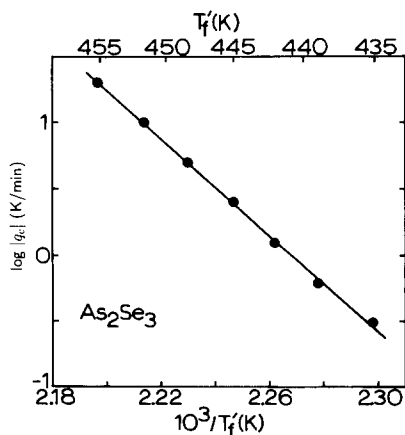


Fig. 5. Logarithm of cooling rate $|q_c|$ versus reciprocal of limiting fictive temperature T_f for As_2Se_3 glass. From Ref. [11].

Table 1

Glass transition temperatures T_g measured at heating rates of 5–20 K min⁻¹, activation energies ΔH^* for structural relaxation determined via Eq. (4) or (5), and activation energies ΔH_η^* for shear viscosity in the glass transition region for various glass-forming liquids

Glass	T_g /(K)	$\Delta H^*/$ (kJ mol ⁻¹)	$\Delta H_\eta^*/$ (kJ mol ⁻¹)	Refs.
5P4E(5-phenyl-4-ether)	244	322	294	[1]
CKN(0.4Ca(NO ₃) ₂ –0.6KNO ₃)	339	590	590	[10, 12]
As ₂ Se ₃	454	342	322	[11, 13]
B ₂ O ₃	557	385	385	[10, 13]
ZBLA(58ZrF ₄ –33BaF ₂ –5LaF ₃ 4AlF ₃)	587	1400	1140	[5, 14]
NBS 711 (lead silicate)	722	374	411	[13, 15]
NBS 710 (alkali lime silicate)	839	612	612	[13, 16]
BSC (alkali borosilicate)	843	615	615	[10, 13]

values of the activation energy ΔH_η^* for the shear viscosity η in the glass transition region. It is generally thought that the atomic or molecular rearrangements taking place during structural relaxation are similar to those occurring during viscous flow in response to a shear stress. In support of this, one finds that the activation energies ΔH^* and ΔH_η^* are equal within experimental error (about 10%) for seven of the eight glass-forming liquids in Table 1. The one apparent exception is the heavy metal fluoride glass ZBLA, where the $\Delta H^*/\Delta H_\eta^*$ ratio appears to be roughly 1.2. This $\Delta H^*/\Delta H_\eta^*$ ratio for ZBLA may still be unity within experimental error, given the extreme steepness of the $\ln |q_c|$ vs. $1/T_f'$ and $\ln \eta$ vs. $1/T$ plots which correspond to these very large ΔH^* and ΔH_η^* values. Angell [17] has noted that some discrepancy between ΔH^* and ΔH_η^* might be expected for very fragile liquids with large $\Delta H_\eta^*/T_g$ values and may be indicative of decoupling near T_g of the faster viscous flow process from the slower structural relaxation process. Nonetheless, as illustrated by the data in Table 1, it appears that ΔH^* values determined via Eq. (4) or (5) give an accurate estimate of the shear viscosity activation energy ΔH_η^* .

4. Activation energies from the width of the glass transition region on DSC or DTA heating curves

The breadth or width of the glass transition region as measured during heating by DSC or DTA may be parameterized as the extrapolated temperatures T_g for onset of rapid rise of the C_p or heat flow vs. T curve and T_g' for completion of the C_p overshoot [13]. These are illustrated in Fig. 6 for a 40Na₂O–60B₂O₃ glass [18]. The shapes of C_p or heat flow reheating curves and hence the relative values of T_g and T_g' are sensitive to the thermal history (cooling rate, time and temperature of sub- T_g anneals) prior to reheating. However, it is found experimentally [13] for a given reheating rate

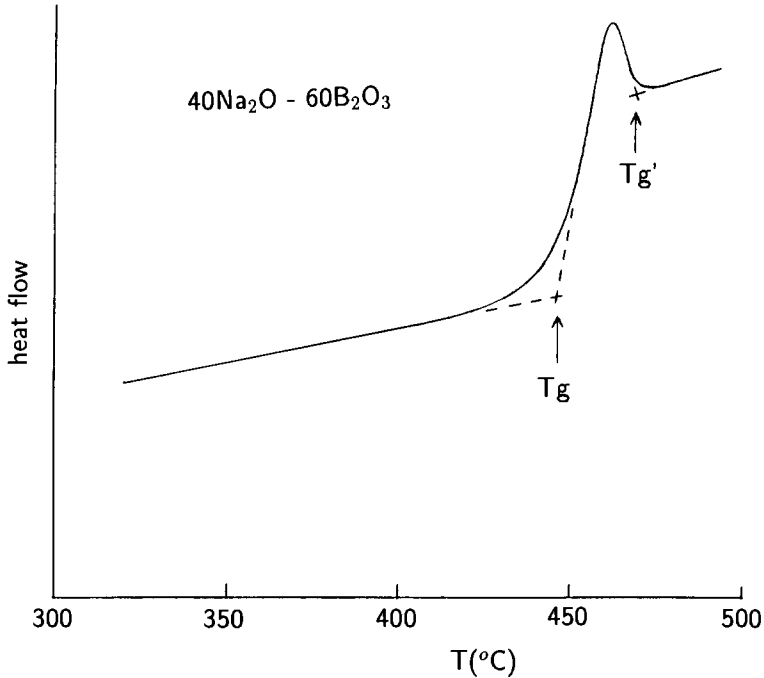


Fig. 6. Heat flow measured by DSC during heating of 40Na₂O–60B₂O₃ glass at 10 K min⁻¹ after cooling through the glass transition region at a slow rate. T_g and T_g' mark respectively the extrapolated onset and finish of the glass transition region during rate heating.

that the values of T_g and T_g' are unaffected within experimental error if the glass is reheated immediately after cooling through the glass transition region and if the ratio of the cooling to reheating rate is kept in the range roughly

$$0.2 \leq |q_c/q_h| \leq 5 \quad (6)$$

As shown in Fig. 2, the low temperature boundary of the glass transition region, T_g , is the temperature at which the structural relaxation times τ_i become on average short enough that the glass can start to exhibit detectable relaxation on the characteristic time scale $\Delta t = \Delta T/q_h$. The high temperature boundary, T_g' , is the temperature at which the τ_i become extremely short, so that the glass can almost completely equilibrate in time Δt . In terms of the parameters of Eqs. (1) and (2), the distance between T_g and T_g' will become larger the smaller the temperature dependence of the relaxation times (the smaller ΔH^*) and the broader the distribution of relaxation times, but will be relatively insensitive to the value of the nonlinearity parameter α [13]. If the experimental constraint of Eq. (6) is met, one thus predicts for glasses with identical distributions of relaxation times on a logarithmic scale that

$$\left(\frac{\Delta H^*}{R}\right)\left(\frac{1}{T_g} - \frac{1}{T_g'}\right) \approx \left(\frac{\Delta H_\eta^*}{R}\right)\left(\frac{1}{T_g} - \frac{1}{T_g'}\right) \equiv \left(\frac{\Delta H_\eta^*}{R}\right)\Delta\left(\frac{1}{T_g}\right) = \text{constant} = C \quad (7)$$

In Ref. [13], Eq. (7) was tested and found to be valid to a high degree of approximation for 17 inorganic glasses with T_g well above ambient temperature. These glasses included the last six entries in Table 1 (As_2Se_3 through BSC), as well as other silicates, chalcogenides and heavy metal fluorides. The observed range in the C values was 4.3–5.6, with a mean of

$$C = 4.8 \pm 0.4 \quad (8)$$

Recently, shear viscosity and DSC heating data have been acquired in the glass transition region for a series of sodium borate glasses with compositions in the range 15–40 mol% Na_2O [18]. The DSC heating curves were measured at a heating rate of 10 K min^{-1} after prior cooling through the glass transition region at a slow rate, so that the constraint of Eq. (6) is approximately satisfied. The DSC heat flow curve is shown in Fig. 6 for one of these glasses. In Table 2 are listed T_g , T_g' and ΔH_η^* values along with the values of $(\Delta H_\eta^*/R)\Delta(1/T_g) = C$ calculated from Eq. (7) for these five sodium borate glasses. For completeness, data for pure B_2O_3 glass taken from Ref. [13] are also included in Table 2. The mean value of C for the six glasses in Table 2 is

$$C = 5.5 \pm 0.4$$

which is at the high end of, but overlaps, the range of C values determined for the 17 glasses in Ref. [13].

An updated generic value of C may be obtained by averaging the C values of the five sodium borate glasses of Table 2 and the C values of the 17 glasses in Ref. [13]. This gives

$$C = 5.0 \pm 0.5 \quad (9)$$

As detailed in Ref. [13], this mean value of C may be used in Eq. (7) to make a very good estimate for high T_g inorganic glasses of the shear viscosity activation energy ΔH_η^* in the glass transition region using only values of T_g and T_g' obtained from a single DSC or DTA heating curve. As also detailed in Ref. [13], however, it should be remembered that the constancy of C is a strictly empirical result, since it depends on the assumption that the distribution of relaxation times is roughly the same for all these glasses. There

Table 2

Lower and upper limits, T_g and T_g' , of the glass transition region during heating at 10 K min^{-1} , shear viscosity activation energy ΔH_η^* in the glass transition region and $(\Delta H_\eta^*/R)\Delta(1/T_g)$ calculated from Eq. (7) for B_2O_3 glass [13] and five sodium borate glasses [18]

Composition (mol%)	T_g (K)	T_g' (K)	$\Delta H_\eta^*/R$ (kJ mol^{-1})	$(\Delta H_\eta^*/R)\Delta(1/T_g)$
B_2O_3	557	591	385	4.8
15 Na_2O –85 B_2O_3	696	731	682	5.6
20 Na_2O –80 B_2O_3	743	774	847	5.5
25 Na_2O –75 B_2O_3	755	785	988	6.0
30 Na_2O –70 B_2O_3	756	781	1137	5.8
40 Na_2O –60 B_2O_3	719	741	1035	5.1

exist low- T_g inorganic glasses, such as the CKN glass in Table 1, for which the experimental value of C is nearly twice that given in Eq. (9).

5. Conclusions

From a pragmatic standpoint, the main virtue of using DSC or DTA data to obtain viscosity activation energies is probably convenience. One can obtain DSC or DTA data on very small samples, and there is no need to fabricate larger samples of precise dimensions, as in the preparation of beam-bending or fiber-elongation viscosity specimens. With some further assumptions about the constancy of the viscosity η at T_g , one can use the ΔH_η^* values from DSC or DTA to make estimates of the melt viscosities up through the working range [13]. The validity of ΔH_η^* ($\approx \Delta H^*$) determinations via Eq. (4) or (5) seems now to be well established, but these determinations require measurement of a number of DSC or DTA heating scans for different prior cooling rates. Evaluation of ΔH_η^* via Eqs. (7) and (9) is much easier, since only one scan is required. However, the implied constancy of C in Eq. (9) needs to be checked out for a much larger number of inorganic glass-forming systems to obtain a better feel for just what classes of glass conform to this empirical correlation.

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