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"Nose Method" of Calculating Critical Cooling Rates for Glass Formation

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In the past, it has been shown that reasonably good estimates of critical cooling rates for glass formation could be obtained by computing the cooling curve which just passes through the nose of a T-T-T (time–temperature–transformation) diagram. Also, it has been noted that critical cooling rates found by this procedure are generally greater than those obtained by other methods. Herein, we provide an explanation of these observations. The nose method of computing critical cooling rates is compared with others, and specific illustrations are given for the glass-forming systems SiO_2, GeO_2, and P_2O_5. [Key words: glass, cooling, silica, germania, phosphates.]

I. Introduction

GLASS formation requires the avoidance of crystallization as the melt is undercooled. The more rapid is the rate of cooling, the less time which is available for crystallization, and hence the greater is the chance of forming a glass.

If one can calculate the crystallization rate as a function of

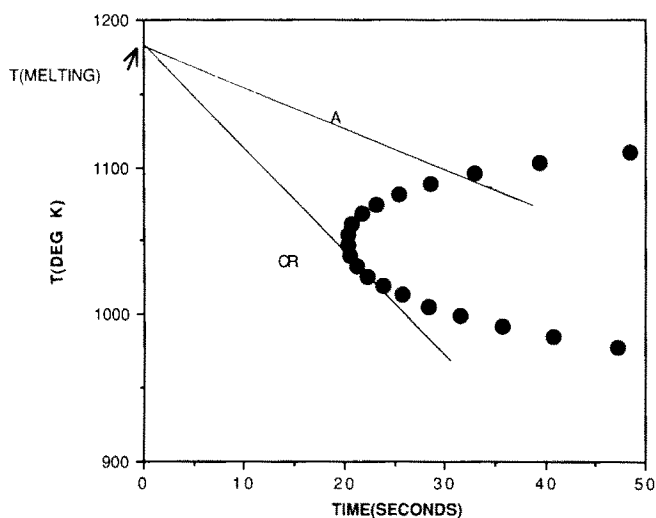**Fig. 1.** Typical T-T-T diagram. CR is critical cooling path and A is an arbitrary path with subcritical rate.

cooling rate, then one can specify the cooling rate needed to avoid any arbitrary value for the volume fraction of crystals, X, which would form. For any cooling path, if $X \leq 10^{-6}$, then one may assert that glass formation has occurred.[1] The cooling rate, R_c, which produces $X_c = 10^{-6}$ is termed the critical cooling rate for glass formation.

Clearly, an important goal of glass science is to have a thorough understanding of the factors which are utilized for calculations of R_c. The critical cooling rate depends upon three factors (assuming that a constant cooling rate is employed): the nucleations rate and its temperature variation, $I(T)$, the crystal growth rate and its temperature dependence, $g(T)$, and the relationship between the two latter quantities and X. Herein, we focus primarily on the last factor.

Previously, many calculations have been performed to predict the critical cooling rates for forming metallic and inorganic glasses.[2-4] In addition, several different methods have been used to compute R_c.[4-6] Numerical methods have been developed which are relatively precise, but laborious to employ. Hence, approximate methods of calculating R_c have been formulated for the sake of convenience. Perhaps the simplest, and most widely employed, method is based on avoiding the nose in a T-T-T (time–temperature–transformation) diagram. This method, hereafter referred to as the nose method, has particular appeal since it relies on the use of isothermal data solely. It may be illustrated by examination of Fig. 1. The T-T-T curve gives the times required to form X_c volume fraction of crystals during an isothermal treatment at various temperatures. The critical cooling rate, line CR, as given by the nose method, is the straight line which connects the melting point, T_m, and the temperature of maximum crystallization rate, T_n (the nose temperature). The slope of the line denoted by A is of smaller magnitude than that of CR, and cooling at the rate indicated by A would produce a partially or totally crystallized body.

It has been observed that the nose method of predicting R_c is in reasonably good agreement with other methods.[7,8] Also, it has been noted that R_c values found by the nose method are typically larger than those computed by other techniques. The origin and generality of these findings have not been examined. Furthermore, it is not readily apparent why the nose method should provide an upper bound for R_c. If a significant degree of crystallization were to occur only in the temperature regime from the melting point to the temperature at the nose, then it would be easy to understand why the nose method produces an upper limit for the critical cooling rate. Under such circumstances one may readily deduce from an inspection of Fig. 1 that $R_{cn} > R_c$ (where R_{cn} is the critical cooling rate found via the nose method). However, it is known that appreciable crystallization *does* occur at temperatures below the nose, and thus the basis for the nose method needs additional inquiry.

The issues raised above will be addressed in the present work. Two alternative methods which may be utilized to calculate R_c will be compared to the nose method. Illustrations will be given with reference to three specific systems: SiO_2, GeO_2, and P_2O_5.

II. Critical Cooling Rates

First, some standard expression for R_c will be reviewed. Next, some relations between these expressions will be given, assuming certain behavior of $I(T)$ and $g(T)$. Finally, these assumptions will be tested via numerical computations.

(1) Standard Expressions

From Fig. 1 it is apparent that R_{cn}, the critical cooling rate obtained by the nose method, is given as

$$R_{cn} = (T_m - T_n)/t_n \tag{1}$$

where t_n is the value of time at the nose. Using the fact that for an isothermal transformation, with I and g independent of time

$$X = \frac{\pi I g^3 t^4}{3} \tag{2}$$

one finds that

$$R_{cn} = \frac{(T_m - T_n)[(\pi/3)I(T_n)\, g^3(T_n)]^{1/4}}{X_c^{1/4}} \tag{3}$$

The precise expression for X is given by

$$X = 1 - \exp\left(\frac{-\pi I g^3 t^4}{3}\right) \equiv 1 - \exp(-X_e) \tag{2'}$$

However, since $X_e = 10^{-6}$ for the critical T-T-T curve, then Eq. (2) is nearly an exact equation for the volume fraction crystallized. For subsequent comparisons it will be more convenient to introduce a quantity ϑ defined as

$$\vartheta = \frac{X_c R_c^4}{\left(\dfrac{\pi}{3}\right) I(T_n)\, g^3(T_n)} \tag{4}$$

Hence

$$\vartheta_n = (T_m - T_n)^4 \tag{5}$$

A precise expression for the volume fraction crystallized after cooling at a constant rate is given by Eq. (6).

$$X = \frac{4\pi}{3}\int_{T_m}^{T_f} dT\, I(T)\left[\int_T^{T_f} g(T')\, dT'\right]^3 R^{-4} \tag{6}$$

In Eq. (6) T_f is the final temperature, I is the steady-state nucleation rate, and g is the crystal growth rate. The expression for ϑ found from Eq. (6) is denoted by ϑ_e:

$$\vartheta_e = 4\int_{T_m}^{T_f} dT\, \frac{I(T)}{I(T_n)}\left[\int_T^{T_f} \frac{g(T')\, dT'}{g(T_n)}\right]^3 \tag{7}$$

Finally, if one assumes that the additivity assumption is valid,[4] one finds that the corresponding ϑ (designated as ϑ_a) is given by

$$\vartheta_a = \left\{\int_{T_m}^{T_f} dT\left[\frac{I(T)\, g^3(T)}{I(T_n)\, g^3(T_n)}\right]^{1/4}\right\}^4 \tag{8}$$

These three expressions for ϑ (Eqs. (5), (7), and (8)) appear quite different in form; and in order to make comparisons among them, one must use physical information concerning the processes being studied, and the typical behavior of $I(T)$ and $g(T)$.

(2) Comparisons and Approximations

First, we emphasize that attention will be restricted to homogeneous crystallization (i.e., homogeneous nucleation followed by growth). Typically, in such cases (as will be illustrated subsequently) the maximum nucleation rate occurs at much larger undercoolings (i.e., lower temperatures) than the maximum crystal growth rate. Also, for standard nucleation and growth expressions, both nucleation and growth rates are sharply peaked functions of temperature, possessing half-widths which are rather narrow in comparison to $T_m - T_f$. Therefore, in both Eqs. (7) and (8) T_f and T_m may be replaced by T_l and T_u, respectively, with $T_m > T_u$ and $T_f < T_l$. T_l and T_u are unspecified at this point.

However, a physical interpretation of $T_u - T_l$ will be given subsequently.

Let us consider Eq. (8). It is clear that the integrand is less than or equal to unity everywhere since T_n corresponds to the temperature of maximum crystallization rate. Hence

$$\vartheta_a = \left\{\int_{T_u}^{T_l} dT\left[\frac{I(T)\, g^3(T)}{I(T_n)\, g^3(T_n)}\right]^{1/4}\right\}^4 < (T_l - T_u)^4 \tag{9}$$

Comparison of Eqs. (5) and (9) shows that a sufficient (but not necessary) condition for $\vartheta_n > \vartheta_a$ is $T_m - T_n > T_l - T_u$. The latter inequality has a very simple physical interpretation. $T_m - T_n$ is the temperature difference between the melting point and the position of maximum crystallization rate, while $T_l - T_u$ is roughly a measure of the breadth of the crystallization curve (difference in temperatures at which $I g^3$ becomes approximately nonzero). Thus, if the temperature difference between the melting point and the temperature of maximum crystallization rate is larger than the "full width" of the crystallization curve, then the nose method will predict a larger critical cooling rate than the additivity method.

Next, one may consider Eq. (7). As stated previously, the maximum crystal growth rate usually occurs at small relative undercoolings (i.e., $\Delta T/T_m \ll 1$). Therefore, in the temperature regime where the crystal growth rate is a decreasing function of temperature (or increasing function of undercooling), the nucleation rate and thus the integrand of Eq. (7) vanish. Thus, in the temperature regime where the integrand of ϑ_e is sensibly nonzero, g is an increasing function of temperature (i.e., decreasing function of undercooling). Hence, one may assert, in reference to Eq. (7), that $g(T) \gtrsim g(T')$. Thus

$$\vartheta_e = 4\int_{T_u}^{T_l} dT\, \frac{I(T)}{I(T_n)}\left[\int_T^{T_l} \frac{g(T')}{g(T_n)}\right]^3$$

$$< 4\int_{T_u}^{T_l} dT\, \frac{I(T)\, g^3(T)}{I(T_n)\, g^3(T_n)}\, (T_l - T)^3$$

$$< (T_u - T_l)^4 \tag{10}$$

Hence, we have the same inequality as derived for the case of additivity. In other words, if $T_u - T_l < T_m - T_n$, then the nose method predicts a larger critical cooling rate than the exact calculation.

Therefore, for systems in which the maximum crystallization rate occurs at rather large undercoolings and the crystallization curve is narrow, then the critical cooling rate found by the nose method is in a sense an upper limit to the actual critical cooling rate. In the next section the position and width of the calculated crystallization curve will be examined for several systems.

III. Calculations

Here, three simple glass-forming systems will be considered for which critical cooling rate calculations have been performed employing different techniques.[8] We select SiO_2, GeO_2, and P_2O_5 as the prototype systems since appropriate thermodynamic and kinetic parameters are available for computation of nucleation and growth rates. In addition, they are three of the simplest glass-forming systems.

The steady-state nucleation rate, I, may be expressed as[9]

$$I = \frac{KT}{\eta}\exp\left(\frac{-K'\alpha^3}{T(\Delta G)^2}\right) \tag{11}$$

where K and K' are constants, η is the shear viscosity, and α is Turnbull's ratio (which typically assumes values from $1/3$ to $1/2$) which relates the liquid-crystal interfacial tension to the enthalpy of melting, and ΔG is the bulk free energy difference between crystal and melt.

For materials which exhibit small entropies of melting ($\Delta S_m/R < 2$), such as the ones chosen above, crystal growth occurs via a normal growth mechanism,[10] and the crystal growth rate is given by Eq. (12). It is, perhaps, somewhat questionable

Table I. Parameters for Nucleation and Crystal Growth

	T_m (K)	$\Delta S_m/R$	A^*	B (K)*
GeO$_2$	1387	1.31	−9.94	17 962
P$_2$O$_5$	853	3.06	−4.87	9 071
SiO$_2$	1996	0.901	−13.51	37 157
		(0.606)[†]	(−6.88)[†]	(27 115)[†]

*log μ(Pa·s) $= A + B/T$. [†]Used only for Table II for consistency with calculation of Ref. 8.

Fig. 2. Integrand of Eq. (9) vs temperature for GeO$_2$ with $\alpha = 0.5$ and $\gamma = 0$.

whether P$_2$O$_5$ crystal growth is described by Eq. (12) since its entropy of melting is a bit large (see Table I). However, for the purpose of comparing various methods of computing R_c, this point is not very significant.

$$g = \frac{K''T}{\eta}\left[1 - \exp\left(\frac{-\Delta G}{RT}\right)\right] \quad (12)$$

If one assumes a constant difference between the specific heats of crystal and melt, ΔC_p, then ΔG is as follows:

$$\Delta G = T_m \Delta S_m[(1 - T_r)(1 - \gamma) - \gamma T_r \ln T_r] \quad (13)$$

In Eq. (13) T_m is the melting point, $T_r = T/T_m$, $\gamma = \Delta C_p/\Delta S_m$, and ΔS_m is the entropy of melting.

(1) Crystallization Curve Widths and Maximum Crystallization Temperature

The temperature of maximum crystallization may be readily obtained by setting $d(Ig^3)/dT$ equal to zero and using Eqs. (11) to (13). However, in order to find $T_u - T_l$, it is most convenient to use numerical computations. The parameters which were employed in the nucleation and crystal growth expressions are given in Table I. In order to find $T_l - T_u$ for the additivity method the integrand in Eq. (9) was computed as a function of temperature. The results for GeO$_2$ and P$_2$O$_5$ are shown in Figs. 2 and 3. For GeO$_2$, $T_u - T_l \approx 250$ K, while for P$_2$O$_5$, $T_u - T_l \approx 150$ K. The melting points for GeO$_2$ and P$_2$O$_5$ are 1387 and 853 K, respectively. For GeO$_2$, $T_m - T_n \approx 410$ K; and for P$_2$O$_5$, $T_m - T_n \approx 340$ K. Since $T_m - T_n > T_u - T_l$, by the results of the previous section one anticipates that $\vartheta_n > \vartheta_u$; and thus $R_{cn} > R_{ca}$ for these two systems. Calculations for SiO$_2$ similarly show $\vartheta_n > \vartheta_u$. For the latter $T_u - T_l \approx 300$ K and $T_m - T_n \approx 480$ K.

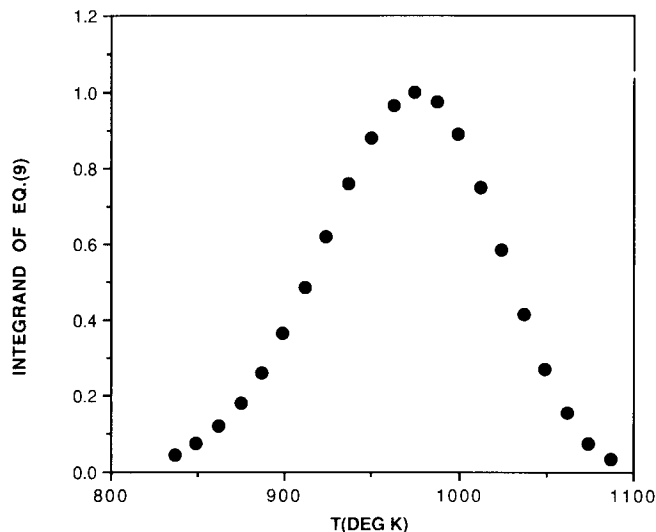Similar calculations were performed to find the values of $T_u - T_l$ for the case of ϑ_e. Here, we chose to use the approximate (right-hand) integrand of Eq. (10) for simplicity. Two points should be made regarding the use of the approximate integrand. First, calculations of the position of the growth rate maxima indicate that the volume fraction crystallized (in the present systems) in the region of decreasing growth rate is negligible. Second, use of the approximate form of the integrand provides a more stringent test of the $\vartheta_n > \vartheta_e$ inequality. The results of a typical calculation are demonstrated for P$_2$O$_5$ in Fig. 4. It is observed that $T_u - T_l \approx 85$ K, while $T_m - T_n \approx 340$ K. Calculations of a similar nature for SiO$_2$ and GeO$_2$ also show $T_m - T_n > T_u - T_l$ indicating that $R_{cn} > R_{ce}$ for these three glasses.

(2) Influence of Nucleation and Growth Parameters

It has been mentioned that Turnbull's ratio, α, typically assumes values in the range $^1/_3$ to $^1/_2$. The above calculations were performed for $\alpha = ^1/_2$. It is of interest to investigate if the precise value of α must be known to draw general conclusions concerning the relative sizes of the predicted R_c, and to study how $T_u - T_l$ and $T_m - T_n$ vary with changing α.
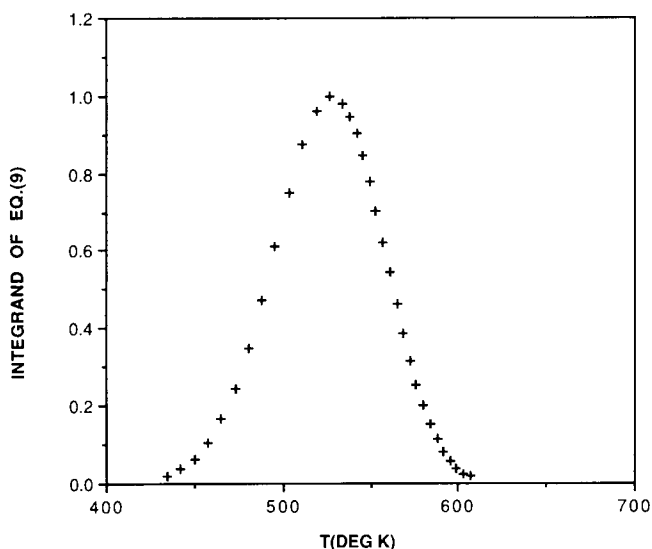

Fig. 3. Integrand of Eq. (9) vs temperature for P$_2$O$_5$ with $\alpha = 0.5$ and $\gamma = 0$; (+) $\beta = 3.06$.
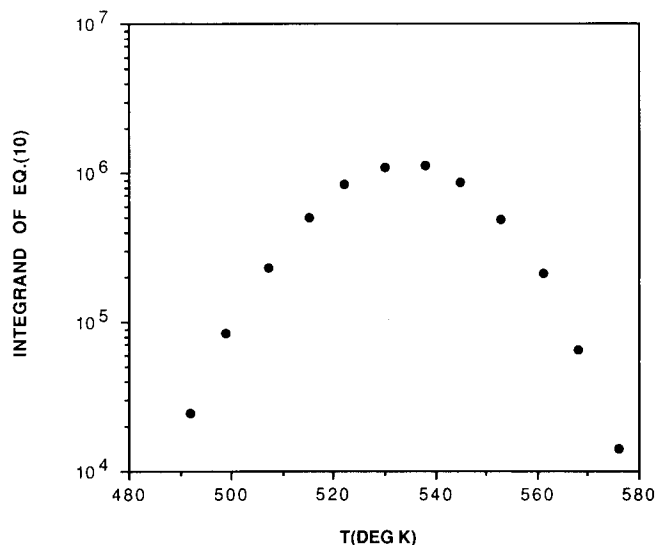

Fig. 4. Integrand (approximate) of Eq. (10) for P$_2$O$_5$ with $\alpha = 0.5$ and $\gamma = 0$.
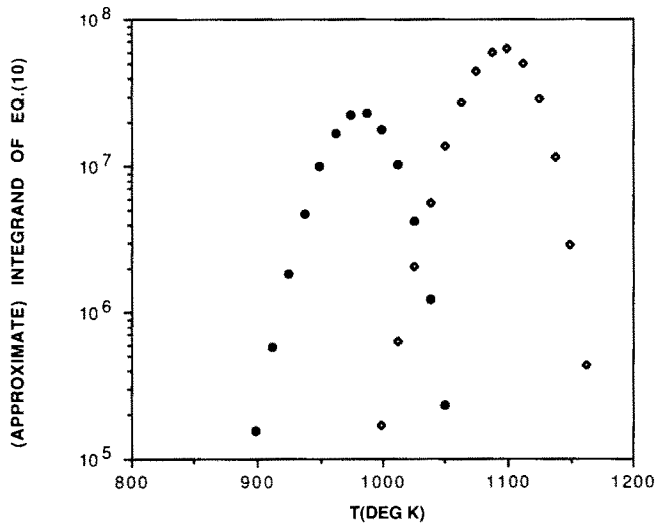
Fig. 5. Integrand (approximate) of Eq. (10) for GeO$_2$ with $\gamma = 0$: ($\diamond$) $\alpha = 0.33$; ($\bullet$) $\alpha = 0.5$.
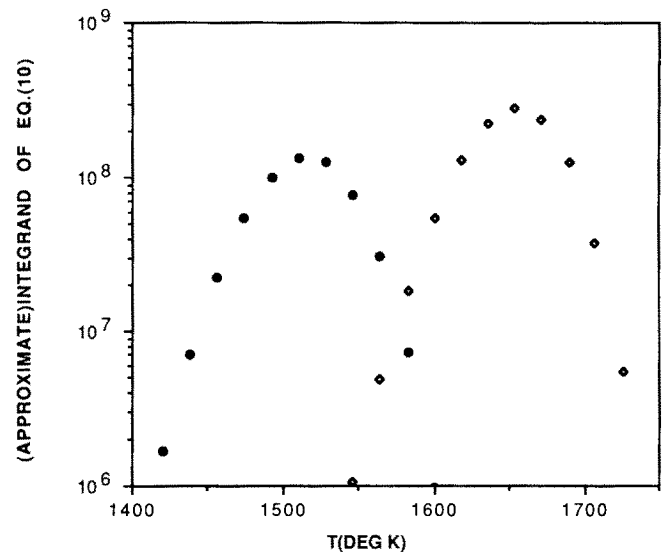

Fig. 6. Same as Fig. 5 for SiO$_2$.

Also, the above calculations have been executed for $\gamma = 0$. This corresponds to the assumption of $\Delta C_p = 0$. Hence, it is important to study the effect of increasing γ on the relevant temperature differences. The influence of α and γ variations are now considered in turn.

It may be shown that as α decreases, $T_m - T_n$ also decreases. However, no such simple general statement may be offered concerning the behavior of $T_u - T_l$ with decreasing α. Hence, this latter feature was studied by direct calculation using the same integrands as in the above. Typical results are shown in Figs. 5 and 6, where the integrands of Eq. (10) are plotted as a function of temperature for GeO$_2$ and SiO$_2$. One notes that the value of $T_u - T_l$ is rather insensitive to α, but as anticipated $T_m - T_n$ declines substantially. However, for all three systems the inequality $T_m - T_n > T_u - T_l$ is preserved, and hence $R_{ce} < R_{cn}$. Similar calculations for these three glasses were performed using Eq. (9). Once again it was found that $T_m - T_n > T_u - T_l$. Thus, one finds that $R_{cu} < R_{cn}$ for these systems, even for $\alpha = \frac{1}{3}$.

Next, we turn to a consideration of the effect of nonzero γ upon the relative temperature differences. It should be noted that the approximation of a constant heat capacity difference will be invalid if γ is much greater than 2. If one computes γ for the three glasses considered here by taking ΔC_p at T_m (rather than the average value over the temperature interval of concern), then $\gamma < 2$ is satisfied.

Figure 7 shows the temperature dependence of integrand in Eq. (9) for P$_2$O$_5$ for three values of γ. Two features should be noted. First, neither the peak position nor the width of the crystallization curve is a very sensitive function of γ. Second, both $T_m - T_n$ and $T_u - T_l$ tend to decrease in magnitude with increasing γ. Hence, there is a compensatory effect; and the differences between $T_m - T_n$ and $T_u - T_l$ vary little with γ. Thus, $T_m - T_n > T_u - T_l$ for all γ.

IV. Discussion

We have shown why the nose method usually gives an upper bound to the predicted critical cooling rate. However, the fact that this method gives reasonable estimates of R_c at all is in a sense fortuitous since the relationship of the location of T_m to T_n is not relevant. For example, for systems with high melting points and large α, $T_m - T_n$ will be large and use of the nose method could be poor since in this case $T_m - T_n \gg T_u - T_l$.

It is clear that the major contribution to the total volume crystallized for nonisothermal cooling comes from the temperature re-

gion in the vicinity of the nose. Hence, if one desires to use a critical T-T-T diagram to make an estimate of R_c, one should utilize this information. A better estimate of R_c could be found by using $T_u - T_l$ rather than $T_m - T_n$; but the former temperature difference is ill-defined. Let us, arbitrarily, assume that the most important temperature regime is bounded by the region where the isothermal transformation time, t, is such that $t \leq 2t_n$. This criterion allows us to determine a ΔT (illustrated in Fig. 8) which can be used to compute R_c.

The latter method for computing R_c (t cutoff) was used to compute the critical cooling rates for SiO$_2$ and GeO$_2$. The results of these calculations are shown in Table II, where they are compared with other values of R_c (Ref. 8) found by the nose method and the numerical integration of the precise form of Eq. (10). The actual predicted values of R_c are not important since they are quite parameter sensitive as shown in Ref. 8. However, it is observed that the cutoff method is in substantially closer agreement with the exact calculations than the nose method.
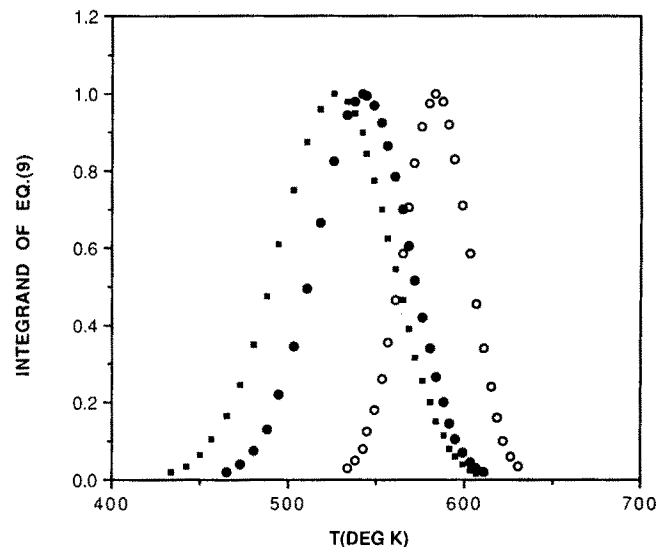

Fig. 7. Integrand of Eq. (9) for P$_2$O$_5$ with $\alpha = 0.5$: ($\blacksquare$) $\gamma = 0$; ($\bullet$) $\gamma = 1.2$; ($\circ$) $\gamma = 2$.
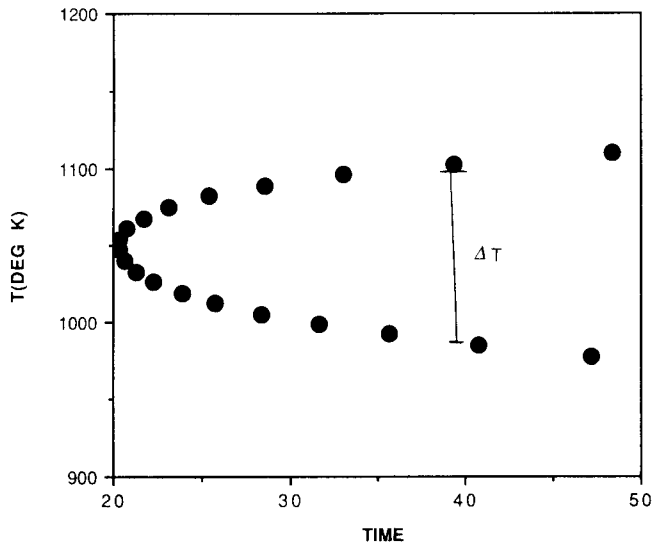
Fig. 8. T-T-T diagram for GeO_2 with $\alpha = 0.39$, $\gamma = 0$.

Table II. Critical Cooling Rates

	R_c (K/s)	
	SiO_2	GeO_2
T-T-T (nose)	3.0×10^{-3}	17
T-T-T (t cutoff)	1.1×10^{-3}	5
Exact	0.47×10^{-3}	3

V. Summary

The use of the nose method for the computation of critical cooling rates has been examined and compared to other methods. It was shown that for homogeneous crystallization it is expected that this procedure will give an overestimate of R_c. This conclusion was drawn after assessing the influence of a range of values for the parameters which control crystal growth and nucleation. Finally, an alternative, simple procedure was proposed to compute critical cooling rates from T-T-T diagrams. The latter technique was shown to be superior to the nose method in the system studied.

References

[1] D. R. Uhlmann, "A Kinetic Treatment of Glass Formation," *J. Non-Cryst. Solids*, **7**, 337–48 (1972).

[2] C. Y. Fang, H. Yinnon, and D. R. Uhlmann, "Cooling Rates for Glass Containing Lunar Compositions," *J. Geophys. Res.*, **88**, A907–A911 (1983).

[3] C. Y. Fang, H. Yinnon, and D. R. Uhlmann, "A Kinetic Treatment of Glass Formation. VII. Critical Cooling Rates for Na_2O–SiO_2 and K_2O–SiO_2 Glasses," *J. Non-Cryst. Solids*, **57**, 465–71 (1983).

[4] D. R. MacFarlane, "Continuous Cooling (CT) Diagrams and Critical Cooling Rages: A Direct Method of Calculations Using the Additivity Concept," *J. Non-Cryst. Solids*, **53**, 61–72 (1982).

[5] H. Yinnon, A. Roshko and D. R. Uhlmann, "On the Barrier to Crystal Nucleation in Lunar Glasses," *Proc. Lunar Plant. Sci. Conf., 11th*, 197–211 (1980).

[6] J. M. Barandiaran and J. Comenro, "Continuous Cooling Approximation for the Formation of a Glass," *J. Non-Cryst. Solids*, **46**, [3] 277–87 (1981).

[7] D. R. Uhlmann, L. Klein, P. I. K. Onorato, and R. W. Hopper, "The Formation of Lunar Breccias: Sintering and Crystallization Kinetics," *Proc. Lunar Sci. Conf., 6th*, 693–705 (1975).

[8] D. R. Uhlmann, B. J. Zelinski, E. D. Zanotto, and M. C. Weinberg, "Sensitivity of Critical Cooling Rate to Model and Kinetic Parameters"; presented at the 15th International Congress on Glass, Leningrad, USSR.

[9] P. F. James, "Kinetics of Crystal Nucleation in Silicate Glasses," *J. Non-Cryst. Solids*, **73**, 517–40 (1985).

[10] D. R. Uhlmann, "Crystal Growth in Glass-Forming Systems: A Ten-Year Perspective"; pp. 80–124 in Advances in Ceramcis, Vol. 4, Nucleation and Crystallization in Glasses. Edited by J. H. Simmons, D. R. Uhlmann, and G. H. Beall. American Ceramic Society, Columbus, OH, 1982   □