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The use of site saturation and Arrhenius assumptions in the interpretation of non-isothermal DTA/DSC crystallization experiments

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Abstract

Two features associated with the interpretation of thermoanalytical crystallization experiments are investigated. First, the generality of the assumption of site saturation is examined. Since this assumption produces a major simplification of the exact expression for the volume fraction crystallized, the domain of applicability of this approximation is explored. Homogeneous crystal nucleation is examined and a broad range of crystallization parameters are considered. Next, an examination is given of a class of models which invoke an Arrhenian assumption for $K(T)$, the crystallization rate constant, and determine crystallization activation energies from plots of $\ln(\ln(1-X)^{-1})$ versus $1/T$. Finally, a discussion is presented of the physical interpretation of the activation energies.

INTRODUCTION

DTA and DSC techniques have been used extensively to study the crystallization behavior of glasses [1–10]. These methods are well adapted for this purpose since data may be acquired rapidly, and a wide range of heating (cooling) rates are possible.

Although many articles have discussed the interpretation of thermoanalytical experiments [11–25], several years ago Yinnon and Uhlmann [26] indicated that all past analyses used the Avrami equation [27] and an Arrhenian form for the temperature dependence of the reaction rate constant, $K(T)$. However, Yinnon and Uhlmann [26] have noted that the latter assumption is often invalid. Also, Weinberg and Kapral [28] have shown that the Avrami equation is inadequate to treat systems of finite size and which exhibit non-random nucleation.

Recently, the use of an Arrhenian assumption for the analysis of DTA/DSC experiments was examined by the present author [29]. However, the latter investigation was limited in two respects. First, the condition of site saturation was assumed without providing a detailed discussion of its applicability. Site saturation corresponds to the case where all nucleation is completed prior to crystal growth, and hence the entire temperature dependence of $K(T)$ arises through the growth process. Second, only the peak crystallization method [25] of analysis was considered.

The present work examines the following issues. The range of applicability of the site saturation approximation is explored. The use of this approximation greatly simplifies the mathematical interpretation of thermoanalytical experiments, and thus its region of validity should be delineated. In the performance of this investigation, only homogeneous crystal nucleation will be considered. This restriction avoids potential pitfalls associated with the use of the Avrami equation, and also permits one to write more definitive expressions for the crystal nucleation rate.

The volume fraction crystallized, $X(T)$, versus T (temperature) method of analysis is also considered. In particular, the validity of the Arrhenian assumption is explored for several crystal growth models.

The final section presents a summary and evaluation of the results, and contains a discussion of the physical interpretation of the activation energy.

However, to begin, the usual governing equations and standard assumptions are reviewed.

GOVERNING EQUATIONS AND STANDARD ASSUMPTIONS

For an isothermal crystallization process with constant nucleation rate, I, and growth rate, g, and spherical growth, the volume fraction transformed as a function of time $X(t)$, is given by the usual Avrami expression [30].

$$X(t) = 1 - \exp(-\tfrac{4}{3}\pi g^3 I t^4) = 1 - \exp(-Kt^4) \tag{1}$$

In eqn. (1) K (or sometimes $K^{1/4}$), the reaction rate constant, can be readily identified. Note that in this case the temperature dependence of K arises from both $I(T)$ and $g(T)$. For a non-isothermal experiment, under similar assumptions, the fraction transformed is [26]

$$X(t) = 1 - \exp\left\{ -\tfrac{4}{3}\pi \int_0^t I(\tau) \left[\int_\tau^t g(t')\mathrm{d}t' \right]^3 \right\} \tag{2}$$

Here the identification of the reaction rate constant is not at all clear. If one assumes that a constant heating (cooling) rate is employed then eqn. (2) can be written in terms of temperature integrals

$$\ln(1-X)^{-1} = \tfrac{4}{3}\pi R^{-4} \int_{T_0}^{T} I(\tilde{T}) \left[\int_{\tilde{T}}^{T} g(T')\mathrm{d}T' \right]^3 \mathrm{d}\tilde{T} \tag{3}$$

In eqn. (3) R is the heating (cooling) rate and T_0 is the temperature at the start of the experiment.

As discussed by Yinnon and Uhlmann [26], several different approaches have been used to analyze data from thermoanalytical experiments. One class of method [12,17,25] relies on the identification and use of the peak crystallization rate temperature, T_p. In this approach various approximations are made to eqn. (3), and ultimately equations are derived involving relationships between T_p and R. Crystallization activation energies are found from the slopes of plots of $f(R, T_p)$ versus T_p^{-1}, where $f(R, T_p)$ represents some particular function of heating rate and peak crystallization temperature. The most widely utilized version of this technique is the Kissinger methods [25]. However, since this method was examined in a previous work [29], it will receive no further attention here.

A second class of method [22,23,31] has utilized approximate forms of eqn. (3), and concludes that plots of $\ln(\ln(1-X)^{-1}$ versus $1/T$ should be linear. The slopes of such plots have been used for the determination of activation energies of crystallization. These techniques have invariably used an Arrhenian assumption, and it is the validity of this assumption which is analyzed herein.

Finally, it should be remarked that there is one approach to the interpretation of non-isothermal crystallization experiments which is almost completely rigorous. In the analysis given by Ozawa [14] only the validity of the Avrami equation was assumed. Hence, for systems which satisfy the assumptions inherent in the derivation of the Avrami equation, Ozawa's method is exact.

SITE SATURATION

If the condition of site saturation applies, then the analysis is greatly simplified since eqn. (3) can be written as

$$\ln\left(\ln(1-X)^{-1}\right) = \ln C + 3 \ln\int_{T_1}^{T} g(T')\, \mathrm{d}T' \tag{4}$$

In eqn. (4) $C = \frac{4}{3}\pi R^{-4}N$, and is constant. N is the integral of the nucleation curve.

In order to assess the reasonableness of this approximation, the overlap of homogeneous crystal nucleation and crystal growth curves will be inspected for a variety of conditions. Since precise values of the overlap are not required, simple expressions for the nucleation and growth rates will be employed.

The nucleation rate is given by the following standard expression [32]:

$$I = \frac{I_0 T_r}{\eta} \exp\left(-\frac{16\pi}{3}\frac{\alpha^3\beta}{T_r(1-T_r)^2}\right) \tag{5}$$

In eqn. (5) T_r is the temperature divided by T_m (the melting temperature),

β is the entropy of fusion in units of the gas constant, η is the shear viscosity, and I_0 is a constant. The precise value of I_0 is unimportant since normalized nucleation rates are employed. Equation (5) contains the Turnbull approximation [33] for the liquid–crystal surface tension, and α is the corresponding Turnbull proportionality constant. Finally, the approximation that there is zero difference in specific heats between glass and crystal was used. The shear viscosity is taken to have Fulcher temperature dependence; i.e.

$$\ln \eta = a + \frac{b}{T_r - T_{r0}} \tag{6}$$

The cases of normal and screw dislocation growth are considered. Hence, the crystal growth rate may be written as [34]

$$g = \frac{g_0 f}{\eta}\left[1 - \exp\left(-\frac{\beta \Delta T_r}{T_r}\right)\right] \tag{7}$$

where $f = 1$ for normal growth, and $f = \Delta T_r \equiv (1 - T_r)$ for screw dislocation growth.

From an inspection of eqns. (5–7) one may see that the overlap between nucleation and growth curves depends upon the values of the four parameters α, β, b, and T_{r0}. Let us consider these in turn. The Turnbull parameter assumes values in the range $1/3 \leqslant \alpha \leqslant 1/2$. Also, the value of α only affects the position of the nucleation curve. Since the maximum of the nucleation curve will shift to higher reduced temperatures as α decreases, the overlap between nucleation and growth curves will be large for smaller α values. In order to provide a conservative estimate (i.e. overestimate) of the degree of overlap $\alpha = 1/3$ is selected in all cases. The value of β affects the position of both nucleation and growth curves. As β becomes smaller the nucleation curve shifts to larger T_r and the growth curve moves to lower T_r. Hence, decreasing β proves to be quite effective in increasing the overlap. Increasing values of b and T_{r0} will tend to move both the nucleation and growth curves to higher reduced temperatures. Since the nucleation curve shifts somewhat more than the growth curve, larger values of the viscosity parameters favor increased overlap. The value of T_{r0}, however, appears to be more important in determining the location of the nucleation curve maximum than b. For example, for $\beta = 2$ and $b = 22$, an Arrhenius temperature dependence of the viscosity (i.e. $T_{r0} = 0$) produces a maximum nucleation temperature at $T_r = 0.63$, while for $T_{r0} = 0.4$ the maximum occurs at $T_r = 0.75$. In contrast, for $\beta = 2$ and $T_{r0} = 0.4$ a change of b from 35.7 to 15, only shifts T_r from 0.78 to 0.73.

In order to draw more definite conclusions, however, the specific growth laws must be employed. For the case of screw dislocation growth $\beta > 2$. In order to select a nearly worse case scenario (i.e. maximum overlap) the

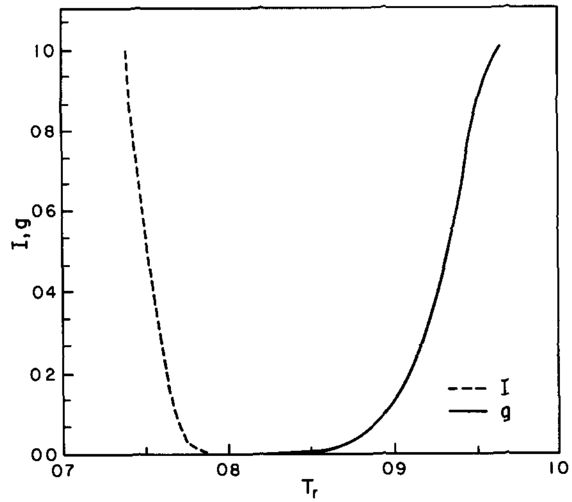

Fig. 1. Overlap of nucleation and screw dislocation growth curves; $\alpha = 1/3$, $\beta = 2.5$, $b = 18.42$, and $T_{r0} = 0.4$.

following choice of parameters is made: $\alpha = 1/3$, $\beta = 2.5$, $b = 18.42$, and $T_{r0} = 0.4$. The normalized nucleation and growth curves for this set of conditions is shown in Fig. 1. It is observed that the overlap is virtually nil. Thus, for homogeneous nucleation followed by screw dislocation growth, one expects in the great majority of instances the nucleation-growth curve overlap to be negligible, and thus site saturation a valid approximation.

However, for the case of normal growth the situation is somewhat different since small β values are possible. In order to illustrate this point a portion of the nucleation and growth curves for the parameter selection $\alpha = 1/3$, $\beta = 0.4$, $b = 22$, and $T_{r0} = 0$ is shown in Fig. 2. An Arrhenius temperature dependence of the viscosity was assumed since this is consistent with the observations for the few inorganic glasses which exhibit normal growth [35]. Clearly, there is some degree of overlap between nucleation and growth curves. Does this feature invalidate the site saturation approximation? It is shown below that overlap between the nucleation and growth curve limits the range of applicability of the site saturation approximation, but does not totally invalidate it.

The volume fraction transformed as a function of final heating temperature was computed using the precise expression (eqn. 3) and the approximate expression where site saturation was invoked (eqn. 4) for the values of the parameters used to produce Fig. 2. The percentage error in $\log(1 - X)^{-1}$ from the use of site saturation was computed as a function of upper heating temperature. The results are shown in Fig. 3. It is observed that for sufficiently large final heating temperature the error in the use of the site saturation approximation is small.

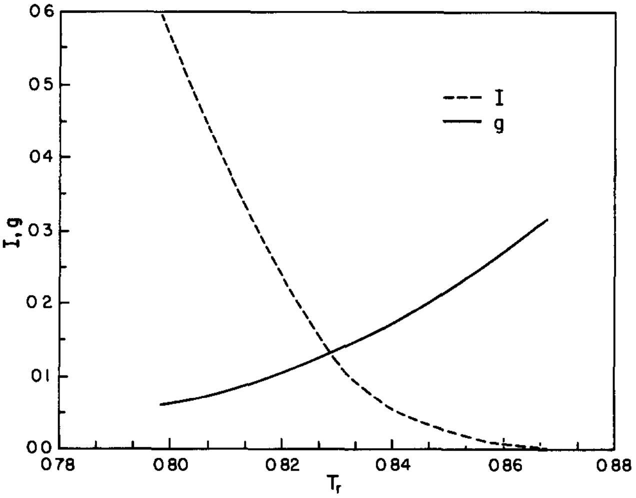

Fig. 2. Overlap of nucleation and normal crystal growth curves; $\alpha = 1/3$, $\beta = 0.4$, $b = 21.87$, and $T_{r0} = 0$.

This latter result can be explained in the following manner. Equation (3) can be rearranged to read

$$\frac{\ln(1-X)^{-1}}{\left(\frac{4}{3}\pi R^{-4}\right)} = \left[\int_{T_0}^{T} g(T')\,\mathrm{d}T'\right]^3 \int_{T_0}^{T} I(\tilde{T}) f(y)\,\mathrm{d}\tilde{T} \tag{8a}$$

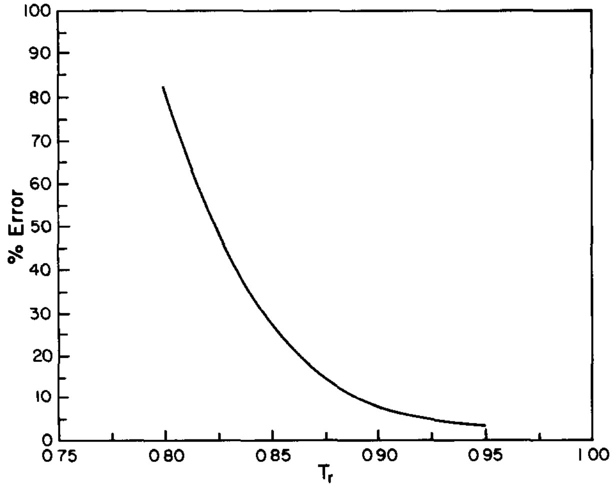

Fig. 3. The percentage error in $\log(1-X)^{-1}$ from the use of site saturation approximation vs. upper heating temperature.

TABLE 1

Ratio of integrand to its maximum value in eqn. (8a) as a function of y for two different upper limits of integration

$T_r = 0.8$		$T_r = 0.95$	
y	I/I_{max}	y	I/I_{max}
0.084	1	0.006	1
0.124	0.988	0.011	0.956
0.180	0.872	0.017	0.778
0.259	0.657	0.028	0.518
0.369	0.391	0.045	0.264
0.520	0.155	0.070	0.095

with

$$y \equiv \frac{\int_{T_0}^{\tilde{T}} g(T')\, \mathrm{d}T'}{\int_{T_0}^{T} g(T')\, \mathrm{d}T'} \tag{8b}$$

and

$$f(y) = 1 - 3y + 3y^2 - y^3 \tag{8c}$$

If one approximates $f(y)$ by unity, then this is equivalent to assuming site saturation. However, it is clear that during the course of integration from T_0 to T, $f(y)$ must vary from 1 to 0. Therefore, for smaller values of $\tilde{T}$, $f(y) \approx 1$. Thus, if the integrand becomes negligible for values of y where $f(y)$ deviates significantly from unity, then site saturation will be a good approximation. One can show that the maximum value of the integrand must lie at T slightly below where the maximum nucleation rate occurs. The rate of decline of the integrand from its maximum value depends not only upon the overlap of the nucleation and growth curves, but also upon the upper limit of integration (final heating temperature). This feature is illustrated in Table 1. For small y, f is close to unity. For an upper heating temperature of 0.95, as the integrand is reduced to less than 0.1 of its maximum value, y grows no larger than 0.07. Hence, one anticipates that site saturation will be valid. This expectation is borne out by the results shown in Fig. 2. However, if the upper heating temperature is 0.8, then $f(y)$ differs significantly from unity over a region where the integrand is not small compared to its maximum value. Thus, site saturation will be a poor approximation in this case.

Since site saturation will be a good approximation whenever the nucleation and growth curves show little overlap, or when there is overlap but a sufficiently high final heating temperature is selected, eqn. (4) will be used in the following section.

TEMPERATURE DEPENDENCE OF VOLUME FRACTION CRYSTALLIZED

The temperature (or time) dependence of the volume fraction of material transformed in a non-isothermal DTA/DSC experiment depends upon the nature of the crystal growth law. Two cases are considered below.

For normal crystal growth with an Arrhenius form for $\eta(T)$, combined use of eqns. (4), (6) and (7) yields

$$\tfrac{1}{3}\ln\left(\ln(1-X)^{-1}\right) - \tfrac{1}{3}\ln C' = \ln\int_{T_{1\mathrm{r}}}^{T_{\mathrm{ru}}}\left[1-\exp\left(-\frac{\beta\Delta T_{\mathrm{r}}}{T_{\mathrm{r}}}\right)\right]\exp\left(-\frac{b}{T_{\mathrm{r}}}\right)\,\mathrm{d}T_{\mathrm{r}} \qquad (9)$$

The constants $\ln g_0$ and $-a$ have been incorporated into C'. The integral appearing on the right side of eqn. (9), I_{R}, can be evaluated analytically to obtain

$$I_{\mathrm{R}} = \frac{y_{\mathrm{m}}}{y}\left[\exp(-y)(1-H(y)) - \exp(\beta)\exp(-z)(1-H(z))\right]$$
$$- \frac{y_{\mathrm{m}}}{y_1}\left[\exp(-y_1)(1-H(y_1)) - \exp(\beta)\exp(-z_1)(1-H(z_1))\right] \qquad (10)$$

In eqn. (10), $y = b/T_{\mathrm{r}}$ and y_{m}, y_1 are y evaluated at the melting temperature and lower integration limit, respectively. Also, in this equation $z = (1 + \beta/y_{\mathrm{m}})y = (1+\gamma)y$, and z_{m}, z_1 are defined in a manner similar to y_{m}, y_1. The function of $H(x)$ is defined by

$$H(x) = x\exp(x)E_1(X) \qquad (11)$$

where $E_1(x)$ is the first exponential integral function [36]. If one selects $T_{1\mathrm{r}}$ as room temperature, then the second term in eqn. (10) (which contains y_1 and z_1) is typically vanishingly small and may be neglected. If one takes the logarithm of eqn. (10) and uses eqn. (9), then one finds

$$\tfrac{1}{3}\ln\left(\ln(1-X)^{-1}\right) - D = -y - \ln y$$
$$+ \ln\left[1 - H(y) - \exp(\beta)\exp(-\gamma y)(1-H(z))\right] \qquad (12)$$

where D is a new constant. One observes that if the quantity within brackets on the right side of eqn. (12) is nearly constant, then a plot of $\tfrac{1}{3}\ln(\ln(1-X)^{-1})$ versus $-y - \ln y$ should give a straight line with unit slope. If one uses the large argument expansion of H and solely retains the first term in the expansion, then one obtains

$$\tfrac{1}{3}\ln\left(\ln(1-X)^{-1}\right) - D \approx -y - 2\log y + \log\left[1 - \frac{\exp(\beta)\exp(-\gamma y)}{1+\gamma}\right] \qquad (13)$$

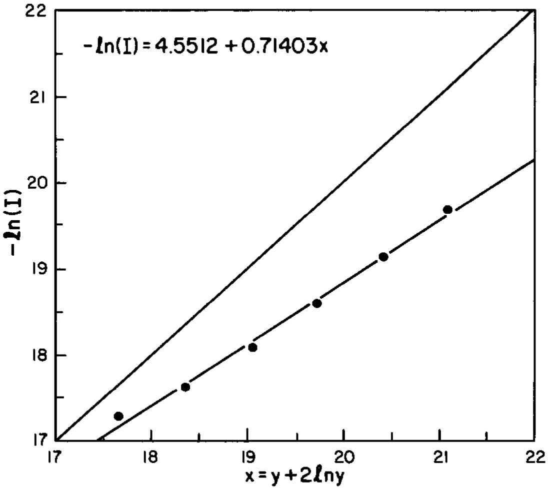

Fig. 4. The negative of the logarithm of the integral of the normal growth expression vs. $y+2\ln y$. $\beta=1.3$, $y_m=12$, and $T_{r0}=0$. Solid line represents approximate calculation and closed points precise computation. Solid curve through points is best linear fit to precise computation.

For sufficiently large y the last term on the right of eqn. (13) may be neglected, and one predicts that a plot of $\frac{1}{3}\ln(\ln(1-X)^{-1})$ versus $-y-2\ln y$ should give a straight line with unit slope.

The latter result is essentially the one obtained by Coates and Redfern [22] and Šesták [23] using an Arrhenius assumption for $K(T)$. These authors found that a plot of $\frac{1}{3}\ln(\ln(1-X)^{-1})-2\ln T$ versus $1/T$ should yield a straight line with slope $(-E/R)$, where E is the activation energy for crystallization. If one recalls that $y=b/T_r$ then not only does the correspondence with the Coates–Redfern–Šesták results become clear, but also one realizes that the activation energy can be identified as the activation energy for viscous flow.

In order to test the viability of this approximation, $\ln I_R$ was computed using the precise expression (eqn. (10)) and the right side of eqn. (13) neglecting the third term. The approximate calculation corresponds to the assumption of an Arrhenian form of the temperature dependence of $K(T)$. The results are shown in Fig. 4, where log I_R is plotted versus $-y-2\ln y$. Several features of this figure warrant comment. First, one notes that the approximate calculation is poor, and would result in a large error for the predicted volume fraction transformed. However, the determination of the activation energy only relies upon the calculated slope. In reduced units, as indicated previously, the slope must be unity. Although the precise calculation differs significantly from the approximate one, it too produces nearly a linear relationship between $\ln I_R$ and $-y-2\ln y$. However, the slope of the line providing the best fit to the exact calculation is about 70% of the

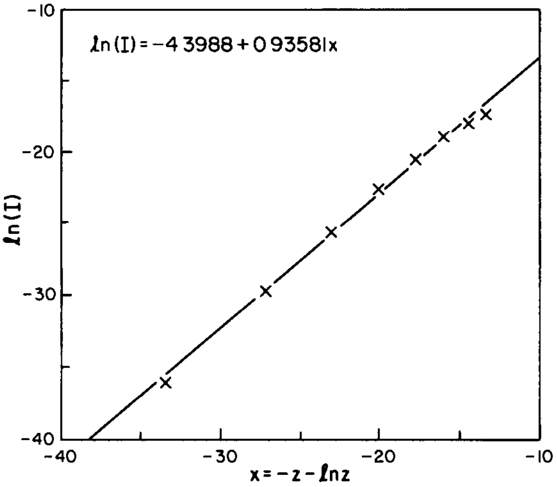

Fig. 5. The logarithm of the integral of the screw dislocation integral vs. $-z - \ln z$. $\beta = 4$, $\gamma = 6$, and $T_{r0} = 0.4$.

one found using the approximate evaluation and thus its use would lead to a similar error in the activation energy.

Next, let us turn to screw dislocation growth where, aside from a constant, the growth rate is given by

$$g = (1 - T_r) \exp\left(\frac{-b}{T_r - T_{r0}}\right)\left[1 - C \exp\left(-\frac{\beta}{T_r}\right)\right] \tag{14}$$

where $C = \exp(\beta)$. The integral of the growth rate was computed numerically for several choices of the growth parameters. The results of a typical calculation are illustrated in Fig. 5, where the logarithm of the integral of the growth rate has been plotted versus $-z - \ln z$, and $z = by = b/(T_r - T_{r0})$. One observes, once again, that the curve is nearly linear. Also, here, the slope is quite close to unity. However, it should be noted that z is not inversely proportional to temperature, but $z \approx 1/(T_r - T_{r0})$. In addition, one sees that departure from linearity occurs at smaller values of $|z|$.

In order to investigate the origin of the nearly linear relation exhibited in Fig. 5 an approximate, but quite accurate, analytical result for the integral of the growth rate was derived. One may write the integral of eqn. (14), I_{sd}, as the difference between two integrals, $I_{sd} = I_1 - I_2$, where

$$I_1 = \int_{T_{1r}}^{T_{ru}} (1 - T_r) \exp\left(\frac{-b}{(T_r - T_{r0})}\right) \mathrm{d}T_r \tag{15a}$$

$$I_2 = \int_{T_{1r}}^{T_{ru}} (1 - T_r) \exp\left(\frac{-b}{T_r - T_{r0}}\right) \exp\left(-\frac{\beta}{T_r}\right) \mathrm{d}T_r \tag{15b}$$

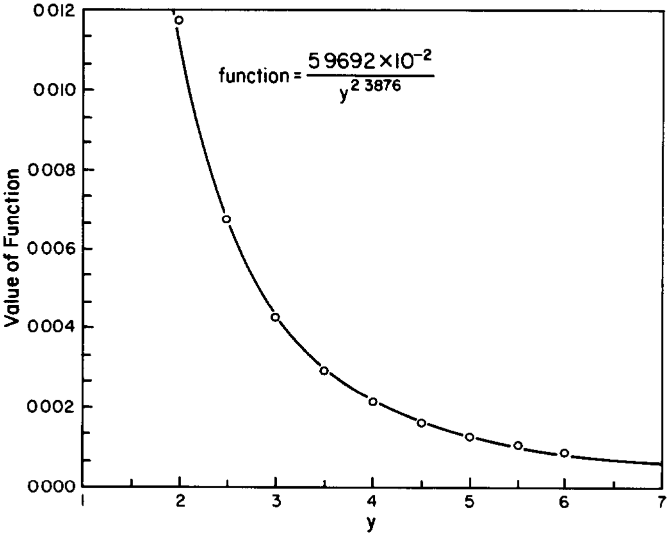

Fig. 6. Approximate fit of exponential of complicated argument in eqn. (17) vs. integration variable.

If one takes the lower temperature, $T_{1r} = 0$ (which introduces virtually no error), then one obtains the precise result given in eqn. (16).

$$I_1 = \frac{b}{z}\exp(-z)\left[\left(1 - T_{r0} + \frac{b}{2}\right)(1 - H(z)) - \frac{b}{2z}\right] \tag{16}$$

All quantities in eqn. (16) retain their former definitions. If one introduces y as the integration variable in eqn. (15b) and uses $T_{1r} = 0$, then one finds

$$I_2 = C\int_{y_e}^{\infty} \mathrm{d}y \frac{\exp(-by)}{y^2}\exp\left(\frac{-\beta y}{1 + T_{r0}y}\right)\left[1 - T_{r0} - \frac{1}{y}\right] \tag{17}$$

Equation (17) could not be integrated, but it was found that if y_e is not too small, then $\exp(-\beta y/(1 + T_{r0}y))$ can be approximated quite well by D/y^{ν}, where D and ν are constants. This feature is illustrated in Fig. 6, where the open circles give the computed values of the former quantity and the solid line gives the latter fit. Thus, if one makes the above replacement in eqn. (17), one obtains

$$I_2 = CD[(1 - T_{r0})I(z,q) - I(z,q+1)] \tag{18a}$$

and

$$I(z,q) = -b^{q-1}\exp(-z)\sum_{j=1}^{3}\frac{z^{j-q}}{(1-q)(2-q)\dots(j-q)} + \frac{b^3 I(z,q-3)}{(1-q)(2-q)(3-q)} \tag{18b}$$

$$I(z,q+1) = -b^{q}\exp(-z)\sum_{j=1}^{4}\frac{z^{j-(q+1)}}{(1-(q+1))\ldots(j-(q+1))} + \frac{b^{4}I(z,q-3)}{(1-q)(2-q)(3-q)(4-q)} \tag{18c}$$

In eqns. (18a–c) $q = 2 + \nu$ and

$$I(q,q-3) = b^{-a}\Gamma(a,z) \tag{19}$$

where $\Gamma(a,z)$ is the incomplete gamma function and $1 - a = \nu - 2$. If the incomplete gamma function is expanded then one finds

$$I_2 = \frac{\exp(-z)}{z}CD\left[(1-T_{r0})\left\{\sum_{j=1}^{3}\frac{b^{q-1}z^{j-3+a}}{(1-b)\ldots(j-b)} + \frac{b^{3-a}z^{a}\left[1+\dfrac{a-1}{z}+\ldots\right]}{(1-b)(2-b)(3-b)}\right\} - \left\{-\sum_{j=1}^{4}\frac{b^{q}z^{j-4+a}}{(1-(q+1))\ldots(j-(q+1))} + \frac{b^{4-a}z^{a}\left[1+\dfrac{a-1}{z}+\ldots\right]}{(1-b)(2-b)(3-b)(4-b)}\right\}\right] \tag{20}$$

Therefore, from an inspection of eqns. (16) and (20), one notes that $I_{sd} \propto \exp(-z)/z$. Although the coefficient of $\exp(-z)/z$ is non-negligible, it can be shown that for sufficiently large z it is a very slowly varying function of z. Since large z corresponds to relatively small T_r, one anticipates linearity in the transformation plot if the final heating temperature is not too high. For the particular values of the parameters chosen in the present calculation ($\beta = 4$, $b = 6$, and $T_{r0} = 0.4$), a plot of $\frac{1}{3}\ln(\ln(1 - X_t)^{-1})$ versus $-z - \ln z$ will be linear, with slope of 0.98 up to a reduced temperature of about 0.8. If b is smaller, then linearity with nearly unit slope will be observed over a more restricted range of T_r. For example, for $b = 3$, one observes linearity with slope of 0.99 to a reduced temperature of about 0.7. As T_{r0} decreases the fit of $\log I$ versus $-z - \ln z$ to a linear plot becomes poorer, and the slope deviates more significantly from unity. This feature is illustrated in Fig. 7, where the values of b and β remain unchanged, but $T_r = 0$, corresponding to an Arrhenius temperature dependence of the viscosity. One can improve "the linearity" by restricting the range of T_r to $T_r \leqslant 0.8$. The procedure would remove the three points in

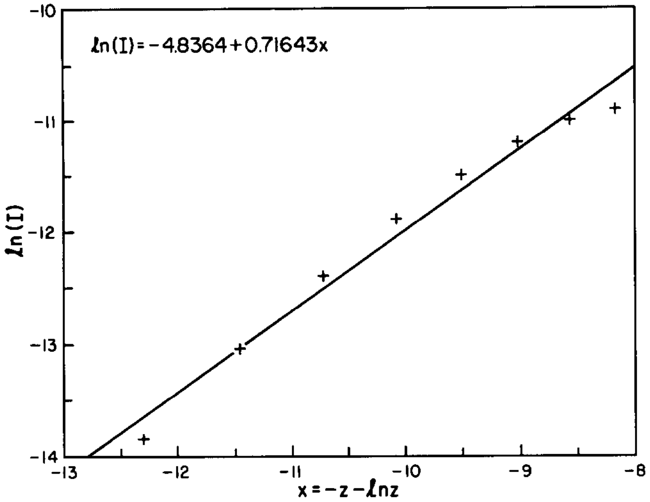

Fig. 7. As Fig. 5, but $T_{r0} = 0$.

Fig. 7 corresponding to the lowest values of z. However, the slope of the resulting line would still deviate significantly from unity. In fact, the reason that the corresponding normal growth plot (i.e. Fig. 4) exhibits such a small slope is due to the assumption that the viscosity is Arrhenius.

DISCUSSION

Most previous analyses of thermoanalytical crystallization experiments have utilized some modified form of eqn. (1) (valid for isothermal experiments) to describe non-isothermal experiments. Furthermore, almost invariably the reaction rate constant, $K(T)$, is assumed to have an exponentional form containing an activation energy, E_a. The constant E_a, termed the activation energy for crystallization, has been measured and reported in a multitude of articles. Yet, this quantity is never well defined. Although many of the procedures which lead to standard interpretations of DTA/DSC experiments appear untenable, quite remarkably the resulting equations usually prove adequate for the analysis of experiments.

Herein, and in a previous work [29], an attempt is made to understand and explain this seeming paradox. In ref. 29, an analysis of the Kissinger method was given, and here the other standard type method of interpretation is examined. In both cases the site saturation assumption is invoked.

Site saturation will be valid if the nucleation and growth curves are well separated. It was shown that if crystal nucleation occurs homogeneously, then for most typical cases involving simple inorganic oxide materials, the nucleation and growth curves are significantly displaced from one another. Furthermore, it was demonstrated that even if overlap does occur, site saturation is a reasonable approximation if one restricts the analysis to sufficiently high temperature in a DTA/DSC heating experiment. Therefore, although caution must be used, for the particular case considered in this work site saturation is applicable.

Next, the use of a $\frac{1}{3}\ln(\ln(1-X)^{-1})$ versus $1/T$ plot for the determination of the activation energy was considered. Several comments and observations are warranted. First, for normal growth with Arrhenius temperature dependence of the viscosity such plots are very close to linear. However, as we can see from inspection of Fig. 4, the use of eqn. (13) with neglect of the third term on the right side of this equation would give the incorrect slope. In other words, $\frac{1}{3}\ln(\ln(1-X)^{-1})$ versus $1/T$ is linear, but the slope of this plot does not necessarily have a simple interpretation. As y_m increases (i.e. b increases or T_m decreases) the curves shown in Fig. 4 would tend to approach one another. In the limiting case of coincidence, the slope of the plot would be proportional to the activation energy for viscous flow. For screw dislocation growth with a Fulcher form of the viscosity the nature of these plots will depend upon the parameters T_{r0}, b, and β, as mentioned previously. For normal growth, β varies over a smaller range and hence its value is less significant. However, for screw dislocation growth β can assume a broad range of values and thus β is more important in this case. As noted, for Fulcher viscosities the appropriate plots should be $\frac{1}{3}\ln(\ln(1-X)^{-1})$ versus $1/(T-T_{r0})$. For $T_{r0}=0.4$, which is a typical value for several common inorganic glasses, and for sufficiently large b (e.g. Fig. 5), the latter plots will be linear with slopes close to unity. Hence, the slopes can be used for the determination of the activation energy for viscous flow. The slope approaches closer to unity for larger values of β and b.

In summary, it is observed that plots of $\frac{1}{3}\ln(\ln(1-X)^{-1})$ versus $1/T$ are expected to be nearly linear often. However, only for certain values of the parameters which control crystallization may the slope be simply associated with an activation energy. Finally, it was shown that this activation energy for crystallization is merely the activation energy for viscous flow.

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