Discussion

Comments on "Activation energy for the crystallization of glass from DDTA curves"

The usual methods of calculating the activation energy of a solid-state reaction from dynamic kinetic data require either multiple experimental curves at different heating rates, or difficult numerical processing of a single curve. It is therefore timely that Marotta *et al.* [1] proposed a method in which the experimental work involves only obtaining data at one heating rate, and the calculation involves merely the values of the temperature at two points that can easily be detected on the curve obtained. Unfortunately, as suggested in this Discussion, their derivation appears to have omitted a correction factor, and may even be basically wrong.

The method in question may briefly be described as follows. Two types of reaction kinetics are considered:

$$1-(1-\alpha)^{1/n} = kt \qquad (1)$$

and

$$-\ln(1-\alpha) = (kt)^n, \qquad (2)$$

where α is the reacted volume-fraction, k a function of the temperature T, and t the time. The rate parameter of interest, namely, activation energy E, is contained in

$$k(T) \propto \exp(-E/RT), \qquad (3)$$

where R is the gas constant.

The authors do well in noting and investigating the possibility that E can be simply calculated from T_1 and T_2, the temperatures at inflection-points (i.e., points of maximum and minimum slope), on an experimental $\mathrm{d}\alpha/\mathrm{d}t$ curve. These points are given by:

$$d^3\alpha/\mathrm{d}T^3 \propto d^3\alpha/\mathrm{d}t^3 = 0. \qquad (4)$$

In this Discussion I shall denote kt by u. The authors noted that

$$d^nu/\mathrm{d}T^n \approx (E/RT^2)^n u. \qquad (5)$$

With these approximations, and if Equations 1 and 2 are used as they stand to express α in terms of u, then Equation 4 becomes:

$$n^2u^2-(3n-1)u+1 = 0, \qquad (6)$$

or

$$(u^n)^2-3u^n+1 = 0 \qquad (7)$$

respectively, after trivial solutions ($u = 0$, 1 or $u \to \infty$, i.e., at the beginning and end of the reaction) have been excluded. E can then be expressed in terms of the ratio of the two solutions for each quadratic equation and thus in terms of T_1, T_2 and the numerical coefficients of the equation.

First of all, a comment on Equation 5 is in order. It is seen that the results:

$$\frac{\mathrm{d}u}{\mathrm{d}T} = \frac{u}{T}-\left(-\frac{E}{RT^2}\right)u \approx \frac{E}{RT^2}u, \qquad (8)$$

$$\frac{\mathrm{d}^2u}{\mathrm{d}T^2} \approx \frac{E}{RT^2}\left(\frac{E}{RT^2}u\right)-\frac{2E}{RT^2}\frac{u}{T} \approx \left(\frac{E}{RT^2}\right)^3 u \qquad (9)$$

and

$$\frac{\mathrm{d}^3u}{\mathrm{d}T^3} \approx \left(\frac{E}{RT^2}\right)^2\frac{E}{RT^2}u-\left(\frac{2E}{RT^2}\right)^2\frac{u}{T} \approx \left(\frac{E}{RT^2}\right)^3 u \qquad (10)$$

are valid under the condition that $E/RT \gg 4$. This condition may with advantage be stated explicitly, since, among solid-state reactions in general, many have relatively low activation energies. As examples, $E/RT < 10$ for the dehydrations of copper sulphate penta- and tri-hydrates, ammonium and potassium alums, $\mathrm{Cu(HCO_2)_2 \cdot 4H_2O}$, $\mathrm{UO_2(NO_3)_2 \cdot 6H_2O}$, and $\alpha\text{-}\mathrm{CaSO_4 \cdot \frac{1}{2}H_2O}$; the dehydroxylation of $\mathrm{Co(OH)_2}$; the decomposition of CrH, $\mathrm{ThH_3}$, $\mathrm{Fe_2(SO_4)_3}$ and $\mathrm{Zn_5O_2(SO_4)_3}$; or the oxidation of zirconium [2, 3], at usual experimental temperatures. The approximations given by Equation 5 are no longer adequate in these cases.

The formulae for E given in [1]:

$$\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = 1.59, \qquad (11)$$

and

$$\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = 0.64 \qquad (12)$$

referred to the special cases of $n = 3$ in Equations 1 and 2, respectively. They have been derived apparently with the assumption that $k(T_1)/k(T_2) = U_1/U_2$, where U_1 and U_2 are the roots of Equation 6 or 7. However, this leaves out the t factors, which are necessarily unequal. The formulae

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should read instead:

$$\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+\ln\frac{T_2-T_0}{T_1-T_0} = 1.59 \text{ or } 0.64; \quad (13)$$

where T_0 is the temperature at zero time. Large errors may result if the second term on the left has been omitted; more often than not it amounts to a significant proportion of 0.64 or 1.59, especially when the data have been obtained at a high heating rate.

Thirdly, and most crucially, it is debatable whether Equations 1 and 2 are applicable to the situation in hand. In a dynamic experiment, when T is a function of t, α cannot simply depend on the instantaneous value of $u(t) \equiv k[T(t)]t$. Rather, the way in which T has been changing with t must also affect α. This effect is taken into account in the equations:

$$1-(1-\alpha)^{1/n} = \int_0^t k \, \mathrm{d}t \quad (14)$$

and

$$-\ln(1-\alpha) = \left(\int_0^t k \, dt\right)^n. \quad (15)$$

The equations used in [1] are valid only in the isothermal case, when k is constant and can be taken out of the integral. The formulae for E proposed there may therefore need more drastic revisions.

References

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3. C. H. BAMFORD and C. F. H. TIPPER (EDS.) "Comprehensive Chemical Kinetics" Vol. 22 (Elsevier, Amsterdam, 1980) pp. 124, 139, 155 and 176–7.

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Reply to 'Comments on "Activation energy for the crystallization of glass from DDTA curves"'

The method of obtaining the value of the activation energy for the crystallization of glass from a single derivative differential thermal analysis (DDTA) curve recently proposed by the authors [1] is criticized by [2].

As the main remark concerns the use under non-isothermal conditions of the two kinetic equations:

$$1-(1-\alpha)^{1/3} = kt \quad (1)$$

and

$$-\ln(1-\alpha) = (kt)^3 \quad (2)$$

where α is the volume fraction of the crystals, k is a constant and t is time, some elucidations are required.

We assumed that under non-isothermal conditions t in Equation 2 represents the time of heating at each temperature T [3] and therefore it has to be considered constant and proportional to the reciprocal of the differential thermal analysis (DTA) heating rate, β, i.e.

$$kt = \frac{k'}{\beta}. \quad (3)$$

Substituting Equation 3 into Equations 1 and 2 we obtained the two kinetic equations proposed by Matusita and Sakka [4, 5] for surface and bulk crystallization of glass from a fixed number of nuclei under non-isothermal conditions.

From the roots of each of the two equations:

$$9(kt)^3 - 8(kt) + 1 = 0 \quad (4)$$

and

$$(kt)^6 - 3(kt)^3 + 1 = 0 \quad (5)$$

that satisfy the condition that at the inflection-point temperatures, T_f, on the DDTA curve (see Fig. 2 [1])

$$\frac{d^2\,\Delta T}{d\,T^2} = \frac{d^3\,\alpha}{d\,T^3} = 0 \quad (6)$$

we obtain

$$\frac{(kt)_{T_{f_2}}}{(kt)_{T_{f_1}}} = \frac{(k')_{T_{f_2}}}{(k')_{t_{f_1}}} = \frac{8+28^{1/2}}{8-28^{1/2}} \quad (7)$$

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