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Notes

CRITICAL REMARKS ON "DETERMINATION OF REACTION KINETIC PARAMETERS FROM VARIABLE TEMPERATURE DSC OR DTA"

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A critical assessment of a published paper (by Bansal and Doremus) is presented. The non-validity of an equation derived by them to calculate the kinetic parameters for the crystallization of fluoride glasses is first reviewed. Then the question of the correct mathematical form is addressed.

A number of mathematical methods have been developed to analyze solid state transformations from non-isothermal studies (see ref. [1] for a critical review).

Recently, Bansal and Doremus [2] have proposed an equation which takes into account the variation of the reaction rate constant with time and temperature. The same equation was used in an earlier paper [3] following the suggestion of a referee. Bansal et al. have adopted this equation, the mathematical treatment of which we believe is incorrect, to calculate the kinetic parameters for crystallization of ZrF_4—BaF_2—LaF_3 glass.

In this communication, we assess the mathematical treatment of the paper by Bansal et al. [2], indicate the sources of error and then address the question of the correct mathematical form.

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Mathematical treatment

Isothermal treatments of the kinetics of phase transformations are usually expressed by the Johnson–Mehl–Avrami equation [4, 5]:

$$-\ln(1-x) = (Kt)^n \tag{1}$$

where x is the volume fraction transformed after time t, n is the Avrami exponent, and K is the overall reaction rate, which is assigned an Arrhenian temperature dependence

$$K = \nu \exp\left[-\frac{E}{RT}\right] \tag{2}$$

where E is the effective activation energy, ν the frequency factor, R the gas constant, and T the isothermal temperature in degrees Kelvin.

In non-isothermal experiments, the temperature is changed at a constant rate $\alpha(= \mathrm{d}T/\mathrm{d}t)$, so that

$$T = T_i + \alpha t \tag{3}$$

where T_i is the initial temperature and T is the temperature after a time t. Substituting Eq. (3) in Eq. (2) gives

$$K(t) = \nu \exp\left[-\frac{E}{R(T_i+\alpha t)}\right] \tag{4}$$

Now, the overall reaction rate is a function of time (i.e. temperature). Let us substitute Kt as $\int_0^t K(t)\,\mathrm{d}t$, so that Eq. (1) becomes

$$-\ln(1-x) = \left[\int_0^t K(t)\,\mathrm{d}t\right]^n \tag{5}$$

or

$$x = 1-\exp[-u^n] \tag{6}$$

where

$$u = \int_0^t K(t)\,\mathrm{d}t \tag{7}$$

If the rate of transformation is maximum at the DTA/DSC peak, the peak position is given by:

$$\ddot{x} = n(1-x)u^{n-2}[u\ddot{u}-\dot{u}^2(nu^n-n+1)] = 0 \tag{8}$$

where

$$\ddot{x} = \frac{\mathrm{d}^2x}{\mathrm{d}t^2},\quad \dot{u} = \frac{\mathrm{d}u}{\mathrm{d}t},\quad \text{and}\quad \ddot{u} = \frac{\mathrm{d}^2u}{\mathrm{d}t^2}$$

The above treatment is based on the method developed by Augis and Bennett [6] and was also used by Bansal and Doremus [2]. The subsequent analysis contains mathematical errors which are discussed below.

Differenting Eq. (7) with respect to time, t, we obtain

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \dot{u} = K(t) \tag{9}$$

and

$$\frac{\mathrm{d}^2u}{\mathrm{d}t^2} = \ddot{u} = qK(t) \tag{10}$$

where

$$q = \frac{E\alpha}{R(T_i + \alpha t)^2} \tag{11}$$

It should be noted that Bansal and Doremus [2] write Eq. (10) in their paper as $\ddot{u} = qK$, where K is independent of time or temperature. But K is defined in the non-isothermal case by Eq. (4) and is dependent on time or temperature.

They [2], introduce a new variable:

$$y = \frac{E}{R(T_i + \alpha t)} \tag{12}$$

So

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{-E\alpha}{R(T_i + \alpha t)^2} = -q \tag{13}$$

(because q has been defined earlier by Eq. (11),
or

$$\mathrm{d}y = -q\,\mathrm{d}t \tag{14}$$

We reconsider Eq. (7):

$$u = \int_0^t K(t)\,\mathrm{d}t = \int_0^t v \exp\left[\frac{-E}{R(T_i + \alpha t)}\right]\mathrm{d}t \tag{15}$$

Substituting Eqs (12) and (14) and changing integration limits, transforms Eq. (15) into:

$$u = -\int_{y_{t=0}}^{y_{t=t}} \frac{ve^{-y}}{q}\,\mathrm{d}y \tag{16}$$

Bansal et al. have obtained:

$$u \simeq \frac{v}{q} e^{-y_{t=t}} = \frac{k}{q} \tag{17}$$

which is Eq. (14) in ref. [2], and hence their final proposed form (Eq. (20) in ref. [2]):

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \ln\left(\frac{E}{R}\right) - \ln v + \frac{E}{RT_p} \tag{18}$$

where T_p is the temperature at the peak, by taking q out of the integral sign in Eq. (16). They have treated q as a constant. But their assumption that q is independent of y is incorrect. Let us justify our claim.

Eq. (12) may be rearranged to give:

$$T_i + \alpha t = \frac{E}{Ry} \tag{19}$$

Substituting Eq. (19) into Eq. (11), one obtains:

$$q = \frac{\alpha R y^2}{E} \tag{20}$$

So q is definitely a function of y (i.e. dependent on time or temperature) and is not a constant. It cannot be taken out of the integral sign.

Substituting q [Eq. (20)] into Eq. (16) gives:

$$u = -\int_{y_{t=0}}^{t_{t=t}} \frac{ve^{-y}}{q} \mathrm{d}y = -\int_{y_{t=0}}^{y_{t=t}} \frac{vE}{\alpha R y^2} \cdot e^{-y} \mathrm{d}y$$

or

$$u = -\frac{vE}{\alpha R} \int_{y_{t=0}}^{y_{t=t}} \frac{e^{-y}}{y^2} \cdot \mathrm{d}y \tag{21}$$

Integrating Eq. (21) gives (limits being disregarded momentarily):

$$u = -\frac{vE}{\alpha R}\left[e^{-y}\int \frac{1}{y^2}\mathrm{d}y - \int (-e^{-y})\left(\int \frac{1}{y^2}\mathrm{d}y\right)\mathrm{d}y\right] =$$

$$= -\frac{vE}{\alpha R}\left[-\frac{e^{-y}}{y} - \int \frac{e^{-y}}{y}\right] \tag{22}$$

Expanding e^{-y} in series and integrating:

$$u = -\frac{vE}{\alpha R}\left[-\frac{e^{-y}}{y} - \int\left(\left(1-y+\frac{y^2}{2!}-\frac{y^3}{3!}\dots\right)\frac{1}{y}\mathrm{d}y\right)\right] =$$
$$= -\frac{vE}{\alpha R}\left[-\frac{e^{-y}}{y} - \int\left(\frac{1}{y}-1+\frac{y}{2!}-\frac{y^2}{3!}+\dots\right)\mathrm{d}y\right] \tag{23}$$

Introducing limits again:

$$u = -\frac{vE}{\alpha R}\left[-\frac{e^{-y}}{y} - \ln y + y - \frac{y^2}{2\cdot 2!} + \frac{y^3}{3\cdot 3!}\dots\right]_{y_{t=0}}^{y_{t=t}} \tag{24}$$

Thus, the above expression [Eq. (24)] is obtained when Eq. (16) is integrated using appropriate assumptions and conditions. The simplified expression, Eq. (17) [or Eq. (14) in Ref. (2)], is obtainable only if q is a constant in Eq. (16), and is therefore non-valid.

The Coates–Redfern–Sestak method has been reviewed [1], where an integral of the type as in Eq. (21) is evaluated using certain approximations. However, we believe that the expression quoted:

$$\int_{\infty}^{y'}\frac{e^{-y}}{y^2}\mathrm{d}y = \frac{-e^{-y'}}{y'^2} \tag{25}$$

which is Eq. (31) in Ref. [1] is unsatisfactory because the authors arrived at the above result using the following integral:

$$\int x^n e^{ax}\,\mathrm{d}x = \frac{e^{ax}}{a}\left(x^n - \frac{nx^{n-1}}{a} + \frac{n(n-1)x^{n-2}}{a^2} - \dots \frac{(-1)^n n!}{a^n}\right) \tag{26}$$

which is only valid for n being a positive integer [7]. Therefore Eq. (25) is acceptable, only if n is a positive integer and higher order terms are neglected.

Based on the assumption that $T_i \ll T$ and $y_{t=t} = y' = E/R(T_i+\alpha t) \gg 1$, an alternative method to evaluate Eq. (21) is to use the correct standard integral:

$$\int\frac{e^{ax}}{x^n}\mathrm{d}x = \frac{-e^{ax}}{(n-1)x^{n-1}} + \frac{a}{n-1}\int\frac{e^{ax}}{x^{n-1}}\mathrm{d}x \tag{27}$$

to obtain:

$$u = -\frac{vE}{\alpha R}\left[-\frac{e^{-y}}{y}\Bigg|_{\infty}^{y'} + \frac{(-1)}{(2-1)}\int_{\infty}^{y'}\frac{e^{-y}}{y}\mathrm{d}y\right] = -\frac{vE}{\alpha R}\left[-\frac{e^{-y'}}{y'} - \int_{\infty}^{y'}\frac{e^{-y}}{y}\mathrm{d}y\right] \tag{28}$$

To evaluate the integral in Eq. (28) we use the standard integral:

$$\int \frac{e^{ax}}{x}\,\mathrm{d}x = \ln x + \frac{ax}{1\cdot 1!} + \frac{(ax)^2}{2\cdot 2!} + \frac{(ax)^3}{3\cdot 3!} + \dots \tag{29}$$

to arrive at the following result:

$$u = -\frac{vE}{\alpha R}\left[-\frac{e^{-y'}}{y'} - \left\{ \ln y + \frac{(-1)y}{1\cdot 1!} + \frac{y^2}{2\cdot 2!} - \frac{y^3}{3\cdot 3!} + \dots \right\} \Bigg|_{\infty}^{y'} \right] \tag{30}$$

which is identical to Eq. (24) obtained by us previously.

Thus our method for solving Eq. (21) using integration by parts followed by a series expansion leads to the same result [Eq. (24)] as when Eq. (21) is solved using approximations [Eq. (30)]; which is obvious.

Concluding remarks

The mathematical treatment of Bansal and Doremus [2], which leads to the proposed equation [Eq. (18)], is questionable.

They [2] have solved Eq. (16), based on an unjustified neglect of the temperature dependence of q, to obtain Eq. (17). Under the appropriate assumption and conditions, Eq. (16) leads to Eq. (21) which is solved by two independent methods to arrive at an identical result [Eq. (24) or Eq. (30)].

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