Discussion

Comments on "Rigorous determination of kinetic parameters from DTA measurements"

Non-isothermal techniques [Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)] are rapidly becoming a valuable tool for the obtaining of kinetic data in a wide range of phase transformations [1, 2]. An important shortcoming of non-isothermal techniques is that it is very common to have several reactions occurring in a particular temperature range. When this happens it is very difficult to obtain kinetic data from a single scan. Kissinger [3, 4] was first to suggest a method for these cases; he showed that, assuming the maximum reaction rate to coincide with the peak of the DTA curve, it was straightforward to obtain kinetic data from various scans performed at different heating rates (multiple scan techniques [4]). Kissinger's assumption does not hold for DTA (DSC will be considered later) if one assumes Borchardt and Daniels' analysis of the DTA techniques [2, 5] to be valid. This is actually the best founded theory of DTA and although originally introduced for the liquid state [5] it might be extended to solid-state reactions. That Kissinger's assumption is wrong for DTA can be easily proved by writing Borchardt and Daniels' basic equation [5].

$$-\frac{d\alpha}{dt} = \frac{1}{KA}\left(hC_p\frac{d\Delta T}{dT} + K\Delta T\right) \qquad (1)$$

This equation being valid for a constant heating rate h, namely, $T = T_0 + ht$, where T_0 is the starting temperature. In Equation 1, α is the fraction of the transformation completed at time t, C_p is the heat capacity of the cell (assumed to be independent of t), K is the heat transfer coefficient of the cell, ΔT is the temperature difference between the sample and the reference and A is the total area under the DTA curve. ΔT is actually the data obtained in a DTA experiment, the outcome of the experiment being a graph of ΔT against time (or temperature).

At the peak (p) of the DTA curve the following relations hold

$$\left.\frac{d\Delta T}{dT}\right|_{T=T_p} = 0 \text{ and } -\frac{d\alpha}{dt} = \left.\frac{1}{A}\Delta T\right|_{T=T_p} \qquad (2)$$

then at T_p, the second derivative of α with respect to t can be written as

$$-\left.\frac{d^2\alpha}{dt^2}\right|_{T=T_p} = \left.\frac{h^2C_p}{KA}\frac{d^2\Delta T}{dT^2}\right|_{T=T_p} \neq 0 \qquad (3)$$

Therefore Kissinger's assumption is invalidated. This result is a consequence of the reaction rate not being directly proportional to ΔT but rather being given by Equation 1. It should be here remarked that although Kissinger's assumption is strictly invalid it has been argued that, in some cases, it approximately holds [6].

In a recent paper Baiocchi *et al.* [7] claimed to have presented a rigorous analysis that allowed them to obtain kinetic parameters through the multiple scan technique [1] and using only peak data not affected by the overlap of several reactions (the peak temperature). The purpose of this paper is twofold: (i) To prove that the analysis presented by Baiocchi *et al.* [7] is wrong as it was obtained through a trivial mathematical error and (ii) to show the validity of Kissinger's assumption for DSC.

The analysis of Baiocchi *et al.* [7] proceeded as follows. They first suggested to work with peak data. Therefore if one borrows Borchardt and Daniel's theory, the basic DTA equations are Equations 2. Then they assumed that α (fraction of the reaction completed at time t) follows the Avrami equation [8]. Here a marginal comment should be made, notice that the usual procedure for the analysis of non-isothermal kinetics is to start with an equation for the reaction rate $d\alpha/dt$ [1, 2] and not for α itself as done by Baiocchi *et al.* [7] and other authors [6]. Once having an equation for α, Baiocchi *et al.* used Equation 2 to obtain an expression for $\Delta T|_{T=T_p}$. Up to this point there is nothing wrong with their analysis [7] but it should be noticed that Equation 2 can hardly be applied to the case of several reactions occurring in a temperature range, as in this case values for $\Delta T|_{T=T_p}$ cannot be trusted. Probably being aware of this fact those authors proceeded further through a completely wrong mathematical argument. Baiocchi *et al.* [7] trying to use the fact that $(d\Delta T/dT)|_{T=T_p} = 0$, differentiated the expression obtained through Equation 2 for $\Delta T|_{T=T_p}$ with respect to T, that is, they differentiated a constant

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and obtained a value different from zero (see Equation 10 of [7]). This mathematical error invalidates the analysis presented by Baiocchi *et al.* [7]. For the correct analysis of DTA curves there are various well founded methods reviewed elsewhere [2]. Finally it should be noticed that the final equation obtained by Baiocchi *et al.* (see Equation 11 of [7]) and the approximate one given at the end of their paper, coincide with those obtained by Augis and Bennett [6, 9]; these authors used Kissinger's assumption and started from the Avrami equation for α. This coincidence can be easily understood if one notices that differentiating $\Delta T|_{T=T_p}$ with respect to T and equating to zero is equivalent to taking the second derivative of α equal to zero (Kissinger's assumption) when in fact it is given by Equation 3. In conclusion Baiocchi *et al.* [7] actually used Kissinger's assumption pretending to have presented a rigorous analysis and stating that Kissinger's one was not.

We now turn to the second point considered in this paper, namely the proof of Kissinger's assumption for DSC. Differential scanning calorimetry directly gives the heat evolved during the reaction, instead of ΔT. This fact allows to obtain $\alpha(t)$ directly from the DSC curve [10, 11], namely

$$\alpha(t) = \frac{A(t)}{A} \qquad (4)$$

where $A(t)$ is the area under the DSC curve from the time (or temperature) at which the reaction is started (t_0) up to time (or temperature) t, namely

$$A(t) = \int_{t_0}^{t} \mathrm{d}t\, \Delta C_p(t) \qquad (5)$$

$\Delta C_p(t)$, the output of the DSC experiment, being the change in specific heat along the linear heating. Now if one differentiates Equation 4 with respect to t, the following expression is obtained

$$\frac{\mathrm{d}\alpha(t)}{\mathrm{d}t} = \frac{1}{A}\Delta C_p(t) \qquad (6)$$

At the peak of the DSC curve it is evident that

$$\frac{\mathrm{d}\Delta C_p(t)}{\mathrm{d}t} = 0 \text{ and therefore } \frac{\mathrm{d}^2\alpha(t)}{\mathrm{d}t^2} = 0 \qquad (7)$$

This proves Kissinger's assumption for DSC.

In conclusion we have shown that although Kissinger's assumption is not valid for DTA (it might be approximately valid if $\mathrm{d}\Delta T/\mathrm{d}T \ll (K/hC_p)\Delta T$ around the peak of the DTA curve [6]) it holds for DSC.

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It is impossible not to agree with Louis and Garcia-Cordovilla [1] about the presence of a trivial error in the derivation of the final expression (Equation 10) of our work [2]. We are very sorry for our mistake. However, we think that it is important to point out the following considerations.

1. We agree with Louis and Garcia-Cordovilla that our deduction of Equation 10 in [2] is implicitly founded on the conclusions of Kissinger [3]. If we start from the theory of Borchardt and

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Daniels [4], we can write an explicit equation for ΔT:

$$\Delta T = A\frac{d\alpha}{dt} - \frac{c_p h}{k}\frac{d\Delta T}{dT}. \qquad (1)$$

The substitution of $d\alpha/dt$ in the expression resulting from the differentiation respect to t of the Avrami–Erofe'ev equation [2] leads to:

$$\Delta T = A\exp\left[-\frac{S}{h}\right]^n \left[nk^n S^n \left(\frac{1}{h}\right)^{n-1} \frac{\beta}{T^2} + nk^n \left(\frac{1}{h}\right)^{n-1} S^{n-1}\right] - \frac{c_p h}{k}\frac{d\Delta T}{dT}, \qquad (2)$$

which differs from our Equation 9 in the presence of the term $(-c_p h/k)(d\Delta T/dT)$. If we differentiate ΔT with respect to T, the maximum condition supplies an equation which, in addition to our previous calculations [2], contains the term $(-c_p h/k)(d^2\Delta T/dT^2)$. From this equation it is possible to obtain an expression like Equation 10 of [2], explicit for k, only supposing $d^2\Delta T/dT^2 = 0$. This has been shown to be equivalent to stating that $d^2\alpha/dt^2 = 0$, which follows from the considerations of Kissinger [3].

2. Augis and Bennett [5], explicitly starting from the conclusions of Kissinger, derived an expression (Equation 12 of [5]) which is not identical, but very similar to ours (Equation 12 of [5]). However, we have suggested (for the first time) the use of a nonlinear regression algorithm for the determination of the kinetic parameters from such an expression, whereas Augis and Bennett proposed the use of a graphical method. Moreover, our approximate equation

$$A = \frac{h}{S_m}\exp\left(\frac{\beta}{T_m}\right) \qquad (3)$$

has been shown to be valid not only when $n = 1$ (as does the one written by Augis and Bennett, Equation 15 of [5]) but for any value of n.

3. The good agreement between the values of the kinetic parameters deduced from our experimental DTA results regarding the devitrification of the $Li_2O \cdot 2SiO_2$ glass and the isothermal ones is not casual. This devitrification reaction is most likely characterized by such a small value of $d\Delta T/dT$ around the DTA peak, that $d\Delta T/dT \ll (k/c_p h)\Delta T$; for this reason our theoretical treatment is adequate.

Lastly, we are persuaded that it is possible to obtain, in agreement with our preliminary remarks [2], a simple and valuable expression which can allow the determination of the kinetic parameters characterizing a solid state reaction from DTA measurements. We are working in this direction and we hope to publish our results as soon as possible.

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