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Note

ON THE USE OF THE DDTA CURVE TO EVALUATE THE KINETIC PARAMETERS OF THE SOLID–GAS DECOMPOSITION REACTION

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In a recent paper Marotta et al. [1] reported an attempt to obtain kinetic information from derivative differential thermal analysis (DDTA) for a solid thermal decomposition reaction, which follows a first-order kinetic equation. The approach used the following statement that the conversion function is given by

$$\mathrm{f}(\alpha) = (1-\alpha)^n \qquad n = 1 \tag{1}$$

This statement is one of the most widely discussed problems of non-isothermal kinetics, its validity being quite doubtful [2]. This note is aimed at presenting a generalization of the method [1] in order to make it useful for any kind of kinetic decomposition law, including the law given above for $n \neq 1$.

Taking the rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\mathrm{f}(\alpha) \tag{2}$$

where

$$k = A\ \exp(-E/RT) \tag{3}$$

A, E, R, T and α having their usual meaning and using the same assumption as in the cited literature [1], we arrive at solving the equation

$$\frac{\mathrm{d}^2\Delta T}{\mathrm{d}t^2} = \frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3} = 0 \tag{4}$$

for $T = T_\mathrm{f}$, where subscript f indicates an inflexion. From eqns. (2) and (4) it turns out that

$$\frac{\mathrm{d}^2k}{\mathrm{d}t^2} + 3k\frac{\mathrm{df}(\alpha)}{\mathrm{d}t}\frac{\mathrm{d}k}{\mathrm{d}t} + k^3\left[\left(\frac{\mathrm{d}f(\alpha)}{\mathrm{d}t}\right)^2 + \mathrm{f}(\alpha)\frac{\mathrm{d}^2\mathrm{f}(\alpha)}{\mathrm{d}t^2}\right] = 0 \tag{5}$$

and as

$$\mathrm{d}k/\mathrm{d}t = ak$$
$$\mathrm{d}^2k/\mathrm{d}t^2 \simeq a^2k \tag{6}$$
$$a = \frac{\mathrm{d}T}{\mathrm{d}t}\frac{E}{RT^2}$$

eqn. (5) can be rewritten as follows

$$\left(\frac{a}{k}\right)^2 - 3\frac{a}{k}\frac{\mathrm{d}f}{\mathrm{d}t} + \left[\left(\frac{\mathrm{d}f}{\mathrm{d}t}\right)^2 + \mathrm{f}\frac{\mathrm{d}^2\mathrm{f}}{\mathrm{d}t^2}\right] = 0 \tag{7}$$

The ratio of the two solutions, corresponding to the two inflexion temperatures $T_{\mathrm{f}1}$ and $T_{\mathrm{f}2}$ is

$$\frac{T_{\mathrm{f}1}^2}{T_{\mathrm{f}2}^2}\mathrm{e}^{E/R(1/T_{\mathrm{f}1} - 1/T_{\mathrm{f}2})} = \lambda = \frac{3 + \left[5 - 4\dfrac{\mathrm{f}\dfrac{\mathrm{d}^2\mathrm{f}}{\mathrm{d}t^2}}{(\mathrm{df}/\mathrm{d}t)^2}\right]^{1/2}}{3 - \left[5 - 4\dfrac{\mathrm{f}\dfrac{\mathrm{d}^2\mathrm{f}}{\mathrm{d}t^2}}{(\mathrm{df}/\mathrm{d}t)^2}\right]^{1/2}} \tag{8}$$

Following Marotta et al. [1], suppose that

$$T_{\mathrm{f}1}^2/T_{\mathrm{f}2}^2 \simeq 1 \tag{9}$$

and taking the logarithms of eqn. (8) we obtain

$$E = \frac{R}{1/T_{\mathrm{f}1} - 1/T_{\mathrm{f}2}}\ln\lambda \tag{10}$$

Since eqn. (10) contains the term λ which is dependent on the form of the function of decomposition, we shall analyse it. For this purpose, the next models of conversion functions are taken into account

$$\mathrm{f}(\alpha) = \alpha^n \tag{11a}$$
$$\mathrm{f}(\alpha) = (1 - \alpha)^n \tag{11b}$$
$$\mathrm{f}(\alpha) = \alpha^m(1 - \alpha)^n \tag{11c}$$

A simple calculus shows that for the models (11a) and (11b), the function λ has the same analytical form

$$\lambda = \frac{3 + (1 + 4/n)^{1/2}}{3 - (1 + 4/n)^{1/2}} \tag{12}$$

which allows eqn. (10) to be rewritten as follows

$$E = \frac{R}{1/T_{\mathrm{f}1} - 1/T_{\mathrm{f}2}}\ln\frac{3 + (1 + 4/n)^{1/2}}{3 - (1 + 4/n)^{1/2}} \tag{10'}$$

It is obvious that the value of $n = 1$ will lead to $\lambda = 6.85$, as cited in ref. 1, and this result points out that the method cannot operate a distinction between the two proposed conversion functions.

Mathematical reasons impose a limitation on the value of n in the above models, i.e.

$$\begin{cases} (1 + 4/n)^{1/2} < 3 \\ 1 + 4/n \geqslant 0 \end{cases}$$

We conclude, therefore, that the method is useless for $-4 \leqslant n \leqslant 4/5$. For the third model of conversion function (11c) the calculus leads to

$$\lambda = \frac{3 + \left(1 + 4\dfrac{n/(1-\alpha)^2 + m/\alpha^2}{[n/(1-\alpha) - m/\alpha]^2}\right)^{1/2}}{3 - \left(1 + 4\dfrac{n/(1-\alpha)^2 + m/\alpha^2}{[n/(1-\alpha) - m/\alpha]^2}\right)^{1/2}} \tag{13}$$

This new form of λ also involves the conversion α. Since the method is independent of α values, the following condition has to be fulfilled

$$\frac{n/(1-\alpha_1)^2 + m/\alpha_1^2}{[n/(1-\alpha_1) - m/\alpha_1]^2} = \frac{n/(1-\alpha_2)^2 + m/\alpha_2^2}{[n/(1-\alpha_2) - m/\alpha_2]^2}$$

where α_1, α_2 are the conversions corresponding to the two inflexion temperatures.

With the assumption that $m, n \neq 0$ (which is fulfilled as we use model 11c) and introducing the notation $\gamma = n/m$ the following relationship is obtained

$$\gamma = \frac{2}{\alpha_1 + \alpha_2} - 1 \tag{14}$$

There are three different cases occurring from eqn. (14), i.e.:

(1) γ tends to 0 if $\alpha_1 + \alpha_2$ tends to 2;

(2) γ tends to ∞ (very large value) if $\alpha_1 + \alpha_2$ tends to 0 (very small value)

(3) γ has a value with one or two digits.

According this discrimination, eqn. (14) can be used as an index of the form of the function of conversion, namely:

(1) if γ tends to 0, n tends to 0, therefore $f(\alpha) = \alpha^m$ fits the reaction well;

(2) if γ tends to a very large value, m tends to 0, therefore $f(\alpha) = (1 - \alpha)^n$ fits the reaction;

(3) if γ has a value of one or two digits, $f(\alpha) = \alpha^m(1 - \alpha)^n$ is the function which fits the reaction, and m (or n) has to be chosen by another method.

CONCLUSIONS

(1) The method of Marotta et al. [1] can be generalized for conversion functions given by $f(\alpha)=\alpha^n$ and $f(\alpha)=(1-\alpha)^n$, in order to obtain the activation energy value from the DDTA curve. The equation which gives the value of the activation energy is

$$E=\frac{R}{1/T_{f1}-1/T_{f2}}\ln\frac{3+(1+4/n)^{1/2}}{3-(1+4/n)^{1/2}}$$

(2) The generalization is useless for $-4 \leqslant n \leqslant 4/5$ and it cannot discriminate between the two forms of the conversion functions, given above.

(3) The method can also be used as an index of the form of the function of conversion.

REFERENCES

1 A. Marotta, S. Saiello and A. Buri, Thermochim. Acta, 56 (1982) 193.
2 J. Šesták, J. Therm. Anal., 16 (1979) 503.