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The use of the derivative differential thermal analysis curve to compute the kinetic parameters of a reaction

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Abstract

A method based on the use of the two temperatures of the inflection determined on a single derivative differential thermal analysis (DDTA) curve and of the temperature of the extremum determined on the differential thermal analysis (DTA) curve is proposed for computing the activation energy and the order of reaction of a chemical process. The obtained formulae do not contain the heating rate. If the conversion degree corresponding to the three temperatures required by the formulae are known, the third kinetic parameter, A, may be also computed. The formulae are fitted to the reaction order model.

INTRODUCTION

In a previous paper [1] we dealt with an extension of a method proposed by Marotta et al. [2] for the analysis of derivative differential thermal analysis (DDTA) curves. The results indicated that the method cannot discriminate between the two forms of the conversion function

$$\begin{aligned} f(1-\alpha) &= (1-\alpha)^n \\ f(\alpha) &= \alpha^n \end{aligned} \qquad (1)$$

The final formula established in that paper gives a relationship between the activation energy and the reaction order if the reaction order model is accepted, i.e. if eqn. (1) is used for the conversion function. This work aims to take a step forward by obtaining a second relationship between the two kinetic parameters, so as to be able to calculate each of them.

EXPERIMENTAL

A Derivatograph C (MOM Budapest) was used to record the DDTA, DTA, T and TG curves. Calcium oxalate ($CaC_2O_4 \cdot H_2O$) and a glass of the system $CaO–MgO–SiO_2–Al_2O_3$ were heated. Heating rates were 10 K

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min^{-1} for the dehydration of calcium oxalate and 3.25, 5, 7.5, 10 and 15 K min^{-1} for the glass crystallization; alumina as reference, alumina holders and an air atmosphere were used.

THEORY

The following assumption and notations [1,2] are used

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(1-\alpha)^n \tag{2}$$

where

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

and the letters have their usual meanings [3].

$$b=\mathrm{d}T/\mathrm{d}t=\mathrm{const.} \tag{4}$$

$$s=E/RT^2b \tag{5}$$

The mathematical requirement for the extremum on the DTG curve, and according to [1] on the DTA curve also is

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}=\frac{\mathrm{d}k}{\mathrm{d}t}(1-\alpha)^n+k\frac{\mathrm{d}}{\mathrm{d}t}(1-\alpha)^n=0 \tag{6}$$

Also, the mathematical condition required for the extremum points on the DDTA curve is [2]

$$\frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3}=\frac{\mathrm{d}^2k}{\mathrm{d}t^2}(1-\alpha)^n+2\frac{\mathrm{d}k}{\mathrm{d}t}\frac{\mathrm{d}}{\mathrm{d}t}(1-\alpha)^n+k\frac{\mathrm{d}^2}{\mathrm{d}t^2}(1-\alpha)^n=0 \tag{7}$$

Taking into account eqns. (3), (4) and (5) one may write

$$\frac{\mathrm{d}k}{\mathrm{d}t}=Ab\frac{E}{RT^2}\exp(-E/RT)=sk \tag{8}$$

and

$$\frac{\mathrm{d}^2k}{\mathrm{d}t^2}=s^2k-\frac{2b}{T}sk=sk\left(s-\frac{2b}{T}\right) \tag{9}$$

As $s \gg 2b/T$ (i.e. $E/RT \gg 2$), eqn. (9) may be rewritten

$$\mathrm{d}^2k/\mathrm{d}t \approx s^2k \tag{10}$$

Taking into account eqns. (2) and (3) one may also write

$$\frac{\mathrm{d}}{\mathrm{d}t}(1-\alpha)^n=-nk(1-\alpha)^{2n-1} \tag{11}$$

and

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}(1-\alpha)^n=n(2n-1)k^2(1-\alpha)^{3n-2}-nsk(1-\alpha)^{2n-1} \tag{12}$$

By introducing eqns. (8), (10), (11) and (12) into eqns. (6) and (7) one obtains

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} = s_\mathrm{m}k_\mathrm{m}(1-\alpha_\mathrm{m})^n - nk_\mathrm{m}^2(1-\alpha_\mathrm{m})^{2n-1} = 0 \tag{13}$$

and

$$\frac{\mathrm{d}^3\alpha}{\mathrm{d}t^3} = n(2n-1)k_\mathrm{f}^3(1-\alpha_\mathrm{f})^{3n-2} - 3ns_\mathrm{f}k_\mathrm{f}^2(1-\alpha_\mathrm{f})^{2n-1} + s_\mathrm{f}^2k_\mathrm{f}(1-\alpha_\mathrm{f})^n = 0 \tag{14}$$

where the subscripts m and f mean the extremum point on the DTA curve and the extremum point on the DDTA curve respectively.

These equations may be divided by $s_\mathrm{m}k_\mathrm{m}(1-\alpha_\mathrm{m})^n$ and $s_\mathrm{f}^2k_\mathrm{f}(1-\alpha_\mathrm{f})^n$ respectively in order to obtain

$$n\left[\frac{k_\mathrm{m}}{s_\mathrm{m}}(1-\alpha_\mathrm{m})^{n-1}\right] - 1 = 0 \tag{15}$$

and

$$n(2n-1)\left[\frac{k_\mathrm{f}}{s_\mathrm{f}}(1-\alpha_\mathrm{f})^{n-1}\right]^2 - 3n\left[\frac{k_\mathrm{f}}{s_\mathrm{f}}(1-\alpha_\mathrm{f})^{n-1}\right] + 1 = 0 \tag{16}$$

The terms in square brackets may be replaced by x for the sake of simplicity, and the solutions of eqns. (15) and (16) thus obtained are

$$\begin{cases} x_\mathrm{m} = 1/n \\ x_{\mathrm{f}1,2} = \dfrac{3 \pm \sqrt{1+4/n}}{2n(2n-1)} \end{cases} \tag{17}$$

The following two ratios may be written

$$\frac{x_{\mathrm{f}1}}{x_\mathrm{m}} = \left(\frac{T_{\mathrm{f}1}}{T_\mathrm{m}}\right)^2\left(\frac{1-\alpha_{\mathrm{f}1}}{1-\alpha_\mathrm{m}}\right)^{n-1}\exp\frac{E}{R}\,\frac{(T_\mathrm{m}-T_{\mathrm{f}1})}{T_\mathrm{m}T_{\mathrm{f}1}} = \frac{3+\sqrt{1+4/n}}{2(2n-1)} \tag{18}$$

and

$$\frac{x_{\mathrm{f}2}}{x_\mathrm{m}} = \left(\frac{T_{\mathrm{f}2}}{T_\mathrm{m}}\right)^2\left(\frac{1-\alpha_{\mathrm{f}2}}{1-\alpha_\mathrm{m}}\right)^{n-1}\exp\frac{E}{R}\,\frac{(T_\mathrm{m}-T_{\mathrm{f}2})}{T_\mathrm{m}T_{\mathrm{f}2}} = \frac{3-\sqrt{1+4/n}}{2(2n-1)} \tag{19}$$

The rough approximations may be made

$T_{\mathrm{f}1} \approx T_\mathrm{m}$; $T_{\mathrm{f}2} \approx T_\mathrm{m}$; $\alpha_{\mathrm{f}1} \approx \alpha_\mathrm{m}$; $\alpha_{\mathrm{f}2} \approx \alpha_\mathrm{m}$

Taking into account these approximations, eqns. (18) and (19) become,

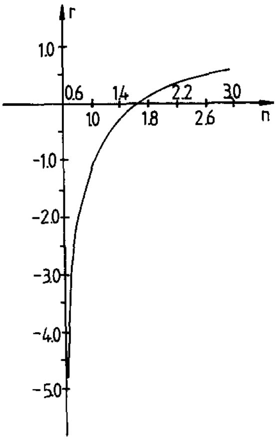

Fig. 1. The index r as a function of the reaction order n.

after taking logarithms

$$\frac{E}{R}\,\frac{(T_{\rm m}-T_{\rm f1})}{T_{\rm m}T_{\rm f1}}=\ln\frac{3+\sqrt{1+4/n}}{2(2n-1)} \tag{20}$$

$$\frac{E}{R}\,\frac{(T_{\rm m}-T_{\rm f2})}{T_{\rm m}T_{\rm f2}}=\ln\frac{3-\sqrt{1+4/n}}{2(2n-1)} \tag{21}$$

Finally, the ratio of eqns. (20) and (21) leads to

$$r=\frac{T_{\rm m}-T_{\rm f1}}{T_{\rm m}-T_{\rm f2}}=\frac{\ln\dfrac{3+\sqrt{1+4/n}}{2(2n-1)}}{\ln\dfrac{3-\sqrt{1+4/n}}{2(2n-1)}} \tag{22}$$

Mathematical reasons demand that n should be higher than 0.5.

Equation (22) may be considered as defining a shape index of the DTA curve, r. A plot of r versus n ranging from 0.60–3 is given in Fig. 1.

Based on these theoretical considerations the following algorithm to compute the kinetic parameters may be set.

1. The three temperatures corresponding to the extremum points on the DTA and DDTA curves obtained at the same heating rate b are used in order to compute the value of r by using the formula

$$r=\frac{T_{\rm m}-T_{\rm f1}}{T_{\rm m}-T_{\rm f2}}$$

2. By means of Fig. 1 and the computed value of r, the value of n is obtained.

3. The temperatures obtained experimentally and the value of n as given by step 2 are used to compute the value of the activation energy E by means of either

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

or

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

4. If the values of the conversion degree corresponding at least to one of the three temperatures and the heating rate used to record the curves are known, the preexponential factor A may be also computed by means of the following general formula

$$A = \frac{x_e\left(\dfrac{E}{RT_e^2}\right) b \exp(E/RT_e)}{(1 - \alpha_e)^{n-1}}$$

TABLE 1

Kinetic parameters computed according to the proposed algorithm as compared with the values obtained by other methods

Substance and process	Heating rate (K min^{-1})	Temperature (K)	Kinetic parameters					
			Computed acc. to algorithm			From other methods		
			n	E (kcal mol^{-1})	A (s^{-1})	n	E (kcal mol^{-1})	A
Calcium oxalate dehydration	10	$T_{f1} = 456$				according to ref. 4		
		$T_{f2} = 490$						
		$T_m = 474$	0.96	25.4	5×10^9	1	23.5	10^9
Glass crystallization	5	$T_{f1} = 1128$						
		$T_{f2} = 1167$						
		$T_m = 1147$	1.02	124.4				
	7.5	$T_{f1} = 1130$						
		$T_{f2} = 1183$						
		$T_m = 1163$	0.85	96.0				
	10	$T_{f1} = 1141$						
		$T_{f2} = 1184$						
		$T_m = 1163$	0.99	118.0				
	15	$T_{f1} = 1163$				according to the		
		$T_{f2} = 1208$				plot of ln b vs. $\frac{1}{T_m}$		
		$T_m = 1178$	1.22	102.6			95.0	

where the subscript e means the extremum point whose conversion and temperature are known.

RESULTS AND CONCLUSIONS

The algorithm was used to analyse the results for the dehydration of calcium oxalate and for the crystallization of a glass. The three temperatures recorded for the two substances are given in Table 1, together with the computed kinetic parameters and the results obtained by other methods.

A good agreement of the values obtained for oxalate dehydration with those given in the literature [4] may be noted.

The temperatures of the extremum point on the DTA curve for the glass heated at different heating rates were processed by means of a method described elsewhere [5] by plotting ln b versus $1/T_m$, and the computed activation energy is also given in Table 1. The two values for the activation energy are also in good agreement.

We may conclude, therefore, that the algorithm we have proposed offers a fast method for estimating the kinetic parameters of both a decomposition reaction and a crystallization process, and gives results in good agreement with those obtained by other methods.

Another feature of the method we propose is that the formulae obtained both for the activation E and for the reaction order n do not contain the heating rate. The same result is obtained even if the approximation $s \gg 2b/T$ is not made. In this case the following equation to replace eqns. (18) and (19) is obtained:

$$\frac{x_{f1,2}}{x_m} = \left(\frac{T_{f1,2}}{T_m}\right)^2 \left(\frac{1-\alpha_{f1,2}}{1-\alpha_m}\right)^{n-1} \exp\frac{E}{R}\left(\frac{1}{T_m} - \frac{1}{T_{f1,2}}\right)$$

$$= \frac{3n \pm \sqrt{n^2(1+16RT_{f1,2}/E) + 4n(1-2RT_{f1,2}/E)}}{2n(2n-1)}$$

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