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A new method to estimate kinetic parameters from a single non-isothermal DSC curve

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According to our previous paper [1], the reaction rate equation used to determine non-isothermal kinetic parameters by a single non-isothermal DSC curve (see Fig. 1) is

$$\frac{d\alpha}{dt} = Af(\alpha)\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right]\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α, T, $f(\alpha)$, T_0, t, R, A and E have the usual meanings [1,2].
Differentiation of eqn. (1) with respect to T gives

$$\frac{d\left(\frac{d\alpha}{dt}\right)}{dT} = Af(\alpha)\, e^{\frac{-E}{RT}}\left\{\frac{E}{RT^2}\left[\frac{2T_0}{T} + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right] + \frac{A}{\phi}\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right]^2 f'(\alpha)\, e^{\frac{-E}{RT}}\right\} \tag{2}$$

where ϕ is the constant heating rate.

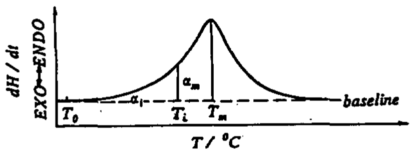

Fig. 1. Schematic diagram of typical DSC curve.

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TABLE 1

Several kinetic functions used for the present analysis

Function No.	Function form: Integral form $G(\alpha)$	Differential form $f(\alpha)$	$f'(\alpha)$	$f''(\alpha)$
1	α^2	$\frac{1}{2}\alpha^{-1}$	$-\frac{1}{2}\alpha^{-2}$	α^{-3}
2	$\alpha+(1-\alpha)\ln(1-\alpha)$	$-[\ln(1-\alpha)]^{-1}$	$-(1-\alpha)^{-1}[\ln(1-\alpha)]^{-2}$	$-[2+\ln(1-\alpha)]$ $(1-\alpha)^{-2}[\ln(1-\alpha)]^{-3}$
3	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	$\frac{3}{2}[(1-\alpha)^{-1/3}-1]^{-1}$	$-\frac{1}{2}(1-\alpha)^{-4/3}[(1-\alpha)^{-1/3}-1]^{-2}$	$-\frac{1}{3}(1-\alpha)^{-7/3}[(1-\alpha)^{-1/3}-1]^{-2}$ $\{2-(1-\alpha)^{-1/3}[(1-\alpha)^{-1/3}-1]^{-1}\}$
4, 5	$[1-(1-\alpha)^{1/3}]^n$	$\frac{3}{n}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-(n-1)}$	$-\frac{2}{n}(1-\alpha)^{-1/3}[1-(1-\alpha)^{1/3}]^{-(n-1)}$ $-\frac{n-1}{n}[1-(1-\alpha)^{1/3}]^{-n}$	$-\frac{2}{3n}(1-\alpha)^{-4/3}$ $[1-(1-\alpha)^{1/3}]^{-(n-1)}+\frac{2}{3}\frac{n-1}{n}$ $(1-\alpha)^{-1}[1-(1-\alpha)^{1/3}]^{-n}$ $+\frac{n-1}{3}(1-\alpha)^{-2/3}[1-(1-\alpha)^{1/3}]^{-(n+1)}$
	$(n=2, \frac{1}{2})$			
6	$[1-(1-\alpha)^{1/2}]^{1/2}$	$4(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{1/2}$	$-2(1-\alpha)^{-1/2}[1-(1-\alpha)^{1/2}]^{1/2}$ $+[1-(1-\alpha)^{1/2}]^{-1/2}$	$-(1-\alpha)^{-3/2}[1-(1-\alpha)^{1/2}]^{1/2}$ $-\frac{1}{2}(1-\alpha)^{-1}[1-(1-\alpha)^{1/2}]^{-1/2}$ $-\frac{1}{4}(1-\alpha)^{-1/2}[1-(1-\alpha)^{1/2}]^{-3/2}$
7	$[(1+\alpha)^{1/3}-1]^2$	$\frac{3}{2}(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$(1+\alpha)^{-1/3}[(1+\alpha)^{1/3}-1]^{-1}$ $-\frac{1}{2}[(1+\alpha)^{1/3}-1]^{-2}$	$-\frac{1}{3}(1+\alpha)^{-4/3}[(1+\alpha)^{1/3}-1]^{-1}$ $-\frac{1}{3}(1+\alpha)^{-1}[(1+\alpha)^{1/3}-1]^{-2}$ $+\frac{1}{3}(1+\alpha)^{-2/3}[(1+\alpha)^{1/3}-1]^{-3}$

8	$[(1-\alpha)^{-1/3}-1]^2$	$\frac{3}{2}(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$-2(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}$ $-\frac{1}{2}[(1-\alpha)^{-1/3}-1]^{-2}$	$\frac{2}{3}(1-\alpha)^{-2/3}[(1-\alpha)^{-1/3}-1]^{-1}$ $+\frac{2}{3}(1-\alpha)^{-1}[(1-\alpha)^{-1/3}-1]^{-2}$ $+\frac{1}{3}(1-\alpha)^{-4/3}[(1-\alpha)^{-1/3}-1]^{-3}$
9	$-\ln(1-\alpha)$	$1-\alpha$	-1	0
10–16	$[-\ln(1-\alpha)]^n$ ($n=\frac{2}{3},\frac{1}{2},\frac{1}{3}$, $4,\frac{1}{4},2,3$)	$\frac{1}{n}(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$	$-\frac{1}{n}[-\ln(1-\alpha)]^{-(n-1)}$ $-\frac{n-1}{n}[-\ln(1-\alpha)]^{-n}$	$\frac{n-1}{n}(1-\alpha)^{-1}[-\ln(1-\alpha)]^{-n}$ $+(n-1)(1-\alpha)^{-1}[-\ln(1-\alpha)]^{-(n+1)}$
17–22	$1-(1-\alpha)^n$ ($n=\frac{1}{2},3,2$, $4,\frac{1}{3},\frac{1}{4}$)	$\frac{1}{n}(1-\alpha)^{-(n-1)}$	$\frac{n-1}{n}(1-\alpha)^{-n}$	$(n-1)(1-\alpha)^{-(n+1)}$
23–27	α^n ($n=1,\frac{3}{2}$, $\frac{1}{2},\frac{1}{3},\frac{1}{4}$)	$\frac{1}{n}\alpha^{-(n-1)}$	$-\frac{n-1}{n}\alpha^{-n}$	$(n-1)\alpha^{-(n+1)}$
28	$(1-\alpha)^{-1}$	$(1-\alpha)^2$	$-2(1-\alpha)$	2
29	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$	$-2(1-\alpha)$	2
30	$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$	$-3(1-\alpha)^{1/2}$	$\frac{3}{2}(1-\alpha)^{-1/2}$

At the point of maximum transformation rate one can obtain from the well-known condition

$$\left[\frac{\mathrm{d}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\mathrm{d}T}\right]_{\substack{T=T_\mathrm{m}\\ \alpha=\alpha_\mathrm{m}}}=0$$

$$\frac{E}{RT_\mathrm{m}^2}\left[\frac{2T_0}{T_\mathrm{m}}+\frac{E}{RT_\mathrm{m}}\left(1-\frac{T_0}{T_\mathrm{m}}\right)\right]+\frac{A}{\phi}\left[1+\frac{E}{RT_\mathrm{m}}\left(1-\frac{T_0}{T_\mathrm{m}}\right)\right]^2 f'(\alpha_\mathrm{m})\,\mathrm{e}^{\frac{-E}{RT_\mathrm{m}}}=0 \tag{3}$$

Differentiation of eqn. (2) with respect to T gives

$$\frac{\mathrm{d}^2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\mathrm{d}T^2}=Af(\alpha)\,\mathrm{e}^{\frac{-E}{RT}}\left\{\frac{E}{RT^4}\left(-6T_0-\frac{3E}{R}+\frac{6ET_0}{RT}+\frac{E^2}{R^2T}-\frac{E^2T_0}{R^2T^2}\right)\right.$$
$$+\frac{A}{\phi}\frac{3E}{RT^3}\left(2T_0+\frac{E}{R}-\frac{ET_0}{RT}\right)\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]f'(\alpha)\,\mathrm{e}^{\frac{-E}{RT}}$$
$$\left.+\left(\frac{A}{\phi}\right)^2\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]^3\left[(f'(\alpha))^2+f(\alpha)f''(\alpha)\right]\mathrm{e}^{\frac{-2E}{RT}}\right\} \tag{4}$$

At the point of inflection of the DSC curve in Fig. 1, one can obtain from the condition

$$\left[\frac{\mathrm{d}^2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\mathrm{d}T^2}\right]_{\substack{T=T_\mathrm{i}\\ \alpha=\alpha_\mathrm{i}}}=0$$

$$\frac{E}{RT_\mathrm{i}^3}\left\{\frac{3T_0}{T_\mathrm{i}}+\left(\frac{E}{RT_\mathrm{i}}-3\right)\left[\frac{3T_0}{T_\mathrm{i}}+\frac{E}{RT_\mathrm{i}}\left(1-\frac{T_0}{T_\mathrm{i}}\right)\right]\right\}$$
$$+\frac{A}{\phi}\frac{3E}{RT_\mathrm{i}^2}\left[\frac{2T_0}{T_\mathrm{i}}+\frac{E}{RT_\mathrm{i}}\left(1-\frac{T_0}{T_\mathrm{i}}\right)\right]$$
$$\times\left[1+\frac{E}{RT_\mathrm{i}}\left(1-\frac{T_0}{T_\mathrm{i}}\right)\right]f'(\alpha_\mathrm{i})\,\mathrm{e}^{\frac{-E}{RT_\mathrm{i}}}+\left(\frac{A}{\phi}\right)^2\left[1+\frac{E}{RT_\mathrm{i}}\left(1-\frac{T_0}{T_\mathrm{i}}\right)\right]^3$$
$$\times\left[(f'(\alpha_\mathrm{i}))^2+f(\alpha_\mathrm{i})f''(\alpha_\mathrm{i})\right]\mathrm{e}^{\frac{-2E}{RT_\mathrm{i}}}=0 \tag{5}$$

TABLE 2

Calculated values of kinetic parameters for the dehydration process for compounds **I–III**

Compd.	Ozawa and Kissinger methods							This work									
	ϕ	T_m	E_O	E_K	log A_K	r_O	r_K	ϕ	T_0	T_i	T_m	α_i	α_m	E	log A	$G(\alpha)$
I	5	126.0	182.0	184.6	22.2	0.99	0.99	5	104.8	120.5	126.0	0.31	0.66	187.8	22.1	$-\ln(1-\alpha)$
	10	130.6														
	15	133.7														
	20	135.8														
II	5	151.6	156.7	157.6	17.4	0.99	0.99	5	128.0	145.5	151.6	0.25	0.55	165.0	17.6	$1-(1-\alpha)^{1/2}$
	10	157.4														
	15	160.3														
	20	164.9														
III	5	125.8	101.2	99.7	10.8	0.96	0.95	5	82.5	118.7	125.8	0.34	0.66	102.2	10.8	$[1-(1-\alpha)^{1/2}]^{1/2}$
	10	138.4														
	15	140.3														
	20	142.2														

Notation: ϕ, heating rate (°C min^{-1}); T, temperature (°C); E, apparent activation energy (kJ mol^{-1}); A, pre-exponential constant (s^{-1}); r, linear correlation coefficient; subscript O, data obtained by Ozawa's method; subscript K, data obtained by Kissinger's method; T_0, the initial point of the deviation from the baseline of the DSC curve (°C); subscript i, the point of inflection of the DSC curve; subscript m, the point of maximum transformation rate of the DSC curve; α, the fraction of the material reacted; $G(\alpha)$, integral mechanism function.

By substituting all the forms of $f(\alpha)$ listed in Table 1 and the corresponding forms of $f'(\alpha)$ and $f''(\alpha)$ and the values of T_0, T_i, T_m, ϕ, α_i and α_m into eqns. (3) and (5), the corresponding values of E and A may be determined by computer. Equations (3) and (5) are suitable for computer programming for fast computations. For example, by substituting the original data of the dehydration process of the ammonium salt monohydrate (**I**), potassium salt monohydrate (**II**) and copper salt tetrahydrate (**III**) of 3-nitro-1,2,4-triazol-5-one, listed in Table 2, and all the forms of $f(\alpha)$, $f'(\alpha)$ and $f''(\alpha)$ into the eqns. (3) and (5), the corresponding values of E and A and the probable mechanism functions (see Table 2) are obtained by the method of logical choices [1]. These values of E and A are in agreement with the calculated values obtained by the methods of Ozawa [3] and Kissinger [4]. This fact shows that eqns. (3) and (5) are suitable for computing the values of E and A.

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