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A method to determine the non-isothermal kinetic parameters and select the most probable mechanism function using a single non-isothermal DSC curve

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Abstract

A method is established that uses only two characteristic points of a single non-isothermal DSC curve, $(d/dT)(d\alpha/dt) = 0$ and $(d^2/dT^2)(d\alpha/dt) = 0$, from the classic isothermal kinetic equation $d\alpha/dt = Af(\alpha)e^{-E/RT}$. Using this method, it is very easy to estimate the non-isothermal kinetic parameters of activation energy E and pre-exponential factor A and to select the most probable mechanism function from those commonly used; this may increase our understanding of the experimental phenomena. Two indexes of peak shape are defined for judging whether the peak is treatable or not. A typical calculation is given. The computed results for E and A coincide very well with those derived by commonly used methods; the selected mechanism function is also reasonable.

Keywords: DSC; Kinetics; Mechanism; Non-isothermal

1. Introduction

The mathematical treatment of experimental results of differential scanning calorimetric (DSC) or thermogravimetric (TG) analysis to estimate the kinetic parameters of a thermal decomposition is very tedious and time consuming. Many mathematical models have been developed to overcome these difficulties. The

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commonly used models may be divided into two categories: differential methods and integration methods. All have their merits and drawbacks. The most frequently employed methods are briefly described below.

The equation of Achar et al. [1] which uses a differential treatment, is as follows, where $f(\alpha)$ is the differential form of the mechanism function

$$\ln\left[\frac{1}{f(\alpha)}\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right] = \ln A - \frac{E}{RT} \tag{1}$$

This method has general applicability. It is clearly shown that there is a linear relationship between the logarithm of the factor $[1/f(\alpha)](\mathrm{d}\alpha/\mathrm{d}t)$ and the reciprocal of the reaction temperature T. From a thermal analysis curve, we can obtain many sets of data of T, α and $(\mathrm{d}\alpha/\mathrm{d}t)$, and then calculate the kinetic parameters A and E using linear regression for every trial of mechanism function $f(\alpha)$. The E and A values obtained with the largest linear regression coefficient might be the chosen results and the corresponding mechanism function might be the most probable mechanism function. The initial data needed for the method must usually comprise more than ten sets to ensure calculation accuracy. The calculated results of the linear regression coefficient are nearly all greater than 0.99. Hence, it is very difficult to choose the most probable results from these calculations.

The famous Kissinger method [2] is also a differential treatment

$$\ln\left(\frac{\phi}{T_{\mathrm{m}}^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_{\mathrm{m}}} \tag{2}$$

This method assumes that the mechanism function $f(\alpha)$ is $(1-\alpha)^n$, that the reaction rate reaches its maximum at the peak summit, that $n(1-\alpha)^{n-1}$ is not affected by the heating rate ϕ, and that $n(1-\alpha)^{n-1} \approx 1$. From thermal analysis curves using different heating rates ϕ_i, we obtain their peak temperatures $(T_{\mathrm{m}})_i$, and then calculate the parameters A and E from Eq. (2) using a linear regression method. For any thermal analysis curves displaying peaks, the values of A and E can always be obtained.

The commonly used integration methods are those of Ozawa [3] and Doyle [4], Setava and Šesták [5], and MacCallum and Tanner [6].

The Ozawa [3] and Doyle [4] equation is as follows, where $G(\alpha)$ represents the integration form of the mechanism function

$$\lg \phi = \lg \frac{AE}{RG(\alpha)} - 2.315 - 0.4567\frac{E}{RT} \tag{3}$$

The mathematical model is irrelevant to the mechanism function for calculating E. Its linearity is better than that of the Kissinger equation. Therefore, this calculated value of E should always be used as a criterion for judging whether or not another method's results are correct. However, it cannot solve the value of A as well as select the mechanism function.

The Satava–Šesták equation [5] is

$$\lg G(\alpha) = \lg \frac{AE}{\phi R} - 2.315 - 0.4567\frac{E}{RT} \tag{4}$$

The MacCallum–Tanner equation [6] is

$$\lg G(\alpha)\ \lg \frac{AE}{\phi R} - 0.4828E^{0.4357} - \frac{0.449 + 0.217E}{0.001} \frac{1}{T} \tag{5}$$

These two methods also need a lot of data to try every possible mechanism function $G(\alpha)$ with linear regression, and values of A and E with large regression coefficients can always be obtained regardless of whether the mechanism function is true or false for the reaction process. Therefore, it is very difficult to choose the most probable mechanism function and corresponding parameters of A and E from the calculated results.

This article describes a method that uses fewer initial data to calculate the values of A and E, and selects the most probable mechanism function more easily.

2. Theoretical

The typical decomposition reaction equation may be expressed as

$$\mathrm{A(s)} \rightarrow \mathrm{B(s)} + \mathrm{C(g)} \tag{6}$$

The classical isothermal reaction rate equation is expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{7}$$

where t is time in s, α is fraction of reacted sample, $f(\alpha)$ is the reaction mechanism function, and k is the reaction rate constant in s^{-1}.

Assuming that the non-isothermal reaction is similar to an isothermal reaction in an infinitesimal time, the reaction rate equation of the non-isothermal reaction may also be expressed as Eq. (7), and the relationship between reaction rate constant and reaction temperature might be expressed in the Arrhenius equation

$$k = A\mathrm{e}^{-E/RT} \tag{8}$$

where A is the pre-exponential factor in s^{-1}, E is reaction activation energy in J mol^{-1}, R is the universal constant, 8.314 J mol^{-1} K^{-1}, and T is reaction temperature in K.

With a linear temperature increase

$$T = T_0 + \phi t \tag{9}$$

where T_0 is the initial temperature at which the peak on the DSC curve deviates from its baseline in K, ϕ is heating rate in K min^{-1}, t is heating time in s^{-1} and T is the reaction temperature at time t in K.

Combining Eqs. (7)–(9)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\phi} f(\alpha)\mathrm{e}^{-E/RT} \tag{10}$$

Eq. (10) describes a DSC curve with a linear heating rate ϕ. The inflections and maxima of the peaks can now be used to establish a kinetic equation.

At the peak summit on a DSC curve, the reaction reaches its maximum, and the boundary conditions may be expressed as

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\bigg|_{T=T_\mathrm{m},\alpha=\alpha_\mathrm{m}}=0 \tag{11}$$

where T_m is the summit temperature in K, and α_m is the fraction of reacted sample from the beginning to the peak summit.

Differentiating Eq. (10) with respect to T, and considering Eq. (9), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)=Af(\alpha)\mathrm{e}^{-E/RT}\left[\frac{A}{\phi}f'(\alpha)\mathrm{e}^{-E/RT}+\frac{E}{RT^2}\right] \tag{12}$$

Therefore, from Eqs. (11) and (12)

$$\frac{A}{\phi}f'(\alpha_\mathrm{m})\mathrm{e}^{-E/RT_\mathrm{m}}+\frac{E}{RT_\mathrm{m}^2}=0 \tag{13}$$

At the peak inflection on the DSC curve, the boundary condition may be expressed

$$\frac{\mathrm{d}^2}{\mathrm{d}T^2}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\bigg|_{T=T_\mathrm{i},\alpha=\alpha_\mathrm{i}}=0 \tag{14}$$

where T_i is the temperature at the peak inflection in K, and α_i is the fraction of reacted sample from the beginning to the inflection.

Differentiating Eq. (12) with respect to T, Eq. (15) is established

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}T^2}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)&=Af(\alpha)\mathrm{e}^{-E/RT}\left\{\frac{A^2}{\phi^2}f'^2(\alpha)\mathrm{e}^{-2E/RT}+\frac{3AE}{\phi RT^2}f'(\alpha)\mathrm{e}^{-E/RT}\right\}\\&\quad+Af(\alpha)\mathrm{e}^{-E/RT}\left\{\frac{A^2}{\phi^2}f''(\alpha)f(\alpha)\mathrm{e}^{-2E/RT}+\frac{E^2-2ERT}{R^2T^4}\right\}\end{aligned} \tag{15}$$

Therefore, combining Eqs. (14) and (15), we obtain

$$\frac{A^2}{\phi^2}f'^2(\alpha_\mathrm{i})\mathrm{e}^{-2E/RT_\mathrm{i}}+\frac{3AE}{\phi RT_\mathrm{i}^2}f'(\alpha_\mathrm{i})\mathrm{e}^{-E/RT_\mathrm{i}}+\frac{A^2}{\phi^2}f''(\alpha_\mathrm{i})f(\alpha_\mathrm{i})\mathrm{e}^{-2E/RT_\mathrm{i}}+\frac{E^2-2ERT_\mathrm{i}}{R^2T_\mathrm{i}^4}=0 \tag{16}$$

Combining Eqs. (13) and (16), we obtain Eqs. (17) and (18)

$$BE\mathrm{e}^{2EU}+CE\mathrm{e}^{EU}+DE\mathrm{e}^{2EU}+\frac{E-2RT_\mathrm{i}}{R^2T_\mathrm{i}^4}=0 \tag{17}$$

$$A=-\frac{E\phi\mathrm{e}^{E/RT_\mathrm{m}}}{RT_\mathrm{m}^2f'(\alpha_\mathrm{m})} \tag{18}$$

where

$$B=\left[\frac{f'(\alpha_i)}{f'(\alpha_m)}\frac{1}{RT_m^2}\right]^2$$

$$C=-\frac{f'(\alpha_i)}{f'(\alpha_m)}\frac{3}{R^2T_m^2T_i^2}$$

$$D=\frac{f''(\alpha_i)f(\alpha_i)}{f'^2(\alpha_m)}\frac{1}{R^2T_m^4}$$

$$U=\frac{T_i-T_m}{RT_iT_m}$$

For DSC analysis, the following relations are true

$$\alpha=\frac{H}{H_0} \tag{19}$$

$$\frac{d\alpha}{dt}=\frac{1}{H_0}\frac{dH}{dt} \tag{20}$$

where H_0 is the total reaction enthalpy in J, H is the reaction enthalpy from the beginning to time t in J, dH/dt is the exothermic rate (or endothermic rate for endothermic reactions) of the reaction in J s^{-1}.

It is clear that Eq. (17) is only related to the reaction activation energy E and mechanism function $f(\alpha)$, as well as to its first-order derivative $f'(\alpha)$ and second-order derivative $f''(\alpha)$. For a measured DSC curve with heating rate ϕ, we can easily obtain values of α_i and α_m corresponding to the inflection temperature T_i and the summit temperature T_m, respectively. In order to solve the equation, we try every possible mechanism function, except the first-order derivative $f'(\alpha)$ which equals zero, assuming E falls in the range 50–500 J mol^{-1}, which is suitable for most decomposition reactions. The calculation is carried out on a computer using a dichotomy method. After computing the value of E from Eq. (17), we can also easily calculate the value of A from Eq. (18). The calculated results show few similar values. Therefore, it is very straightforward to choose the most probable mechanism function and the corresponding values of A and E. The commonly used mechanism functions in non-isothermal reaction kinetics are summarized in Table 1.

3. Indexes of peak shape

Because the thermal behaviour of real samples is very complicated, their DSC curves might be very different. Not all measured curves are mathematically treatable. Therefore, we define two indexes of peak shape for judging whether the peak is treatable or not

$$H_w=\frac{H_{max}}{W_{hp}} \tag{21}$$

$$\tau_m=\frac{\left(\frac{dH}{dt}\right)_{max}}{(T_m-T_0)M} \tag{22}$$

Table 1
Commonly used mechanism functions for non-isothermal reaction kinetics

No.	Name	Mechanism	$f(\alpha)$	Ref.
1	Parabolic law	1-D diffusion	$\frac{1}{2}\alpha^{-1}$	7
2	Valensi eq.	2-D diffusion	$[-\ln(1-\alpha)]^{-1}$	7
3	Jander eq.	2-D diffusion $n=\frac{1}{2}$, 2	$\frac{2}{n}(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{1-n}$	8
4	Jander eq.	3-D diffusion $n=\frac{1}{2}$, 2	$\frac{3}{n}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{1-n}$	9
5	G.-B. eq. [a]	3-D diffusion	$\frac{3}{2}[(1-\alpha)^{-1/3}-1]^{-1}$	7
6	Anti-Jander eq.	3-D diffusion	$\frac{3}{2}(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	7
7	Z.-L.-T. eq. [b]	3-D diffusion	$\frac{3}{2}(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	7
8	Avrami–Erofeev eq.	Nucleation and growth, $n=\frac{1}{4}, \frac{1}{3}, \frac{2}{5}, \frac{1}{2}, \frac{2}{3}, \frac{3}{4}, 1, \frac{3}{2}, 2, 3, 4$	$\frac{1}{n}(1-\alpha)[-\ln(1-\alpha)]^{1-n}$	10, 11
9	P.–T. eq. [c]		$\alpha(1-\alpha)$	10
10	Mampel power law	$n=\frac{1}{4}, \frac{1}{3}, \frac{1}{2}, \frac{3}{2}, 2$	$\frac{1}{n}\alpha^{1-n}$	7
11	Chemical reaction	$n=\frac{1}{4}, \frac{1}{3}, \frac{1}{2}, 2, 3, 4$	$\frac{1}{n}(1-\alpha)^{1-n}$	7, 10, 1
12	Chemical reaction		$(1-\alpha)^2$	7, 8
13	Chemical reaction		$2(1-\alpha)^{3/2}$	7
14	Exponent law	$n=1, 2$	$\frac{1}{n}\alpha$	10

[a] Ginstling–Brounstein equation. [b] Zhuralev–Lesokin–Tempelman equation. [c] Prout–Tompkins equation.

where H_{max} is the peak height at its summit in mm, W_{hp} is the peak width at half H_{max} in mm, $(dH/dt)_{max}$ is the exothermic rate at the peak summit on the DSC curve in mJ s^{-1}, T_m is the summit temperature in K, T_0 is the initial temperature of the peak in K and M is the sample mass in g.

Our results confirm that only when these indexes satisfy both the conditions $0.13 \leq H_w \leq 1.0$ and $1.8 \times 10^{-2} \leq \tau_m \leq 9.7 \times 10^{-2}$ is the peak treatable.

4. Computed example

4.1. Sample

The hydrated copper salt of 3-nitro-1,2,4-triazol-5-one [$Cu(NTO)_2 \cdot 4H_2O$] was synthesized and purified just before use.

4.2. Instruments and conditions

In the present experiments, the initial data needed for calculating the kinetic parameters A and E were all obtained using a CDR-1 differential scanning calorimeter (Shanghai Tianping Instrument Factory, China) with an aluminium cell (diameter 5 mm, height 3 mm), whose side is rolled up with a lid. The conditions of DSC analysis were: sample mass, less than 1 mg; heating rates, 2, 5, 10 and 20 K min^{-1}, respectively; calorimetric sensitivity, ±10.5 mJ s^{-1}; the atmosphere was self-generating; reference sample, α-Al_2O_3.

4.3. Initial data

The DSC curve of $Cu(NTO)_2 \cdot 4H_2O$ has a flat endothermic peak corresponding to its dehydration process. When the heating rate ϕ is 5.1 K min^{-1}, H_m equals 1.0, and τ_m equals 0.096 mJ (K s mg)$^{-1}$. These index values confirm that this peak is mathematically treatable.

The data needed for this method are: $\phi = 5.1$ K min^{-1}, $T_i = 397.6$ K, $\alpha_i = 0.50$, $T_m = 402.4$ K, and $\alpha_m = 0.75$.

The data needed for Ozawa's method and Kissinger's method are: $\phi_1 = 2.1$ K min^{-1}, $T_{m1} = 390.2$ K; $\phi_2 = 5.1$ K min^{-1}, $T_{m2} = 402.7$ K; $\phi_3 = 10.4$ K min^{-1}, $T_{m3} = 410.2$ K; $\phi_4 = 21.0$ K min^{-1}, $T_{m4} = 414.4$ K.

The data needed for the equations of the differential and integration methods are summarized in Table 2.

4.4. Calculation results

The results obtained with our method, together with those calculated with the Ozawa equation, the Kissinger equation, the Achar–Brindley–Sharp equation, the Phadnis equation [10], the MacCallum–Tanner equation, the Satava–Šesták equation, the Agrawal equation [12], and the Universal equation [9] are all listed comparatively in Table 3. It is clear that the values of E and A, as well as the

Table 2
Data for equations of differential and integration methods

Data No. j	T_j	α_j	$(dH/dt)_j$
	K		mJ s^{-1}
1	382.7	0.0676	1.255
2	385.2	0.0915	1.757
3	387.6	0.1392	2.510
4	389.9	0.1968	3.213
5	392.4	0.2883	4.033
6	395.2	0.3852	4.770
7	397.6	0.5030	5.255
8	400.2	0.6243	5.690
9	402.4	0.7515	5.891

$\phi = 5.1$ K min^{-1}
$T_0 = 368.2$ K
$H_0 = 1262$ mJ

Table 3
Calculated results of kinetics

Method	Equation	Mech. funct. no.	E/ kJ mol^{-1}	lg A	r [a]	S [b]
This one		8, $n=2/3$	114.1	12.57		
Ozawa	Ozawa		117.4		−0.984	0.095
Kissinger	Kissinger		116.8	13.09	−0.982	0.218
Differential	Achar et al.	8, $n=2/3$	113.8	12.79	−0.997	0.024
	Phadnis	8, $n=2/3$	124.4		0.992	0.024
Integration	Satava et al.	8, $n=2/3$	124.1	14.11	−0.999	0.012
	MacCallum	8, $n=2/3$	122.8	13.90	−0.999	0.012
	Agrawal	8, $n=2/3$	123.9	17.66	−0.999	0.027
	Universal	8, $n-2/3$	126.2	12.92	−0.999	0.027

[a] Linear regression coefficient. [b] Standard error.

mechanism function selected with our method are almost the same as those with the commonly used methods, but the initial amount of data required for our method is the lowest of all the methods.

The results obtained indicate that the reaction mechanism of the dehydration process of $Cu(NTO)_2 \cdot 4H_2O$ is classified as nucleation and growth, and the mechanism function is No. 8, the Avrami–Erofeev equation with $n = 2/3$.

Substituting $f(\alpha)$ with $3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, E with 114.1 kJ mol^{-1}, ϕ with 5.1 K min^{-1} and A with 3.71×10^{12} s^{-1} in Eq. (10), we can now establish the kinetics equation of the dehydration process of $Cu(NTO)_2 \cdot 4H_2O$ as follows

$$\frac{d\alpha}{dT} = 6.56 \times 10^{13}(1-\alpha)[-\ln(1-\alpha)]^{1/3}e^{-1.37 \times 10^4/T}$$

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