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A consideration of errors and accuracy in the isoconversional methods

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Abstract

The conventional isoconversional plots, ln β versus $1/T$ and $\ln(\beta/T^2)$ versus $1/T$, have some errors in calculating the activation energy due to the use of an approximate value of $p(x)$. In order to obtain the 'exact' value of activation energy of a reaction, an iterative procedure has been established after the ratios, $H(x)$ and $h(x)$, were introduced to determine 'exact' $p(x)$ instead of the approximate values of $p(x)$ used in the conventional isoconversional plots. The iterative procedure is wide applicable, no matter how little or how great the E/RT value of the reaction is. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The isoconversional methods, Ozawa method [1] and Kissinger–Akahira–Sunose method [2,3], have been widely used to estimate activation energies regardless of the rate expressions of the reactions. The successful application is ascribed to the approximate expressions used in the integration of Arrhenius equation [4,5]. For the same reason, however, the calculated activation energies contain some errors, which are dependent on E/RT value. An analysis of the error of Kissinger–Akahira–Sunose method was reported by Ortega et al. [6]. In their work, the error was evaluated at separate E/RT values in comparison to the 'exact' integral of the Arrhenius equation. In practice, calculation of activation energy in the isoconversional methods is made over a range of E/RT values corresponding to the temperatures at different heating rates. The error of calculated activation energy is thus concerned in a regressive way with all the errors at the E/RT values within the range. This is the reason why Ozawa method can give a useful estimate of the activation energy usually although the approximation adopted in integrating the Arrhenius equation is rather rough. Nevertheless, the errors in the calculated activation energy will become larger as E/RT value decreases below 15. In the present work, through a thorough consideration of the errors of the conventional isoconversional methods, we present an improved scheme to obtain exact values for the activation energy, no matter how little or how great the E/RT value of the reaction is.

2. Theoretical

In non-isothermal analyses, the reaction rate is generally expressed by the derivative of the fractional

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conversion as Eq. (1).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E/RT} f(\alpha) \tag{1}$$

Furthermore

$$\begin{aligned} g(\alpha) &= \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_0^{t} A\mathrm{e}^{-E/RT}\,\mathrm{d}t \\ &= \frac{AE}{\beta R}\int_x^{\infty} \frac{\exp(-x)}{x^2}\,\mathrm{d}x = \frac{AE}{\beta R}p(x) \end{aligned} \tag{2}$$

where $x = E/RT$, $T_0 = 0$ K, β is the heating rate of a linear temperature-programmed process. As is well known, the p function has no analytical solution and is expressed by several approximate expressions [4,5].

$$p(x) = 0.0048\exp(-1.0516x) \tag{3}$$

$$p(x) = \frac{\exp(-x)}{x^2} \tag{4}$$

From Eq. (3) Ozawa adopted a linear plot of ln β against $1/T$ at the same fractional conversion. Similarly, a linear plot of $\ln(\beta/T^2)$ against $1/T$ from Eq. (4) was adopted by Kissinger et al.

$$\ln\beta = \left(\ln\frac{0.0048AE}{R} - \ln g(\alpha)\right) - \frac{1.0516E}{RT} \tag{5}$$

$$\ln\frac{\beta}{T^2} = \left(\ln\frac{AR}{E} - \ln g(\alpha)\right) - \frac{E}{RT} \tag{6}$$

These two methods of plotting a linear regressive curve at the same fractional conversion are the so-called isoconversional methods. The plot of $\ln(\beta/T^2)$ against $1/T$ in Eq. (6) has been proved to give an activation energy with an error within 1% when x is greater than 15 compared with the use of the 'exact' integral of Arrhenius equation [6]. The 'exact' $p(x)$ was regarded as Eq. (7).

$$p(x) = \frac{\exp(-x)}{x^2}h(x) \tag{7}$$

where

$$h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{8}$$

As a matter of fact, reaction rate should be expressed by derivative of mass decrease of a reactant (or mass increase of reaction product) as Eq. (9) in the strictest sense.

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = A\mathrm{e}^{-E/RT} f(m) \tag{9}$$

Of course, because $m = m_0(1-\alpha)$, Eq. (9) can be rewritten as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E/RT}\frac{1}{m_0} f(m_0,\alpha) \tag{10}$$

When the reaction under study is a nth order reaction, m_0 can be separated from α, that is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E/RT} m_0^{n-1}(1-\alpha)^n \tag{11}$$

In this way, Eqs. (5) and (6) should be rewritten as Eqs. (12) and (13).

$$\begin{aligned} \ln\beta = &\left(\ln\frac{0.0048AE}{R} - \ln g(m_0,\alpha) - \ln m_0\right) \\ &- \frac{1.0516E}{RT} \end{aligned} \tag{12}$$

$$\ln\frac{\beta}{T^2} = \left(\ln\frac{AR}{E} - \ln g(m_0,\alpha) - \ln m_0\right) - \frac{E}{RT} \tag{13}$$

It is evident that the initial mass of sample m_0 must be kept at constant in all measurements at different heating rates to maintain a rigorous linear relationship for Eqs. (12) and (13). However, it is often seen that the initial mass of sample was not kept constant in the literature [7,8]. When m_0 is separated with α in $f(m_0, \alpha)$, keeping the same initial mass in all measurements is not necessary since the term of m_0 can be combined into the term containing β.

If it is supposed that the initial mass of sample is kept constant in all measurements at different heating rates, then Eqs. (5) and (6) can be adopted in the following discussion for convenience. Here, we also regard Eq. (7) as exact $p(x)$, then evaluate the errors of activation energies obtained from Eqs. (5) and (6) in comparison to the exact $p(x)$. It is certain that more accurate the used approximate expression of $p(x)$, more accurate the calculated activation energies. Even although, if there is an approximate $p(x)$, no matter how rough it is, having a constant ratio to the exact $p(x)$, the approximate $p(x)$ will give the same value of activation energy as the exact $p(x)$ does. The ratio of the exact $p(x)$ (Eq. (7)) to Eq. (4) is $h(x)$ (Eq. (8)), which varies slightly with x, from 0.8910 to 0.9729

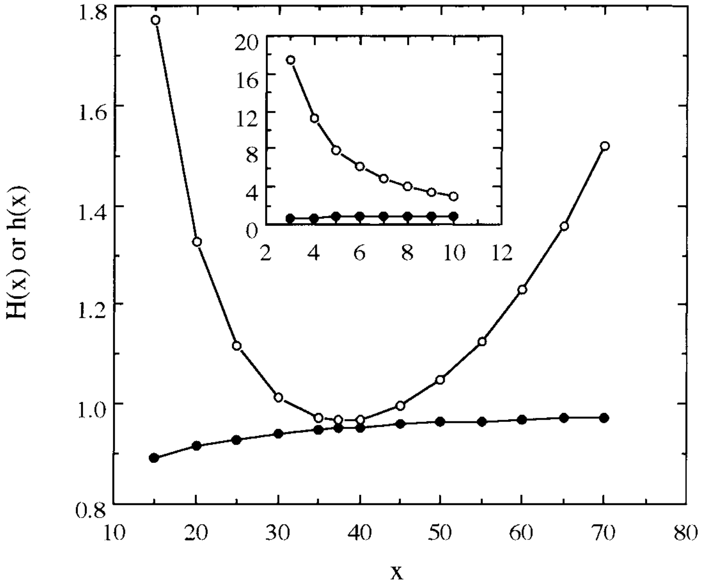

Fig. 1. The variations of $H(x)$ (open circle) and $h(x)$ (black circle) with x.

corresponding to $x = 15$–70. The ratio of the exact $p(x)$ to Eq. (3) is defined as $H(x)$.

$$H(x) = \frac{\exp(-x)h(x)/x^2}{0.0048\exp(-1.0516x)} \tag{14}$$

$H(x)$ was found to vary greatly with x value. The variations of $H(x)$ and $h(x)$ with x are shown in Fig. 1. The form of the function $H(x)$ can be obtained by fitting the ratios against x, but it has to be a long polynomial to reflect accurately these variations. After taking $h(x)$ and $H(x)$ into account, Eqs. (5) and (6) can be rewritten as Eqs. (15) and (16).

$$\ln\frac{\beta}{H} = \left(\ln\frac{0.0048AE}{R} - \ln g(\alpha)\right) - \frac{1.0516E}{RT} \tag{15}$$

$$\ln\frac{\beta}{hT^2} = \left(\ln\frac{AR}{E} - \ln g(\alpha)\right) - \frac{E}{RT} \tag{16}$$

Eqs. (15) and (16) are perfect relations since the exact function of $p(x)$ is used. It can be seen that plots of $\ln\beta$ versus $1/T$ and $\ln(\beta/T^2)$ versus $1/T$ in the conventional isoconversional methods are consequences of ignoring the variation of $H(x)$ and $h(x)$ with x. This is the reason for errors in the conventional isoconversional methods. In an accurate kinetic study, an iterative calculation should be performed by the use of Eq. (15) or Eq. (16). The iterative procedure is as follows.

- Step 1: supposing $H(x) = 1$ or $h(x) = 1$ to estimate the initial value of the activation energy E_1. The conventional isoconversional methods stop calculating at this step.
- Step 2: using E_1 calculate $H(x)$ or $h(x)$, then from Eq. (15) or Eq. (16) calculate a new value E_2 for the activation energy from the plot of $\ln(\beta/H)$ versus $1/T$ or $\ln(\beta/hT^2)$ versus $1/T$.
- Step 3: repeat step 2, replacing E_1 with E_2.

And so on until the absolute difference of $(E_i - E_{i-1})$ is less than a defined small quantity such as 0.1 kJ mol^{-1} generally. The last value E_i is the exact value of activation energy of the reaction. The error in the conventional isoconversional calculation of activation energy can then be given by value of $(E_1 - E_i)/E_i$. If the reaction mechanism is known, the exact pre-exponential factor A can be calculated from the intercept of the plot at the same time.

On the other hand, one can fit an approximate $p(x)$ more accurate than Eq. (3) over the range of x of the being considered reaction for evaluating error of activation energy calculated from Ozawa plot with the use of Eq. (3). As ordinary reactions correspond to

Table 1
The fitted $p(x)$ at the intervals of $\Delta x = 5$ from the values of the exact $p(x)$ vs. x

x	The fitted $p(x)$
10–15	$0.0376\exp(-1.1516x)$
15–20	$0.0202\exp(-1.1095x)$
20–25	$0.0126\exp(-1.0858x)$
25–30	$0.0086\exp(-1.0706x)$
30–35	$0.0063\exp(-1.0600x)$
35–40	$0.0048\exp(-1.0521x)$
40–45	$0.0038\exp(-1.0461x)$
45–50	$0.0030\exp(-1.0413x)$
50–55	$0.0025\exp(-1.0375x)$
55–60	$0.0021\exp(-1.0342x)$
60–65	$0.0018\exp(-1.0315x)$
65–70	$0.0015\exp(-1.0292x)$

range of Δx around 3–4 at usual heating rates, the fitting of a more accurate approximate $p(x)$ in the form of Eq. (3) from the exact $p(x)$ (Eq. (7)) was made at several intervals of $\Delta x = 5$. The approximate $p(x)$ function are indicated in Table 1. It can be seen that Eq. (3) is very similar to the fitted $p(x)$ at $x = 35$–40. So it is obvious that Ozawa plot using Eq. (3) will lead to a larger value at lower x values and a less value at higher x values than the exact values of activation energy.

3. Experimental

Thermal decomposition of a polyamide 6 (lot No. 1013B, Ube Industries Ltd., Japan) was carried out in a thermogravimetric analyzer (Shimadzu, TGA-50, Japan) in a flowing atmosphere of dry nitrogen (flow rate 40 $\mathrm{cm^3\,min^{-1}}$) from 373 to 873 K at heating rate of 2, 4, 6 and 10 $\mathrm{K\,min^{-1}}$, respectively. The sample cells were platinum crucibles. The sample mass was 4.867–5.384 mg. Calcium oxalate monohydrate (of special grade, Kanto Chemical Co., Japan) was dehydrated in the same thermogravimetric analyzer in nitrogen gas flow of 40 $\mathrm{cm^3\,min^{-1}}$ from ambient temperature at heating rate of 1, 2, 5 and 10 $\mathrm{K\,min^{-1}}$, respectively. The sample mass was 3.687–7.110 mg.

4. Results and discussion

It is reported that the polyamide 6 decomposes by a first-order reaction [9,10] with the formation of the charred residue about 4 wt.% at the end [11]. So the initial mass of the sample should have no effect on the calculation of the activation energy for polyamide 6 according to Eq. (11) except the last part of the decomposition. To illustrate the iterative method, iterative calculations of the activation energy for the thermal decomposition of the polyamide 6 were carried out at $\alpha = 0.3$. The results are indicated in Tables 2 and 3. It can be seen from Tables 2 and 3 that the same value of activation energy was obtained at their last step of iterative calculations. This is because the same 'exact' $p(x)$ (Eq. (7)) was used in both Eqs. (15) and (16). But Eq. (5) contained a larger error than Eq. (6) in the initial activation energy. This can be understood from Fig. 1. Here, $h(x)$ is slowly varying with x, whereas $H(x)$ varies greatly with a small change of x except in the range of $x = 35$–40. So Eq. (4) is better for calculating the activation energy.

Similar results were seen in the iterative calculations on the dehydration of calcium oxalate monohydrate as shown in Tables 4 and 5. The effect of the initial mass of the sample was not considered as the mechanism of the dehydration was not known. Discussion of the mechanism is beyond the scope of this paper. In this case Ozawa plot exhibited a slightly larger error (2.6%) in the activation energy because the E/RT values were around 24, lower than those (around 34) for the thermal decomposition of the polyamide 6. According to Fig. 1, the Ozawa plot

Table 2
An iterative calculation of activation energy for the thermal decomposition of the polyamide 6 by use of the plot of $\ln(\beta/H)$ vs. $1/T$ at $\alpha = 0.3$

β (K min^{-1})	T (K)	$h_1(x)$	E_1 (kJ mol^{-1})	$h_2(x)$	E_2 (kJ mol^{-1})	$h_3(x)$	E_3 (kJ mol^{-1})
2	684.8	1.0	197.6	0.9827	196.6	0.9836	196.5
4	697.4	1.0		0.9858		0.9869	
6	706.6	1.0		0.9884		0.9896	
10	716.0	1.0		0.9914		0.9927	

Table 3
An iterative calculation of activation energy for the thermal decomposition of the polyamide 6 by use of the plot of $\ln(\beta/hT^2)$ vs. $1/T$ at $\alpha = 0.3$

β (K min^{-1})	T (K)	$h_1(x)$	E_1 (kJ mol^{-1})	$h_2(x)$	E_2 (kJ mol^{-1})	$h_3(x)$	E_3 (kJ mol^{-1})
2	684.8	1.0	196.2	0.9475	196.5	0.9476	196.5
4	697.4	1.0		0.9466		0.9467	
6	706.6	1.0		0.9460		0.9461	
10	716.0	1.0		0.9453		0.9454	

Table 4
An iterative calculation of activation energy for dehydration of the calcium oxalate monohydrate by use of the plot of $\ln(\beta/H)$ vs. $1/T$ at $\alpha = 0.4$

β (K min^{-1})	T (K)	$h_1(x)$	E_1 (kJ mol^{-1})	$h_2(x)$	E_2 (kJ mol^{-1})	$h_3(x)$	E_3 (kJ mol^{-1})
1	397.5	1.0	85.6	1.0919	83.5	1.1090	83.4
2	407.9	1.0		1.1094		1.1277	
5	422.7	1.0		1.1355		1.1555	
10	434.1	1.0		1.1565		1.1779	

Table 5
An iterative calculation of activation energy for dehydration of the calcium oxalate monohydrate by use of the plot of $\ln(\beta/hT^2)$ vs. $1/T$ at $\alpha = 0.4$

β (K min^{-1})	T (K)	$h_1(x)$	E_1 (kJ mol^{-1})	$h_2(x)$	E_2 (kJ mol^{-1})	$h_3(x)$	E_3 (kJ mol^{-1})
1	397.5	1.0	83.1	0.9303	83.4	0.9305	83.4
2	407.9	1.0		0.9287		0.9289	
5	422.7	1.0		0.9264		0.9266	
10	434.1	1.0		0.9246		0.9248	

is good only with $x = 35$–40, the plot of $\ln(\beta/T^2)$ against $1/T$ is better when x is greater than 15. When x is lower than 15, the plot of $\ln(\beta/T^2)$ against $1/T$ will also exhibit an increased error in value of calculated activation energy. Maybe the increased error in value of calculated activation energy is still smaller than the experimental error in some cases. But a perfect calculation method is always expected, at least to know how much the calculation error involved in a calculated result from the experimental data. Therefore, the iterative calculation by means of Eq. (15) or Eq. (16) is essential for obtaining the exact value of activation energy of an interested reaction, especially for the reaction of which E/RT is lower than 15.

5. Conclusions

Errors in calculating the activation energy of conventional isoconversional plots, $\ln\beta$ versus $1/T$ and $\ln(\beta/T^2)$ versus $1/T$, are due to ignoring the variation of $H(x)$ and $h(x)$ with x. Iterative calculations based on consideration of change in $H(x)$ and $h(x)$ by means of plots of $\ln(\beta/H)$ versus $1/T$ or $\ln(\beta/hT^2)$ versus $1/T$ give the 'exact' value of activation energy, no matter how little or how great the E/RT value of the reaction is. The 'exact' value of activation energy is dependent on the 'exact' $p(x)$ adopted. The procedure of iterative calculations is general applicable, no matter what $p(x)$ is regarded as exact $p(x)$.

The effect of the initial mass of sample on calculation of kinetic parameters should be considered. In the cases where mechanism of the being considered reaction is unknown, keeping initial mass of sample at a fixed constant in all measurements is safe. If initial mass of sample is different in the measurements at different heating rates, the exact value of pre-exponential factor cannot be obtained at least.

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