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Iterative method to improve calculation of the pre-exponential factor for dynamic thermogravimetric analysis measurements

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Abstract

The conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ usually has a large error of about -10% in calculation of the pre-exponential factor as a consequence of assuming $h(x)=1$. Iterative calculation using the plot of $\ln(\beta/hT^2)$ versus $1/T$ is thus suggested. It is illustrated that the iterative method can greatly improve calculation for the pre-exponential factor. Success in calculation for the pre-exponential factor is accompanied by an enhanced accuracy in value of activation energy given by the iterative method in comparison with the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$. One explanation is due to the compensation effect of the Arrhenius parameters. The iterative method has been applied to thermal degradation reactions of poly(methyl methacrylate) (PMMA) and polyethylene.

Keywords: Iterative method; Pre-exponential factor; Isoconversional plot

1. Introduction

Dynamic measurement is a rapid and efficient method to investigate any physical and/or chemical change of a material with temperature. Thermogravimetric analysis (TGA) is a widely used technique in dynamic measurements. The innovative works of Kissinger [1], Coats and Redfern [2], Ozawa [3] and Flynn and Wall [4] allow it possible to estimate activation energy from dynamic measurements regardless of reaction mechanism. In the previous paper [5], we reported an iterative method to improve calculation of activation energy for the isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$. The results show that the iterative calculation improved activation energy by 0.3 kJ/mol for the two reactions. The small improvement (by 0.3 kJ/mol) illustrates the isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ is quite accurate in calculation of activation energy. Recently we evaluated error of the isoconversional plot in calculation of the pre-exponential factor by using theoretically designed α–T data [6]. It is found that the isoconversional plot usually has a large error of about -10% in calculation for the pre-exponential factor. In the present paper, we intend to apply the iterative method to improve the estimate of the pre-exponential factor.

2. Theoretical approach

In the present paper, we adopt nth-order reactions as examples to introduce the iterative method. For nth-order reaction, the rate expression is written as Eq. (1).

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)\times(1-\alpha)^n \tag{1}$$

In which, α is the degree of conversion, n is the reaction order, E and A are activation energy and pre-exponential factor of the Arrhenius equation, respectively. At a given heating rate β, i.e. $T=T_0+\beta t$, integrating Eq. (1) gives

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_{T_0}^{T} e^{-E/RT}\,dT \tag{2}$$

The function $g(\alpha)$ has two forms depending on the value of the reaction order.

$$g(\alpha) = -\ln(1-\alpha) \qquad n=1 \tag{3}$$

$$g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n} \qquad n\neq 1 \tag{4}$$

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Unfortunately, the temperature integral of the exponential of the Arrhenius equation has no analytical solution. Approximate expressions had to be proposed [7]. The most well used one is Eq. (5).

$$\int_0^T \mathrm{e}^{-E/RT}\mathrm{d}T = \frac{E}{R}\frac{\mathrm{e}^{-x}}{x^2}h(x) \tag{5}$$

In which, $x = E/RT$, T_0 is taken as 0 K for convenience of achieving the temperature integral, and $h(x)$ has several forms with different accuracy [7]. The more accurate form is Eq. (6), that is, the fourth Senum and Yang approximation [7,8].

$$h(x) = \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{6}$$

For most reactions, x is within 15–70, $h(x)$ is correspondingly variable from 0.8879 to 0.9726. Since the variation is not large, it is generally ignored. Thus, regarding $h(x) = 1$, one obtains

$$g(\alpha) = \frac{AE}{\beta R}\frac{\mathrm{e}^{-x}}{x^2} = \frac{AR}{E}\frac{T^2}{\beta}\mathrm{e}^{-E/RT} \tag{7}$$

Taking logarithms for Eq. (7) leads to Eq. (8).

$$\ln\left(\frac{\beta}{T^2}\right) = -\frac{E}{RT} + \left[\ln\left(\frac{AR}{E}\right) - \ln g(\alpha)\right] \tag{8}$$

Eq. (8) is relation of the so-called isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ for several heating rates at a defined degree of conversion. This plot can give an estimate for activation energy regardless of reaction mechanism. The pre-exponential factor can be estimated from the intercept after the kinetic expression $g(\alpha)$ is known. In the case the kinetic expression is known, Eq. (9) can also be applied to calculate activation energy.

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \frac{-E}{RT} + \left[\ln\left(\frac{AR}{E}\right) - \ln\beta\right] \tag{9}$$

Eq. (9) is single heating rate plot of $\ln[g(\alpha)/T^2]$ against $1/T$ for a measurement at a heating rate β.

As stated above, Eq. (8) is an approximate relation with regarding $h(x)$ as unity, although $h(x)$ is in deed variable with temperature. In order to calculate activation energy more accurately, an iterative procedure was proposed [5]. In this procedure, except for the first step, $h(x)$ is not approximately regarded as unity and is calculated based on the value of activation energy obtained at the past step. Thus, the iterative calculation is repeated according to Eq. (10).

$$\ln\left(\frac{\beta}{hT^2}\right) = \frac{-E}{RT} + \left[\ln\left(\frac{AR}{E}\right) - \ln g(\alpha)\right] \tag{10}$$

In the present paper, the pre-exponential factor is calculated by use of the iterative method. The detail of the iterative procedure is as follows.

Step 1: supposing $h(x) = 1$ to estimate the initial value (E_0) of activation energy. The pre-exponential factor (A_0) is then calculated from the intercept. This is in fact the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ (Eq. (8)).
Step 2: using the E_0 value to calculate $h(x)$, then from the plot of $\ln(\beta/hT^2)$ versus $1/T$ to calculate a new value E_1 for activation energy. Corresponding to the E_1 value, a new value A_1 of the pre-exponential factor is then calculated from the intercept.
Step 3: using the E_1 value to calculate $h(x)$, and plot $\ln(\beta/hT^2)$ versus $1/T$ again. New values of E_2 and A_2 are obtained similarly to step 2.
Step 4: repeat step 3 by replacing E_2 with E_1.

And so on until the absolute difference of $(E_i - E_{i-1})$ is zero or less than a defined small quantity such as 0.01 kJ/mol. The last E_i is regarded as the 'exact' value of activation energy of the reaction under study. Correspondingly, the last value A_i is the 'exact' value of the pre-exponential factor.

For single heating rate plot of $\ln[g(\alpha)/hT^2]$ versus $1/T$, an iterative calculation can be done in a similar way to the isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$.

3. Design of theoretical α–T data

The theoretically designed α–T data in the previous paper [6] are used here again. Two sets of values of Arrhenius parameters were assumed to calculate theoretical α–T data, i.e. $E = 180.00$ kJ/mol, $A = 1.000 \times 10^{10}\ \mathrm{s}^{-1}$, and $E = 260.00$ kJ/mol, $A = 1.000 \times 10^{16}\ \mathrm{s}^{-1}$. Five linear heating rates, 4, 6, 8, 10 and 20 K/min, were selected. The temperature integral in Eq. (2) was achieved by numerical integration using trapezoidal rule with a step size of 0.1 K between the limits of T_0 and T, corresponding to the time from zero to t [9]. The degree of conversion was then calculated from Eqs. (3) or (4) when reaction order was given. Three reaction orders, $n = 0.5$, 1.0 and 1.5, were selected. As examples, theoretical α–T data of the first-order model reactions are listed in Tables 1 and 2.

4. Results and discussion

Iterative calculations using the theoretical α–T data were carried out at the four degrees of conversion $\alpha = 0.1$, 0.3, 0.6 and 0.9. Theoretically speaking, one can expect the iterative

Table 1
Theoretical α–T data* of a model first-order reaction with $E = 180.00$ kJ/mol and $A = 1.000 \times 10^{10}\ \mathrm{s}^{-1}$

α	T_4 (K)	T_6 (K)	T_8 (K)	T_{10} (K)	T_{20} (K)
0.1	697.6	706.3	712.6	717.5	733.4
0.2	713.8	722.9	729.5	734.7	751.2
0.3	724.3	733.7	740.5	745.8	762.9
0.4	732.6	742.2	749.1	754.5	772.0
0.5	739.8	749.5	756.6	762.1	779.9
0.6	746.4	756.4	763.5	769.2	787.3
0.7	753.1	763.2	770.5	776.2	794.7
0.8	760.3	770.5	778.0	783.9	802.7
0.9	769.3	779.8	787.5	793.5	812.7

*The symbols T_4, T_6, T_8, T_{10} and T_{20} denote the temperature values calculated at 4, 6, 8, 10 and 20 K/min, respectively.

Table 2
Theoretical α–T data* of a model first-order reaction with $E=260.00$ kJ/mol and $A=1.000\times10^{16}$ s^{-1}

α	T_4 (K)	T_6 (K)	T_8 (K)	T_{10} (K)	T_{20} (K)
0.1	702.5	708.7	713.2	716.7	727.7
0.2	714.0	720.4	725.0	728.6	740.0
0.3	721.4	727.9	732.6	736.3	748.0
0.4	727.2	733.8	738.6	742.3	754.2
0.5	732.2	738.9	743.7	747.5	759.5
0.6	736.8	743.6	748.4	752.3	764.5
0.7	741.3	748.2	753.1	757.0	769.4
0.8	746.2	753.2	758.2	762.1	774.6
0.9	752.4	759.4	764.5	768.5	781.2

*The symbols T_4, T_6, T_8, T_{10} and T_{20} denote the temperature values calculated at 4, 6, 8, 10 and 20 K/min, respectively.

calculations reproduce the set values of the activation energy and the pre-exponential factor. However, from Tables 3–8 it is seen that the results are not as that as expected. It should be considered that the iterative method is a perfect method. This kind of calculation has been adopted in quantum chemistry calculation. The fourth Senum and Yang approximation $h(x)$ [Eq. (6)] also has a very high accuracy relative to the numerical integration in the reaction temperature range, with relative error being of the order of 10^{-5} or even smaller. Therefore, the reason for the discrepancy between the calculated Arrhenius parameters and the set ones should be attributed to the low accuracy of temperature values in the theoretical α–T data, since the step size is assumed to be 0.1 K to make numerical integration for the Arrhenius equation. This is because usually we take temperature value precision to the order from experimental thermogravimetric curve. Results of iterative calculations for the simulated data with the two sets of Arrhenius parameters are discussed, respectively below.

4.1. Iterative calculation for the theoretical α–T data with the set values of $E=180.00$ kJ/mol and $A=1.000\times10^{10}$ s^{-1}

After the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$, iterative calculation using the plot of $\ln(\beta/hT^2)$ versus $1/T$ was performed for the theoretical α–T data designed at $E=180.00$ kJ/mol and $A=1.000\times10^{10}$ s^{-1}. The both kinds of plots were fitted. The fitted functions are sequentially shown in Tables 3–5.

Table 3
Iterative calculation for the theoretical α–T data designed at $n=0.5$, $E=180.00$ kJ/mol and $A=1.000\times10^{10}$ s^{-1}

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})
0.1	$y=-21582x+15.160$	179.43	0.850×10^{10}
	$y=-21624x+15.281$	179.78	0.961×10^{10}
	$y=-21624x+15.280$	179.78	0.960×10^{10}
0.3	$y=-21598x+14.028$	179.57	0.873×10^{10}
	$y=-21643x+14.153$	179.94	0.991×10^{10}
	$y=-21643x+14.153$	179.94	0.991×10^{10}
0.6	$y=-21600x+13.219$	179.58	0.874×10^{10}
	$y=-21647x+13.347$	179.97	0.996×10^{10}
	$y=-21647x+13.347$	179.97	0.996×10^{10}
0.9	$y=-21579x+12.571$	179.41	0.850×10^{10}
	$y=-21629x+12.702$	179.82	0.971×10^{10}
	$y=-21628x+12.701$	179.82	0.970×10^{10}
	$y=-21628x+12.701$	179.82	0.970×10^{10}

Table 4
Iterative calculation for the theoretical α–T data designed at $n=1.0$, $E=180.00$ kJ/mol and $A=1.000\times10^{10}$ s^{-1}

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})
0.1	$y=-21579x+15.130$	179.41	0.846×10^{10}
	$y=-21621x+15.251$	179.76	0.957×10^{10}
	$y=-21621x+15.251$	179.76	0.957×10^{10}
0.3	$y=-21562x+13.890$	179.27	0.829×10^{10}
	$y=-21607x+14.015$	179.64	0.941×10^{10}
	$y=-21607x+14.015$	179.64	0.941×10^{10}
0.6	$y=-21605x+13.006$	179.62	0.881×10^{10}
	$y=-21653x+13.135$	180.02	1.005×10^{10}
	$y=-21653x+13.135$	180.02	1.005×10^{10}
0.9	$y=-21598x+12.075$	179.57	0.872×10^{10}
	$y=-21648x+12.207$	179.98	0.998×10^{10}
	$y=-21648x+12.207$	179.98	0.998×10^{10}

From Tables 3–5, it is seen that the iterative calculations greatly improve the results of the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$. Both for activation energy and for pre-exponential factor, the iterative calculation makes the calculated values much closer to the set ones.

The conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ actually gave good estimate for activation energy with relative error within -0.5% for each of the plots in Tables 3–5. But, estimates for the pre-exponential factor are found to have errors at high level of about -10 to -15%. In contrast, the iterative calculation using the plot of $\ln(\beta/hT^2)$ versus $1/T$ improved estimates of the pre-exponential factor into smaller errors of about -5 to $+2\%$.

Improvement on value of the pre-exponential factor is accompanied by change of value of activation energy. A little variation of activation energy has a large effect on value of the pre-exponential factor. This can be understood from the compensation effect, i.e. $\ln A=a\times E+b$, which is observed

Table 5
Iterative calculation for the theoretical α–T data designed at $n=1.5$, $E=180.00$ kJ/mol and $A=1.000\times10^{10}$ s^{-1}

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})
0.1	$y=-21616x+15.155$	179.72	0.893×10^{10}
	$y=-21658x+15.276$	180.07	1.009×10^{10}
	$y=-21658x+15.276$	180.07	1.009×10^{10}
0.3	$y=-21619x+13.877$	179.74	0.898×10^{10}
	$y=-21665x+14.003$	180.12	1.020×10^{10}
	$y=-21665x+14.003$	180.12	1.020×10^{10}
0.6	$y=-21618x+12.785$	179.73	0.897×10^{10}
	$y=-21667x+12.915$	180.14	1.023×10^{10}
	$y=-21667x+12.914$	180.14	1.022×10^{10}
0.9	$y=-21575x+11.415$	179.38	0.846×10^{10}
	$y=-21628x+11.551$	179.82	0.972×10^{10}
	$y=-21628x+11.550$	179.82	0.971×10^{10}

Table 6
Iterative calculation for the theoretical α–T data designed at $n=0.5$, $E=260.00$ kJ/mol and $A=1.000\times10^{16}$ s^{-1}

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})
0.1	$y=-31282x+28.734$	260.08	0.967×10^{16}
	$y=-31312x+28.820$	260.33	1.055×10^{16}
	$y=-31312x+28.820$	260.33	1.055×10^{16}
0.3	$y=-31166x+27.419$	259.11	0.824×10^{16}
	$y=-31197x+27.507$	259.37	0.900×10^{16}
	$y=-31197x+27.507$	259.37	0.900×10^{16}
0.6	$y=-31237x+26.707$	259.70	0.911×10^{16}
	$y=-31270x+26.796$	259.98	0.997×10^{16}
	$y=-31270x+26.796$	259.98	0.997×10^{16}
0.9	$y=-31226x+26.069$	259.61	0.896×10^{16}
	$y=-31260x+26.159$	259.90	0.981×10^{16}
	$y=-31260x+26.159$	259.90	0.981×10^{16}

quite often [10–13]. In Tables 3–5, the compensation effect is also observed. The coefficient (slope) for every Table is found to be $a=$ca. 0.3 (note: a in unit s^{-1}, E in unit kJ/mol). Therefore, if activation energy is increased by 0.1 kJ/mol, the pre-exponential factor will be increased to $A_i=1.03A_{i-1}$. It can be seen in Tables 3–5that the iterative calculation increases activation energy usually by 0.3–0.4 kJ/mol. The pre-exponential factor is therefore improved greatly in the iterative calculation.

It should be noted that the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ gives divergent values of activation energy from 179.4 to 179.7 kJ/mol at the four degrees of conversion (see Tables 3–5). And the plot of $\ln(\beta/hT^2)$ versus $1/T$ also shows different values for activation energy at the four different degrees of conversion at each of the reaction orders. Since the α–T data are simulated data, it can be considered that the calculated activation energy should be the same value independent of the degree of conversion. The reason for this variation of activation energy with the degree of conversion can be only the low accuracy of temperature values in the theoretical α–T data, which were calculated by numerical integration with step size of 0.1 K. For example, for a defined degree of conversion, the temperature at a heating rate is 718.14 K, we take it as 718.1 K; at another heating rate the temperature is 756.26 K, we take it as 756.3 K. This kind of deviations in temperature for different heating rates certainly result in deflection of the isoconversional plot at the defined degree of conversion, because the isoconversional plot is very sensitive to temperature value. It is found that, if one changes (or by mistake) a temperature value at a heating rate by 0.1 K in Table 1, the isoconversional plot at the degree of conversion for the five heating rates will be subjected to a notable influence. Unfortunately, it is usually not certain in experiment to read a temperature value more accurately than 0.1 K.

Table 7
Iterative calculation for the theoretical α–T data designed at $n=1.0$, $E=260.00$ kJ/mol and $A=1.000\times10^{16}$ s^{-1}

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})
0.1	$y=-31210x+28.608$	259.48	0.874×10^{16}
	$y=-31240x+28.694$	259.73	0.953×10^{16}
	$y=-31240x+28.694$	259.73	0.953×10^{16}
0.3	$y=-31171x+27.339$	259.16	0.830×10^{16}
	$y=-31203x+27.428$	259.42	0.908×10^{16}
	$y=-31203x+27.428$	259.42	0.908×10^{16}
0.6	$y=-31233x+26.478$	259.67	0.903×10^{16}
	$y=-31266x+26.568$	259.95	0.990×10^{16}
	$y=-31266x+26.568$	259.95	0.990×10^{16}
0.9	$y=-31296x+25.643$	260.19	0.987×10^{16}
	$y=-31331x+25.734$	260.49	1.082×10^{16}
	$y=-31331x+25.734$	260.49	1.082×10^{16}

Table 8
Iterative calculation for the theoretical α–T data designed at $n=1.5$, $E=260.00$ kJ/mol and $A=1.000\times10^{16}$ s^{-1}

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})
0.1	$y=-31123x+28.460$	258.76	0.771×10^{16}
	$y=-31153x+28.546$	259.01	0.842×10^{16}
	$y=-31153x+28.546$	259.01	0.842×10^{16}
0.3	$y=-31301x+27.426$	260.24	0.996×10^{16}
	$y=-31333x+27.514$	260.50	1.088×10^{16}
	$y=-31333x+27.514$	260.50	1.088×10^{16}
0.6	$y=-31231x+26.240$	259.66	0.903×10^{16}
	$y=-31264x+26.331$	259.93	0.990×10^{16}
	$y=-31264x+26.331$	259.93	0.990×10^{16}
0.9	$y=-31251x+24.951$	259.82	0.927×10^{16}
	$y=-31286x+25.044$	260.11	1.018×10^{16}
	$y=-31286x+25.044$	260.11	1.018×10^{16}

4.2. Iterative calculation for the theoretical α–T data with the set values of $E=260.00$ kJ/mol and $A=1.000\times10^{16}$ s^{-1}

Iterative calculations were performed for the theoretical α–T data with the set values of $E=260.00$ kJ/mol and $A=1.000\times10^{16}$ s^{-1}. The results are listed in Tables 6–8. Some discussions made above are applicable here. Similarly, in comparison with the initial plot of $\ln(\beta/T^2)$ versus $1/T$, the iterative calculation always leads to an increase in activation energy and therefore an increase in value of the pre-exponential factor. However, in a few of calculations the gains are of overplus. Besides, the values of activation energy in Tables 6–8scatter slightly broader than those in Tables 3–5. These can be ascribed to the narrower reaction temperature range of the reaction with the larger activation energy and pre-exponential factor (compare Table 2 with Table 1). The narrower reaction temperature range led to more deviations in values of temperature in the theoretical α–T data. And note that the deviations of temperature are random. These finally result in larger scattering of the Arrhenius parameters in the iterative calculation for the α–T data theoretically designed with the set values of $E=260.00$ kJ/mol and $A=1.000\times10^{16}$ s^{-1}. Nevertheless, the iterative

Table 9
The average values* of Arrhenius parameters calculated from the isoconversional plot at the four degrees of conversion $\alpha=0.1$, 0.3, 0.6 and 0.9

n	E (kJ/mol)	A (s^{-1})	E_0 (kJ/mol)	A_0 (s^{-1})	E_i (kJ/mol)	A_i (s^{-1})
0.5	180.00	1.000×10^{10}	179.50	0.862×10^{10}	179.88	0.979×10^{10}
1.0	180.00	1.000×10^{10}	179.47	0.857×10^{10}	179.85	0.975×10^{10}
1.5	180.00	1.000×10^{10}	179.64	0.883×10^{10}	180.04	1.005×10^{10}
0.5	260.00	1.000×10^{16}	259.63	0.900×10^{16}	259.89	0.983×10^{16}
1.0	260.00	1.000×10^{16}	259.63	0.899×10^{16}	259.90	0.983×10^{16}
1.5	260.00	1.000×10^{16}	259.62	0.899×10^{16}	259.89	0.984×10^{16}

*E and A are the set values of activation energy and pre-exponential factor for calculating theoretical α–T data at a given reaction order (n) and at a given heating rate. E_0 and A_0 are the calculated values from the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$. E_i and A_i are the calculated values by means of the iterative calculation method using the plot of $\ln(\beta/hT^2)$ versus $1/T$.

calculation remarkably improved the result of the conventional isoconversional plot of $\ln(\beta/T^2)$ verus $1/T$ as a whole. This has been clearly indicated in Table 9, where the average values of the Arrhenius parameters calculated at the four degrees of conversion are summarized.

4.3. Application of the iterative method to degradations of PMMA and polyethylene

The PMMA sample was found to be degraded in the first-order kinetics [12]. The experimental α–T data is reproduced in Table 10. Iterative calculation by use of the plot of $\ln(\beta/hT^2)$ versus $1/T$ was made for the degradation at the four degrees of conversion ($\alpha=0.1$, 0.3, 0.6 and 0.9) and the results are listed in Table 11. It can be seen that the iterative calculation greatly improved the result of the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$. With taking the A_i value of the last step of the iteration as the 'exact' value, the relative error of the pre-exponential factor (A_0) estimated from the plot of $\ln(\beta/T^2)$ versus $1/T$ was calculated according to $(A_0-A_i)/A_i\times100\%$. The errors are found from -9.6 to -12.1%.

The iterative method was also applied to the degradation of the polyethylene, of which the reaction order was found to be $n=0.55$ [13]. Based on the experimental α–T data represented in Table 12, iterative calculation was performed and the results are listed in Table 13. Consistent with the above calculations, the iterative method greatly improved value of the pre-exponential factor. The relative errors of the estimates (A_0) obtained from the plot of $\ln(\beta/T^2)$ versus $1/T$ are found at -10.1 to -11.3%.

4.4. Further discussion on validity and applicability of the iterative procedure

Generally, non-isothermal analysis is always started from Eq. (11). The Eq. (1) is just a special case of Eq. (11). A lot of efforts have been made in the past several decades by many researchers in the field of thermal analysis. One of the remarkable achievements is that for obtaining integration of the Arrhenius equation since its exponential has no analytical solution. As the result, several approximate expressions are given [7]. Based on the approximations, the isoconversional plots were proposed to estimate activation energy without prerequisite to know kinetics expression of the reaction under study. Eq. (8) is also called Kissinger–Akahira–Sunose (KAS) plot [14]. Another plot is Eq. (12), called Flynn–Wall–Ozawa plot [14].

$$\frac{d\alpha}{dt}=A\exp\left(\frac{-E}{RT}\right)\times f(\alpha) \tag{11}$$

$$\ln\beta=-1.0516\frac{E}{RT}+\left[\ln\left(0.0048\frac{AE}{R}\right)-\ln g(\alpha)\right] \tag{12}$$

Since the isoconversional plots are proposed from the approximate expressions of integration of the Arrhenius equation, the plots are only approximately linear plots. Eq. (10) is a more accurate plot instead of Eq. (8). The more accurate form of Eq. (12) is described in the previous paper [5]. Ortega et al. evaluated error of the activation energy estimated from the plot of $\ln(\beta/T^2)$ against $1/T$ [15]. Error of pre-exponential factor due to the same plot is reported by Gao et al. [6], and then expressed into a mathematical equation by Chen

Table 10
Experimental α–T data* measured for the dynamic degradation of the PMMA sample

α	T_4 (K)	T_6 (K)	T_8 (K)	T_{10}(K)	T_{20} (K)
0.1	595.8	601.0	609.8	612.8	626.7
0.2	612.5	618.2	624.2	627.9	640.0
0.3	621.2	627.0	632.2	636.1	647.8
0.4	627.5	633.3	638.3	642.2	653.9
0.5	632.9	638.6	643.6	647.4	659.2
0.6	637.8	643.6	648.5	652.4	664.3
0.7	642.7	648.7	653.5	657.6	669.7
0.8	648.3	654.4	659.1	663.4	675.8
0.9	655.9	662.0	666.7	671.3	684.2

*The symbols T_4, T_6, T_8, T_{10} and T_{20} denote the temperature values measured at 4, 6, 8, 10 and 20 K/min, respectively.

Table 11
Iterative calculation for the dynamic degradation of the PMMA sample (experimental α–T data shown in Table 10)

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})	Relative error (%) * of the pre-exponential factor (A_0)
0.1	$y=-17559x+14.023$	145.99	2.277×10^{9}	−12.08
	$y=-17596x+14.150$	146.29	2.590×10^{9}	
	$y=-17596x+14.150$	146.29	2.590×10^{9}	
0.3	$y=-22818x+21.179$	189.71	1.284×10^{13}	−9.89
	$y=-22850x+21.282$	189.97	1.425×10^{13}	
	$y=-22850x+21.282$	189.97	1.425×10^{13}	
0.6	$y=-24203x+22.346$	201.22	1.124×10^{14}	−9.57
	$y=-24234x+22.446$	201.48	1.243×10^{14}	
	$y=-24234x+22.446$	201.48	1.243×10^{14}	
0.9	$y=-23911x+20.810$	198.80	6.005×10^{13}	−10.00
	$y=-23945x+20.914$	199.08	6.672×10^{13}	
	$y=-23945x+20.914$	199.08	6.672×10^{13}	

*Relative error of the pre-exponential factor (A_0) estimated from the plot of $\ln(\beta/T^2)$ versus $1/T$ is calculated according to $(A_0-A_i)/A_i\times100\%$, in which A_i is the value obtained at the last step of the iterative calculation of $\ln(\beta/hT^2)$ versus $1/T$.

et al. quite recently [16]. It is clear that the plot of $\ln(\beta/T^2)$ versus $1/T$ always gives lower value for the pre-exponential factor, usually with an error of about −10%. Meanwhile, the plot also shows a little bit lower value for activation energy by 0.2–0.5 kJ/mol usually. Budrugeac reported that the plot of $\ln(\beta/T^2)$ against $1/T$ gives activation energy value of 179.8 kJ/mol from the simulated data with set value of 180.0 kJ/mol, in contrast 182.9 kJ/mol obtained from the plot of $\ln\beta$ versus $1/T$ [14]. The previous paper [5] has illustrated that the iterative procedure leads to a mediate value of the estimates of the two plots for activation energy. So it can be concluded that the mediate value obtained by use of the iterative procedure is more accurate than every one estimated, respectively from the two conventional plots. Especially improvement of activation energy for the plot of $\ln\beta$ versus $1/T$ with the use of the iterative procedure is much obvious, by 1–3 kJ/mol as seen for the simulated data [14] and the experimental data [5]. It should be noticed that the two conventional isoconversional plots, $\ln(\beta/T^2)$ versus $1/T$ and $\ln\beta$ versus $1/T$, give the same value at the final iterative step when both applied in the iteration calculation. This is because the iterative procedure adopted the same and more accurate integration, the fourth Senum and Yang approximation [7,8], for the Arrhenius equation. As shown in Table 9 (for simulated data), Tables 11 and 13 (for experimental data), the iterative method corrected (increased) values of the pre-exponential factor by about 10%. This magnitude is in consistence with the prediction of error level (about −10%) of the plot (i.e. $\ln(\beta/T^2)$ versus $1/T$) for the pre-exponential factor [6,16].

Iteration procedure has been adopted in molecular orbital calculation of quantum chemistry. Iteration is terminated when the difference of total energy of the molecule in the last two iterative steps is smaller than a defined quantity such as 10^{-5} eV. At this point, the iterative calculation is regarded as self-consistence. Eq. (10) is a rigorously linear plot as long as the adopted $h(x)$ function is accurate enough compared to the numerical integration. It is true that in some cases we are difficult to know the real values of the activation energy and the pre-exponential factor of a polymer decomposition process. But we always try to calculate them more accurately from experimental data. The phenomenon of the compensation effect, i.e. $\ln A=a\times E+b$, which is often observed in non-isothermal analyses, is still a tiring question. Besides we are still suffering from incomplete list of kinetic models [17]. Many publications appeared for discussion of these issues. Vyazovkin and Lesnikovich noticed the change pattern of E with α (the degree of conversion) in association with mechanism of a complex process [18]. The invariant kinetic parameter method (IKP method) was suggested [19,20] and applied to determine the kinetic triplet (E, A and $f(\alpha)$) [21]. The iterative method suggested by us can of course improve calculation accuracy of the IKP method, too.

In addition, it should be stressed again that the accuracy of the isoconversional plots is very strongly dependent on the

Table 12
Experimental α–T data* measured for the dynamic degradation of the polyethylene

α	T_4 (K)	T_6 (K)	T_8 (K)	T_{10} (K)	T_{20} (K)
0.1	687.8	695.9	700.9	706.8	722.1
0.2	700.1	708.3	713.3	719.7	734.7
0.3	708.1	716.1	721.1	727.5	742.4
0.4	714.1	721.9	726.9	733.3	747.9
0.5	718.9	726.6	731.7	737.8	752.3
0.6	723.2	730.7	735.8	741.7	756.1
0.7	727.2	734.7	739.8	745.6	759.8
0.8	731.2	738.7	743.8	749.5	763.6
0.9	735.9	743.4	748.5	754.1	768.3

*The symbols T_4, T_6, T_8, T_{10} and T_{20} denote the temperature values measured at 4, 6, 8, 10 and 20 K/min, respectively.

Table 13
Iterative calculation for the dynamic degradation of the polyethylene sample (experimental α–T data shown in Table 12)

α	Fitted function for the isoconversional plot	Calculated activation energy (kJ/mol)	Calculated pre-exponential factor (s^{-1})	Relative error (%)* of the pre-exponential factor (A_0)
0.1	$y=-21783x+15.914$	181.10	1.828×10^{10}	−11.35
	$y=-21824x+16.033$	181.44	2.063×10^{10}	
	$y=-21823x+16.033$	181.44	2.062×10^{10}	
	$y=-21823x+16.033$	181.44	2.062×10^{10}	
0.3	$y=-22991x+16.656$	191.15	1.297×10^{11}	−11.04
	$y=-23032x+16.772$	191.49	1.460×10^{11}	
	$y=-23032x+16.771$	191.49	1.458×10^{11}	
0.6	$y=-25009x+18.729$	207.92	2.556×10^{12}	−10.47
	$y=-25048x+18.838$	208.25	2.855×10^{12}	
	$y=-25048x+18.838$	208.25	2.855×10^{12}	
0.9	$y=-26367x+19.938$	219.22	1.724×10^{13}	−10.07
	$y=-26405x+20.043$	219.53	1.917×10^{13}	
	$y=-26405x+20.043$	219.53	1.917×10^{13}	

*Relative error of the pre-exponential factor (A_0) estimated from the plot of $\ln(\beta/T^2)$ versus $1/T$ is calculated according to $(A_0-A_i)/A_i\times100\%$, in which A_i is the value obtained at the last step of the iterative calculation of $\ln(\beta/hT^2)$ versus $1/T$.

precision of α–T data. Errors in reading temperature value certainly lead to deviations of estimates of the Arrhenius parameters. In Tables 6–8, it is seen that the iterative calculations gave overestimates for the Arrhenius parameters in a few cases. The reason should be ascribed to the random reading errors of the temperature values in the α–T data. Comparing Table 2 with Table 1, it is apparent that the former has a narrower conversion temperature range than the latter. This means presence of relatively more reading errors in the temperature values for the reaction with $E=260.00$ kJ/mol and $A=1.000\times10^{16}\ s^{-1}$. Even though the presence of reading errors in temperature values in α–T data, statistical calculation using more sets of α–T data should give more accurate estimates for the Arrhenius parameters. Table 9 shows the average values of the individual calculations at the four degrees of conversion. In all cases it is found that the average values are very close to the set values of the Arrhenius parameters. This illustrates validity and applicability of the iterative procedure.

5. Conclusions

The conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ can give quite good estimate for activation energy, with relative error within −0.5%. However, the pre-exponential factor calculated from the plot of $\ln(\beta/T^2)$ versus $1/T$ usually has a large error of about −10 to −15%. Such the large error of the pre-exponential factor can be accounted for the general existence of the compensation effect, i.e. $\ln A=a\times E+b$. That implies that a little deviation in value of activation energy can result in a large change in value of the pre-exponential factor.

In mathematical principle, errors of the Arrhenius parameters calculated from the plot of $\ln(\beta/T^2)$ versus $1/T$ is a consequence of assuming $h(x)=1$.

The iterative calculation using the plot of $\ln(\beta/hT^2)$ versus $1/T$ greatly improves the result of the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$. Both for activation energy and for pre-exponential factor, the improvement is remarkable. Table 9 is a summary that indicates that a fairly small error within −3 to +1% can be achieved for the pre-exponential factor by the iterative calculation.

In some cases we may be difficult to know the real values of activation energy and pre-exponential factor for a reaction process. If we take the iterative calculation results, i.e. E_i and A_i as the exact values, the relative errors of the conventional isoconversional plot of $\ln(\beta/T^2)$ versus $1/T$ can be estimated from $(E_0-E_i)/E_i\times100\%$ and $(A_0-A_i)/A_i\times100\%$.

The isoconversional plot is very sensitive to temperature values in α–T data. Obtaining accurately temperature value is the most important to reduce errors of calculated Arrhenius parameters from the isoconversional plot.

In addition, the iterative method is not only applicable for nth-order reactions, but also for any other reactions.

References

[1] Kissinger HE. Anal Chem 1957;29:1702.
[2] Coats AW, Redfern JP. Nature 1964;201:68.
[3] Ozawa T. Bull Chem Soc Jpn 1965;38:1881.
[4] Flynn JH, Wall LA. J Polym Sci B 1966;4:323.
[5] Gao Z, Nakada M, Amasaki I. Thermochim Acta 2001;369:137.
[6] Gao Z, Amasaki I, Kaneko T, Nakada M. Polym Degrad Stab 2004;83:67.
[7] Flynn JH. Thermochim Acta 1997;300:83.
[8] Senum GI, Yang RT. J Therm Anal 1977;11:445.
[9] Lyon RE. Thermochim Acta 1997;297:117.
[10] Koga N, Sestak J. Thermochim Acta 1991;182:201.
[11] Galwey AK, Brown ME. Thermochim Acta 1997;300:107.
[12] Gao Z, Kaneko T, Hou D, Nakada M. Polym Degrad Stab 2004;84:399.
[13] Gao Z, Amasaki I, Nakada M. J Anal Appl Pyrolysis 2003;67:1.
[14] Budrugeac P. Polym Degrad Stab 2005;89:265.
[15] Ortega A, Perez-Maqueda LA, Criado JM. Thermochim Acta 1996; 282/283:29.
[16] Chen H, Liu N, Shu L. Polym Degrad Stab 2005;90:132.
[17] Vyazovkin S. Int Rev Phys Chem 2000;19:45.
[18] Vyazovkin S, Lesnikovich AI. Thermochim Acta 1990;165:273.
[19] Lesnikovich AI, Levchik SV. J Therm Anal 1983;27:83.
[20] Lesnikovich AI, Levchik SV. J Therm Anal 1985;30:667.
[21] Budrugeac P, Segal E, Perez-Maqueda LA, Criado JM. Polym Degrad Stab 2004;84:311.