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Supplement on applicability of the Kissinger equation in thermal analysis

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Abstract The relative errors ($e\%$) in the determination of the activation energy from the slope of the Kissinger straight line $\ln(\beta/\beta T_p^2)$ vs. $1/T_p$ (β is the heating rate) are in-depth discussion. Our work shows that the relative errors is a function containing the factors of x_p and Δx_p, not only x_p ($x_p = E/RT_p$, E is the activation energy, T_p is the temperature corresponding to maximum process rate, R is the gas constant). The relative error between E_k and E_p will be smaller with the increase of the value of x and/or with the decrease of the value of Δx. For a set of different heating rates in thermal analysis experiments, the low and close heating rates are proposed from the kinetic theory.

Keywords Kissinger equation · Activation energy · Non-isothermal kinetics · Thermal analysis · Differential thermalanalysis (DTA) · Chemical kinetics

Introduction

The kinetic equation of a chemical reaction in the linear heating process can be described as

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where $f(\alpha)$ is the function of conversion, A is the pre-exponential factor, E is the activation energy, R is the gas constant, T is the temperature, β is the linear heating rate, $\beta = dT/dt$.

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According to the generalization of Kissinger method [1] by Elder method [2], at the peak temperature, $(d^2\alpha/dT^2)_p = 0$. Equation 2 may be obtained by the differentiation of Eq. 1

$$\ln\frac{\beta}{T_p^2} = \ln\frac{AR}{E} + \ln\left[-f'(\alpha_p)\right] - \frac{E_p}{RT_p} \tag{2}$$

where T_p is the of peak temperature, α_p is the degree of conversion at T_p, E_p is defined as the real activation energy at T_p. The Kissinger method has been wildly used to evaluate the kinetic parameters until now [3–12].

The differential form of Eq. 2 [13] can be written as

$$E_p = -R\frac{d\left(\ln\frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)}\frac{1}{1-\frac{d\ln\delta_p}{dx_p}} \tag{3}$$

where $\delta_p = (-f'(\alpha_p))$, $x_p = E/RT_p$. When $\Delta T < 150$ K, the literature [13] pointed out that

$$\frac{1}{1-\frac{d\ln\delta_p}{dx_p}} = \frac{1}{1-\overline{\frac{d\ln\delta_p}{dx_p}}} \tag{4}$$

According to Kissinger method,

$$\frac{1}{1-\frac{d\ln\delta_p}{dx_p}} \approx 1 \tag{5}$$

At time, the formula (3) may be converted as

$$E_k = -R\frac{d\left(\ln\frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} \tag{6}$$

where E_k is the activation energy at T_p calculated by Kissinger method.

Combining the formula (3) and (6), the expression of the relative error in the reference [13] is

$$e\% = \frac{E_k - E_p}{E_p} \times 100 = -100\left(\frac{\mathrm{d}\ln\delta_p}{\mathrm{d}x_p}\right) \quad (7)$$

The literature [13] proposes a good method to evaluate the relative error between E_k and E_p.

But, the literature reference [13] does not prove the validity of the formula (4). Are the values of d $\ln\delta_p/\mathrm{d}x_p$ an average value or a constant in the different heating rates?

(1) If $E/RT_{p1} = 5$, $E/RT_{p2} = 4.5$ and $T_1 = 500$ K, and then $T_2 = 500 \times 5/4.5 = 556$, $\Delta T = 556 - 500 = 56 < 150$ K which accords with the temperature range given by the literature [13]. But 5/5.4 = 0.93, an original error of 7% is introduced in the formula (4).

(2) According to the data in Table 3 (Seeing Table 1) in the literature [13], the values of d $\ln\delta_p/\mathrm{d}x_p$ range from −0.0770 to −0.1427. Apparently the values of d $\ln\delta_p/\mathrm{d}x_p$ in different heating rates are not a constant.

As the values of d $\ln\delta_p/\mathrm{d}x_p$ in the different heating rates are not of the same, one may doubt whether the conclusion in the literature [13] is right.

Our work is to correct the expression on the relative error between the E_k and E_p and to calculate the relative error.

The relative error of *E* in Kissinger equation

The value of E_p calculated by Eq. 2 is

$$\ln\frac{\beta_1 T_{p2}^2}{\beta_2 T_{p1}^2} = \ln\frac{f'(\alpha_{p1})}{f'(\alpha_{p2})} + E_p\left(\frac{1}{RT_{p2}} - \frac{1}{RT_{p1}}\right) \quad (8)$$

The value of E_k calculated by Kissinger equation is

$$\ln\frac{\beta_1 T_{p2}^2}{\beta_2 T_{p1}^2} = E_k\left(\frac{1}{RT_{p2}} - \frac{1}{RT_{p1}}\right) \quad (9)$$

The relative error between E_p and E_k is

$$e\% = \frac{E_k - E_p}{E_p} \times 100\% = \frac{1}{x_{p2} - x_{p1}} \ln\frac{f'(\alpha_{p1})}{f'(\alpha_{p2})} \times 100\% \quad (10)$$

Because the value of α_p cannot be obtained directly from the test of Differential Thermal Analysis (DTA), we need to convert $f'(\alpha_p)$ to the function of $R(x_p, n)$, n is the reaction order. $R(x_p, n)$ is a function without the factor α_p.

The integral and differential forms of Eq. 1 are shown separately,

$$G(\alpha) = \frac{AE}{R\beta} \times P(x) \quad (11)$$

$$-f'(\alpha_p) = \frac{E\beta}{ART_p^2} e^{\frac{E}{RT_p}} \quad (12)$$

T_p in Eq. 12 is the peak temperature. According to Senum and Yang [14], the integral of $p(x)$ may be expressed as follows:

$$P(x) = \frac{e^{-x}}{x^2} \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} = \frac{e^{-x}}{x^2} \times H(x) \quad (13)$$

When Eqs. 11, 12, and 13 are combined together, the following result is obtained:

$$-f'(\alpha_p) \times G(\alpha_p) = H(x_p) \quad (14)$$

Taking the differential and integral forms of $f(\alpha)$ (Table 2), the relation (14) can be converted to

$$-f'(x_p) = R(x_p, n) \quad (15)$$

(1) When $f(\alpha) = (1 - \alpha)^n$ ($n \neq 1$), Eq. 10 may be written as:

$$e\% = \frac{E_k - E_p}{E_p} \times 100\% = \frac{1}{x_{p2} - x_{p1}} \ln\frac{n - (n-1)H(x_{p1})}{n - (n-1)H(x_{p2})} \times 100\% \quad (16)$$

(2) When $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{n-1/n}$, Eq. 10 may be written as

$$e\% = \frac{E_k - E_p}{E_p} \times 100\% = \frac{1}{x_{p2} - x_{p1}} \ln\left[\frac{(n-1)B_1^{-\frac{1}{n}} - nB_1^{\frac{n-1}{n}}}{(n-1)B_2^{-\frac{1}{n}} - nB_2^{\frac{n-1}{n}}}\right] \times 100\% \quad (17)$$

Table 1 The characteristic parameters of the simulated non-isothermal data [13]

β/K min^{-1}	T_p/K	x_p	$\ln\delta_p$	d $\ln\delta_p/x_p$
2	665.15	7.344	2.70277	−0.0770
5	732.65	6.567	2.77096	−0.1012
10	790.65	6.085	2.82345	−0.1185
15	828.65	5.806	2.85851	−0.1323
20	857.15	5.613	2.88518	−0.1427

Table 2 The expression of $f(\alpha)$ and $f'(\alpha)$

Equation type	$f(\alpha)$	$-f'(x_p) = R(x_p, n)$
Fn ($n \neq 1$ or $n \neq 0$)	$(1-\alpha)^n$	$n - (n-1)H(x_p)$
An	$n(1-\alpha)^n [-\ln(1-\alpha)]^{n-1/n}$	$n\left[-B^{\frac{n-1}{n}} + \frac{(n-1)}{n}B^{-\frac{1}{n}}\right]$

Note: $B = (H(x_p) + n - 1)/n$

The relative error between E_k and E_p

According to Eq. 16 or 17, taking a fixed value of n and changing values of x_1 and x_2 ($x_2 = x_1 + \Delta x$), the relative error between E_k and E_p can be calculated.

(1) If $f(\alpha) = (1-\alpha)^n (n \neq 1)$, $n = 1.5$, $x_1 = 1$–10, $\Delta x = 0.1$–1, the values and curves of relative error are shown Fig. 1 and Table 3:

(2) If $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{n-1/n}$, $n = 1.5$, $x_1 = 1$–10, $\Delta x = 0.1$–1, the curves of relation error are shown in Fig. 2 and Table 4

Figures 1 and 2 show that the relative error between E_k and E_p will be bigger when the value of x becomes smaller or when the value of Δx becomes bigger. Second, when $f(\alpha) = (1-\alpha)^n$, the relative error between E_k and E_p is a positive error. When $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{n-1/n}$, the relative error between E_k and E_p is a negative error.

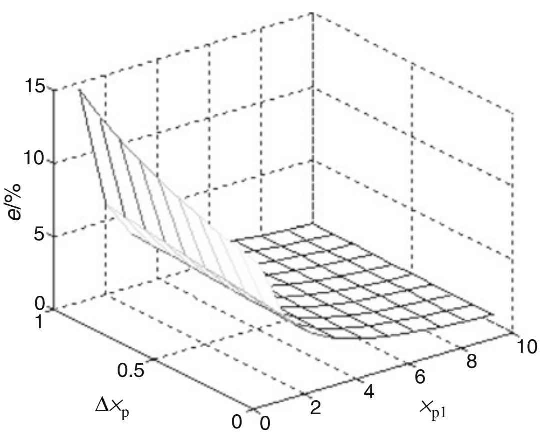

Fig. 1 The $e\%$ vs. x and Δx for $f(\alpha) = (1-\alpha)^n (n = 1.5; x = 1$–$10$; $\Delta x = 0.1$–$1)$

Table 3 The |e%| calculated by Eq. 16. and |e%|′ calculated by ref. [13]for $f(\alpha) = (1-\alpha)^n$ $n = 1.5$

X_p / Δx_p	|e%|								
	1	2	3	4	5	6	7	8	9	10
0.1	8.76	4.69	3.00	2.1	1.57	1.21	0.97	0.80	0.66	0.56
0.2	9.13	4.81	3.06	2.14	1.59	1.23	0.98	0.80	0.67	0.57
0.3	9.54	4.95	3.12	2.18	1.61	1.24	0.99	0.81	0.68	0.57
0.4	9.99	5.09	3.19	2.21	1.63	1.26	1.00	0.82	0.68	0.58
0.5	10.5	5.24	3.26	2.25	1.66	1.28	1.01	0.83	0.69	0.58
0.6	11.08	5.40	3.33	2.29	1.68	1.29	1.03	0.84	0.69	0.59
0.7	11.74	5.57	3.41	2.33	1.71	1.31	1.04	0.84	0.70	0.59
0.8	12.50	5.76	3.49	2.38	1.73	1.33	1.05	0.85	0.71	0.60
0.9	13.41	5.96	3.57	2.42	1.76	1.34	1.06	0.86	0.71	0.60
1.0	14.54	6.17	3.66	2.47	1.79	1.36	1.07	0.87	0.72	0.61
|e%|’	6.87	4.13	2.95	2.24	1.81	1.47	1.24	1.00	<1	<1

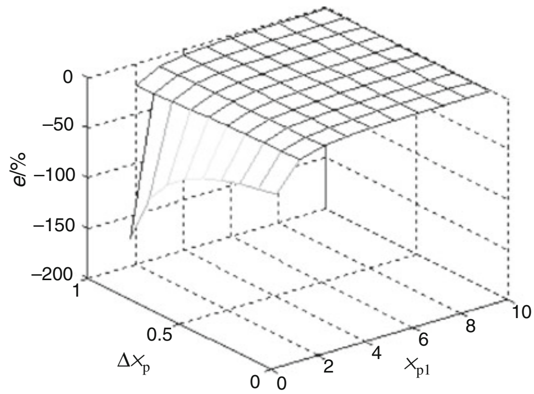

Fig. 2 The e vs. x and Δx for $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{n-1/n}$ $(n = 1.5; x = 1$–10; $\Delta x = 0.1$–$1)$

Table 4 The |e%| calculated by Eq. 17 and |e%|′ calculated from ref. [13] for $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{n-1/n}$ $n = 1.5$

X_p / Δx_p	|e%|								
	1	2	3	4	5	6	7	8	9	10
0.1	40.99	13.41	6.84	4.20	2.85	2.07	1.58	1.24	1.01	0.83
0.2	44.71	14.00	7.04	4.29	2.90	2.10	1.60	1.26	1.02	0.84
0.3	49.26	14.65	7.26	4.39	2.96	2.14	1.62	1.27	1.03	0.85
0.4	54.95	15.36	7.48	4.49	3.01	2.17	1.64	1.29	1.04	0.85
0.5	62.31	16.14	7.73	4.60	3.07	2.20	1.66	1.30	1.05	0.86
0.6	72.28	17.02	7.99	4.71	3.13	2.24	1.69	1.32	1.06	0.87
0.7	86.72	18.01	8.26	4.83	3.19	2.28	1.71	1.33	1.07	0.88
0.8	110.0	19.13	8.56	4.95	3.26	2.31	1.73	1.35	1.08	0.89
0.9	157.6	20.41	8.89	5.09	3.32	2.35	1.76	1.37	1.09	0.90
1.0	-Inf	21.89	9.24	5.22	3.39	2.39	1.78	1.38	1.11	0.90
|e%|’	9.14	6.19	4.84	4.13	3.62	3.22	2.94	2.70	2.51	2.35

(3) Taking the data of β, x_p, and $\ln\delta_p$ in Table 1[13], the relative error between E_p and E_k in the different heating rate can be calculated by Eq. 10.

The data in No.1 show that the relative error between E_p and E_k increases with the increase of the heating rate (β). The data in No.2 show that the relative error between E_p and E_k becomes bigger with the decrease of the ratio (β_1/β_2).

From Table 1, it can be found that the value of T_p becomes bigger gradually with the increase of β, the change of the values $x_p(x_p = E/RT_p)$ is on the contrary. In other words, the bigger the value of β is, the smaller will be the value of x_p. Second, the value of Δx becomes smaller when the chosen two heating rates are very close to each other. According to Table 5, the values of $|e\%|$ are the smallest when $\beta = 2$, while are the largest when $\beta = 15$.

Table 5 The |e%| calculated from Eq. 10 in the different heating rate

No.	1				2			
β_1/β_2	2/5	5/10	10/15	15/20	2/5	2/10	2/15	2/20
$e\%$	8.8	10.9	12.6	13.8	8.8	9.6	10.1	10.5

Conclusion

Equations 10, 16, and 17 show that the relative error between E_p and E_k is a function containing the factors of x and Δx, not only x.

Figures 1 and 2 show that the relative error between E_k and E_p will be bigger when the value of x becomes smaller or when the value of Δx becomes bigger.

The thermal analysis experiments with lower heating rates can promise more accurate values of activation energy, so do those with closely values of different hating rates. However, the experimental data in DTA are sometimes bad in these cases. Hence, the heating rates should be chosen for one given test and sample.

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