

Deviation of activation energy caused by neglecting a temperature term in Ozawa Equation

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Abstract In the non-isothermal kinetic equation, the temperature integral from 0 to T_0 never equals to zero, so a deviation of activation energy is introduced when the term is neglected. We propose a new evaluation method on Ozawa Equation. The results show that neglecting this term in Ozawa Equation leads to large activation energy errors, when small absolute values of $\Delta x = x - x_0$ ($x = E/RT$). The deviation of the activation energy is less than 0.55% when $|\Delta x| > 5$, but may exceed 10% if $|\Delta x| < 2$. The application of this method on the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ shows that the theoretical error was close to the actual error.

Keywords Activation energy · Temperature integral · Ozawa Equation · Non-isothermal kinetics · Thermal analysis

1 Introduction

In linear heating process, the kinetic equation of many chemical reactions can be expressed as:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp(-E/RT) dT$$
$$= \frac{A}{\beta} \left[\int_0^T \exp(-E/RT) dT - \int_0^{T_0} \exp(-E/RT) dT \right]$$

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$$= \frac{A}{\beta} [I(T) - I(T_0)] \tag{1}$$

where $f(\alpha)$ is the reaction model, α is the degree of conversion, T is Kelvin temperature, A is the pre-exponential factor, β is the linear heating rate ($\beta = dT/dt$), R is the gas constant and E is the activation energy. Furthermore, $I(T) = \int_0^T \exp(-E/RT)dT$ and $I(T_0) = \int_0^{T_0} \exp(-E/RT)dT$.

Kissinger [1], Coats [2], KAS [3] and Ozawa [4] consider that the rate of the reaction is very low at low temperature, so Eq. (1) [1–4] was expressed as:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} I(T) \tag{2}$$

In other words, they neglect the value of $I(T_0)$.

According to Doyle’s approximate integral method [5],

$$I(T) \cong \frac{E}{R} \left(0.00484e^{-1.0516 \frac{E}{RT}} \right) \tag{3}$$

Combining Eq. (3) with Eq. (2) gives:

$$\ln \beta = \ln \left(\frac{AE}{RG(\alpha)} \right) - 5.3308 - 1.0516 \frac{E}{RT} \tag{4}$$

where $G(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$. Equation (4) is Ozawa Equation.

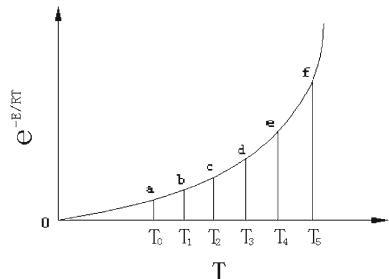
In fact, the value of $I(T_0)$ is never equal to zero so that it is unsafe to neglect it without further analysis of its significance [6–8]. Equation (2) is correct only when the ratio r in Eq. (5) is very close to zero [8].

$$r = I(T_0)/I(T) \tag{5}$$

For a given value of E , the curve and the integral area of $\exp(-E/RT)$ are indicated in Fig. 1.

In Fig. 1, the integral areas represent the values of $I(T)$. For example, the value of $I(T_0)$ is the integral area from 0 to T_0 . When the interval between T and T_0 is

Fig. 1 Curve and integral areas of $\exp(-E/RT)$ [8]



small enough, the value of $I(T_0)$ in Eq. (1) cannot be neglected, and Eq. (2) cannot be applied. If the value of $I(T_0)$ is neglected, the activation energy calculated using Ozawa Equation (4) will be inaccurate.

Starink [7] proposed an evaluation equation (15) on the deviation of activation energy due to neglecting the value of $I(T_0)$. Our work shows that the evaluation equation is unreasonable, and an improved method is proposed.

2 Basic analysis

Typical thermogravimetry curves of a reaction at different linear heating rates are shown in Fig. 2.

In the isoconversional method (a fixed value of α and variable linear heating rate β), we can obtain Eq. (6) as follows:

$$G(\alpha)_{\beta_1} = G(\alpha)_{\beta_2} = G(\alpha)_{\beta_3} = \dots \quad (6)$$

Taking $\alpha = \alpha_1$, $T = T_{11}$ when $\beta = \beta_1$ and $T = T_{21}$ when $\beta = \beta_2$ (see Fig. 2). According to Eqs. (1) and (6), we can obtain

$$[I(T_{11}) - I(T_0)]/\beta_1 = [I(T_{21}) - I(T_0)]/\beta_2 = \dots \quad (7)$$

and then Eq. (7) can be rewritten as:

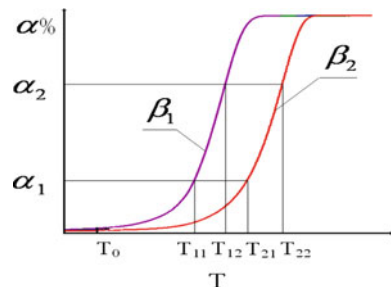
$$\begin{aligned} \frac{\beta_2}{\beta_1} &= \left[\frac{I(T_{21}) - I(T_0)}{I(T_{11}) - I(T_0)} \right]_{E_r} \\ &= \left[\frac{I(T_{21})}{I(T_{11})} \times \frac{1 - I(T_0)/I(T_{21})}{1 - I(T_0)/I(T_{11})} \right]_{E_r} \end{aligned} \quad (8)$$

where the value of E_r in $I(T)$ is the accurate activation energy.

If $I(T_0)$ is neglected (the necessary condition in Ozawa Equation 4), Eq. (8) can be rewritten as:

$$\frac{\beta_2}{\beta_1} = \left[\frac{I(T_{21})}{I(T_{11})} \right]_{E_0} \quad (9)$$

Fig. 2 The thermogravimetry curves



where the value of E_0 in $I(T)$ is an approximate activation energy due to neglecting the value of $I(T_0)$.

Combining Eq. (8) with Eq. (9) gives [7]:

$$\ln \left[\frac{1 - I(T_0)/I(T_{21})}{1 - I(T_0)/I(T_{11})} \right]_{E_r} = \ln \left[\frac{I(T_{21})}{I(T_{11})} \right]_{E_0} - \ln \left[\frac{I(T_{21})}{I(T_{11})} \right]_{E_r} \quad (10)$$

According to Doyle's approximate integral method (Eq. 3),

$$\ln \frac{I(T_{21})}{I(T_{11})} \cong 1.0516 \frac{E}{R} \left(\frac{1}{T_{11}} - \frac{1}{T_{21}} \right) \quad (11)$$

Substituting Eq. (11) into Eq. (10) [7]:

$$\ln \left[\frac{1 - I(T_0)/I(T_{21})}{1 - I(T_0)/I(T_{11})} \right]_{E_r} \cong 1.0516 \frac{\Delta E}{R} \left(\frac{1}{T_{11}} - \frac{1}{T_{21}} \right) \quad (12)$$

where $\Delta E = E_0 - E_r$. ΔE is the deviation introduced by neglecting $I(T_0)$.

3 The calculation of ΔE in Eq. (12)

By finding the value of ΔE in Eq. (12), the relative error between E_0 and E_r may be evaluated.

3.1 The present solution of Eq. (12)

Starink [7] states that "As long as $I(T_0)$ is small compared with $I(T_{11})$ and $I(T_{21})$ it is justified to make a first order approximation" (page 485):

$$\begin{aligned} \ln \frac{1 - I(T_0)/I(T_{21})}{1 - I(T_0)/I(T_{11})} &\cong \ln \left[1 + \frac{I(T_0)}{I(T_{11})} - \frac{I(T_0)}{I(T_{21})} \right] \\ &\cong \frac{I(T_0)}{I(T_{11})} - \frac{I(T_0)}{I(T_{21})} \end{aligned} \quad (13)$$

Here, Eq. (13) depends mightily on $I(T_0)$ is small compared with $I(T_{11})$ and $I(T_{21})$. But the condition disobeys the title "Deviations due to neglecting the low temperature end of the temperature integral" of the literature [7].

Secondly, what is the meaning of "small"?

1. If $I(T_0) < I(T_1)$ and $I(T_0) < I(T_2)$, the first order approximation cannot be adopted in Eq. (13). For instance, if $I(T_0)/I(T_{11}) = 0.27$, $I(T_0)/I(T_{21}) = 0.02$ when $E = 50$ kJ/mol, $T_0 = 300$ K, $T_1 = 320$ K and $T_2 = 365$ K, the result of the left side in Eq. (13) is 0.29 and the result of the right side in Eq. (13) is 0.22. The difference between them is 0.07, and the relative error is about 24.1%.

2. Because T_{21} always exceeds T_{11} (See Fig. 2), in all analyses, $I(T_{21}) > I(T_{11})$ (See Fig. 1). If $I(T_0)/I(T_{11}) \approx 0$, we can conclude that $I(T_0)/I(T_{21}) \approx 0$ from $I(T_{21}) > I(T_{11})$, and then Eq. (13) is equal to zero.
3. If $I(T_0)/I(T_{21}) \approx 0$ and $I(T_0)/I(T_{11}) > 0$, it can be obtained directly from Eq. (13) that

$$\ln \frac{1 - I(T_0)/I(T_{21})}{1 - I(T_0)/I(T_{11})} = \ln \left[\frac{1}{1 - I(T_0)/I(T_{11})} \right] \quad (14)$$

Equation (14) appears to be inconsistent with Eq. (13).

This inconsistency calls into question the evaluation Eq. (15) [7] derived from Eq. (13):

$$\frac{\Delta E}{R} = \frac{\exp[-1.0516E(1/T_{21} - 1/T_0)/R] - \exp[-1.0516E(1/T_{11} - 1/T_0)/R]}{1.0516(1/T_{21} - 1/T_{11})} \quad (15)$$

3.2 New solution of Eq. (12)

Rewriting (12):

$$\ln \left[\frac{1 - I(T_0)/I(T_{21})}{1 - I(T_0)/I(T_{11})} \right]_{E_r} = 1.0516 \frac{\Delta E}{E_r} \left(\frac{E_r}{RT_{11}} - \frac{E_r}{RT_{21}} \right) \quad (16)$$

Taking $E/RT = x$, $e\% = \Delta E/E_r \times 100$, and substituting Eq. (3) into Eq. (16). Equation (16) becomes

$$\ln \frac{1 - \exp[1.0516(x_2 - x_0)]}{1 - \exp[1.0516(x_1 - x_0)]} = \frac{e\%}{100} \times 1.0516(x_1 - x_2) \quad (17)$$

where $x_0 = E/RT_0$, $x_1 = E/RT_{11}$ and $x_2 = E/RT_{21}$. Taking $\Delta x_1 = x_1 - x_0$, $\Delta x_2 = x_2 - x_0$, Eq. (17) can be expressed as:

$$e\% = \frac{\ln \frac{1 - \exp[1.0516\Delta x_2]}{1 - \exp[1.0516\Delta x_1]}}{1.0516(\Delta x_1 - \Delta x_2)} \times 100 \quad (18)$$

In linear heating programs, T_{21} is always larger than T_{11} when $\beta_2 > \beta_1$, in fact $T_{21} > T_{11} > T_0$. Because $x_0 > x_1 > x_2$, $\Delta x = x - x_0$ is negative and $|\Delta x_1| < |\Delta x_2|$. The Δx_1 and Δx_2 dependency of $e\%$ are shown in Fig. 3.

Only parts of the data in Fig. 3 are available, where $|\Delta x_1| < |\Delta x_2|$.

3.3 Discussions

1. Starink [7] states that “For reactions with $E > 70$ kJ/mol and $T_{11} > 375$ K, $\Delta E/E_r$ is smaller than 0.5% provided $T_{11} - T_0 > 65$ K, and if $E > 100$ kJ/mol,

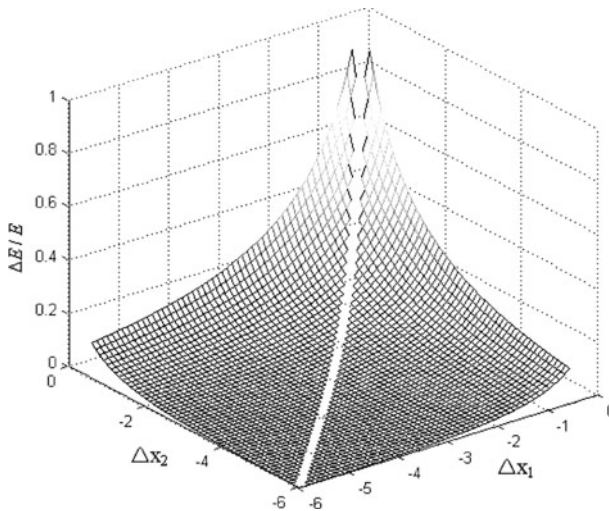


Fig. 3 A three-dimensional figure on the $e\%$ vs Δx_1 and Δx_2 ($\Delta x = -0.6 \sim -6$)

$T_{11} - T_0$ needs to be larger than 50K to achieve $\Delta E/E_r < 0.005$ "(page 486). Hence Starink [7] thought that "only when E and T_0 are relative low, significant deviations are introduced". However, our work show that if $E=120$ kJ/mol ($E > 70$ and 100 kJ/mol), $T_0 = 710$ K ($T_0 > 375$ K), $T_{11} = 775$ K ($T_{11} - T_0 = 65$ K) and $T_{21} = 810$ K, $|\Delta x_1| = 1.71$. By Eq. (18), the relative error will be 12.8%. Equation (18) and Fig. 3 show that the relative error will depend mainly on $|\Delta x|$. In other words, the relative error is significant when the value of $|\Delta x|$ is suitably small.

- Set Δx_1 as $-2, -3, -4, -5$ and -6 . Because the relative error is inversely proportional to $\Delta x_1 - \Delta x_2$ according to Eq. (18), take $\Delta x_1 - \Delta x_2 = 0.01$. According to these data, the values of $e\%$ can be calculated by Eq. (18). The results are listed in Table 1.

From the data in Table 1, the deviations of the activation energy due to neglecting the value of $I(T_0)$ are less than 0.55% only when $|\Delta x_1| > 5$, and may be larger than 10% if $|\Delta x_1| < 2$.

4 The deviation analysis of activation energy for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

4.1 Experimental

The $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ used was analytically pure. TG was performed on a Mettler-Toledo STAR SW9.00 with selected heating rates 2 and $5^\circ\text{C}/\text{min}$ in the range $30\text{--}300^\circ\text{C}$. The samples with masses of 10 mg were put in Alumina $30\ \mu\text{l}$ pans in an atmosphere of dry nitrogen at a flow of 20 ml/min. The TG results are listed in Table 2.

Table 1 The deviations of activation energy due to neglecting the value of $I(T_0)$

No.	Δx_1	Δx_2	$\Delta x_1 - \Delta x_2$	$e\%$
1	-2	-2.01	0.01	13.82
2	-3	-3.01	0.01	4.43
3	-4	-4.01	0.01	1.50
4	-5	-5.01	0.01	0.52
5	-6	-6.01	0.01	0.18

Table 2 The TG data of the dehydration reaction of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

β	α									
	0	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
1	371.21	383.25	389.55	394.07	397.73	400.73	403.48	405.9	408.23	410.57
2	371.21	388.95	396.55	401.65	405.75	409.25	412.25	415.05	417.75	420.35
5	371.21	398.23	407.82	414.23	419.23	423.48	427.15	430.57	433.65	436.75
10	371.21	407.15	418.07	425.48	431.23	436.07	440.23	444.07	447.73	451.48
20	371.21	413.95	426.95	435.55	442.25	447.85	452.75	457.15	461.35	465.75

4.2 Calculation on activation energy

(1) Ozawa method

For any two linear heating rate tests in TG, Ozawa Equation (Eq. 4) may be rewritten:

$$\ln \frac{\beta_2}{\beta_1} \cong 1.0516 \frac{E_0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (19)$$

This is a kinetic equation which neglects the temperature integral part from 0 to T_0 . For a given value of α , the activation energy can be calculated when the temperature points on two linear heating rate are introduced, as in Eq. (19).

(2) Iterative method [8]

According to Eqs. (3) and (7), a kinetic equation can be described as follows:

$$\frac{\beta_2}{\beta_1} = \left(e^{-\frac{E_r}{RT_2}} - e^{-\frac{E_r}{RT_0}} \right) / \left(e^{-\frac{E_r}{RT_1}} - e^{-\frac{E_r}{RT_0}} \right) \quad (20)$$

This is a kinetic equation that considers the temperature integral part from 0 to T_0 . The ratio β_2/β_1 can be calculated when two temperature points for a given value of α are given, and assumptive values of E_r are introduced in Eq. (20). If the calculated ratio is not equal to the real ratio of the two linear heating rates in the test, we should change the value of E until it is. Here, the value of E_r is the exact value we are looking for. The activation energies calculated by the two methods are listed in Table 3.

Table 3 Activation energy in a dehydration reaction of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

α	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
E_O	119.09	103.53	96.33	92.04	88.85	86.50	84.54	82.85	80.97
E_r	107.33	97.39	92.35	89.17	86.52	84.69	83.99	81.51	79.87

Table 4 Relative error between E_0 and E_r

α		0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
Theoretical error ($e_T\%$)		13.32	7.56	5.49	4.34	3.68	3.16	2.81	2.50	2.25
Actual error ($e_A\%$)		10.96	6.30	4.31	3.22	2.69	2.14	0.65	1.64	1.38

4.3 The relative error between E_0 and E_r

(1) Theoretical error between E_0 and E_r

Taking two temperature points for a given α in Table 1, the corresponding E_0 and E_r are listed in Table 3, then the theoretical error (E_T) between E_0 and E_r can be calculated by Eq. (18) (See Table 4).

(2) Actual error between E_0 and E_r

$$e_A\% = \frac{E_0 - E_r}{E_r} \times 100 \quad (21)$$

According to the data in Table 3, the actual errors are calculated by Eq. (21) (See Table 4).

4.4 Analysis and discussion

Figures 4 and 5 represent the data in Tables 3 and 4.

From Fig. 4, the differences between E_0 and E_r become small with the increase of α . In other words, because the temperature T at α is trend to T_0 when the value of α is smaller (see Fig. 2), the integral values of $I(T_0)$ in Ozawa Equation can not be neglected at low temperature.

Figure 5 shows that the theoretical error is close to the actual error.

5 Conclusions

We have proposed an evaluation method for the relative error of activation energy caused by neglecting the temperature integral part from 0 to T_0 in Ozawa Equation. The work shows the following:

- (1) When the temperature integral part from 0 to T_0 in Ozawa method is neglected, a greater relative error of activation energy will be introduced when the value of $|\Delta x|$ is smaller.
- (2) The relative error depends mainly on the magnitude of $|\Delta x|$, not only on the low temperature and low activation energy.

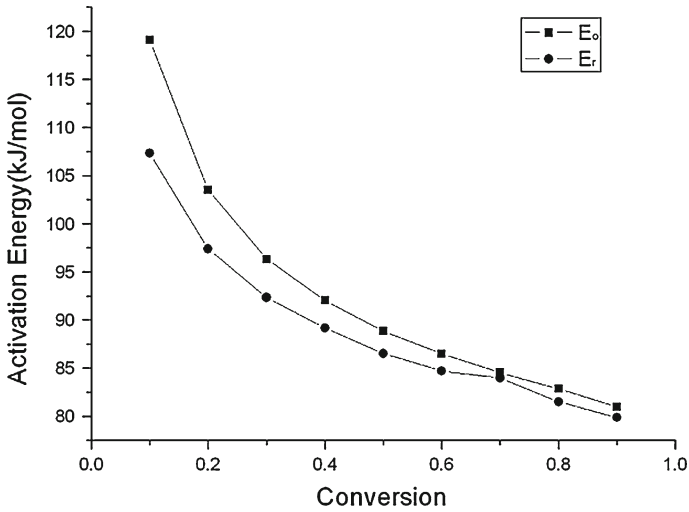


Fig. 4 E_r and E_0 vs α

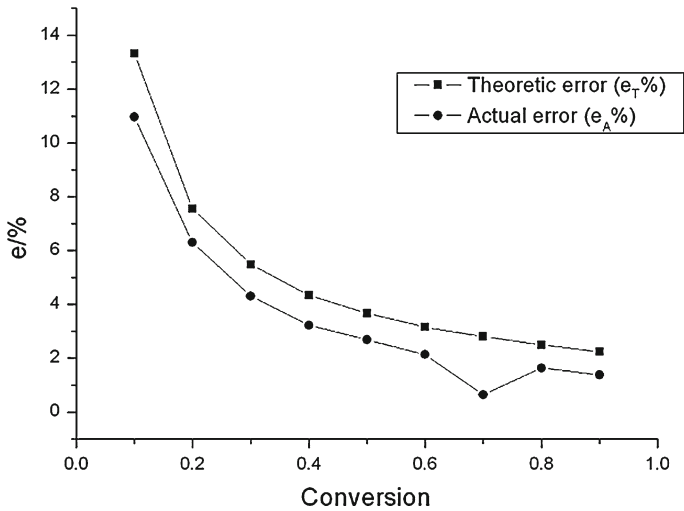


Fig. 5 $e_T\%$ and $e_A\%$ vs α

- (3) To avoid the relative error of activation energy calculated by using Ozawa Equation neglecting $I(T_0)$, we propose using some non-isothermal kinetic equations [6,8,9].
- (4) The application of this method in the dehydration reaction of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ shown that the theoretical error was close to the actual error.

References

1. H.E. Kissinger, *Anal. Chem.* **29**(11), 1702–1706 (1957)
2. A.W. Coats, J.P. Redfern, *Nature* **201**, 68–69 (1964)
3. T. Ozawa, *Bull. Chem. Soc. Jap.* **38**(11), 1881–1886 (1965)
4. T. Akahira, T. Sunose, *Trans. Joint Convention of Four Electrical Institutes*, Paper No. 246, 1969
Research Report, Chiba Institute of Technology Sci. Technol., vol. **16**, pp. 22–31 (1971)
5. C.D. Doyle, *J. Appl. Polymer Sci.* **5**(15), 285–292 (1961)
6. C. Popescu, *Thermochimica Acta* **285**(2), 309–323 (1996)
7. M.J. Starink, *J. Mater. Sci.* **42**(2), 483–489 (2007)
8. Y. Cheng, *Chinese J. Inorg. Chem.* **22**(2), 287–292 (2006)
9. S. Vyazovkin, *J. Comput. Chem.* **22**(2), 178–183 (2001)