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ERROR EVALUATION OF INTEGRAL METHODS BY CONSIDERATION ON THE APPROXIMATION OF TEMPERATURE INTEGRAL

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In this paper, the integral methods in general use are divided into two types in terms of their different ways to in order to deal with the temperature integral $p(x)$: for Type A the function $h(x)=p(x)x^2e^x$ is regarded as constant *vs*. x, while for Type B $h(x)$ varies *vs*. x and $\ln[p(x)]$ is assumed to have the approximation form of $\ln[p(x)]=a\ln x+bx+c$ (the coefficients a, b, and c are constant). The errors of kinetic parameters calculated by these two types of methods are derived as functions of x and analyzed theoretically. It is found that Type A methods have the common errors of activation energy, while the Coats-Redfern method can lead to more accurate value of frequency factor than others. The accuracy of frequency factor can be further enhanced by adjusting the expression of the Coats-Redfern approximation. Although using quite simple approximation of the temperature integral, the Coats-Redfern method has the best performance among Type A methods, implying that usage of a sophisticated approximation may be unnecessary in kinetic analysis. For Type B, the revised MKN method has a lower error in activation energy and an acceptable error in frequency factor, and thus it can be reliably used. Comparatively, the Doyle method has higher error of activation energy and great error of the frequency factor, and thus it is not recommended to be adopted in kinetic analysis.

Keywords: *error evaluation, kinetic analysis, temperature integral*

Introduction

Thermal analysis techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC) have been widely used to study the kinetics and mechanism of solid thermal decomposition reactions, generally carried out under a linear temperature program. The kinetic triplet (activation energy E, frequency factor A and kinetic model) can be derived from the experimental data based on the kinetic equation of solid-gas phase decomposition as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\exp(-E/RT)f(\alpha) \tag{1}$$

where $\alpha(0<\alpha<1)$ is the fractional conversion, ß (K min^{-1}) the heating rate, E (kJ mol^{-1}) the activation energy, A (min^{-1}) the pre-exponential factor, and R the gas constant. T(K) is the absolute temperature. The specific form of $f(\alpha)$ represents the hypothetical model of the reaction mechanism. Approaches to extract the kinetic triplet from the above expression can be generally divided into two categories according to the kind of data used, i.e. differential method by usding derivative thermogravimetry (DTG) data and integral method using TG data.

For integral methods, integrating Eq. (1) and substituting $x=E/RT$ for T gives:

$$G(\alpha)=\frac{AE}{\beta R}p(x) \tag{2}$$

where $G(\alpha)=\int\limits_0^{\alpha}\frac{d\alpha}{f(\alpha)}$, $p(x)=\int\limits_{\infty}^{x}\frac{-e^{-x}}{x^2}dx$

here $p(x)$ is the Arrhenius temperature integral. Although the integral methods are believed to be more reliable and accurate than the differential methods [1], the temperature integral has been a subject of much concern and controversy for a long time, since it cannot be analytically integrated. Many authors have proposed extensive approximations of $p(x)$ with different mathematical complexities and numerical precisions [2–13], and the researchers were always seeking to prove how closely their formulae approach the precise values of $p(x)$. Flynn [14] provided a review on the various approximate expressions for the

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temperature integral, in which he reappraised the accuracies and utilities of these approximations according to their percentage deviations. In a recent paper, Heal [15] proposed an accurate method to evaluate the temperature integral by a series of Chebyshev polynomials. More recently, Tang *et al.* [16] also presented a precise formula for the temperature integral by using two-step linear fitting process. Moreover, some papers proposed a kind of approximations of $p(x)$ through integration over small temperature intervals to enhance the accuracy [17–20].

Sestak ever presented a good discussion on the applicability of the $p(x)$-function in the kinetic analysis under non-isothermal conditions [21]. In the evaluation of the temperature integral, an important point is that it should not be regarded as a pure mathematical problem, but should be considered in connection with the aim of kinetic analysis, i.e. accurate extraction of kinetic parameters and model description. Any approximation leading to accurate enough evaluation of the kinetic parameters should be regarded as reasonable. In this sense, some approximations with higher mathematical complexities may have no remarkable advantage over some other simple approximations. With this idea in mind, in this paper we propose a new consideration on the published approximations and compare them by examining their performances in kinetic analysis, whereby the integral methods are evaluated and compared in terms of error analysis.

Theoretical consideration

Before the error analysis of integral methods, we first propose a new classification of the methods to divide them into two types. The error analysis will be conducted in section 3 respectively with regard to the two types.

It is known that besides $p(x)$, another function $h(x)$ introduced by Senum and Yang [12] can also be used to express the integral form (2) as follows:

$$G(\alpha)=\frac{AE}{\beta R}p(x)=\frac{AE}{\beta R}\frac{e^{-x}}{x^2}h(x),\ \text{with} \qquad (3)$$
$$h(x)=p(x)x^2e^x$$

The values of $p(x)$ and $h(x)$ are calculated *vs.* x by numerical integral and shown in Fig. 1. Compared with $p(x)$, $h(x)$ varies slowly and has an asymptotic value of 1 as x increases, and so it may be easier to explore reasonable approximations for $h(x)$.

The logarithmic form of Eq. (3) is adopted in almost all the integral methods for convenience of analysis:

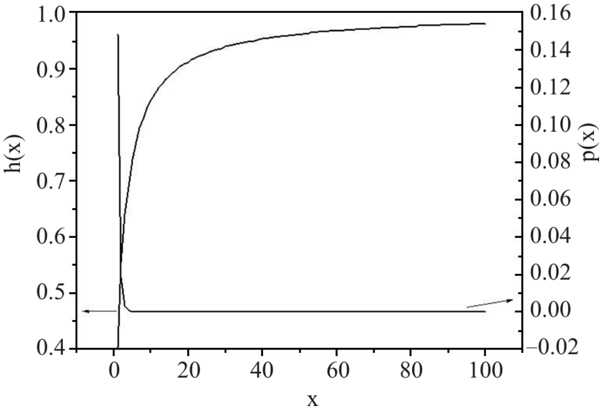

Fig. 1 Values of $h(x)$ and $p(x)$in the domain of $1\le x\le 100$

$$\ln G(\alpha)=\ln\left[\frac{AE}{\beta R}\right]+\ln[p(x)]= \qquad (4)$$
$$\ln\left[\frac{AE}{\beta R}\right]+\ln[h(x)]-2\ln x-x$$

Various integral methods differ from each other just in their different ways to deal with the term of $\ln[h(x)]$. In terms of the different ways the integral methods fall into two types as follows.

Type A: Merging the term of $\ln[h(x)]$ *into* $\ln\left[\frac{AE}{\beta R}\right]$ [2–7]

This process leads to the expression:

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}h\left(\frac{E}{RT}\right)\right]-\frac{E}{RT} \qquad (5)$$

This type assumes that the term of $\ln\left[\frac{AR}{\beta E}h\left(\frac{E}{RT}\right)\right]$ can be regarded as a constant for T, and thus the plot of $\ln\frac{G(\alpha)}{T^2}$ *vs.* the reciprocal of T would result in a straight line for a correct reaction model function. The activation energy E is obtained from the slope term of the regression line, and then the frequency factor A can be evaluated from the intercept term. For the methods of this type, the differences among them lie in the involved different approximations of temperature integral:

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(1-2\frac{RT}{E}\right)\right]-\frac{E}{RT} \qquad (6\text{–}1)$$

(Coats-Redfern's method [2])

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(\frac{1-2\frac{RT}{E}}{1-4\left(\frac{RT}{E}\right)^2}\right)\right]-\frac{E}{RT} \quad (6\text{–}2)$$

(Lee-Beck's method [4])

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(\frac{1-2\frac{RT}{E}}{1-6\left(\frac{RT}{E}\right)^2}\right)\right]-\frac{E}{RT} \quad (6\text{–}3)$$

(Li Chung-Hsiung's method [5])

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(\frac{1-2\frac{RT}{E}}{1-5\left(\frac{RT}{E}\right)^2}\right)\right]-\frac{E}{RT} \quad (6\text{–}4)$$

(Agrawal's method [6])

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(\frac{1-2\frac{RT}{E}}{1-4.6\left(\frac{RT}{E}\right)^2}\right)\right]-\frac{E}{RT} \quad \text{(a) and}$$

(6–5) (Ran-Ye's method [7])

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(\frac{1-2\frac{RT}{E}}{1-5.2\left(\frac{RT}{E}\right)^2}\right)\right]-\frac{E}{RT} \quad \text{(b)}$$

The simplest one is the simplified Coats-Redfern's method:

$$\ln\frac{G(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\right]-\frac{E}{RT} \quad (6\text{–}6)$$

Obviously, this method adopts Frank-Kameneskii's approximation [3]:

$$p(x)=\exp(-x)/x^2\text{, i.e. } h(x)=1 \quad (7)$$

Whether the term of $\ln\left[\frac{AR}{\beta E}h\left(\frac{E}{RT}\right)\right]$ can be viewed as a constant has been a subject of considerable discussions. In most cases, the inequality of $\frac{E}{RT}$ » 1 holds for the general range of E and temperatures of decomposition reactions, and thus $\ln\left[\frac{AR}{\beta E}h\left(\frac{E}{RT}\right)\right]$ can be regarded as constant.

Type B: Merging the term of ln[h(x)] into –2lnx–x:

For this type, the term $\ln[h(x)]$ isn't combined with $\ln\left[\frac{AE}{\beta R}\right]$ to organize a nearly constant term, but integrated with the term of $-2\ln x-x$ which varies with x. The major point of this method is that $\ln[h(x)]$ is assumed to have the following approximation form:

$$\begin{aligned}&\ln[h(x)]=a'\ln x+b'x+c'\text{, or}\\&\ln[p(x)]=a\ln x+bx+c\end{aligned} \quad (8)$$

by which we obtain the integral expression:

$$\ln\frac{G(\alpha)}{T^{-a}}=c+\ln\left[\frac{AE}{\beta R}\left(\frac{E}{R}\right)^a\right]+b\frac{E}{RT} \quad (9)$$

The plot of $\ln\frac{G(\alpha)}{T^{-a}}$ *vs.*1/*T* should result in a straight line of slope *bE*/*R* for the correct reaction model. *E* and *A* can be obtained respectively from the slope and intercept terms.

A method of this kind was first proposed by Madhusudanan *et al.* [10], for which the approximate formula of $\ln[p(x)]$ is

$$\ln[p(x)]=-1.921503\ln x-1.000953x-0.297580 \quad (10)$$

Due to its simplicity, the formula has been widely used in thermal analysis [22–25]. Two other formulae [26] in this form, which were usually referred to [27–29], were proposed as below:

$$\ln[p(x)]=-1.920620\ln x-1.000974x-0.299963 \quad (11)$$

$$\ln[p(x)]=-1.884318\ln x-1.001928x-0.389677 \quad (12)$$

The following formula developed recently is due to Tang *et al.* [16] by using a two-step linear fitting process:

$$\begin{aligned}&\ln[p(x)]=-1.89466100\ln x-\\&-1.00145033x-0.37773896\end{aligned} \quad (13)$$

It should be pointed out that the difference of the parameter sets of (a, b, c) in the Eqs (10–13) is due to the corresponding different deriving procedures and as well the accuracy of the original tabulated values of $p(x)$ used in the derivation. Equations (10) and (11) were respectively derived by the two- and threeterm truncations of MKN expansion of $p(x)$ while for Eq. (12) all terms were reserved. All these three equations share some common linear relationship assumptions.

Comparatively, Eq. (13) should be more accurate since it was derived directly from the numerical linearly fitting calculation.

An extreme situation of Eq. (8) is a=0, i.e. $\ln[p(x)] = bx + c$. Doyle [9] found that within a certain interval of x the term $\ln[p(x)]$ varies almost linearly *vs.* x. He proposed the approximation of this form by taking the first two terms of the asymptotic expansion of $p(x)$ as the approximation:

$$\ln[p(x)] = -1.0516x - 5.3308 (20 \le x \le 60) \quad (14)$$

We can improve the parameters by using linear fitting calculation, and obtain a more accurate approximation:

$$\begin{aligned}\ln[p(x)] = -1.05162960x - \\ -5.26936572 (20 \le x \le 60)\end{aligned} \quad (15)$$

In mathematics, there's another simplified form of Eq. (8), i.e. $\ln[p(x)] = a \ln x + c\,(b = 0)$. However, since the term varies nonlinearly with ln$x$ during the general interval $\ln[p(x)]$ of x, there's no possibility to obtain an approximation in this form.

Error analysis of the integral methods

In this section we conduct the error analysis of kinetic parameters respectively for the above two types of integral methods. Let us use (E_e, A_e) to denote the evaluated values of (E, A). The relative error of can then be defined by the following expression:

$$\varepsilon_E = \frac{E_e - E}{E} \quad (16)$$

Error analysis of Type A methods

The integral methods of Type A share a common process of calculating the activation energy, i.e. viewing $\ln\left[\frac{AR}{\beta E} h\left(\frac{E}{RT}\right)\right]$ as a const. and plotting $\ln\frac{G(\alpha)}{T^2}$ *vs.* $1/T$. The activation energy is obtained from the slope term of the regression curve:

$$\delta \ln\frac{G(\alpha)}{T^2} / \delta\frac{1}{T} = -\frac{E_e}{R} \quad (17)$$

Therefore, it's obvious that all these methods have the same errors ε_E in calculating the activation energy and differ from each other only in the intercept of the regression line which is related to the frequency factor. Hence, even the simplest form (Eq. (6–6)) may be good enough to evaluate the activation energy.

Ortega [30] derived the error of the activation energy regarding the simplest form of approximations, as follows:

$$\varepsilon_E = \frac{E_e - E}{E} = -\frac{\mathrm{d}\ln h(x)}{\mathrm{d}x} \quad (18)$$

By using $h(x)e^{-x}x^{-2} = p(x)$and the definition of $p(x)$-function, we can derive:

$$h'(x) = h(x)\left(1 + \frac{2}{x}\right) - 1 \quad (19)$$

Thus

$$\varepsilon_E = -\frac{d\ln h(x)}{\mathrm{d}x} = \frac{1}{h(x)} - \left(1 + \frac{2}{x}\right) \quad (20)$$

Although Eqs (18) and (20) are derived for the simplest form of $p(x)$, since all the methods of Type A share the same evaluated values of activation energy, these methods should all satisfy both equations. Error ε_E only depends on the variable $x=E/RT$, and thus can be computed by numerical integral. Figure 2 shows the values of ε_E in the domain of $5 \le x \le 100$. It can be seen that the error is less than 2% when $x \ge 10$. The evaluated value of activation energy is always less than its real value. Since an error less than 2% is generally acceptable, the results indicate that it's unnecessary to use sophisticated approximations in practice, and even the simplest form of $p(x)$ (Eq. (7)) is accurate enough to calculate the activation energy.

The error of frequency factor A should be analyzed correlated with the approximation form of $h(x)$, since A is involved in the intercept term of the regression expression. We take the simplified Coats-Redfern method as an example to evaluate the error. Rewriting Eq. (6–6) gives:

$$\ln\frac{G(\alpha)}{T^2} = \ln\left[\frac{A_e R}{\beta E_e}\right] - \frac{E_e}{RT} \quad (21)$$

Combining it with Eq. (5) gives:

$$\ln\left[\frac{AR}{\beta E} h\left(\frac{E}{RT}\right)\right] - \frac{E}{RT} = \ln\left[\frac{A_e R}{\beta E_e}\right] - \frac{E_e}{RT}$$

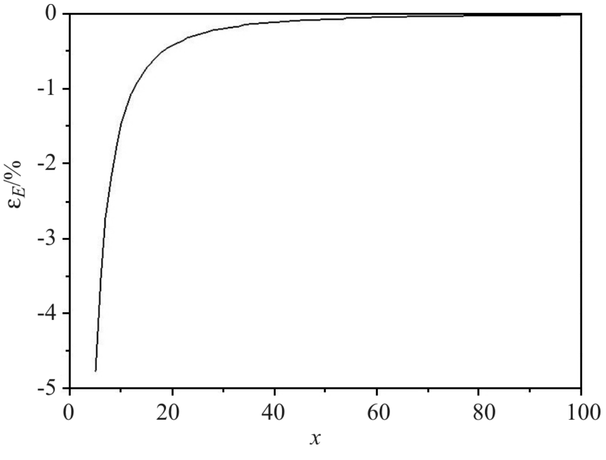

Fig. 2 Error of activation energy for Type A method in the domain of $5 \le x \le 100$

Table 1 The ratios $r=A_e/A$ of Type A methods $\varepsilon_E = \frac{1}{h(x)} - \left(1+\frac{2}{x}\right)$

Simplified Coats-Redfern's method	$(1+\varepsilon_E)h(x)e^{\varepsilon_E x}$
Coats-Redfern's method	$(1+\varepsilon_E)^2 h(x)e^{\varepsilon_E x}x/[(1+\varepsilon_E)x-2]$
Lee-Beck's method	$h(x)e^{\varepsilon_E x}[(1+\varepsilon_E)x+2]/x$
Li Chung-Hsiung's method	$h(x)e^{\varepsilon_E x}[(1+\varepsilon_E)^2x^2-6]/[(1+\varepsilon_E)x^2-2x]$
Agrawal's method	$h(x)e^{\varepsilon_E x}[(1+\varepsilon_E)^2x^2-5]/[(1+\varepsilon_E)x^2-2x]$
Ran-Ye's method	$h(x)e^{\varepsilon_E x}[(1+\varepsilon_E)^2x^2-4.6]/[(1+\varepsilon_E)x^2-2x]$ $h(x)e^{\varepsilon_E x}[(1+\varepsilon_E)^2x^2-5.2]/[(1+\varepsilon_E)x^2-2x]$

if we define $r=A_e/A$, this ratio can be easily deduced as the function of x:

$$r=\frac{A_e}{A}=(1-\varepsilon_E)h(x)e^{\varepsilon_E x}= \\ =\left(1-\frac{2h(x)}{x}\right)\exp\left[\left(\frac{1}{h(x)}-1\right)x-2\right] \tag{22}$$

The r ratios of other integral methods of this type are deduced in the same way and presented in Table 1. Figure 3 gives the values of these ratios in the domain of $5\le x\le 100$. It can be seen that the simplified Coats-Redfern method has the greatest error (the mean absolute error is 10% in $20\le x\le 60$), while the Coats-Redfern method shows the best performance among all these methods. This result is interesting since, except the simplified Coats-Redfern method, the Coats-Redfern method adopts the simplest approximation of the temperature integral:

$$h(x)=1-\frac{2}{x} \tag{23}$$

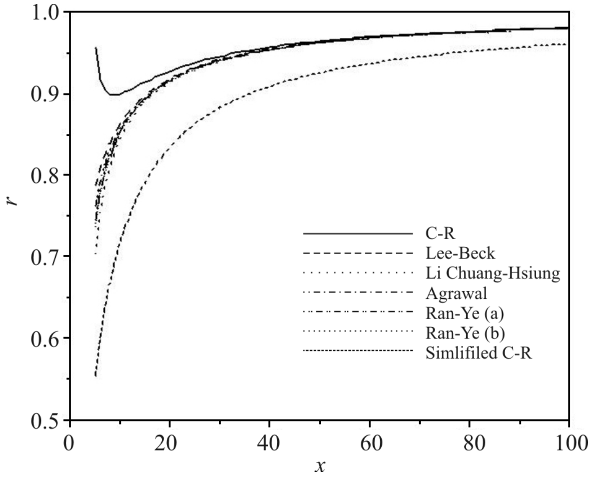

Fig. 3 Ratios $r=A_e/A$ for Type A methods in the domain of $5\le x\le 100$

This further indicates that sophisticated approximations of the temperature integral may be unnecessary for the extraction of kinetic parameters by using the Type A methods.

The error of pre-exponential factor for the Coats-Redfern method can be further reduced based on Eq. (23). Taking the form of this equation for reference, we suppose an approximate form of $h(x)$:

$$h(x)=a\left(1-\frac{b}{x}\right) \tag{24}$$

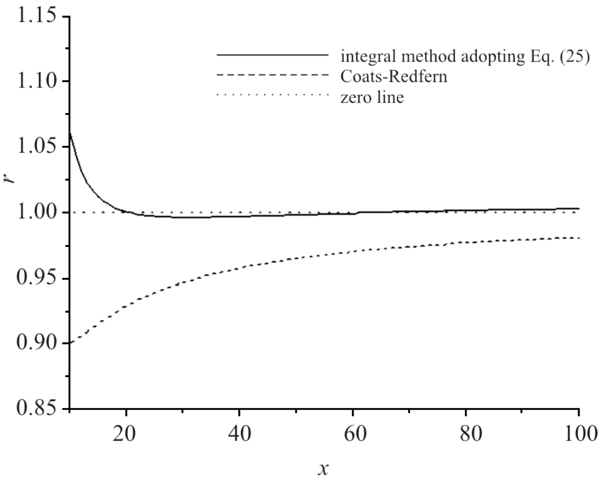

Fig. 4 Ratios $r=A_e/A$ for the Coats-Redfern method and the method using the approximation $h(x)=0.98985(1–3.12028/x)$

It is easy to obtain the coefficients a and b by linear regression, and the result in the domain of $20\le x\le 100$ is:

$$h(x)=0.98985(1-3.12028/x) \tag{25}$$

By this approximate form of $h(x)$, we can see from Fig. 4 that the error of frequency factor is less than 0.5% in the domain of $20\le x\le 100$. Comparatively, the error by Coats-Redfern method exceeds

2%. During $10 \le x \le 20$, the error by Coats-Redfern method is nearly two folds of the error by the new form of $h(x)$.

Error analysis of Type A methods

For the Type B methods, since the simulated activation energy E_e satisfies Eq. (9), we differentiate the left term with respect to $1/T$ and obtain:

$$\delta \ln \frac{G(\alpha)}{T^{-a}} / \delta \frac{1}{T} = b\frac{E_e}{R} \tag{26}$$

The true value of activation energy E satisfies Eq. (4), which can be rewritten as:

$$\ln \frac{G(\alpha)}{T^{-a}} = \ln\left[\frac{AE}{\beta R} h(x)\right] + (a+2)\ln T - \frac{E}{RT} \tag{27}$$

Differentiating the above logarithmic form with respect to $1/T$ gives:

$$\begin{aligned}\delta \ln \frac{G(\alpha)}{T^{-a}} / \delta \frac{1}{T} = \\ = \left[\delta \ln h\left(\frac{E}{RT}\right) / \delta \frac{1}{T}\right] - (a+2)T - \frac{E}{R}\end{aligned} \tag{28}$$

Combining Eqs (26) and (28) gives:

$$b\frac{E_{\mathrm{e}}}{R} = \left[\delta \ln h\left(\frac{E}{RT}\right) / \delta \frac{1}{T}\right] - (a+2)T - \frac{E}{R} \tag{29}$$

by which the error of activation energy can be easily derived as:

$$\varepsilon_{\mathrm{E}} = \frac{E_{\mathrm{e}} - E}{E} = \frac{1}{b}\left[-\frac{1}{h(x)} - \frac{a}{x}\right] - 1 \tag{30}$$

In what follows the revised MKN method with new parameters by Tang (Eq. (13)) and the Doyle method (Eq. (14)) are compared by the above error expression. For the revised MKN method, the error of activation energy is:

$$\begin{aligned}\varepsilon_{\mathrm{E-MKN}} = \frac{1}{-1.00145033} \\ \left[-\frac{1}{h(x)} - \frac{-1.89466100}{x}\right] - 1\end{aligned} \tag{31}$$

and for Doyle method (a=0):

$$\varepsilon_{\mathrm{E-Doyle}} = \frac{1}{-1.0516}\left[-\frac{1}{h(x)}\right] - 1 \tag{32}$$

The ratio $r=A_e/A$ is also deduced in the similar way as indicated above for the error analysis of Type A:

$$r = h(1+\varepsilon_{\mathrm{E}})^{-1-\mathrm{a}} x^{-2-\mathrm{a}} e^{-\mathrm{b}\varepsilon_{\mathrm{E}}\mathrm{x}-\mathrm{bx}-\mathrm{x}-\mathrm{c}} \tag{33}$$

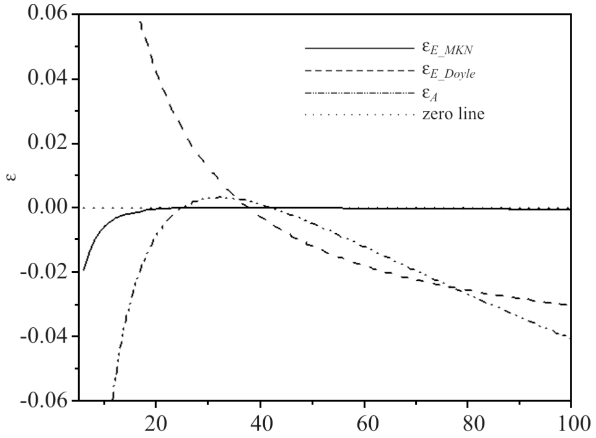

Fig. 5. Errors of the kinetic parameters for Type B method. ε_{E_MKN} ,ε_{A}: errors of activation energy and frequency factor for revised MKN method; ε_{E_Doyle}: error of activation energy for Doyle's method

Figure 5 shows the errors of activation energy ($\varepsilon_{\mathrm{E-MKN}}$, $\varepsilon_{\mathrm{E-Doyle}}$) for the revised MKN method and Doyle method, and the error of frequency factor ($\varepsilon_{\mathrm{A}}=(A_e-A)/A=r-1$) for the revised MKN method. It can be seen that the revised MKN method has excellent performance in calculating activation energy. The error $\varepsilon_{\mathrm{E-MKN}}$ is less than 1% in most cases of $x \ge 10$, and even approaches zero when $x>15$. The error $\varepsilon_{\mathrm{E-Doyle}}$ is much higher, though it is less than 4% when $x>20$. The error of frequency factor ε_{A} of the revised MKN method is less than 4% at most values of x. The error of frequency factor of Doyle method is not listed here since it has too large values (mean absolute error >55% in $20 \le x \le 60$). The results indicate that the revised MKN method can lead to enough accurate activation energy and acceptable frequency factor, while Doyle method should be used cautiously.

Conclusions

In the extraction of the kinetic triplet (activation energy E, frequency factor A and kinetic model) from the decomposition data, different approximations of the temperature integral are used for various integral methods. In this paper, we first propose a new classification approach to divide the integral methods into two types, in terms of their different ways to treat the temperature integral. The two types of integral methods and their adopted temperature integral approximations are analyzed in detail. The error analysis of activation energy shows that Type A methods share the same errors of activation energy, while the Coats-Redfern method can lead to more accurate value of frequency factor than others. The accuracy of frequency factor can be further enhanced by adjusting the expression of the Coats-Redfern approximation. The Coats-Redfern method, although with quite simple temperature integral approximation, has the best performance in Type A methods. This implies that the usage of a sophisticated approximation of the temperature integral may be unnecessary in kinetic analysis. For Type B, the revised MKN method has a lower error in calculating activation energy and an acceptable error in frequency factor, and thus it can be reliably used. Comparatively, the Doyle method has higher error of activation energy and produces great error of the frequency factor, and thus it is not recommended to be used in kinetic analysis.

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