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APPROXIMATIONS FOR THE TEMPERATURE INTEGRAL
Their underlying relationship

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The temperature integral cannot be analytically integrated and many simple closed-form expressions have been proposed to use in the integral methods. This paper first reviews two types of simple approximation expressions for temperature integral in literature, i.e. the rational approximations and exponential approximations. Then the relationship of the two types of approximations is revealed by the aid of a new equation concerning the 1st derivative of the temperature integral. It is found that the exponential approximations are essentially one kind of rational approximations with the form of $h(x)=[x/(Ax+k)]$. That is, they share the same assumptions that the temperature integral $h(x)$ can be approximated by $x/(Ax+k)$. It is also found that only two of the three parameters in the general formula of exponential approximations are needed to be determined and the other one is a constant in theory. Though both types of the approximations have close relationship, the integral methods derived from the exponential approximations are recommended in kinetic analysis.

Keywords: *Approximation, temperature integral, thermal analysis, underlying relationship*

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-state thermal decomposition process, 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-state decomposition process as follows:

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

where α ($0<\alpha<1$) is the fractional conversion, β (K s^{-1}) the heating rate, E (kJ mol^{-1}) the activation energy, A (s^{-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 kinetic model of the reaction mechanism. The approaches to extract the kinetic triplet (E–A–$f(\alpha)$) from the above expression may be generally classified as the differential methods and the integral methods. The main difference between the two classes of methods is that the differential methods refer to local data and offer the values of the kinetic parameters in the given point, whilst the integral ones refer to interval data and offer the values of the kinetic parameters averaged for the considered interval [1]. For the integral methods, integrating Eq. (1) and substituting $x=E/RT$ for T gives:

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

where

$$G(\alpha)=\int_0^\alpha\frac{\mathrm{d}(\alpha)}{f(\alpha)},\quad p(x)=\int_\infty^x\frac{-\mathrm{e}^{-x}}{x^2}\mathrm{d}x \tag{2}$$

Here $p(x)$ is the well-known Arrhenius temperature integral. Although the integral methods are believed to be more reliable and accurate than the differential methods [2], 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 for the temperature integral $p(x)$ with different mathematical complexities and numerical precisions [3–16]. Flynn [17] provided a review on the various approximate expressions for the temperature integral, in which the solutions of the temperature integral are classified into three categories, i.e. series solution, complex approximations and simple approximations. In fact, most of the complex and simple approximations can be derived from one-term, two-term or three-term

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truncations of different series solutions [17]. Besides, some simple approximations are obtained through data-fitting process [11–13], and another kind of approximations are proposed through integration over small temperature intervals to enhance the accuracy [18]. Recently, some new simple approximations with high precision are proposed [11–13, 19]. Though so many approximations for the temperature integral have appeared in the literature, it seems that there are very few papers considering the critical appraisal of the approximations and especially, the inherent relationship of the approximations.

In this work, an equation concerning the 1st order derivative of the temperature integral is proposed and then, the relationship of various approximations for the temperature integral is presented. It is shown that many approximations share the same assumption.

Theoretical background

A range of the approximations for the temperature integral $p(x)$ have been suggested in literature, and here we will consider the best known and the most accurate approximations.

Firstly we introduce another function, $h(x)$ [10, 12, 20], to simplify the mathematical forms of some approximations. $h(x)$ is defined as:

$$h(x) = p(x)x^2e^x \text{ or } p(x)=\frac{e^{-x}}{x^2}h(x) \tag{3}$$

The values of $p(x)$ and $h(x)$ are calculated *vs*. x by numerical integral and showed in Fig. 1. Compared with $p(x)$, $h(x)$ varies slowly and has an asymptotic value of 1 as x increases, and consequently it may be more easy to explore or appraise the approximations for the temperature integral. Both $p(x)$ and $h(x)$ can be called the temperature integral.

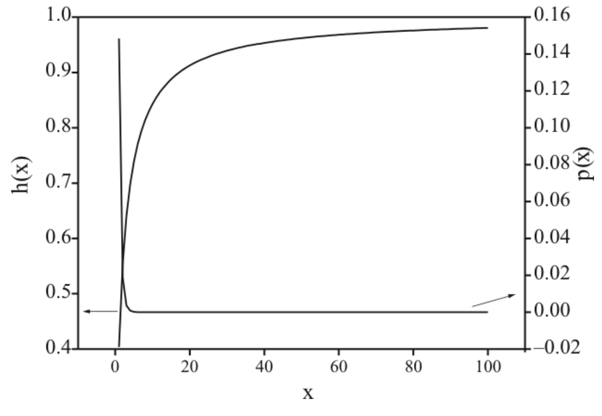

Fig. 1 Values of $h(x)$and $p(x)$ in the domain of $1\leq x\leq 100$

As pointed out in our previous paper [20], the integral methods can be generally classified into two categories. The difference is that one type of integral methods uses the ‘rational’ approximations for the temperature integral and the other uses the ‘exponential’ approximations.

The term of ‘rational’ approximations was first proposed by Senum and Yang [10], who provided a series of such approximations. The fourth order approximation, which is believed to hold very high accuracy, is given by:

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

The simplest one of rational approximations is Frank–Kameneskii’s approximation [4]:

$$h(x)=1 \tag{5}$$

and the classical one is Coats–Redfern’s approximation [3]:

$$h(x)=1-\frac{2}{x} \tag{6}$$

There are many other forms of rational approximations [5–7, 14, 16, 19]. Recently, some new ones were proposed, for example:

$$h(x)=\frac{x}{1.00198882x+1.87391198}$$

(Wanjun–Yumen [13]) (7)

$$h(x)=\frac{x+0.66691}{x+2.64943}$$

(Cai [12]) (8)

It seems that exploring new approximations through data-fitting process or parameter optimization has become fashionable. The new approximations are often more accurate. However, it should be noted that only very simple approximations can be considered for use in thermal analysis [20, 21]. In mathematical sense, reasonable approximations should be able to be justified by their accordance with the mathematical features of the temperature integral. For example, the approximation is anticipated to approach unity as x increases since the function of $h(x)$ has an asymptotic value of 1. In this sense, Eq. (7) is somewhat of deviation.

The term of ‘exponential’ approximations refers to the approximations which contain exponential function, or equivalently logarithmic function, as follows [20]:

$$\ln[h(x)]=a\ln x+bx+c \text{ or } \ln[p(x)]=a'\ln x+b'x+c' \tag{9}$$

where a, b, c, a', b', c' are the parameters and a, b are not both zero (otherwise it will become a rational

Table 1 Typical values of the parameters appeared in the 'exponential' approximation as $p(x)=\exp(-Ax+B)/x^{k}$

Source	A	k	B	No.
Doyle [22]	1.0516	0	–5.3308	1
Starink [23]	1	1.95	–0.235	2
Starink [23]	1.0008	1.92	–0.312	3
Madhusudanan *et al.* [15]	1.000953	1.921503	–0.297580	4
Madhusudanan *et al.* [8]	1.000974	1.920620	–0.299963	5
Madhusudanan *et al.* [8]	1.001928	1.884318	–0.389677	6
Tang *et al.* [11]	1.00145033	1.89466100	–0.37773896	7

approximation, for example, Frank–Kameneskii's approximation).

The most famous exponential approximation was suggested by Doyle [22]:

$$p(x)=\exp(-1.0516x-5.3308) \tag{10}$$

Another widely-used approximation of this kind was first proposed by Madhusudanan *et al.* [15], for which the approximate formula of ln[$p(x)$] is

$$\ln[p(x)]=-1.921503\ln x-1.000953x-0.297580 \tag{11}$$

Madhusudanan *et al.* [15] also proposed the general formula of 'exponential' approximations as $p(x)=e^{a_1+b_2}x^{a_2}e^{b_1x}$. Starink [23] provided another general formula as $p(x)=\exp(-Ax+B)/x^{k}$ recently. It is obvious that the two formulae are identical in mathematics. Table 1 lists some typical values of the parameters appeared in Starink's general formula of 'exponential' approximations.

Relationship of the exponential and the rational approximations

The exponential and rational approximations are deduced from different mathematical approaches and both are widely used in thermal analysis as two types of integral methods [20]. It seems that no discussion concerning the relationship of the two types of approximations appeared in literature. Here we will consider how the two types of approximations are related to each other.

The general formula of exponential approximations $p(x)=\exp(-Ax+B)/x^{k}$ can be arranged into the form of Eq. (9): $\ln[h(x)]=(2-k)\ln x+(1-A)x+B$. The differential form of this equation is:

$$\frac{h'(x)}{h(x)}=\frac{2-k}{x}+(1-A) \tag{12}$$

By differentiating the definition equation of $h(x)$, $h(x)e^{-x}x^{-2}=p(x)$, we can obtain the 1st order derivative of the function $h(x)$:

$$h'(x)=\left(1+\frac{2}{x}\right)h(x)-1 \tag{13}$$

This equation seems to appear firstly in our previous paper [20]. It has many applications for the research of temperature integral, for example, higher order derivative can be deduced and then a series of new approximations for the temperature integral can be obtained [19].

Combining the Eqs (12) and (13), one can obtain:

$$h(x)=\frac{x}{Ax+k} \tag{14}$$

It is very interesting that Eq. (14) is just one kind of the rational approximations. That is to say, the exponential approximations in essence belong to the rational approximations, and are very simple rational approximations. They share the same assumption that the temperature integral $h(x)$ can be approximated by $x/(Ax+k)$. If $A=1$, Eq. (14) becomes ordinary rational approximations, for example, Gorbachev's approximation [5]. It is surprising that the rational approximation with the form of Eq. (14) and $A\neq1$, i.e. Eq. (7), was proposed just a few years ago. And in the above part, it is pointed out that Eq. (7) is somewhat of deviation from mathematical features of $h(x)$. Maybe this consideration delays the discovery of more rational approximations with the form of Eq. (14).

Two parameters of the exponential approximation $p(x)=\exp(-Ax+B)/x^{k}$, A and k, appear in Eq. (14). Where is B? It can be deduced that B is an integral constant. Integrating Eq. (12) in the range $[x_0, x]$ will produce:

$$\ln[h(x)]=(2-k)\ln x+(1-A)x+B \tag{15}$$

with

$$B=\ln[h(x_0)]-(2-k)\ln x_0-(1-A)x_0 \tag{16}$$

From this equation, it is obvious that B is a constant and can be calculated directly, however, many papers have regarded it as a variable which needs to be determined. In fact, the values of B calculated from Eq. (16) will vary a little with x_0 (see below), which roots in the assumption that the temperature integral can be approximated by $p(x)=\exp(-Ax+B)/x^{k}$. Thus the rationality of the exponential approximations can be assessed through the deviation degree of B from its average value.

In the following, we will analyze all the three parameters (A–k–B) of the exponential approximations presented in Table 1 in detail.

No. 1: Doyle's approximation

In Doyle's approximation (Eq. (10)), k=0. So Eq. (14) can be converted into:

$$h(x)=\frac{1}{A} \tag{17}$$

i.e. the underlying assumption of Doyle's approximation is that the function $h(x)$ can be regarded as a constant. The parameter A has a physical meaning that it is the reciprocal of averaged value (represented by $\langle h(x)\rangle$ in the following) of $h(x)$. So it can be obtained theoretically other than through Doyle's approaches. In the range of $x\in[20, 60]$ which is the valid domain of Doyle's approximation, $\langle h(x)\rangle$ can be calculated as:

$$\langle h(x)\rangle=\int_{20}^{60}h(x)\mathrm{d}x/\int_{20}^{60}1\mathrm{d}x=\int_{20}^{60}p(x)x^{2}\mathrm{e}^{x}\mathrm{d}x/40 \tag{18}$$

By combining the asymptotic expansion of $p(x)$, Eq. (18) becomes:

$$\begin{aligned}\langle h(x)\rangle&=\int_{20}^{60}\frac{\mathrm{e}^{-x}}{x^{2}}\left(1-\frac{2}{x}+\sum_{j=2}^{\infty}\frac{(-1)^{j}(j+1)!}{x^{j}}\right)x^{2}\mathrm{e}^{x}\mathrm{d}x/40\\&=\left[x-2\ln x+\sum_{j=2}^{\infty}\frac{(-1)^{j}(j+1)!}{1-j}x^{1-j}\right]_{20}^{60}/40\approx0.9495\end{aligned} \tag{19}$$

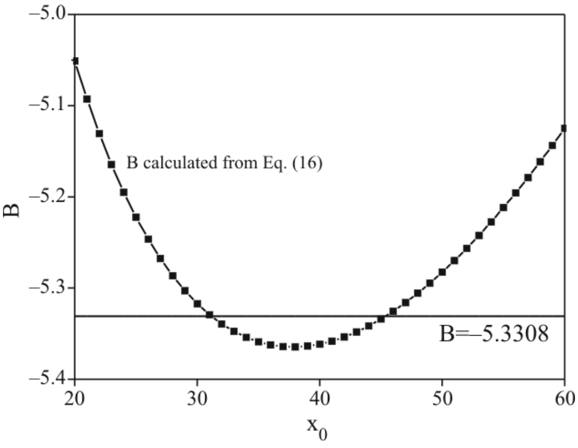

Fig. 2 Comparison of the values of B calculated from Eq. (16) with the value from Table 1 for Doyle's approximation

Thus from Eq. (17), A equals 1.0532, which is very close to 1.0516 in Doyle's approximation.

As for the parameter B, it can be calculated from Eq. (16). Figure 2 gives the theoretical value of B when x_0 is sampled from the range of [20, 60]. Here $h(x)$ is approximated by Eq. (4) and A=1.0516. It can be seen that B varies with the value of x_0 and differs from –5.3308 which appeared in Doyle's approximation. This is because Doyle's assumption (Eq. (17)) is too simple and deviates much from the true values. Therefore this approximation should be used carefully.

No. 2: Starink's approximation

According to Eq. (14), Starink's approximation is equal to:

$$h(x)=\frac{x}{x+1.95} \tag{20}$$

It can be regarded as an improvement of Gorbachev's approximation [5], where $h(x)=x/(x+2)$. Because Eq. (20) is also very simple, it can be deduced that the values of B from Eq. (16) will differ from –0.235 in Starink's approximation, as Fig. 3 shows.

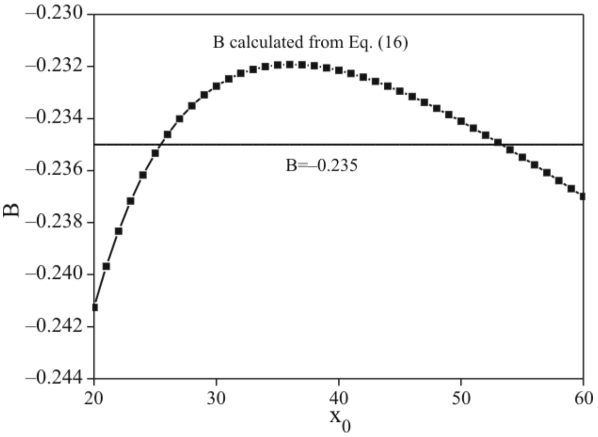

Fig. 3 Comparison of the values of B calculated from Eq. (16) with the value from Table 1 for Starink's approximation (No. 2)

No. 3–7: M-approximations

The approximations represented by No. 3–7 (named as M-approxiamtions for convenience) in Table 1 have some common features. Madhusudanan's approximations (No. 4–6) are derived from the two- or three-term truncations of MKN expansion of $p(x)$ [15]. No. 3 and 7 can be regarded as the improved forms of Madhusudanan's approximations. Especially, No. 7 used two-step linearly fitting process to obtain more accurate (A–k–B) values and the corresponding integral methods are more reliable.

Here we can point out that only the first-step linearly fitting process (to determine A and k) in their paper is necessary and the second-step (to determine B) can be omitted because B is an integral constant.

M-approximations are identical to Eq. (14) with more accurate values of (A–k). Up to now, the most accurate values appear in Eq. (7) with A=1.00198882 and k=1.87391198. Then the value of B can be determined from Eq. (16). Obviously, the values of (A–k) depend on the range of x and the accuracy can be enhanced by reasonable manipulation of Eq. (14). For example, Eq. (14) can be linearized as:

$$y=Ax+k,\ y=\frac{x}{h(x)} \tag{21}$$

In the range of $x\in[15, 60]$ (in which the overwhelming majority of reactions occur [23]), the fitted line will produce the parameters with A=1.0014452 and k=1.8915041 (Fig. 4, data points are sampled from $x\in[15, 60]$ with the interval of 0.01).

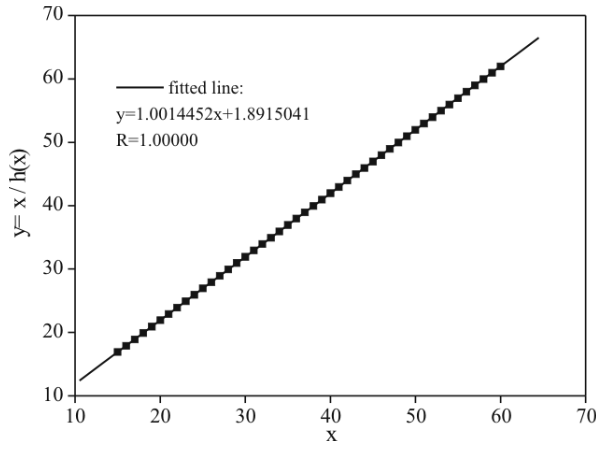

Fig. 4 The linear relationship of $y=x/h(x)$ with x in the range of [15, 60]

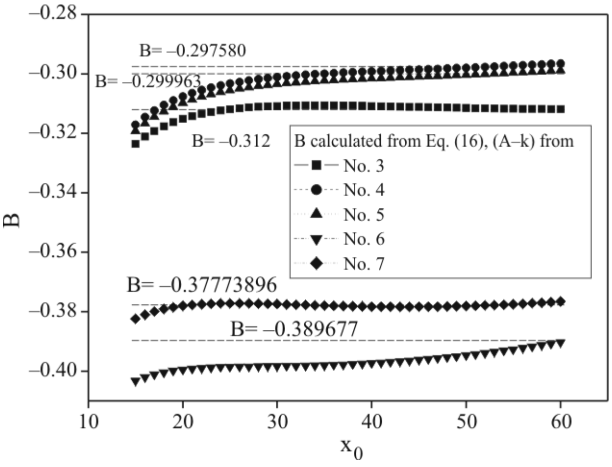

Fig. 5 Comparison of the values of B calculated from Eq. (16) with the value from Table 1 for M-approximation (No. 3–7)

When (A–k) are set, the value of B can be calculated by Eq. (16). Figure 5 presents the theoretical B values compared with the values from Table 1. It can be seen that Starink's and Tang's approximations hold higher precision than others and thus they are recommended in thermal analysis.

Conclusions

'The temperature integral has played a somewhat enigmatic role in the development of thermal analysis reaction kinetics' [17]. Many of the problems have resulted from the inability to accurately approximate the temperature integral by a simple closed-form expression which is suitable for use in the integral methods. So various approximations for the temperature integral have appeared in literature. As two main types of approximations, the rational and exponential approximations have been proposed separately and developed into two types of integral methods.

In this paper, the relationship of the rational and exponential approximations is revealed by the aid of a new equation concerning the 1st derivative of the temperature integral. It is found that the exponential approximations are essentially one kind of the rational approximations with the form of $h(x)=x/(Ax+k)$. That is, they share the same assumptions that the temperature integral $h(x)$ can be approximated by $x/(Ax+k)$. It is also found that only two of the three parameters in the general formula of exponential approximations are needed to be determined and the other one is a constant in theory.

Though the exponential approximations belong to the rational approximations, their corresponding integral methods use them in different ways. For example, the rational approximation Eq. (7) is used as:

$$\begin{aligned}&\ln\left[\frac{G(\alpha)}{T^2}\right]=\\&=\ln\left[\frac{AR}{\beta(1.00198882E+1.87391198RT)}\right]-\frac{E}{RT}\end{aligned} \tag{22}$$

The integral method still needs to assume that $\ln\left[\frac{AR}{\beta(1.00198882E+1.87391198RT)}\right]$ is nearly a constant for T and the plot of $\ln[G(\alpha)/T^2]$~$1/T$ would result in a straight line for the correct reaction model. While the exponential approximation No. 7 [11] is used as:

$$\ln\left[\frac{G(\alpha)}{T^{1.89466100}}\right]= \left[\ln\frac{AE}{\beta R}+3.63504095-1.89466100\ln E\right]- -1.00145033\frac{E}{RT} \qquad (23)$$

The plot of $\ln[G(\alpha)/T^{1.89466100}]\sim 1/T$ will result in a straight line for the correct reaction model. This integral method adopts no assumptions other than the approximation for the temperature integral and will be more accurate in the calculation of kinetic parameters [20]. Therefore, the integral methods, which are derived from the exponential approximations, are recommended to be a prior choose in kinetic analysis, though the exponential approximations in essence are one kind of the rational approximations.

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