New Approximate Formula for the Generalized Temperature Integral

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The generalized temperature integral $\int_0^T T^m \exp(-E/RT)dT$ *frequently occurs in nonisothermal kinetic analysis. This article has proposed a new approximate formula for the generalized temperature integral, which is in the following form:*

$$h_m = x^{(0.11168+0.04426m)} e^{(-0.00150-0.00055m)x-(0.39922+0.16360m)}.$$

For commonly used values of m in kinetic analysis, the deviation of the new approximation from the numerical values of the integral is within 0.4%. More importantly, the new formula represents the exponential approximation, which is not found earlier, and it can result in a new and very accurate integral method in kinetic analysis.
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Introduction

Nonisothermal thermal–analytical techniques, such as thermogravimetry and differential scanning calorimetry, have been widely used to study the kinetics and mechanism of solid thermal decomposition reactions. Rate of the processes in condensed state is generally a function of temperature and conversion. If the assumption of the single-step kinetics approximation is used,[1] the rate of the processes can be formally described as a product of two separable functions, $k(T)$ and $f(\alpha)$,

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \tag{1}$$

where α is the fractional conversion and T is the absolute temperature. Various equations of the function $k(T)$ were proposed since 19th century,[2] one of which is expresses as

$$k(T) = AT^m \exp(-E/RT), \tag{2}$$

where E is the activation energy, A the constant, and R the universal gas constant. The exponent m arises from the temperature dependence of the pre-exponential factor, which is undoubtedly often present in the kinetically complex condensed phase systems.[3] The case $m = 0$ occurs in famous Arrhenius theory, $m = -1/2$ in the Langmuir evaporation theory, and $m = 1/2$ in the collision theory. In the transition-state theory, the power of the temperature is 1 or greater (for example, 2) depending on the number of reacting species involved in the geometry of the activated complex.[2]

Combining Eqs. 1 and 2, one obtains at constant heating rate, β, upon integration,

$$G(\alpha) = \int_0^\alpha d\alpha/f(\alpha) = \int_0^T AT^m \exp(-E/RT)dT/\beta = \frac{A}{\beta}I(m,T). \tag{3}$$

A serious difficulty of the mathematical modeling of the nonisothermal processes results from the fact that the integral $I(m,T)$ cannot be solved in a close form in most cases. Miscellaneous approximations,[4–9] with varying complexity and precision, have been proposed for the evaluation of the integral $I(m,T)$ for the special case of $m = 0$. For arbitrary values of the temperature exponent m, Singh et al.[10] developed a technique based on the complementary incomplete gamma function for the evaluation of the integral $I(m,T)$.

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However, the evaluation of the complementary incomplete gamma function is complex and takes much computing time. So, an approximation for the integral $I(m,T)$, which can be easily programmed and carried out in a personal computer with enough precision, will be preferred in evaluating kinetic parameters from the data of nonisothermal experiments. Wanjun et al.[11] published this kind of research first and proposed two approximate formulae for calculation of the integral $I(m,T)$ by using integration-by-parts approaches. Later, an approximation with first-degree rational fraction was proposed by Cai and Liu,[12] and a procedure to yield a series of the approximations with different complexity and accuracy is proposed by Chen and Liu.[13] Recently, Cai et al. have proposed two new approximations, which are more accurate.[14,15] It is noteworthy to point out that all these formulae are of rational approximations. As we know, there is another type of approximations for the ordinary temperature integral $I(0,T)$, that is, the exponential approximations, which is believed to be more accurate in the calculation of kinetic parameters.[16] In this article, we will try to find the exponential approximation for the generalized temperature integral $I(m,T)$.

Theory

With the substitution $x = E/RT$, $I(m,T)$ in Eq. 3 can be expressed as

$$I(m,T) = (E/R)^{m+1} \int_x^\infty \frac{\exp(-x)}{x^{m+2}} dx \tag{4}$$

Define

$$h_m = \int_x^\infty \frac{\exp(-x)}{x^{m+2}} dx \Big/ \frac{\exp(-x)}{x^{m+2}} \tag{5}$$

Then

$$I(m,T) = (E/R)^{m+1} \frac{\exp(-x)}{x^{m+2}} h_m. \tag{6}$$

Thus, the problem of approximating the integral $I(m,T)$ is converted to finding the approximation for h_m. Figure 1 presents the numerical integration values of h_m at commonly used m values ($m = -0.5$–3) in the range of $5 \leq x \leq 100$. It is found that the values of h_m are higher than 0.5 and gradually approaching to 1 with the rise of x.

If Eqs. 3 and 6 are taken into account, the following expression is obtained

$$\ln G(\alpha) = \ln\left[\frac{A}{\beta}(E/R)^{m+1}\right] - x - (m+2)\ln x + \ln h_m. \tag{7}$$

To develop the integral methods for kinetic analysis, the term of $\ln h_m$ must be properly dealt with. In the special case of $m = 0$, the integral methods in general use can be divided into two types in terms of their different ways to deal with the term of $\ln h_m$ ($m = 0$): one type regards it as a constant vs. x and the other approximates it with the linear combination of the items of $\ln x$ and x.[16] These two types of integral methods naturally result in two types of approximations for $h_m(m = 0)$, that is, the rational approximations and the exponential approximations. For h_m with arbitrary values of m, all of the published approximated approximations are of the rational approximations.[11–13] Here, we try to approximate h_m in the exponential form to propose a new type of integral methods, that is to say, we suppose $\ln h_m$ can be approximated by the linear combination of $\ln x$ and x as follows:

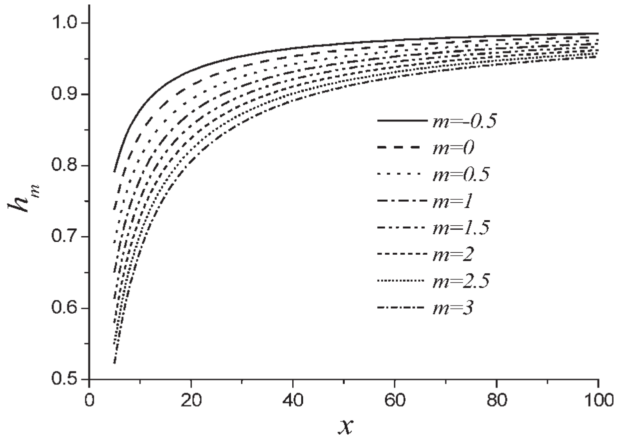

Figure 1. Numerical values of h_m as a function of x at different m values.

$$\ln h_m \approx (m+2+a_m)\ln x + (1+b_m)x + c_m, \tag{8}$$

Here, a_m, b_m, c_m are constant for x but vary with m. The corresponding integral method (Eq. 7) for the evaluation of the kinetic parameters can be rearranged as

$$\ln\frac{G(\alpha)}{T^{-a_m}} = \ln\left[\frac{A}{\beta}\left(\frac{E}{R}\right)^{m+1+a_m}\right] + c_m + \frac{b_m E}{R}\frac{1}{T}. \tag{9}$$

Because the above integral method is based on the approximation of Eq. 8, the validity of the new approximation should be certified.

The differential form of Eq. 8 is:

$$\frac{h'_m}{h_m} \approx (m+2+a_m)\frac{1}{x} + (1+b_m) \tag{10}$$

In a recently published article,[13] we obtained the expression of the first-order derivative of h_m:

$$h'_m = h_m\left(1 + \frac{m+2}{x}\right) - 1 \tag{11}$$

So, Eq. 10 can be rearranged as

$$\frac{x}{h_m} \approx -b_m x - a_m \tag{12}$$

The validity of Eq. 12 can be testified by checking whether the variable of x/h_m is linear function of x. For example, Figure 2 plots x/h_m vs. x with $m = 2$ and $15 \leq x \leq 60$. The overwhelming majority of reactions occur for $15 \leq x \leq 60$.[17] Figure 2 proves that the values of x/h_m increase linearly with the rise of x at $m = 2$. At other values of m,

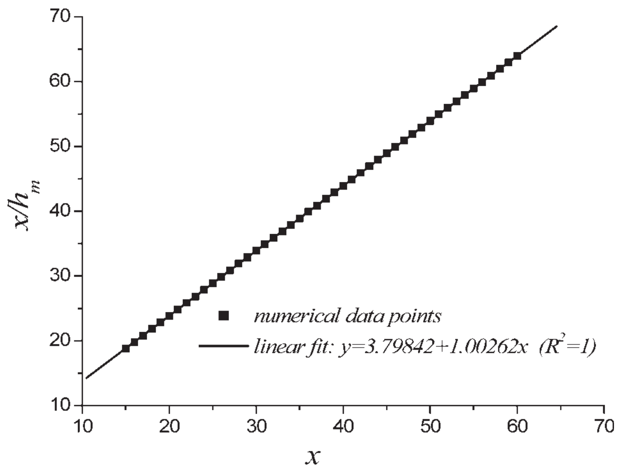

Figure 2. The linear relationship of x/h_m with x at $m = 2$.

such linearity can be also testified. Table 1 presents the values of $-b_m$ and $-a_m$, which are obtained from the slope and intercept of the fitted lines, respectively. Once the values of b_m and a_m are determined, the value of c_m can be calculated from Eq. 8 as

$$c_m \approx \ln h_m - (m + 2 + a_m)\ln x - (1 + b_m)x. \tag{13}$$

From the aforementioned expression, it seems that c_m varies with x. Indeed, c_m varies but very little (for example, see Figure 3, the maximum relative error is 0.5%). The variation comes from the assumption that ln h_m can be approximated by the expression of Eq. 8. On the other hand, the very small variation indicates the assumption is reasonable. The values of c_m in Table 1 are the average of the values calculated by Eq. 13. All of the values of a_m, b_m and c_m at different m values in Table 1 are plotted in Figure 4. It is found that there is a linear relationship among the values of $-a_m$, $-b_m$, or $-c_m$ and m. The fitted lines are

$$-a_m = 1.89021 + 0.95479m \tag{14}$$

$$-b_m = 1.00147 + 0.00057m \tag{15}$$

$$-c_m = 0.39329 + 0.16656m \tag{16}$$

So, the new approximation for h_m, Eq. 8, can be rearranged as

$$h_m \approx h_{ma} = x^{(0.10979+0.04521m)} e^{(-0.00147-0.00057m)x-(0.39329+0.16656m)} \tag{17}$$

Here, h_{ma} represents the approximation of the generalized temperature integral.

So, the integral method, Eq. 9, becomes

$$\ln\frac{G(\alpha)}{T^{1.89021+0.95479m}} = \ln\left[\frac{A}{\beta}\left(\frac{E}{R}\right)^{0.04521m-0.89021}\right] - (0.39329 + 0.16656m) - (1.00147 + 0.00057m)\frac{E}{RT} \tag{18}$$

The aforementioned integral method can be also rearranged into an isoconversional method, which is preferred in kinetic analysis:

$$\ln\frac{\beta}{T^{1.89021+0.95479m}} = \text{const.} - (1.00147 + 0.00057m)\frac{E}{RT}. \tag{19}$$

Evaluation of accuracy of the new approximate formula

The aim of this section is to assess the precision of the newly proposed approximation for the generalized temperature integral at commonly used m values in their range of applicability in kinetic studies, that is, $m = -0.5$, 0, 0.5, 1, and 2. The relative error of the approximation is defined by the expression:

$$\varepsilon = \frac{h_{ma} - h_m}{h_m}. \tag{20}$$

Here, h_m is the numerical integration value, which is showed in Figure 1, and h_{ma} represents the value calculated by the approximation of Eq. 17. Figure 5 presents the relative errors. It is clearly seen that the relative errors are very low (<0.4%) in all four cases. It is also shown that the errors are zero around $x = 36$ and 63. Compared with the published approximations proposed by Wanjun et al.,[11] Chen and Liu,[13] and Cai et al.,[12,14,15] it can be found that the new approximation is a little more accurate in some domains of x and less accurate in other domains. However, it must be recalled that the new approximation represents a new type of approximations (i.e., the exponential approximations), and from the new approximation, some new and more reliable integral methods, Eqs. 18 and 19, can be obtained.

Precision of the new integral method in calculating the activation energy

The main purpose of approximating the generalized temperature integral is for the calculation of the kinetic parameters, in particular, the activation energy. The integral methods derived from the new approximation are desired to be more reliable and easier to use. This section will analyze the precision of the new integral method for the determination of the activation energy.

Table 1. The Values of the Parameters Appeared in ln $h_m = (m + 2 + a_m)$ln $x + (1 + b_m)x + c_m$

m	−0.5	0	0.5	1	1.5	2	2.5	3
$-a_m$	1.41613	1.89062	2.36618	2.84265	3.32007	3.79842	4.27773	4.75776
$-b_m$	1.00113	1.00146	1.00177	1.00207	1.00236	1.00262	1.00287	1.00311
$-c_m$	0.29963	0.39200	0.48104	0.56722	0.65039	0.73067	0.80803	0.88298

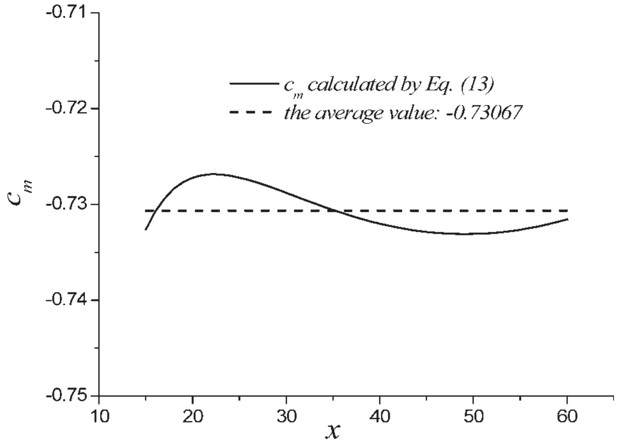

Figure 3. Comparison of c_m calculated by Eq. 13 and its average value at $m = 2$.

In the usage of the new integral method to calculate the activation energy, we need to differentiate the left term of Eq. 9 with respect to $1/T$:

$$d\left[\ln\frac{G(\alpha)}{T^{-a_m}}\right]\Big/ d\left(\frac{1}{T}\right)=\frac{b_m E_e}{R}. \tag{21}$$

Here, E_e refers to the apparent value of the activation energy obtained from the integral method.

The true value of activation energy E satisfies Eq. 4. Rearranging and differentiating this equation with respect to $1/T$ will lead to

$$d\left[\ln\frac{G(\alpha)}{T^{-a_m}}\right]\Big/ d\left(\frac{1}{T}\right)=\frac{E}{R}\left[-1-\frac{m+2+a_m}{x}+\frac{a(\ln h_m)}{dx}\right] \tag{22}$$

Combining Eqs. 21 and 22 gives

$$\frac{E_e}{E}=\frac{1}{b_m}\left[-1-\frac{m+2+a_m}{x}+\frac{d(\ln h_m)}{dx}\right] \tag{23}$$

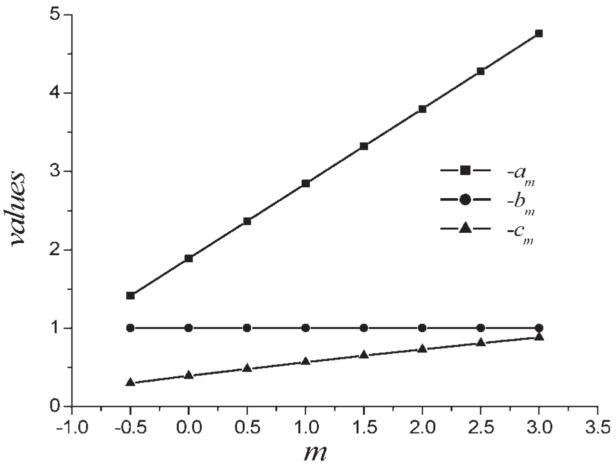

Figure 4. The relationships of $-a_m$, $-b_m$, and $-c_m$ with m.

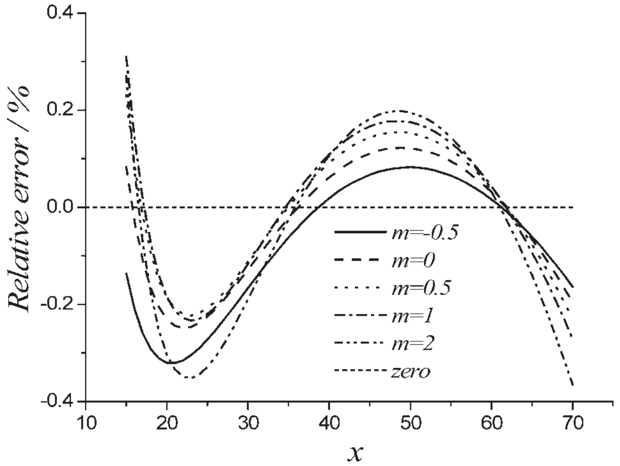

Figure 5. The relative error of the approximation of Eq. 17.

Considering that $h'_m = h_m(1+\frac{m+2}{x})-1$ (Eq. 11), the aforementioned expression can be simplified as

$$\frac{E_e}{E}=-\frac{1}{b_m}\left(\frac{a_m}{x}+\frac{1}{h_m}\right). \tag{24}$$

The relative error of the apparent activation energy obtained from the new integral method can be defined and calculated by the following expression

$$\varepsilon_E=\frac{E_e-E}{E}=-\frac{1}{b_m}\left(\frac{1}{h_m}+\frac{a_m}{x}\right)-1. \tag{25}$$

It is obvious that the relative error is dependent on the parameters $x = E / RT$ and m. Figure 6 shows the relative error of the activation energy calculated by using the new integral method. It can be seen that the new integral method has excellent performance in calculating the activation energy. The relative error ε_E is less than 0.8% in most cases of $x \geq 10$. It even approaches zero (less than 0.04%) when $20 \leq x \leq 60$. The results show that the new integral method proposed in this article is very accurate in the determination of the activation energy.

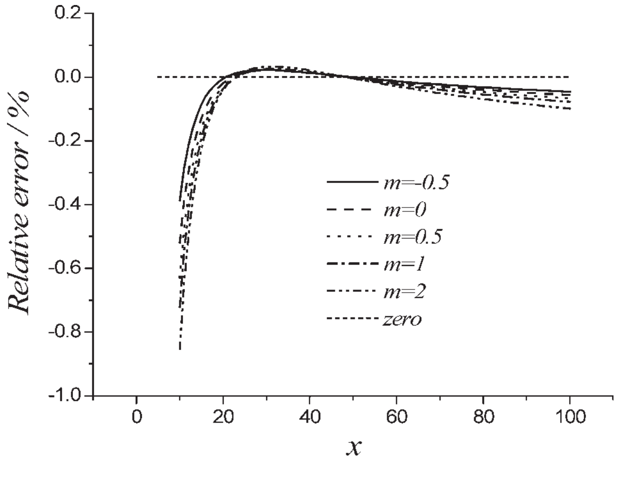

Figure 6. The relative error of the apparent activation energy obtained from the new integral method.

Conclusions

In this article, we have proposed a new approximate formula for the generalized temperature integral $I(m,T) = \int_0^T T^m \exp(-E/RT)dT$, which frequently occurs in nonisothermal thermal analysis. For commonly used values of m, the deviation of the new approximation from numerical values of $I(m,T)$ is within 0.4% when $15 \leq x \leq 60$. The new approximation belongs to the exponential approximation, which is different from the published rational approximations. The new integral methods derived from the new approximation show very good performance in calculating the activation energy and can play an important role in the evaluation of kinetic parameters from nonisothermal kinetic analysis.

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