

A PROCEDURE TO APPROXIMATE THE GENERALIZED TEMPERATURE INTEGRAL

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In the paper a new procedure to approximate the generalized temperature integral $\int_0^T T^m \exp(-E/RT) dT$, which frequently occurs in non-isothermal thermal analysis, are presented. A series of the approximations for the temperature integral with different complexity and accuracy are proposed from the procedure. For commonly used values of m in kinetic analysis, the deviation of most approximations from the numerical values of the integral is within 0.7%, except the first approximation (within 4.0%). Since they are simple in calculation and hold high accuracy, the approximations are recommended to use in the evaluation of kinetic parameters from non-isothermal kinetic analysis.

Keywords: approximation, integral, kinetic analysis, non-isothermal

Introduction

Non-isothermal thermal-analytical 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. 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 employed [1], the rate of the processes can be formally described as a product of two separable functions, $k(T)$ and $f(\alpha)$,

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

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 expressed as

$$k(T) = AT^m \exp(-E/RT) \quad (2)$$

where E is the activation energy, A the pre-exponential factor, 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, and the cases $m=1/2$ occurs in the collision theory. In the transition state theory, the power of the temperature is 1 or greater (for example, 2) depending

upon 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,

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

A serious difficulty of the mathematical modeling of the non-isothermal processes results from the fact that the integral $I(m, T)$ can not be solved in a close form in most cases. Miscellaneous approximations [4–7], 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.* [8] developed a technique based on the complementary incomplete gamma function for the evaluation of the integral $I(m, T)$. 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 non-isothermal experiments. Recently, Wanjun *et al.* [9] published this kind of research firstly and proposed two approximate formulae for calculation of the integral $I(m, T)$ by using integration-by-parts approaches. In the present paper,

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we will present a new procedure to approximate the integral $I(m, T)$ for arbitrary values of the temperature exponent m . The approximations for the integral $I(m, T)$ produced by the procedure are validated by comparing their values with those from numerical integration.

Theory

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

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

Define

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

then $I(m, T) = (E/R)^{m+1} \frac{\exp(-x)}{x^{m+2}} h_m$. Thus the problem of approximating the integral $I(m, T)$ is converted to finding the approximation for h_m .

Equation (5) can be arranged as $h_m \frac{\exp(-x)}{x^{m+2}} = \int_x^{\infty} \frac{\exp(-x)}{x^{m+2}} dx$. By differentiating this equation, one can obtain the expression of the 1st order derivative of h_m :

$$h'_m = h_m \left(1 + \frac{m+2}{x} \right) - 1 \quad (6)$$

Higher order derivatives of $h(x)$ are listed in the following:

$$h_m^{(2)} = h_m \left[1 + 2 \frac{m+2}{x} + \frac{(m+1)(m+2)}{x^2} \right] - \left(1 + \frac{m+2}{x} \right) \quad (7)$$

$$h_m^{(3)} = h_m \left[1 + 3 \frac{m+2}{x} + 3 \frac{(m+1)(m+2)}{x^2} + \frac{m(m+1)(m+2)}{x^3} \right] - \left[1 + 2 \frac{m+2}{x} + \frac{m(m+2)}{x^2} \right] \quad (8)$$

$$h_m^{(4)} = h_m \left[1 + 4 \frac{m+2}{x} + 6 \frac{(m+1)(m+2)}{x^2} + 4 \frac{m(m+1)(m+2)}{x^3} + \frac{(m-1)m(m+1)(m+2)}{x^4} \right] - \left[1 + 3 \frac{m+2}{x} + \frac{(3m+1)(m+2)}{x^2} + \frac{m(m-1)(m+2)}{x^3} \right] \quad (9)$$

$$h_m^{(5)} = h_m \left[1 + 5 \frac{m+2}{x} + 10 \frac{(m+1)(m+2)}{x^2} + 10 \frac{m(m+1)(m+2)}{x^3} + 5 \frac{(m-1)m(m+1)(m+2)}{x^4} + \frac{(m-2)(m-1)m(m+1)(m+2)}{x^5} \right] - \left[1 + 4 \frac{m+2}{x} + 3 \frac{(2m+1)(m+2)}{x^2} + 2 \frac{(m-1)(m+2)(2m+1)}{x^3} + \frac{(m-2)(m-1)m(m+2)}{x^4} \right] \quad (10)$$

Figure 1 presents the numerical integration values of h_m and its derivatives at commonly used m values ($m=0, 1/2, 1, 2$) in the range of $5 \leq x \leq 100$, which covers the overwhelming majority of reactions [10]. Some features can be found in these curves. Firstly and most importantly, most values of h_m in the subfigures are higher than 0.6 and gradually approach to 1 with the rise of x , whereas most values of all derivatives are lower than 0.04 and gradually close to zero with the rise of x . That is to say, compared with the values of h_m , the values of its derivatives are very low. Secondly, when the order of the h_m derivatives increases, the absolute values of the derivatives become lower and lower. This indicates that compared with h_m , the higher order derivative can be more reasonable to be deemed as zero. Therefore, if the derivatives are assumed to be zero compared with the values of h_m , one can obtain some approximations of h_m from Eqs (6)–(10):

$$h_{ma}^1 = 1 / \left(1 + \frac{m+2}{x} \right) \quad (11)$$

$$h_{ma}^2 = \left(1 + \frac{m+2}{x} \right) / \left[1 + 2 \frac{m+2}{x} + \frac{(m+1)(m+2)}{x^2} \right] \quad (12)$$

$$h_{ma}^3 = \left[1 + 2 \frac{m+2}{x} + \frac{m(m+2)}{x^2} \right] / \left[1 + 3 \frac{m+2}{x} + 3 \frac{(m+1)(m+2)}{x^2} + \frac{m(m+1)(m+2)}{x^3} \right] \quad (13)$$

$$h_{ma}^4 = \left[1 + 3 \frac{m+2}{x} + \frac{(3m+1)(m+2)}{x^2} + \frac{m(m-1)(m+2)}{x^3} \right] / \left[1 + 4 \frac{m+2}{x} + 6 \frac{(m+1)(m+2)}{x^2} + 4 \frac{m(m+1)(m+2)}{x^3} + \frac{(m-1)m(m+1)(m+2)}{x^4} \right] \quad (14)$$

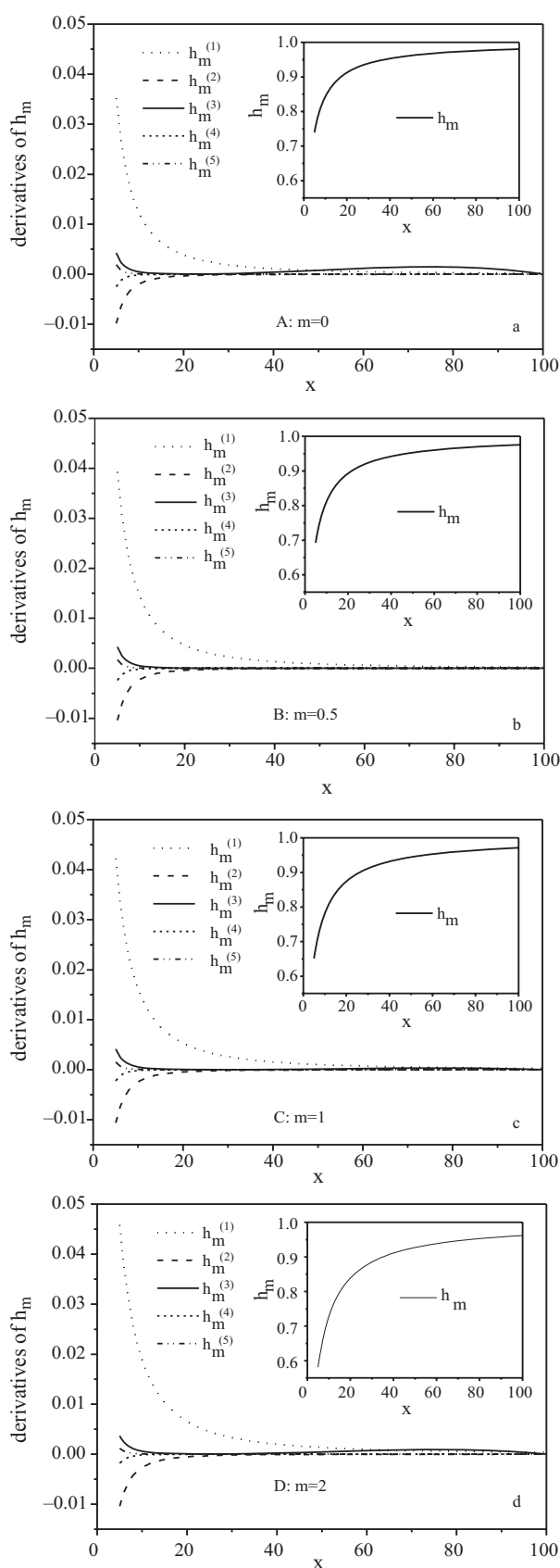


Fig. 1 Values of h_m and its derivatives in the range of $5 \leq x \leq 100$. A – $m=0$; B – $m=1/2$; C – $m=1$; D – $m=2$

$$h_{ma}^5 = \left[1 + 4 \frac{m+2}{x} + 3 \frac{(2m+1)(m+2)}{x^2} + 2 \frac{(m-1)(m+2)(2m+1)}{x^3} + \frac{(m-2)(m-1)m(m+2)}{x^4} \right] / \left[1 + 5 \frac{m+2}{x} + 10 \frac{(m+1)(m+2)}{x^2} + 10 \frac{m(m+1)(m+2)}{x^3} + 5 \frac{(m-1)m(+1)(m+2)}{x^4} + \frac{(m-2)(m-1)m(m+1)(m+2)}{x^5} \right] \quad (15)$$

Here the subscript ‘a’ means ‘approximation’. Obviously, the approximation of $h_{ma}^1 = 1 / \left(1 + \frac{m+2}{x} \right)$

(Eq. (11)) is just the first approximation proposed in the article of Wanjun *et al.* [9]. The deviation of this approximation from the numerical integration is less than 4.0% in most x values [9]. From Fig. 1, it can be expected that the other four approximations appeared in Eqs (12)–(15) will hold higher and higher accuracy. The following part will assess the precision of these approximations for commonly used m values in kinetic analysis.

Evaluation of the accuracy of the approximations

If all the derivatives of h_m (Eqs (6)–(10)) are denoted as $h_m^{(i)} = h_m A_i - B_i$, $i=1,2,3,\dots$, then $h_{ma}^i = B_i / A_i$. The relative error of the approximations can be defined as follows:

$$\varepsilon_i \% = \frac{h_{ma}^i - h_m}{h_m} 100\% = \frac{-h_m^{(i)}}{A_i h_m} 100\% \quad (16)$$

As an estimation, $\varepsilon_i \% = \frac{-h_m^{(i)}}{A_i h_m} \approx \frac{-h_m^{(i)}}{A_i h_m^i} = \frac{-h_m^{(i)}}{B_i} \approx -h_m^{(i)}$.

Therefore, from Fig. 1, it can be seen that the absolute relative errors are very low (<4.0% in most cases) and decrease with the increase of the order of the derivatives, i.e., the approximation deduced from higher derivatives will hold higher precision. As an example, here gives the accurate relative error of h_{ma}^2 by numerical calculation in Fig. 2. It can be clearly seen that the relative errors are very low (<0.7%) in all four cases. Compared with the relative error of h_{ma}^1 published in the article of Wanjun *et al.* [9], it can be concluded that h_{ma}^2 presents better accuracy in approximating the integral $I(m,T)$. The approximations $h_{ma}^3, h_{ma}^4, h_{ma}^5 \dots$ are undoubtedly more accurate.

Potential applications of the proposed procedure

Obviously, the proposed procedure has produced a series of new approximations for the temperature integral. Especially in the case of $m=0$, the procedure can provide many approximations with high accuracy, which are often required in the integral methods in practical thermal analysis. For example, in the case of $m=0$, Eq. (12) becomes:

$$h_{ma}^2 = x(x+2)/(x^2+4x+2) \quad (17)$$

This approximation seems to be appeared firstly and holds high precision as showed in Fig. 2. More new and accurate approximations can be obtained from the procedure if necessary.

As for the arbitrary value of m , the integral form of the rate equation, Eq. (3), can be rearranged as:

$$\ln \left[\frac{G(\alpha)}{T^{m+2}} \right] = \ln \left[\frac{AR}{\beta E} h_m \right] - \frac{E}{RT} \quad (18)$$

The proposed approximations can be used to replace the generalized temperature integral h_m in the above equation. Then, if Eq. (2), other than Arrhenius equation, is adopted in thermal analysis, Eq. (18) will yield the kinetic parameters (if m is prior known) by regression plot, or by iterative computation (if m is not prior known). In fact, Eq. (2) has been proved in the reactions of some chemical radicals [11]. It will be a meaningful try to use this equation in practical thermal analysis.

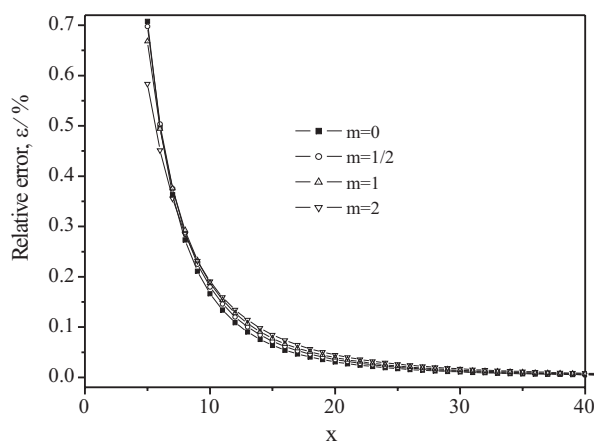


Fig. 2 The relative error of the approximation h_{ma}^2

Conclusions

In the present article we have proposed a new procedure to approximate the generalized temperature integral $I(m,T) = \int_0^T T^m \exp(-E/RT) dT$, which frequently occurs in non-isothermal thermal analysis. This new procedure has yielded a series of the approximations for $I(m,T)$ with different complexity and accuracy. For commonly used values of m , the deviation of the approximation h_{ma}^1 (Eq. (11)) from numerical values of $I(m,T)$ is within 4.0%, and the approximation h_{ma}^2 (Eq. (12)) within 0.7%. Other approximations hold higher precision. Since the approximations h_{ma}^1 and h_{ma}^2 retain simplicity in calculation and high accuracy, they are recommended to use in the evaluation of kinetic parameters from nonisothermal kinetic analysis.

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