Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 1, 175–178

NEW APPROXIMATE FORMULAE FOR THE GENERALIZED TEMPERATURE INTEGRAL

H. X. Chen[*] *and N. A. Liu*[**]

State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

The generalized temperature integral $\int_0^T T^m \exp(-E/RT)\mathrm{d}T$ frequently occurs in non-isothermal kinetic analysis. Here E is the activation energy, R the universal gas constant and T the absolute temperature. The exponent m arises from the temperature dependence of the pre-exponential factor. This paper has proposed two new approximate formulae for the generalized temperature integral, which are in the following forms:

$$h_m(x)=\frac{x}{(1.00141+0.00060m)x+(1.89376+0.95276m)}$$

$$h_m(x)=\frac{x+(0.74981-0.06396m)}{(1.00017+0.00013m)x+(2.73166+0.92246m)}$$

where $h_m(x)$ is the equivalent form of the generalized temperature integral. For commonly used values of m in kinetic analysis, the deviations of the new approximations from the numerical values of the integral are within 0.2 and 0.03%, respectively. In contrast to other approximations, both the present approaches are simple, accurate and can be used easily in kinetic analysis.

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

Introduction

Non-isothermal thermoanalytical 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 $f(\alpha)$,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{1}$$

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 expressed 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 Arrhenuis 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,

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

A serious difficulty of the mathematical modeling of the non-isothermal 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

---

[*] Author for correspondence: hxchen@ustc.edu.cn

[**] Author for correspondence: liunai@ustc.edu.cn

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

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. Wanjun *et al.* [11] 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. Recently an approximation with first-degree rational fraction was proposed by Cai *et al.* [12] and a procedure to yield a series of the approximations with different complexity and accuracy is proposed by Chen *et al.* [13].

It is noteworthy to point out that various type of approximations for the ordinary temperature integral $I(0,T)$ can provide some clues to discovering new approximations for $I(m,T)$. In a recent paper, we have reported that the exponential approximations for $I(0,T)$ 'are essentially one kind of rational approximations with the form of $h(x)=x/(Ax+k)$' [14]. In the present work, we try to find some similar expressions to approximate the generalized temperature integral. It will be shown that the new formulae are very accurate and simple.

Theory

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

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

define

$$h_{\mathrm{m}}(x)=\frac{\displaystyle\int_{\mathrm{x}}^{\infty}\frac{\exp(-x)}{x^{\mathrm{m}+2}}\mathrm{d}x}{\dfrac{\exp(-x)}{x^{\mathrm{m}+2}}} \tag{5}$$

then

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

Thus the problem of approximating the integral $I(m,T)$ is converted to finding the approximation for $h_{\mathrm{m}}(x)$. Figure 1 presents the numerical integration values of $h_{\mathrm{m}}(x)$ at commonly used m values ($m=-1.5$~3 [15]) in the range of $5\le x\le 100$. It is indicated that the values of $h_{\mathrm{m}}(x)$ are higher than 0.5 and gradually approaching to 1 with the increase of x.

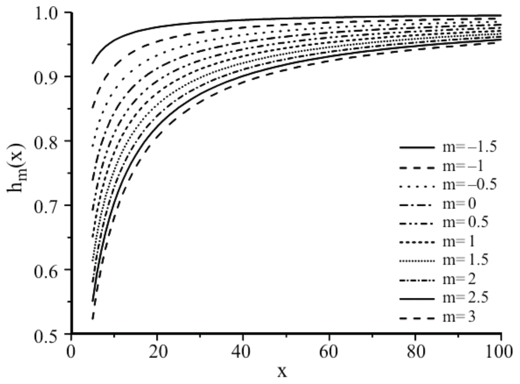

Fig. 1 Numerical values of $h_{\mathrm{m}}(x)$ as a function of x at commonly used m values

For the special case of $m=0$, it is found that the approximation $h(x)=x/(Ax+k)$, where A and k are the coefficients, can represent all of the exponential approximations and a type of rational approximations for the temperature integral [14]. We hope to find new approximation for the generalized temperature integral which holds the similar form of $h(x)=x/(Ax+k)$, that is, we assume the generalized temperature integral can be approximated by

$$h_{\mathrm{m}}(x)=\frac{x}{A_{\mathrm{m}}x+k_{\mathrm{m}}} \tag{7}$$

where A_{m} and k_{m} are the coefficients which are dependent on m. In order to testify the rationality of the assumption and determine the coefficients, the above expression can be rewritten as

$$\frac{x}{h_{\mathrm{m}}(x)}=A_{\mathrm{m}}x+k_{\mathrm{m}} \tag{8}$$

For a given value of m, plotting of $x/h_{\mathrm{m}}(x)$ *vs.* x will result in a straight line with the slope A_{m} and intercept k_{m}. For example, Fig. 2 plots $x/h_{\mathrm{m}}(x)$ *vs.* x with $m=2$ and $15\le x\le 60$. The overwhelming majority of reactions occur for $15\le x\le 60$ [16]. Figure 2 proves that the values of $x/h_{\mathrm{m}}(x)$ indeed increases linearly with the rise of x at $m=2$. At other values of m, such linearity can be also testified. Table 1 presents the values of A_{m} and k_{m} which are obtained from the slope and intercept of the fitted lines, respectively.

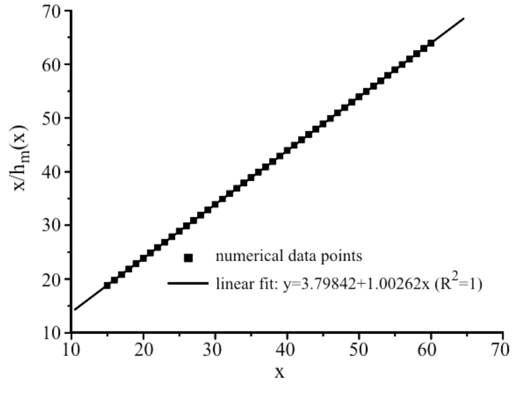

Fig. 2 The linear relationship of $x/h_{\mathrm{m}}(x)$ with x at $m=2$

Table 1 The values of the parameters A_m and k_m in Eq. (7) ($15\leq x\leq 60$)

m	–1.5	–1	–0.5	0	0.5	1	1.5	2	2.5	3
A_m	1.00040	1.00077	1.00113	1.00146	1.00177	1.00207	1.00236	1.00262	1.00287	1.00311
k_m	0.47083	0.94289	1.41613	1.89062	2.36618	2.84265	3.32007	3.79842	4.27773	4.75776

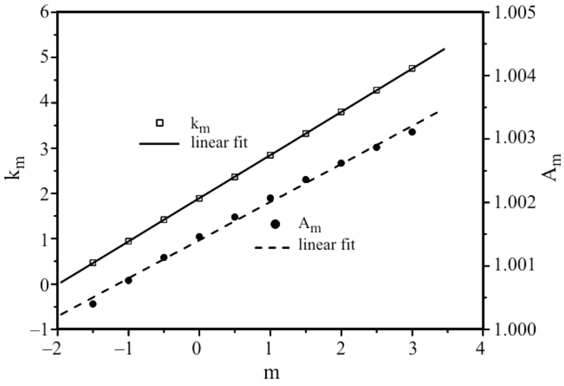

Fig. 3 The relationships of A_m and k_m in Eq. (7) with m

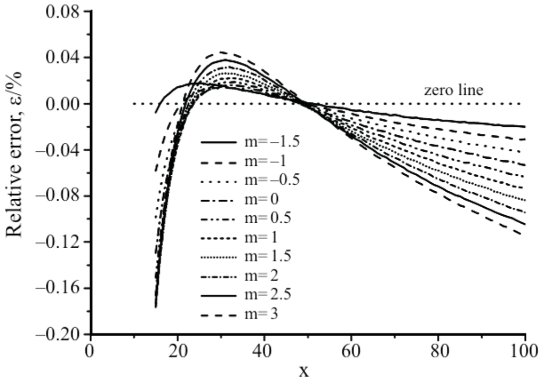

Fig. 4 The relative error of the approximation of Eq. (11)

All the values of A_m and k_m at different m values in Table 1 are plotted in Fig. 3. It is obvious that there is a linear relationship between the values of A_m, or k_m, with those of m. The fitted lines are

$$A_m=1.00141+0.00060m \tag{9}$$

$$k_m=1.89376+0.95276m \tag{10}$$

So the new approximation for $h_m(x)$, Eq. (7), can be rearranged as

$$h_{ma}(x)=\frac{x}{(1.00141+0.00060m)x+(1.89376+0.95276m)} \tag{11}$$

The subscript *a* means it is an approximation.

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. The relative error is defined by the expression:

$$\varepsilon=\frac{h_{ma}(x)-h_m(x)}{h_m(x)} \tag{12}$$

where $h_m(x)$ is the numerical integration value which is presented in Fig. 1 and $h_{ma}(x)$ represents the value calculated by the approximation of Eq. (11). The result of the relative errors is illustrated in Fig. 4. It is clearly seen that the relative errors are very low (<0.2%) when $x\geq 15$. In the range of $20\leq x\leq 60$, the relative errors are less than 0.04%, which are very accurate. However, the relative error is somewhat higher in other ranges. In the following, we will present a modified version of Eq. (7) to approximate the generalized temperature integral more accurately.

Another approximate formula – modified version of Eq. (7)

In order to enhance the accuracy of the approximation, we modify Eq. (7) as the following form:

$$h_m(x)=\frac{x+B_m}{A_m x+k_m} \tag{13}$$

In this expression, a term B_m is added in order to decrease the relative error. Using the non-linear curve fit function of Origin software, all the three coefficients of the above expression can be determined, which is listed in Table 2. It is also found that there is a linear relationship between the values of A_m, or k_m, or B_m, with those of m as showed in Fig. 5. The fitted lines are

$$A_m=1.00017+0.00013m \tag{14}$$

Table 2 The values of the parameters A_m, k_m and B_m in Eq. (13) ($15\leq x\leq 60$)

m	–1.5	–1	–0.5	0	0.5	1	1.5	2	2.5	3
A_m	1.00003	1.00005	1.00009	1.00016	1.00019	1.00029	1.00037	1.00041	1.00050	1.00061
k_m	1.35534	1.81074	2.26778	2.72896	3.19030	3.65030	4.11049	4.57519	5.03931	5.50661
B_m	0.85765	0.81659	0.77826	0.74468	0.71208	0.67925	0.64753	0.62026	0.59313	0.56900

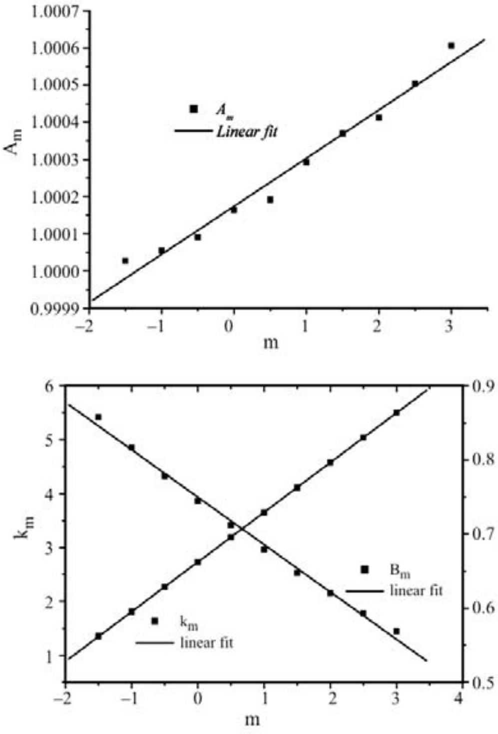

Fig. 5 The relationships of A_m, k_m and B_m in Eq. (13) with m

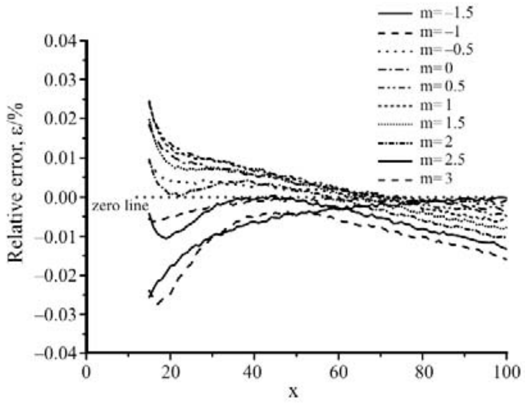

Fig. 6 The relative error of the approximation of Eq. (17)

$$k_m=2.73166+0.92246m \tag{15}$$

$$B_m=0.74981-0.06396m \tag{16}$$

So the new approximation with the form of Eq. (13) becomes

$$h_{ma2}(x)=\frac{x+(0.74981-0.06396m)}{(1.00017+0.00013m)x+(2.73166+0.92246m)} \tag{17}$$

The relative error of this new formula deviated from the real values of the generalized temperature integral is presented in Fig. 6. It is clear that the relative errors are very low (<0.03%) when $x\geq15$. Compared with Eq. (11) and the newly published approximations proposed by Wanjun *et al.* [11], Cai *et al.* [12] and Chen *et al.* [13], it can be concluded that this new approximation holds highest accuracy. Moreover, the expression of the new approximation is simple and it is easily used in non-isothermal kinetic analysis.

Conclusions

In the present article we have proposed two new approximate formulae for the generalized temperature integral

$$I(m,T)=\int_0^T T^m \exp(-E/RT)\,\mathrm{d}T$$

which frequently occurs in non-isothermal thermal analysis. For commonly used values of m, the deviation of the new approximations from numerical values of $I(m,T)$ is within 0.2 and 0.03% when $x\geq15$, respectively. Compared with the published approximations, the second one of this paper is significantly most accurate. Since they are simple and easy to use, both of the new approximations proposed in this paper could play important roles in non-isothermal kinetic analysis.

Acknowledgements

This work was sponsored by China NSFC 50576090 and the Program for New Century Excellent Talents in University. Support from SKLFS is also greatly acknowledged.

References

1 P. Šimon, J. Therm. Anal. Cal., 82 (2005) 651.
2 J. H. Flynn, Thermochim. Acta, 300 (1997) 83.
3 J. H. Flynn, J. Thermal Anal., 36 (1990) 1579.
4 Q. Y. Ran and S. Ye, J. Thermal Anal., 44 (1995) 1147.
5 J. M. Cai, F. S. Yao, W. M. Yi and F. He, AIChE J., 52 (2006) 1554.
6 C. H. Li, AIChE J., 31 (1985) 1037.
7 W. J. Tang, Y. W. Liu, H. Zhang and C. X. Wang, Thermochim. Acta, 408 (2003) 39.
8 H. X. Chen and N. A. Liu, AIChE J., 52 (2006) 4181.
9 J. J. M. Orfao, AIChE J., 53 (2007) 2905.
10 S. D. Singh, W. G. Devi, A. K. M. Singh, M. Bhattacharya and P. S. Mazumdar, J. Therm. Anal. Cal., 61 (2000) 1013.
11 T. Wanjun, L. Yuwen, Y. Xil, W. Zhiyong and W. Cunxin, J. Therm. Anal. Cal., 81 (2005) 347.
12 J. M. Cai and R. H. Liu, J. Therm. Anal. Cal., 90 (2007) 469.
13 H. X. Chen and N. A. Liu, J. Therm. Anal. Cal., 90 (2007) 449.
14 H. X. Chen and N. A. Liu, J. Therm. Anal. Cal., 92 (2008) 573.
15 J. M. Criado, L. A. Perez-Maqueda and P. E. Sanchez-Jimenez, J. Therm. Anal. Cal., 82 (2005) 671.
16 M. J. Starink, Thermochim. Acta, 404 (2003) 163.

Received: July 6, 2008
Accepted: November 4, 2008

DOI: 10.1007/s10973-008-9388-1