

New approximate formula for the generalized temperature integral

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Abstract A new procedure to approximate the generalized temperature integral $\int_0^T T^m e^{-E/RT} dT$, which frequently occurs in non-isothermal thermal analysis, has been developed. The approximate formula has been proposed for calculation of the integral by using the procedure. New equation for the evaluation of non-isothermal kinetic parameters has been obtained, which can be put in the form:

$$\ln \left[\frac{g(\alpha)}{T^{(m+2)0.94733}} \right] = \left[\ln \frac{A_0 E}{\beta R} - (m+2)0.18887 - (m+2)0.94733 \ln \frac{E}{R} \right] - (1.00145 + 0.00069m) \frac{E}{RT}$$

The validity of the new approximation has been tested with the true value of the integral from numerical calculation. Compared with several published approximation, the new one is simple in calculation and retains high accuracy, which indicates it is a good approximation for the evaluation of kinetic parameters from non-isothermal kinetic analysis.

Keywords Approximation · Integral method · Non-isothermal kinetic analysis

Introduction

Thermally stimulated solid-state reactions, such as decompositions, solid–solid reactions, crystallizations, and desorption of gases adsorbed on solid surface and sintering are heterogeneous processes. It has been generally assumed that the reaction rate of such processes can be kinetically described by the following expression:

$$\frac{d\alpha}{dt} = kf(\alpha) = Ae^{-E/RT}f(\alpha) \quad (1)$$

where k is the constant rate, A is the pre-exponential factor, E is the activation energy, R is the gas constant, T is the temperature, t is the time and α is the extent of reaction ranging from 0 before the process starts to 1 when it is over.

It is noteworthy to point out that all the integral method for the kinetic analysis generally used have been developed by assuming that the frequency factor can be considered as a constant all over the temperature range investigated. However, to some solid-state reactions, the frequency factor is connected with the temperature through the following relationship.

$$A = A_0 T^m \quad (2)$$

where A_0 is a constant and the values of the exponent m range from -1.5 to 2.5 for some solid-state reactions [1].

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

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta} \int_0^T T^m e^{-E/RT} dT \quad (3)$$

The integral $\int_0^T T^m e^{-E/RT} dT$ on the right-hand side of Eq. 3 does not have an exact analytical solution in most cases. Miscellaneous approximations, with varying

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complexity and precision, have been proposed for the evaluation of the integral for the special case of $m = 0$ [2–5]. For arbitrary values of the temperature exponent m , Singh et al. [6] developed a technique based on the complementary incomplete gamma function for the evaluation of the integral. However, the evaluation of the complementary incomplete gamma function is complex and takes much computing time. So an approximation for the integral, 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. Many authors have proposed extensive approximations for the integral with different mathematical complexities and numerical precisions. Wanjun et al. [7] published this kind of research firstly and proposed two approximate formulae for calculation of the integral by using integration-by-parts approaches. Recently, several approximations with rational fraction were proposed by Cai and co-workers [8–11]. Also, a procedure to yield a series of the approximations with different complexity and accuracy is proposed by Chen et al. [12]. An iterative technique is usually necessary to obtain kinetic parameters using the above methods. The aim of this work is to present a new approximation for the integral. It will be shown that the new approximation is simply used, accurate, and can be used for arbitrary values of m .

Theory

With the substitution $u = E/RT$, $\int_0^T T^m e^{-E/RT} dT$ can be expressed as

$$\int_0^T T^m e^{-E/RT} dT = \left(\frac{E}{R}\right)^{m+1} \int_u^\infty \frac{\exp(-u)}{u^{m+2}} du \tag{4}$$

The integral in the right-hand side of Eq. 4 has no exact analytical solution, but can be integrated by parts to obtain the expression as below:

$$\int_u^\infty \frac{\exp(-u)}{u^{m+2}} du = \frac{\exp(-u)}{u^{m+2}} - (m+2) \int_u^\infty \frac{\exp(-u)}{u^{m+3}} du \tag{5}$$

Rearrangement of Eq. 5 leads to:

$$\int_u^\infty \left(1 + \frac{m+2}{u}\right) \frac{\exp(-u)}{u^{m+2}} du = \frac{\exp(-u)}{u^{m+2}} \tag{6}$$

Both sides of Eq. 6 are divided by $\int_u^\infty [\exp(-u)/u^{m+2}] du$ and it follows:

$$1 + (m+2) \frac{\int_u^\infty \frac{\exp(-u)}{u^{m+3}} du}{\int_u^\infty \frac{\exp(-u)}{u^{m+2}} du} = \frac{\exp(-u)}{u^{m+2}} \frac{1}{\int_u^\infty \frac{\exp(-u)}{u^{m+2}} du} \tag{7}$$

Define

$$k(m, u) = \int_u^\infty \frac{\exp(-u)}{u^{m+3}} du / \int_u^\infty \frac{\exp(-u)}{u^{m+2}} du \tag{8}$$

By rearranging Eq. 7:

$$p(m, u) = \int_u^\infty \frac{\exp(-u)}{u^{m+2}} du = \frac{\exp(-u)}{u^{m+2} [1 + (m+2)k(m, u)]} \tag{9}$$

The above procedure has been described in detail by Wanjun et al. [7].

Taking logarithm on both sides of Eq. 9, we get

$$-\ln[p(m, u)] = u + (m+2) \ln u + \ln[1 + (m+2)k(m, u)] \tag{10}$$

Since the values of $k(m, u) \rightarrow 0$ in the domain of $20 \leq u \leq 60$ [7], Eq. 10 can be rewritten as

$$-\ln[p(m, u)] \approx u + (m+2) \ln u + (m+2)k(m, u) \tag{11}$$

It was reported [13] that the expression of $\ln[p(m, u)]$ can be put into the following expression in the case of $m = 0$.

$$-\ln[p(0, u)] = 1.00145u + 1.89466 \ln u + 0.37774 \tag{12}$$

Comparing Eq. 11 with 12, a new form of approximation for the generalized temperature integral is shown as below

$$-\ln[p(m, u)] = a_m u + (m+2)0.94733 \ln u + (m+2)0.18887 \tag{13}$$

Here, a_m is constant for u but varies with m . Define

$$q(m, u) = -\ln[p(m, u)] - (m+2)0.94733 \ln u - (m+2)0.18887 \tag{14}$$

Main of thermal decomposition reactions takes place in the range of $20 \leq u \leq 60$. In this range, Simpson’s procedure is used to evaluate numerical integral values for various u at interval of 1. Figure 1 presents the values of $q(m, u)$ at commonly used m values ($m = -1.0-2.0$) in the range of $20 \leq u \leq 60$. It is found that the values of $q(m, u)$ increase linearly with the rise of u . The values of a_m at different m are obtained from the sloped of the fitted lines and are plotted in Fig. 2. It is found that there is a linear relationship between the values of a_m and m . The value of a_m can be calculated from Fig. 2 as

$$a_m = 1.00145 + 0.00069m \tag{15}$$

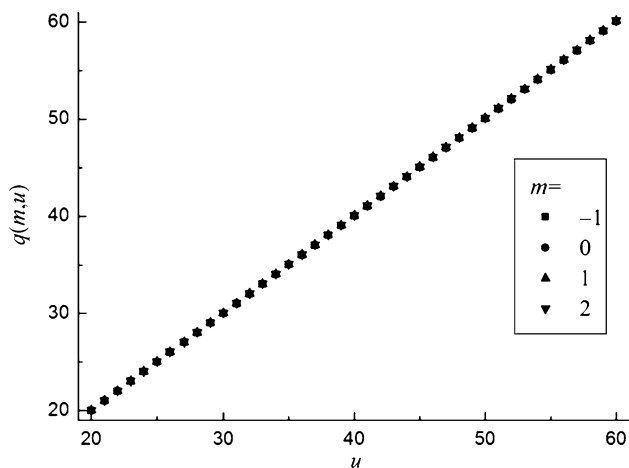


Fig. 1 Numerical values of $q(m, u)$ as a function of u at different m values

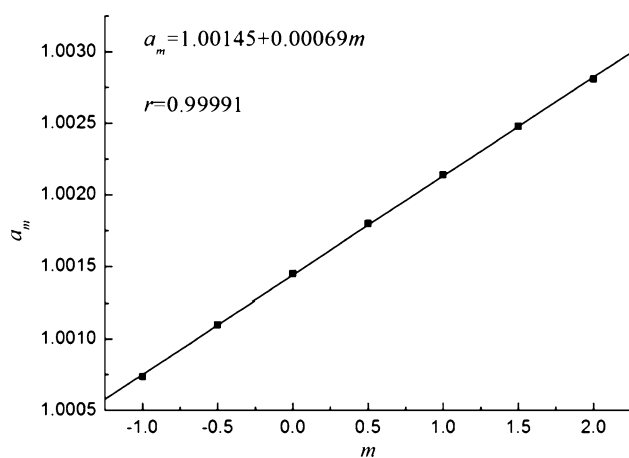


Fig. 2 Linear relationship of a_m with m

Thus, the approximation for the generalized temperature integral is obtained and gives below:

$$-\ln[p(m, u)] = (1.00145 + 0.00069m)u + (m + 2)0.94733 \ln u + (m + 2)0.18887 \quad (16)$$

In the case of $m = 0$, the expression of Eq. 16 can be put into the same form as Eq. 12. This fact confirms the feasibility of the used mathematical approach for the derivation of Eq. 16.

Inserting Eq. 16 into Eq. 3, and taking logarithm on both sides of Eq. 3, it follows:

$$\ln \left[\frac{g(\alpha)}{T^{(m+2)0.94733}} \right] = \left[\ln \frac{A_0 E}{\beta R} - (m + 2)0.18887 - (m + 2)0.94733 \ln \frac{E}{R} - (1.00145 + 0.00069m) \frac{E}{RT} \right] \quad (17)$$

Plotting $\ln[g(\alpha)/T^{(m+2)0.94733}]$ versus $1/T$, the activation energy E is obtained from the slope and the pre-exponential

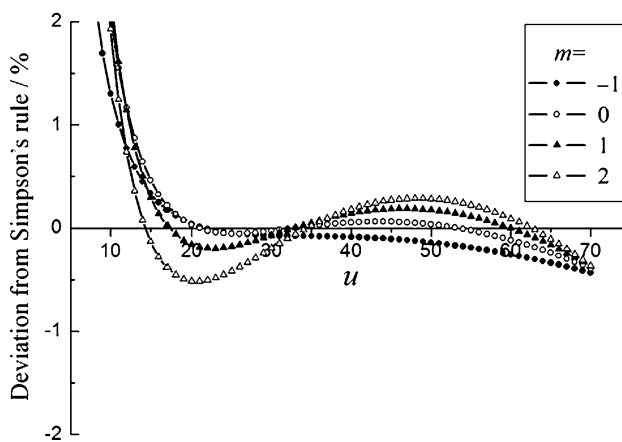


Fig. 3 Deviation of the approximation for different values of m

factor A can be calculated by inserting E and heating rate β in to the interception.

$$\left[\ln \frac{A_0 E}{\beta R} - (m + 2)0.18887 - (m + 2)0.94733 \ln \frac{E}{R} \right]$$

The iterative technique is unnecessary to obtain kinetic parameters using the newly proposed Eqs. 16 and 17.

Evaluation of accuracy of the approximate formula

The aim of this analysis is to assess the precision of the present approximation for commonly used m in their range of applicability in kinetic studies. All numerical values are computed and plotted on a Pentium IV PC by programming MATLAB 6.5. The values of $p(m, u)$ for $m = -1, 0, 1$ and 2 for Eq. 16 are evaluated in a physically realistic range of u . Its deviation from the Simpson's procedure of the integral for different values of m is shown in Fig. 3. It can be clear seen that the present approximate formula gives accurate results and works well for both zero and non-zero values of m with a wide range of application. It is obvious that the proposed approximate formula is more easily applicable than that have been developed.

Conclusions

In the present paper, an approximate formula has been developed for the evaluation of the generalized temperature integral $\int_0^T T^m e^{-E/RT} dT$, which frequently occurs in non-isothermal thermal analysis. The approximation gives values of the integral quite close to theoretical values for arbitrary values of m in a physically realistic range of E/RT . The approximation can be directly applied to obtain kinetic parameters and the iterative technique is unnecessary,

which is different from the published approximations. The results confirm the validity of this newly proposed procedure. Because of its simplicity, reliability and high accuracy, the approximation may be commonly used in the evaluation of kinetic parameters from nonisothermal kinetic analysis.

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