

APPROXIMATE FORMULAE FOR CALCULATION OF THE INTEGRAL

$$\int_0^T T^m \exp(-E / RT) dT$$

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In this paper two approximate formulae have been developed for calculation of the integral $\int_0^T T^m \exp(-E / RT) dT$ by using integration-by-parts approaches. They are in the following forms:

$$I(m, T) = \frac{RT^{m+2}}{E + (m+2)RT} \exp\left(-\frac{E}{RT}\right)$$

$$I(m, T) = \frac{RT^{m+2}}{E + (m+2)(0.00099441E + 0.93695599RT)} \exp\left(-\frac{E}{RT}\right)$$

The validity of the two formulae has been confirmed and their accuracies have been tested with data from numerical calculating. In contrast to existing other integral methods, both the present approaches are simply used, accurate, and can be used for arbitrary values of m .

Keywords: approximate formulae, integral, integration-by-parts, non-isothermal analysis

Introduction

Non-isothermal methods such as differential thermal analysis (DTA), thermogravimetry (TG), differential scanning calorimetry (DSC) etc., have been widely used to study the kinetics and mechanism of variety of reactions [1–4]. These methods usually involve in the integral

$$I(m, T) = \int_0^T T^m \exp(-E / RT) dT \quad (1)$$

where E is energy, R is universal gas constant, T is absolute temperature, and the exponent m arises from the temperature dependence of the pre-exponential factor [5, 6]. The case $m = -1/2$ occurs in the Langmuir evaporation theory [7, 8]. The case $m = 0$ occurs in Arrhenius theory [9]. And the cases $m = 1/2$ and 1 occur in the collision theory [10] and transition state theory [11], respectively. However, this integral cannot be solved in a closed form. Miscellaneous approximations [12–15], with varying complexity and precision, have been proposed for the evaluation of the integral for the special case of $m = 0$. Recently Singh *et al.* [16] developed a technique based on the complementary incomplete gamma function for evaluation of the integral for arbitrary values of the temperature exponent m .

In the past few years, calculation of the kinetic parameters from non-isothermal data has been subjects of considerable interests [17, 18]. Thus, it is very important to suggest a reasonable approach by which kinetic parameters can be evaluated from the data of non-isothermal experiments both accurately and conveniently [19, 20]. Kinetic parameters are usually evaluated iteratively by linear or non-linear regression. It has been demonstrated that the technique developed by Singh *et al.* [16] leads to almost accurate results. But the evaluation of the complementary incomplete gamma function, which is necessary to obtain the integral, is complex and takes much computing time. So an approximation method, which can be easily programmed and carried out in a personal computer with accurate enough results, will be welcome [21]. The aim of this paper is to present new integral approximate formulae for evaluation of the integral for arbitrary values of the temperature exponent m . Comparing the results with those determined with numerical integration validates both methods. Furthermore, both new methods are simple, easily applied, and can be used over a wide range of values of E/RT .

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Theory

With the substitution $u=E/RT$, Eq. (1) can be expressed [16] as

$$I(m, T) = \left(\frac{E}{R}\right)^{m+1} \int_u^\infty \frac{\exp(-u)}{u^{m+2}} du \quad (2)$$

The integral in the right-hand side of Eq. (2) has no exact analytical solution, but can be integrated by parts [22] to obtain the expression shown below:

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

Rearrangement of Eq. (3) gives to Eq. (4)

$$\int_u^\infty \left(1 + \frac{m+2}{u}\right) \frac{\exp(-u)}{u^{m+2}} du = \frac{\exp(-u)}{u^{m+2}} \quad (4)$$

Since $(m+2)RT/E$ is much less than unity at moderate temperatures T and high energies E , the value of $1+(m+2)/u$ is in the neighborhood of unity. Therefore, $1+(m+2)/u$ is assumed constant and removed out of the integral symbol to give Eq. (5).

$$\left(1 + \frac{m+2}{u}\right) \int_u^\infty \frac{\exp(-u)}{u^{m+2}} du \approx \frac{\exp(-u)}{u^{m+2}} \quad (5)$$

Equation (5) is then rearranged to give Eq. (6)

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

That is

$$I(m, T) = \frac{RT^{m+2}}{E + (m+2)RT} \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Equation (7) can be reverted to Gorbachev–Lee–Beck equation [23, 24] for $m=0$.

In order to improve the preciseness of the approximation further, we divide both sides of Eq. (4) by $\int_u^\infty [\exp(-u) / u^{m+2}] du$ and get

$$1 + (m+2) \frac{\int_u^\infty \frac{\exp(-u)}{u^{m+3}} du}{\int_u^\infty \frac{\exp(-u)}{u^{m+2}} du} = \frac{\exp(-u)}{u^{m+2}} \frac{1}{\int_u^\infty \frac{\exp(-u)}{u^{m+2}} du} \quad (8)$$

Let

$$k(m, u) = \left[\int_u^\infty \frac{\exp(-u)}{u^{m+3}} du \right] / \left[\int_u^\infty \frac{\exp(-u)}{u^{m+2}} du \right] \quad (9)$$

$$I(m, T) = \frac{RT^{m+2}}{E + (m+2)(0.00099441E + 0.93695599RT)} \exp\left(-\frac{E}{RT}\right) \quad (13)$$

Rearranging Eq. (8), we get

$$\int_u^\infty \frac{\exp(-u)}{u^{m+2}} du = \frac{\exp(-u)}{u^{m+2} [1 + (m+2)k(m, u)]} \quad (10)$$

In a recently published literature [25], we reported that the expression of $k(m, u)$ can be put into the following form in the case of $m=0$.

$$k(0, u) = 0.00099441 + 0.93695599/u \quad (11)$$

The results of our calculations lead us to propose that the expression of $k(m, u)$ can be also put into the same form as Eq. (11) for arbitrary values of m . Introducing the expression of $k(m, u)$ into Eq. (10), the following approximation of the integral

$$\int_u^\infty [\exp(-u) / u^{m+2}] du \text{ is obtained:} \\ \int_u^\infty \frac{\exp(-u)}{u^{m+2}} du = \frac{\exp(-u)}{u^{m+2} \left[1 + (m+2) \left(0.00099441 + \frac{0.93695599}{u} \right) \right]} \quad (12)$$

Equation (13) gives the higher accuracy, whereas Eq. (7) seems simpler. The form of Eq. (13) is the same as that presented in [25] but the exponent m . And the integral equation in [25] can be obtained from Eq. (13) for $m=0$, too.

Evaluation of accuracy of the approximate formulae

The aim of this analysis is to assess the precision of the two present methods 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 $\int_u^\infty [\exp(-u) / u^{m+2}] du$ for $m=-1, 0, 1$ and 2 for Eqs (6) and (12) are evaluated in a physically realistic range of u . Their deviation from the Simpson’s procedure of the integral for different values of m is shown in Figs 1 and 2, respectively. It can be clear seen that the values from both recommended methods be in excellent accordance. Both the present approximate formulae give accurate results and works well for both zero and non-zero values of m with a wide range of application. And Eq. (13) gives a more accurate than Eq. (7). It is obvious that the proposed approximate formulae are more easily applicable than that developed by Singh *et al.* [16].

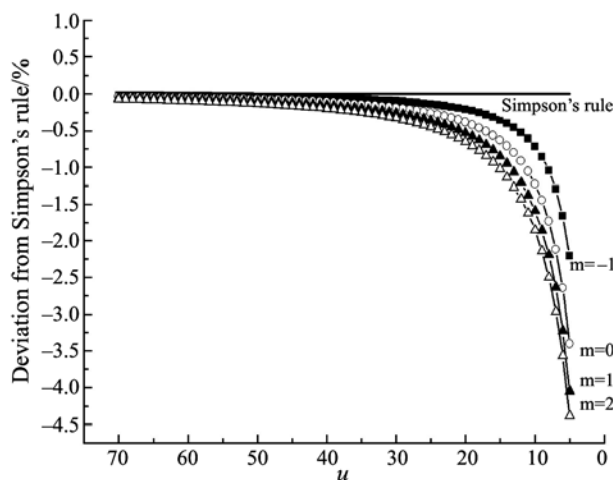


Fig. 1 Percent deviation of the approximation Eq. (6) from Simpson's procedure of the integral for different values of m : ■ – $m=-1$, ○ – $m=0$, ▲ – $m=1$ and △ – $m=2$

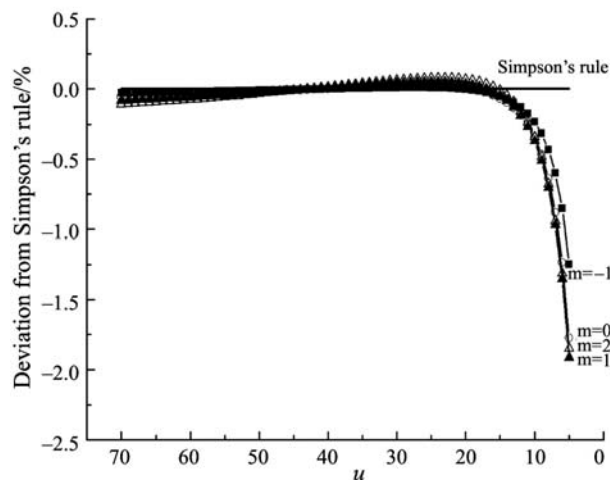


Fig. 2 Percent deviation of the approximation Eq. (12) from Simpson's procedure of the integral for different values of m : ■ – $m=-1$, ○ – $m=0$, ▲ – $m=1$ and △ – $m=2$

Conclusions

In the present paper we have developed two approximate formulae for the evaluation of the integral $\int_0^T T^m \exp(-E/RT) dT$, which frequently occurs in non-isothermal thermal analysis. The present methods give values of the integral quite close to theoretical values of the integral for arbitrary values of m in a physically realistic range of u . The results also confirmed the plausibility of the used mathematical approach for the derivation of Eqs (7) and (13). In addition, both the equations retain simplicity in calculation and formulation. Furthermore, the present methods are reliable and accurate enough in a wide range of applicability.

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