

## NEW TEMPERATURE INTEGRAL APPROXIMATE FORMULA FOR NON-ISOTHERMAL KINETIC ANALYSIS

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### Abstract

A new approximate formula for temperature integral is proposed. The linear dependence of

$\int_0^x x e^{-1/x} dx / \int_0^x e^{-1/x} dx$  on  $x$  has been established. Combining this linear dependence and integration-by-parts, new equation for the evaluation of kinetic parameters has been obtained from the above dependence, which can be put in the form

$$\ln \left[ \frac{G(\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta(1.00198882E+1.87391198RT)} \right] - \frac{E}{RT}$$

The validity of this equation has been tested with data from numerical calculating. And its deviation from the values calculated by Simpson's numerical integrating was discussed. Compared with several published approximate formulae, this new one is much superior to all other approximations and is the most suitable solution for the evaluation of kinetic parameters from TG experiments.

**Keywords:** approximate formula, non-isothermal kinetic analysis, temperature integral, TG

### Introduction

Thermal analysis, especially modern thermogravimetric analysis (TG), provides a quantitative understanding of non-isothermal solid decomposition under controlled laboratory conditions, for the development of modern thermal analysis techniques. Consequently, the validity of TG data for kinetic analysis of non-isothermal solid decomposition is enhanced greatly. In the most TG studies the temperature of samples increases linearly. Knowledge of kinetic parameters, such as kinetic model, activation energy, and the pre-exponential factor, can be obtained through various TG data treating methods [1–5]. Integral method is one of basic approaches to analysis of non-isothermal TG data. For its many inherent advantages, integral method has been used widely. Unfortunately, this method involves in an integration of Arrhenius function, also called 'temperature integral' as shown below, which cannot be analytically

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integrated. A large number of solutions for this question, with varying complexity and precision, have been presented. In 1964 Coats and Redfern [6] provided a widely used integral approximate formula. Gorbachev–Lee–Beck [7, 8] proposed a two-term approximation, which is considered simple and more precise than Coats–Redfern equation. Li Chung-Hsiung [9] and Agrawal [10] proposed two three-term approximate formulae, which are precise but more complex. Senum and Yang [11] put forward a series of multi-order rational approximations with the degree of the polynomial in the denominator from 1 to 4, and Perez-Maqueda *et al.* [12] further proposed rational approximations, some of which have high accuracy but horrendous complicated. Urbanovici *et al.* [13] presented an improved version of the Coats–Redfern method of evaluating non-isothermal kinetic parameters. A number of different approaches have been proposed in the literature during the last century as can be found in excellent reviews of Flynn [14]. How to evaluate an integral of the Arrhenius function had been reviewed recently [15]. And if an approximation method of temperature integral is both simple and accurate enough in the range of its applicability, the sophisticated approximation of temperature integral, which requires the use of tedious non-linear optimization for calculating the kinetic parameters, is not necessary [16]. It seems to be of great interests to find out a suitable approximation for temperature integral. The aims of this paper is to present a better approximation of temperature integral, which is simple, precise and reliable.

### Theory

It is usually assumed that the basic kinetic equation for solid state decomposition process under non-isothermal conditions can be expressed as a function of the fractional conversion  $\alpha$  ( $0 < \alpha < 1$ ) in the following form:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (1)$$

where  $A$  is the pre-exponential factor of the Arrhenius type rate constant, and  $E$  the apparent activation energy,  $\beta$  heating rate, and  $f(\alpha)$  a function depending on reaction mechanism.

Rearranging Eq. (1) and integrating both sides of the equation the following expression is obtained.

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \quad (2)$$

The right side of Eq. (2) cannot be analytically integrated, but can be integrated by parts to obtain the expression showed in Eq. (3).

$$\int_0^T e^{-E/RT} dT = \frac{RT^2}{E} e^{-E/RT} - \int_0^T \frac{2RT}{E} e^{-E/RT} dT \quad (3)$$

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

$$\int_0^T \left(1 + \frac{2RT}{E}\right) e^{-E/RT} dT = \frac{RT^2}{E} e^{-E/RT} \quad (4)$$

that is

$$\int_0^x (1+2x)e^{-1/x} dx = x^2 e^{-1/x} \quad (5)$$

where  $x=RT/E$ ,  $u=E/RT$ . Dividing both sides of Eq. (5) by  $\int_0^x e^{-1/x} dx$ , we get

$$1+2 \frac{\int_0^x x e^{-1/x} dx}{\int_0^x e^{-1/x} dx} = \frac{x^2 e^{-1/x}}{\int_0^x e^{-1/x} dx} \quad (6)$$

Let

$$\frac{\int_0^x x e^{-1/x} dx}{\int_0^x e^{-1/x} dx} = k(x) \quad (7)$$

Rearranging Eq. (6), we get

$$\int_0^x e^{-1/x} dx = \frac{x^2 e^{-1/x}}{1+2k(x)} \quad (8)$$

Main of thermal decomposition reactions takes place in the range of  $15 \leq u \leq 55$ , i.e.,  $1/55 \leq x \leq 1/15$ . In this range, Simpson's procedure is used to evaluate numerical integral values for various  $u$  at interval of 1. A close examination of Eq. (7) shows that  $k(x)$  varies linearly with  $x$  in the range  $1/55 \leq x \leq 1/15$ . Plotting  $k(x)$  vs.  $x$  is shown in Fig. 1. The values of intercept, slope and regression coefficient for linear plot of  $k(x)$  vs.  $x$  are 0.00099441, 0.93695599 and 0.99995584, respectively. And the expression of  $k(x)$  is

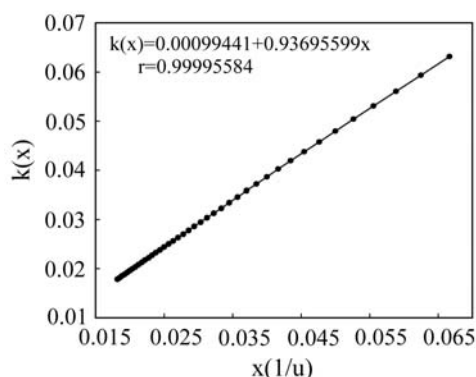
$$k(x) = 0.00099441 + 0.93695599x \quad (9)$$

Combining Eq. (8) and Eq. (9), a new approximation equation for temperature integral is obtained

$$\int_0^T e^{-E/RT} dT = \frac{RT^2}{1.00198882E + 1.87391198RT} e^{-E/RT} \quad (10)$$

Inserting Eq. (10) into Eq. (2), and logarithm on both sides of Eq. (2), we get

$$\ln \left[ \frac{G(\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta(1.00198882E + 1.87391198RT)} \right] - E/RT \quad (11)$$



**Fig. 1** Linear fitting of  $k(x)$  vs.  $x(1/u)$

## Results and discussion

The objective of this analysis is to compare the proposed method with several known integral approximate methods in order to determine its range of applicability in kinetic studies. All numerical values were computed and plotted on a PC by a MATLAB program. The expressions of Coats–Redfern equation, Gorbachev–Lee–Beck equation, Li Chung-Hsiung equation, Agrawal equations, which are introduced for comparison, are shown in Table 1. The deviation from Simpson’s procedure of Arrhenius integral

**Table 1** Expressions for some proposed rational approximations for Arrhenius integral

Author	$\int_0^T e^{-E/RT} dT$	Equation
Li Chung-Hsiung	$\frac{RT^2}{E} \left[ \frac{1-2\left(\frac{RT}{E}\right)}{1-6\left(\frac{RT}{E}\right)^2} \right] e^{-E/RT}$	(12)
Agrawal	$\frac{RT^2}{E} \left[ \frac{1-2\left(\frac{RT}{E}\right)}{1-5\left(\frac{RT}{E}\right)^2} \right] e^{-E/RT}$	(13)
Gorbachev–Lee–Beck	$\frac{RT^2}{E+2RT} e^{-E/RT}$	(14)
Coats–Redfern	$\frac{RT^2}{E} \left( 1 - \frac{2RT}{E} \right) e^{-E/RT}$	(15)
New equation	$\frac{RT^2}{1.00198882E+1.87391198RT} e^{-E/RT}$	(10)

**Table 2** Percentage deviation from Simpson's procedure for some approximate formula at various  $u$ 

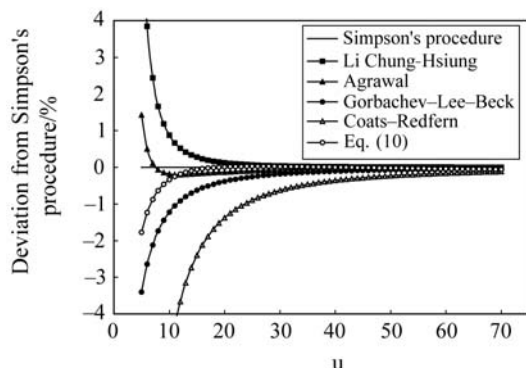
$u$	Li Chung-Hsiung	Agrawal	Gorbachev-Lee-Beck	Coats-Redfern	Eq. (10)
5	6.7656	1.4273	-3.4025	-18.8581	-1.7727
10	0.8768	-0.1851	-1.2248	-5.1758	-0.3428
15	0.2786	-0.1772	-0.6289	-2.3955	-0.0631
20	0.1231	-0.1303	-0.3825	-1.3787	0.0098
25	0.0651	-0.0963	-0.2572	-0.8955	0.0257
30	0.0386	-0.0732	-0.1847	-0.6284	0.0229
35	0.0247	-0.0573	-0.1391	-0.4652	0.0135
40	0.0168	-0.0459	-0.1085	-0.3583	0.0023
45	0.0119	-0.0376	-0.0871	-0.2844	-0.0092
50	0.0088	-0.0313	-0.0714	-0.2313	-0.0201
55	0.0066	-0.0265	-0.0596	-0.1917	-0.0303
60	0.0051	-0.0227	-0.0505	-0.1615	-0.0396
65	0.0041	-0.0196	-0.0433	-0.1379	-0.0481
70	0.0033	-0.0172	-0.0376	-0.1192	-0.0558

for these approximate formulae at various  $u$  is shown in Table 2, respectively. The relative percent error associated with the use of above approximations as solution of the Arrhenius integral for a physically realistic domain of  $u$  are plotted in Fig. 2 along with the error for the present result, Eq. (10). The range of  $u$  and their corresponding precisions are shown in Table 3.

As shown in Fig. 2, hard line represents the 'exact' values of temperature integral used for the error calculation was obtained by double precision numerical integration of Arrhenius integral using the Simpson's procedure with a step size of 1 for  $u$ . Similar plots are drawn for other equations. Figure 2 shows that Eq. (10) is significantly more accurate than either Coats-Redfern method or Gorbachev-Lee-Beck

**Table 3** Typical percentage deviation of various approximate equations from Simpson's procedure of temperature integral

Approximate equation	Range of $u$		
	Deviation from Simpson's procedure/%		
	<0.1	<1.0	<2.0
Li Chung-Hsiung	≥22	≥10	≥8
Agrawal	≥25	≥6	≥5
Gorbachev-Lee-Beck	≥42	≥12	≥8
Coats-Redfern	–	≥24	≥17
Equation (10)	≥14	≥7	≥5



**Fig. 2** Comparison of various approximate methods at different values of  $u$ . Related data are given in Table 2

method in all the range of  $u$ , as a solution of Arrhenius integral. Furthermore, Eq. (10) is better than Li Chung-Hsiung method and Agrawal method in the main range  $u \geq 12$ . In the low range  $5 \leq u \leq 11$ , Eq. (10) is better than Li Chung-Hsiung method and the ratio of deviation lower than 2%. And this new equation is more simple than the two latter. Equation (10) under-predicts the true value of the Arrhenius integral by less than 0.1% over the domain  $u \geq 14$  most normally encountered in experimental studies.

Accurate approximation is the most favorable characteristic for the newly developed approximation formulae [14]. Equation (10) remains the simplicity of Coats-Redfern method and Gorbachev-Lee-Beck method in calculation and formation. And its accuracy is better than Li Chung-Hsiung method and Agrawal method. So it has both simplicity and accuracy. Although Eq. (10) is derived in the range of  $15 \leq u \leq 55$ , it has high precision in the range  $5 \leq u \leq 70$ , in which most of thermal decompositions take place. Furthermore, Eq. (10) is directly derived from numerical temperature integral, so it is reliable.

The program mentioned above is also available in MATLAB 5.3 language, which is a powerful software for numerical calculation and symbol calculation. The precision of numerical calculation performed was higher than 10–11% [17].

## Conclusions

- It is found that  $\frac{\int_0^x x e^{-1/x} dx}{\int_0^x e^{-1/x} dx}$  varies linearly with  $x$  in the range  $1/55 \leq x \leq 1/15$ . Com-

binning this linear correlation and integration-by-parts, a new approximation for temperature integral has been proposed.

- The validity of Eq. (10) has been tested with data from a numerical calculation. Equation (10) gives values close to the theoretical values of temperature integral. Meanwhile Eq. (10) gives more accurate values than those from other approximations compared by the numerical analysis. The results showed that Eq. (10) is an ideal choice for temperature integral. It can be concluded that this newly proposed approximation leads to reasonably good results.
- Because of its simplicity, reliability and high accuracy, Eq. (10) may be commonly used as integral methods of thermal analysis.
- The results also confirmed the plausibility of the used mathematical approach for the derivation of Eq. (10).

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