

An improved version of Junmeng–Fang–Weiming–Fusheng approximation for the temperature integral

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An improved version of Junmeng–Fang–Weiming–Fusheng approximation for the temperature integral has been developed. The accuracy of the improved approximation for the temperature integral has been tested by some numerical analyses. The systematic analysis of the relative errors involved in the kinetic parameters obtained from Junmeng–Fang–Weiming–Fusheng integral method and its improved version has been also carried out. The results have shown that the improved approximation is more accurate than Junmeng–Fang–Weiming–Fusheng approximation as the solution of the temperature integral, and that more accurate kinetic parameters can be determined from the integral method based on the improved temperature integral approximation.

KEY WORDS: nonisothermal kinetics, temperature integral, approximation

1. Introduction

The temperature integral, which is frequently occurs in the nonisothermal kinetic analysis of solid-state reactions, does not have an exact analytical solution [1]. Recently, Junmeng *et al.* proposed a first degree rational fraction approximation for the temperature integral, which is accurate and reliable [2]. Here we call it Junmeng–Fang–Weiming–Fusheng approximation for the temperature integral. The corresponding integral method for nonisothermal kinetics based on Junmeng–Fang–Weiming–Fusheng approximation for the temperature integral is called Junmeng–Fang–Weiming–Fusheng integral method.

In this paper, an improved version of Junmeng–Fang–Weiming–Fusheng approximation has been presented, which is more accurate. As is well known, the main application of the temperature integral approximation is the determination of the kinetic parameters, not the computation of the temperature integral [3, 4]. It is necessary to estimate the relative errors of the kinetic parameters obtained

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from the integral methods based on the temperature integral approximations. Thus, the precision of the Junmeng–Fang–Weiming–Fang approximation integral methods and its improved version for the determination of the kinetic parameters has also been presented in this paper.

2. Theory

The temperature integral is a special integral which is frequently occurs in the nonisothermal kinetic analysis when the dependence of the reaction rate on the temperature is described by the Arrhenius law [5]. Usually, the temperature integral is expressed by the following equation [6, 7]:

$$\int_0^T e^{-(E/RT)} dT = \frac{RT^2}{E} e^{-(E/RT)} h(x) \quad (1)$$

where

$$x = \frac{E}{RT} \quad (2)$$

$$h(x) = x^2 e^x \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (3)$$

Junmeng *et al.* proposed a approximation in the form of $h_1(x) = \frac{x+a \ln x+b}{x+c \ln x+d}$ (where a , b , c , and d are constants) for the $h(x)$ function [2].

In this paper, an improved approximation in the form of $h_1(x) = \frac{p_1 x + p_2 \ln x + p_3}{x + p_4 \ln x + p_5}$ (where p_1 , p_2 , p_3 , p_4 , and p_5 are indeterminate parameters) for the $h(x)$ function has been put forward. Based on the numerical values of the $h(x)$ function obtained by means of the Mathematica software system (detailed information about the Mathematica software system can be found in the literature [8]), using the pattern search method (detailed information about the pattern search method can be found in the literature [9, 10]), the new approximation has been obtained:

$$h_1(x) = \frac{0.999940083636437x + 0.278603058646963 \ln x + 0.367233903690375}{x + 0.264770161932887 \ln x + 2.43832629069336} \quad (4)$$

The corresponding approximation for the temperature integral is given below:

$$\int_0^T e^{-(E/RT)} dT = \frac{RT^2}{E} e^{-(E/RT)} \frac{0.999940083636437E + 0.278603058646963RT \ln(E/RT) + 0.367233903690375RT}{E + 0.264770161932887RT \ln(E/RT) + 2.43832629069336RT} \quad (5)$$

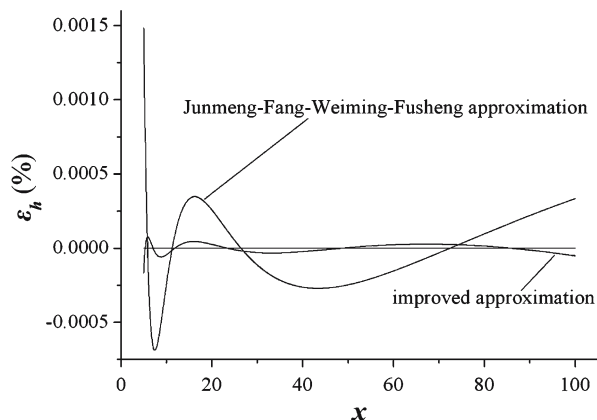


Figure 1. The relative error of the two $h(x)$ approximations for the estimation of the $h(x)$ function.

3. Accuracy evaluation of the improved approximation for the temperature integral

Since the $h(x)$ function is the variable-transformed expression of the temperature integral, the accuracy evaluation of the temperature integral approximation is identical to that of the corresponding $h(x)$ approximation [11]. To perform the accuracy evaluation of the $h(x)$ approximation, the relative errors of the Junmeng–Fang–Weiming–Fusheng approximation and its improved approximation for the $h(x)$ function for the estimation of the $h(x)$ function have been calculated. The relative error of the $h(x)$ approximation can be defined by the following expression:

$$\varepsilon_h = \frac{h_1(x) - h(x)}{h(x)} \cdot 100\% \tag{6}$$

In the above equation, $h_1(x)$ is the value obtained by the $h(x)$ approximation, $h(x)$ is the value obtained by the numerical results of the $h(x)$ function.

The relative error percentages of the two $h(x)$ approximations for the estimation of the $h(x)$ function are shown in figure 1. It is obviously seen that the improved approximation is more accurate than Junmeng–Fang–Weiming–Fusheng approximation with regard to the numerical values of the $h(x)$ function.

4. The precision of Junmeng–Fang–Weiming–Fusheng integral method and its improved version for the determination of the kinetic parameters

For linear heating conditions, the kinetic equation of the solid-state reactions can be described by the following expression:

$$g(\alpha) = \frac{A}{\beta} \frac{RT^2}{E} e^{-(E/RT)} h(x), \tag{7}$$

where $g(\alpha)$ is the integral conversion function depending on the reaction mechanism.

If the integral methods were used for performing the kinetic analysis of solid-state reactions, the apparent activation energy, E_e , would satisfy the following equation [12]:

$$g(\alpha) = \frac{A_e RT^2}{\beta E_e} e^{-(E_e/RT)} h_1(x_e), \quad (8)$$

where the subscript e stands for the apparent values from the integral methods.

From equation (8), one can obtain:

$$\frac{d \ln[g(\alpha)/T^2]}{d(1/T)} = -\frac{E_e}{R} \left(1 - \frac{d \ln h_1(x_e)}{dx_e} \right). \quad (9)$$

The real value of the left hand side of equation (9) as a function of the true activation energy, E , can be determined from equation (7).

$$\frac{d \ln[g(\alpha)/T^2]}{d(1/T)} = -\frac{E}{R} \left[1 - \frac{d \ln h(x)}{dx} \right]. \quad (10)$$

The relative error, ε_E , of the apparent activation energy (E_e) can be defined by the following equation:

$$\varepsilon_E = \frac{E_e - E}{E} \cdot 100\%. \quad (11)$$

Thus, from equations (9), (10), and (11), it follows:

$$(\varepsilon_E + 1) \left(1 - \frac{d \ln h_1[(\varepsilon_E + 1)x]}{d[(\varepsilon_E + 1)x]} \right) = 1 - \frac{d \ln h(x)}{dx}. \quad (12)$$

The above equation for the relative error of the apparent activation energy cannot be analytically solved. But for certain x values, the equation can be solved by numerical techniques. In this study, the Mathematica software system has been used for the numerical solutions of equation (12).

From equations (7) and (8), it follows:

$$\frac{A_e RT^2}{\beta E_e} e^{-(E_e/RT)} h_1(x_e) = \frac{A RT^2}{\beta E} e^{-(E/RT)} h(x). \quad (13)$$

We define the relative error of the frequency factor $\varepsilon_A = \frac{A_e - A}{A} \cdot 100\%$, and ε_A can be easily derived from equation (13):

$$\varepsilon_A = (\varepsilon_E + 1) e^{\varepsilon_E x} \frac{h(u)}{h_1[(\varepsilon_E + 1)x]} - 1. \quad (14)$$

Equations (12) and (14) indicate that that values of ε_E and ε_A depend on $x = (E/RT)$, and therefore, on the value of the activation energy and on the range of temperature of the reaction process.

Table 1

The relative error percentages of the activation energy and frequency factor obtained by Junmeng–Fang–Weiming–Fusheng integral method and the improved version.

x	Activation energy		Frequency factor	
	Junmeng–Fang–Weiming–Fusheng integral method	Improved integral method	Junmeng–Fang–Weiming–Fusheng integral method	Improved integral method
5	–2.4747E-03	7.3321E-04	–1.5741E-02	4.3922E-03
10	2.1153E-04	2.1819E-05	2.5393E-03	2.8040E-04
15	2.5795E-05	4.2961E-06	7.8412E-05	2.5162E-05
20	–3.7481E-05	–7.5588E-06	–1.0423E-03	–1.8362E-04
30	–2.6978E-05	–1.9774E-06	–7.2173E-04	–3.1091E-05
50	6.5755E-06	2.5900E-06	5.8248E-04	1.2871E-04
100	1.0808E-05	–4.3411E-06	7.5847E-04	–3.8658E-04

The relative error percentages of the activation energy and frequency factor obtained by Junmeng–Fang–Weiming–Fusheng integral method and its improved version have been computed from a program developed in the Mathematica language. The resulting ε_E and ε_A values as a function of the parameter x are included in Table 1. The values included in Table 1 illustrate that there is a significant influence of x in the precision of the calculated activation energy and frequency factor values. Furthermore, the precision of the improved integral method is higher than that of Junmeng–Fang–Weiming–Fusheng integral method for the determination of the kinetic parameters.

5. Conclusions

The temperature integral, which is frequently occurs in the nonisothermal kinetic analysis of solid-state reactions, does not have an exact analytical solution. In this paper, we have proposed an improved version of the temperature integral approximation presented by Junmeng *et al.* [2]. The accuracy of the improved approximation for the temperature integral has been analyzed by means of some numerical calculations. The results have shown that the improved approximation is more accurate than Junmeng–Fang–Weiming–Fusheng approximation with regard to the numerical values of the temperature integral. Since the main application of the temperature integral approximation is the determination of the kinetic parameters, not the computation of the temperature integral, the precision of Junmeng–Fang–Weiming–Fusheng integral method and its improved version for the determination of the kinetic parameters has been performed. The results have shown that the improved integral method is more accurate than Junmeng–Fang–Weiming–Fusheng integral method for the determination of the kinetic parameters.

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