Improved version of Doyle integral method for nonisothermal kinetics of solid-state reactions

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An improved version of Doyle integral method for the determination of the kinetic parameters from nonisothermal thermoanalytical data has been presented. The relative errors involved in the activation energy and frequency factor determined from Doyle integral method and its improved integral method have been estimated. The results have shown that the precision of the improved version of Doyle integral method for the determination the kinetic parameters (including the activation energy and frequency factor) is much higher than that of Doyle integral method.

KEY WORDS: Doyle integral method, nonisothermal kinetics, kinetic parameter

1.   Introduction

The integral methods are extensively used for performing the nonisothermal kinetic analysis of solid-state reactions [1]. The number of publications where the integral methods have been used for determining the kinetic parameters is vast [2]. Thus, according to ISI Web of Science Database, more than 4000 citations can be found in the literatures for the integral methods of nonisothermal kinetics. More than 1200 of these citations have been found in the last 5 years. Additionally, Doyle integral method is also extensively used as indicated by more than 450 citations received during the last 5 years. Despite the popularity of Doyle integral method, its accuracy for the estimation of the kinetic parameters are still in doubt, thus some authors have claimed that Doyle integral method are not proper for determining the accurate kinetic parameters [3–6]. Junmeng et al. have calculated the errors in the kinetic parameters (including the activation energy and frequency factor) obtained from Doyle integral method, concluding that the errors are quite large [7].

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The aim of this paper is to develop an improved version of Doyle integral method. It will be shown that the precision of the modified Doyle integral method for the determination of the kinetic parameters is much higher than that of Doyle integral method.

2. Theoretical

In nonisothermal kinetic analysis, the reaction rate of thermally stimulated solid-state reactions can be generally described by the following expression [8]:

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

Furthermore,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} e^{-E/RT} dT = \frac{AE}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx = \frac{AE}{\beta R} p(x), \tag{2}$$

where α is the extent of reaction, T is the absolute temperature, A is the frequency factor, β is the heating rate, E is the activation energy, R is the ideal gas constant, $f(\alpha)$ is the differential kinetic model function depending on the reaction mechanism, and $x = E/RT$. As is well known $p(x)$ has no exact analytical solution, and is expressed by the approximation proposed by Doyle [9].

$$p(x) = 0.0048 e^{-1.0516x}. \tag{3}$$

Equation (2) can be written in the logarithm form as

$$\ln(g(\alpha)) = \ln \frac{AE}{\beta R} + \ln(p(x)). \tag{4}$$

The expression $\ln(p(x))$ of the right hand side of the above equation has no exact analytical solution, but can be solved by numerical techniques. In this study, we use the Mathematica software system to numerically calculate $\ln(p(x))$. Figure 1 illustrates the $\ln(p(x))$ versus x curve.

As ordinary reactions correspond to the range of Δx around 3–4 at common heating rates, a more accurate approximation for the $p(x)$ function in the form of $p(x) = e^{p_1 + p_2 x}$ (as the same with Doyle approximation) from the numerical values of $\ln(p(x))$ has been made at several intervals of $\Delta x = 5$. The calculation has been performed by means of the DataFit software (detailed information about the DataFit software can be found in the website:
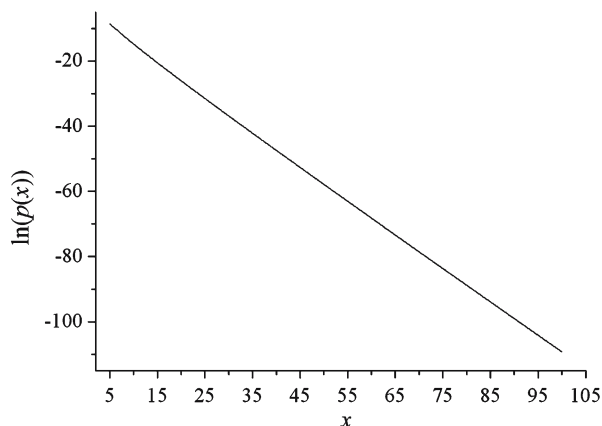
Figure 1. The $\ln(p(x))$ versus x curve.

http://www.oakdaleengr.com/). The expressions of the newly proposed approximation for the $p(x)$ function at various ranges of x are given below:

$$p(x) = \begin{cases} e^{-3.28911330177196-1.15121234630742x}, & 10 \leqslant x < 15, \\ e^{-3.90838558635278-1.1093207210243x}, & 15 \leqslant x < 20, \\ e^{-4.37682243791985-1.08570680852686x}, & 20 \leqslant x < 25, \\ e^{-4.75461564627948-1.07051592145543x}, & 25 \leqslant x < 30, \\ e^{-5.07154962843782-1.05991302577339x}, & 30 \leqslant x < 35, \\ e^{-5.34468086877182-1.05208840691833x}, & 35 \leqslant x < 40, \\ e^{-5.58472986824859-1.04607488429738x}, & 40 \leqslant x < 45, \\ e^{-5.79888947665438-1.04130806963680x}, & 45 \leqslant x < 50, \\ e^{-5.99793094099841-1.03732939479791x}, & 50 \leqslant x < 55, \\ e^{-6.16844631285637-1.03422877181582x}, & 55 \leqslant x < 60, \\ e^{-6.33034410081178-1.03152800995092x}, & 60 \leqslant x < 65, \\ e^{-6.48007938879614-1.02922259552574x}, & 65 \leqslant x \leqslant 70. \end{cases} \tag{5}$$

Substituting the above equation into equation (4), an improve version of Doyle integral method is obtained. To perform a kinetic analysis by the mean of the new method, an iterative calculation should be carried out. The iterative procedure is as follows:

- Step 1: supposing the initial value of the activation energy E_1, calculating $x = E/RT_{\alpha=0.5}$ ($T_{\alpha=0.5}$ is the temperature corresponding to $\alpha = 0.5$), selecting the expression of $p(x)$ corresponding to x from equation (5), then calculating a new value E_2 for the activation energy from the plot of $\ln(g(x))$ versus $1/T$ using equation (4).

- Step 2: replacing E_1 with E_2, repeating step 1.

And so on until $E_i = E_{i-1}$. The last value E_i is the resulting value of activation energy of the reaction.

3.   Results and discussion

The aim of this section is to evaluate the accuracy of the newly proposed $p(x)$ approximation for the estimation of the $p(x)$ function and perform a systematic analysis of the errors involved in the determination of the activation energy and frequency factor obtained by the improved version of Doyle integral method.

Figure 2 shows the evolution of the relative errors of Doyle approximation and its improved version for the estimation of the $p(x)$ function versus x. The relative error has been defined by the expression:

$$\varepsilon_p = \frac{p_a(x) - p(x)}{p(x)} \cdot 100\%, \tag{6}$$

where $p_a(x)$ is the value obtained by the $p(x)$ approximation and $p(x)$ is the value obtained by numerical calculation. Figure 2 indicates that the improved approximation is much more accurate than Doyle approximation for the estimation of $p(x)$.

Doyle approximation and the newly proposed approximation for the $p(x)$ function can be expressed in the form of $p(x) = e^{p_1 + p_2 x}$. In their previous paper, Junmeng and Ronghou have proposed a method for analyzing the precision of the integral methods based on the $p(x)$ approximation in the form of $p(x) = e^{p_1 + p_2 x + p_3 \ln x}$ [7]. Using the method (detailed information of the method is presented in the appendix), we can obtain the relative errors of the activation energy and frequency faction obtained by Doyle integral method and its improve version.

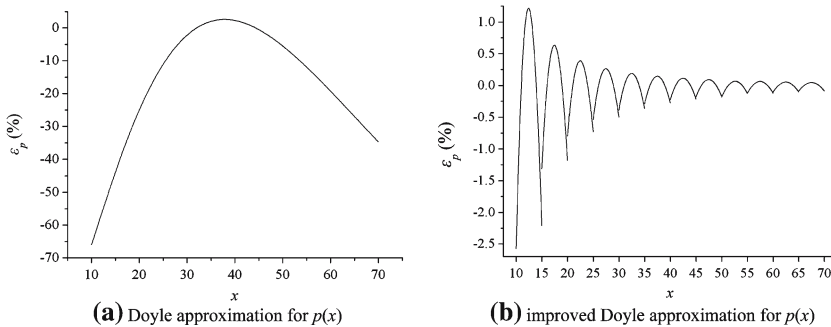(a) Doyle approximation for $p(x)$ (b) improved Doyle approximation for $p(x)$

Figure 2. Evolution of the relative errors of Doyle approximation and its improved version for the estimation of the $p(x)$ function versus the value of x.

(a) Doyle integral method
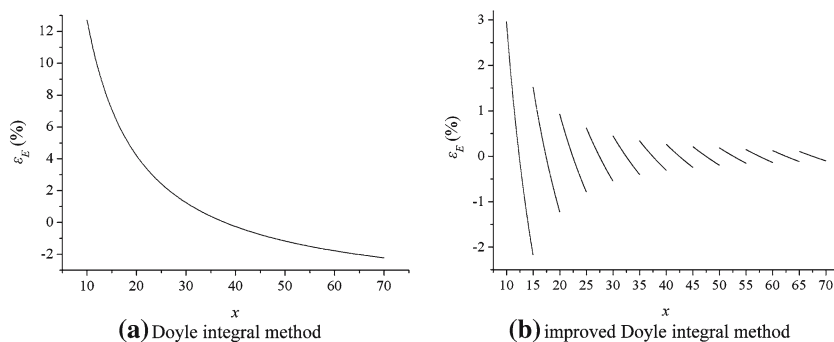
(b) improved Doyle integral method

Figure 3. Relative error percentages of the activation energy obtained from Doyle integral method and its improved integral method its improved integral method.

(a) Doyle integral method
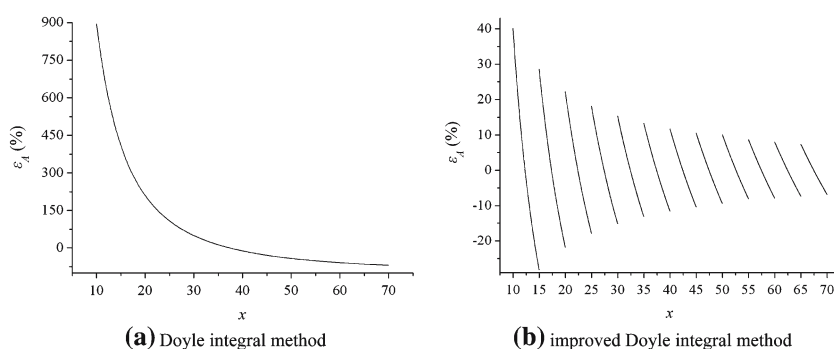
(b) improved Doyle integral method

Figure 4. Relative error percentages of the frequency factor obtained from Doyle integral method and its improved integral method.

Figure 3 illustrates the relative error involved in the determination of the activation energy calculated by Doyle integral method and the improved integral method.

Figure 4 illustrates the relative error involved in the determination of the frequency factor calculated by Doyle integral method and the improved integral method.

It can be observed that the relative errors of the activation energy and frequency factor are dependent on x (E/RT), and therefore, on the value of the activation energy and on the range of temperature of the process from figures 3 and 4. Furthermore, the precision of the improved integral method is much higher than Doyle integral method.

All calculation of this section has been performed by means of the Mathematica software system, which is powerful for the numerical calculation and symbolic computation [10].

4.   Conclusions

Doyle integral method is extensively used in the nonisothermal kinetic analysis of solid-state reactions. However, the errors involved in the determination of the activation energy and frequency factor calculated by Doyle integral method are quite large. In this work, an improved version of Doyle integral method have been developed, A systematic analysis of the errors in the activation energy and frequency factor from the new integral method has been performed. The results have shown that the improved method is much more accurate than Doyle integral method for the determination of the kinetic parameters.

Appendix

The precision of the integral methods based on the $p(x)$ approximations in the form of $p(x) = e^{p_1 + p_2 x}$ for the determination of the kinetic parameters.

If the integral methods were used for performing the kinetic analysis of solid-state reactions, the apparent activation energy, E_a, would satisfy the following expression:

$$\ln(g(\alpha)) = \ln \frac{A_a E_a}{\beta R} + p_1 + p_2 x_a. \tag{7}$$

In the above equation, the subscript a stands for the apparent value of the kinetic parameters from the integral methods, and $x_a = E_a/RT$.

By differentiating equation (7), one can get

$$\frac{\partial \ln(g(\alpha))}{\partial(1/T)} = p_2 \cdot \frac{E_a}{R}. \tag{8}$$

The real value of the left hand side of the above equation as a function of the true activation energy can be easily determined by differentiating equation (4):

$$\frac{\partial \ln(g(\alpha))}{\partial(1/T)} = \frac{E}{R} \frac{d \ln(p(x))}{dx}. \tag{9}$$

We define the relative error in the activation energy $\varepsilon_E = \frac{E_a - E}{E} \cdot 100\%$, and the following expressions can be obtained

$$E_a = (\varepsilon_E + 1)E, \tag{10}$$

$$x_a = (\varepsilon_E + 1)x. \tag{11}$$

From equations (8), (9), (10), and (11), we can obtain the expression of the relative error in the activation energy:

$$\varepsilon_E = \frac{1}{p_2}\frac{\mathrm{d}\ln(p(x))}{\mathrm{d}x} - 1. \tag{12}$$

From equations (4) and (7), it follows:

$$\frac{AE}{\beta R}p(x) = \frac{A_a E_a}{\beta R}\mathrm{e}^{p_1 + p_2 x}. \tag{13}$$

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

$$\varepsilon_A = \frac{p(x)}{(\varepsilon_E + 1)\mathrm{e}^{p_1 + p_2[(\varepsilon_E + 1)x]}} - 1. \tag{14}$$

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