

Kinetic analysis of nonisothermal solid-state reactions: determination of the kinetic parameters by means of a nonlinear regression method

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Abstract A nonlinear regression method has been proposed for a simultaneous calculation of the activation energy, frequency factor, and reaction order from a single TG curve. This method was based on the new temperature integral approximation proposed in this paper and the Levenberg–Marquardt method. The newly proposed nonlinear regression method was applied for determining the kinetic parameters from two simulated TG curves. The results of the calculations were compared with values obtained by the traditional method. It can be concluded from this comparison that the new nonlinear regression method is more accurate than the traditional method for the determination of the kinetic parameters of solid-state heterogeneous reactions.

Keywords Nonlinear regression · Nonisothermal kinetics · Activation energy · Frequency factor · Reaction order

1 Introduction

The nonisothermal thermogravimetry with a linear temperature ramp is a convenient technique for studying the kinetics of processes involving solids, such as decomposition and gas–solid reactions, by following the mass loss of the samples with

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time/temperature [1]. In addition, it enables to determine the kinetic parameters of solid-state reactions. There are two types of calculation methods for the determination of the kinetic parameters of heterogeneous reactions: one type is based on a single TG curve (“model-fitting” methods [2]), the other one require several TG curves measured at various heating rates (“model-free” methods, isoconversional methods [3]). The development of computing technologies and software products make the iterative methods utilizing the direct nonlinear evaluating of TG curves possible [4–6]. The aim of the present short paper is to investigate the possibility of applying a nonlinear regression method for the determination of the kinetic parameters of solid-state heterogeneous reactions.

2 Theoretical

If it is taken into account that a solid-state reaction can be approximated by an n th-order kinetic model, the kinetic law of the reaction is described by the following differential equation [7]:

$$\frac{dw}{dt} = -k(T)w^n \quad (1)$$

with the boundary condition $w = 1$ at $t = 0$. In the above equation, w stands for the mass fraction of reaction material, t is the time, n is the reaction order, $k(T)$ is its corresponding reaction rate constant, given by the Arrhenius law [8]:

$$k(T) = Ae^{-E/RT} \quad (2)$$

If the temperature of the process is increase at a constant rate $\beta = dT/dt$, Eq. (1) can be integrated:

$$\begin{aligned} g(w) &= \int_1^w \frac{dw}{w^n} = -\frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT \\ &= -\frac{A}{\beta} \left[\int_0^T e^{-E/RT} dT - \int_0^{T_0} e^{-E/RT} dT \right] \end{aligned} \quad (3)$$

where T_0 is the starting temperature of the linear heating program.

The $g(w)$ function has two forms depending on the value of the reaction order [9].

$$g(w) = \begin{cases} \frac{w^{1-n}-1}{1-n} & n \neq 1 \\ \ln w & n = 1 \end{cases} \quad (4)$$

2.1 Traditional method

The integrals $I(E, T) = \int_0^T e^{-E/RT} dT$ and $I(E, T_0) = \int_0^{T_0} e^{-E/RT} dT$ in the right hand side of Eq. (3) is termed in the literature the temperature integral or Arrhenius

integral [10–12], which cannot be expressed in a closed form. Usually, it is considered that the integral $I(E, T_0)$ is negligible, which is an acceptable hypothesis, since T_0 is usually near room temperature, and the activation energy is usually not too low [13]. In this case

$$\begin{cases} \frac{w^{1-n}-1}{1-n} = -\frac{A}{\beta} \int_0^T e^{-E/RT} dT & n \neq 1 \\ \ln w = -\frac{A}{\beta} \int_0^T e^{-E/RT} dT & n = 1 \end{cases} \tag{5}$$

Since $I(E, T)$ has no exact analytical solution, $e^{-E/RT}$ can be expressed as an asymptotic series and integrated, with the higher-order terms ignored.

$$\begin{cases} \frac{w^{1-n}-1}{1-n} = -\frac{A}{\beta} \frac{RT^2}{E} \left(1 - \frac{2RT}{E}\right) e^{-E/RT} & n \neq 1 \\ \ln w = -\frac{A}{\beta} \frac{RT^2}{E} \left(1 - \frac{2RT}{E}\right) e^{-E/RT} & n = 1 \end{cases} \tag{6}$$

Expressing Eq. (6) in logarithmic form

$$\begin{cases} \ln \left[\frac{1-w^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} & n \neq 1 \\ \ln \left(\frac{-\ln w}{T^2} \right) = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} & n = 1 \end{cases} \tag{7}$$

If $2RT/E \ll 1$ is assumed, Eq. (7) becomes

$$\begin{cases} \ln \left[\frac{1-w^{1-n}}{T^2(1-n)} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT} & n \neq 1 \\ \ln \left(\frac{-\ln w}{T^2} \right) = \ln \frac{AR}{\beta E} - \frac{E}{RT} & n = 1 \end{cases} \tag{8}$$

Thus, a plot of $\ln \left[\frac{1-w^{1-n}}{T^2(1-n)} \right]$ versus $\frac{1}{T}$ if $n \neq 1$ or $\ln \left(\frac{-\ln w}{T^2} \right)$ versus $\frac{1}{T}$ if $n = 1$ should result in a straight line of slope $-E/R$ for the proper value of n . The criterion used for acceptable value of E and A is that the final value of n should yield values of E whose linear correlation coefficients are the best [14].

2.2 Nonlinear regression method

The temperature integral has no exact analytical solution, and a large number of approximated equations have been proposed in the literature for performing the kinetic analysis of solid-state reactions from integral experimental data [15, 16]. Some empirical approximations are imprecise in the evaluation of the temperature integral if the temperature integral approximations are compared with the values calculated by numerical calculation [17].

In this study, a new approximation has been proposed, which is very accurate as a solution of the temperature integral. The derivation of the new approximation is as follows.

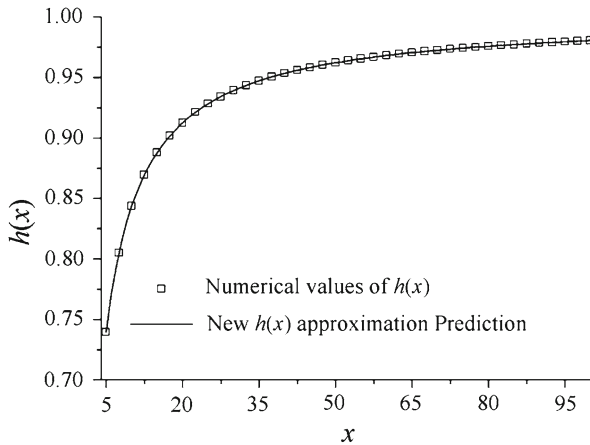


Fig. 1 Overlay of numerical values of $h(x)$ and its approximation prediction

With $x = E/RT$, the temperature integral can be rewritten:

$$\int_0^T e^{-E/RT} dT = \frac{RT^2}{E} e^{-E/RT} h(x) \quad (9)$$

where

$$h(x) = x^2 e^x \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (10)$$

The $h(x)$ function has no exact analytical solution, but can be calculated from numerical methods. In this study, the Simpson's 1/3 rule has been employed to perform the numerical calculation of the $h(x)$ function. The plot of $h(x)$ versus x is depicted in Fig. 1.

From numerical values of $h(x)$ shown in Fig. 1, it can be seen that the $h(x)$ function changes slowly with x and is close to unity for high values of x . Based on the above analysis, we have proposed the following approximating formula for the estimation of the $h(x)$ function:

$$h_a(x) = \left(\frac{x+a}{x+b} \right)^c \quad (11)$$

where $h_a(x)$ is the approximation of the $h(x)$ function, a, b, c are indeterminate parameters.

Based on the numerical values of the $h(x)$ function, the values of the parameters a, b and c can be easily obtained using a certain nonlinear regression method: $a = -0.566552207341865$, $b = 4.42348301307593$, $c = 0.400350661295612$. For comparison, the prediction of the $h(x)$ function with the $h(x)$ approximation is also included in Fig. 1. Figure 2 shows the evolution of the relative error of the new

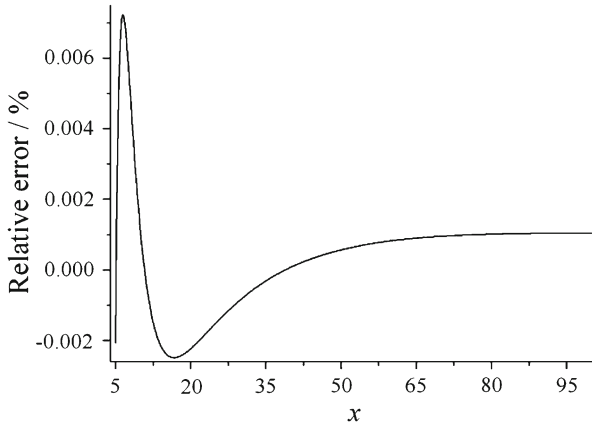


Fig. 2 Evolution of the relative error of the new $h(x)$ approximation for the estimation of the $h(x)$ function versus the value of x . The relative error has been defined by the expression: $[h_a(x) - h(x)]/h(x) \cdot 100\%$, being $h_a(x)$ the value obtained by the new $h(x)$ approximation and $h(x)$ the value obtained by numerical integration

approximated $h(x)$ function for the estimation of the $h(x)$ function versus x . Figures 1 and 2 indicate that the newly proposed $h(x)$ approximation is very accurate as a solution of the $h(x)$ function.

From Eqs. (6) and (8), and $x = E/RT$, we can get the approximation for the temperature integral:

$$\int_0^T e^{-E/RT} dT \approx I_a(E, T) = \frac{RT^2}{E} e^{-E/RT} \left(\frac{E - 0.566552207341865 RT}{E + 4.42348301307593 RT} \right)^{0.400350661295612} \tag{12}$$

where $I_a(E, T)$ is the newly proposed approximation for the temperature integral.

By substituting Eqs. (4) and (12) into Eq. (3), one gets

$$w = \begin{cases} \left\{ 1 - \frac{A}{\beta} (1 - n) [I_a(E, T) - I_a(E, T_0)] \right\}^{1/(1-n)} & n \neq 1 \\ e^{-\frac{A}{\beta} [I_a(E, T) - I_a(E, T_0)]} & n = 1 \end{cases} \tag{13}$$

To evaluate the parameters A , E , and n , the residual sum of squares of the real values of w and w values calculated from Eq. (13) is used. It is defined for Eq. (14) by the following relation:

$$RSS = \sum_{i=1}^{n_d} (w_{r,i} - w_{c,i})^2 \tag{14}$$

where $w_{r,i}$ and $w_{c,i}$ are the mass fractions in individual points of the real curve and the values calculated from Eq. (13) in the corresponding points, respectively; n_d is the number of points. The least RSS values are obtained for the best parameter estimates.

There are a number of algorithms for minimizing Eq. (14) enabling to find the best values of the parameters. In this study, the Levenberg–Marquardt method has been used for the calculation of the parameter values that minimize Eq. (14). The Levenberg–Marquardt method is a nonlinear regression method. Many methods use the gradient of the objective function. The Levenberg–Marquardt method uses Jacobian instead of gradient. More detailed information about this method can be found in the literature [18]. For performing the Levenberg–Marquardt method, either general purposed mathematical software or a computer program developed in any programming language is used. In this work, the DataFit software [19] has been used for performing the optimization procedure.

3 Results and discussion

The nonisothermal simulated data, which unlike experimental data are not affected by noises, have been analyzed. The two different theoretical curves have been simulated assuming different kinetic parameters. The simulated curves have been computed by solving the system of two differential equations constituted by Eq. (3) and $dT/dt = \beta$ by means of the Runge-Kutta method of the fourth order using the MATLAB software and a tolerance of 10^{-6} . The first curve (Fig. 3a) has been simulated for $\beta = 10 \text{ K min}^{-1}$, $T_0 = 400 \text{ K}$, $E = 30 \text{ kJ mol}^{-1}$, $A = 10 \text{ min}^{-1}$, $n = 1.2$. The second curve (Fig. 3b) has been computed for $\beta = 10 \text{ K min}^{-1}$, $T_0 = 400 \text{ K}$, $E = 115 \text{ kJ mol}^{-1}$, $A = 6 \times 10^9 \text{ min}^{-1}$, and $n = 2.5$.

These curves have been analyzed by means of both the traditional method and the nonlinear regression proposed in this paper. The resulting values of the kinetic para-

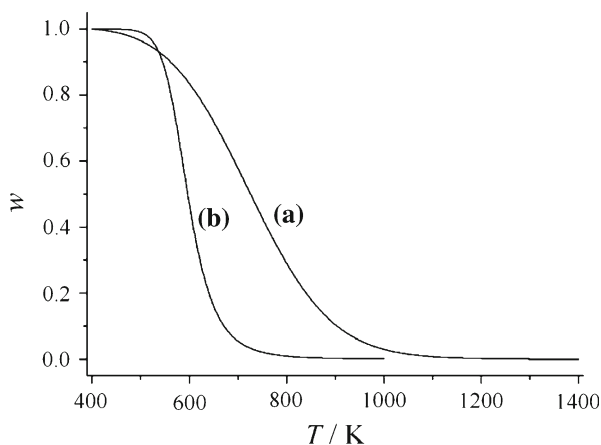


Fig. 3 Simulated curves (a) $\beta = 10 \text{ K min}^{-1}$, $T_0 = 400 \text{ K}$, $E = 30 \text{ kJ mol}^{-1}$, $A = 10 \text{ min}^{-1}$, $n = 1.2$; and (b) $\beta = 10 \text{ K min}^{-1}$, $T_0 = 400 \text{ K}$, $E = 115 \text{ kJ mol}^{-1}$, $A = 6 \times 10^9 \text{ min}^{-1}$, and $n = 2.5$

Table 1 Values of the kinetic parameters and the corresponding relative error obtained in the analysis of the simulated curves included in Fig. 3a and b by means of the different methods^a

		Real value	Nonlinear regression method		Traditional method	
			Calculated value	Relative error (%)	Calculated value	Relative error (%)
Simulated curve Fig. 3a	E (kJ mol ⁻¹)	30	30.19198	0.63994	29.79476	-0.68415
	A (min ⁻¹)	10	10.37791	3.77912	7.16499	-28.35011
	n	1.2	1.20582	0.48536	1.24901	4.08436
Simulated curve Fig. 3b	E (kJ mol ⁻¹)	115	115.00279	0.00243	114.71386	-0.24882
	A (min ⁻¹)	6×10^9	6.00362×10^9	0.06031	5.22132×10^9	-12.97793
	n	2.5	2.50005	0.00202	2.50228	0.09132

^a The relative error has been defined by the following expression:

$$\text{Relative error} = (\text{Calculated value} - \text{Real value}) / \text{Real value} \times 100\%$$

meters and the corresponding relative errors are given in Table 1. It can be obtained that values of the kinetic parameters calculated by the nonlinear regression method proposed in this paper are more accurate than those by traditional method. In the nonlinear regression method, a new accurate approximation for the temperature integral is used and the low temperature end of the temperature integral is not neglected. Furthermore, the simultaneous calculation of the activation energy, frequency factor and reaction order can be performed by means of the nonlinear regression method.

4 Conclusions

In the present short paper, a new method for determination of the kinetic parameters of solid-state reactions has been presented. The newly proposed method was based on the newly proposed approximation for the temperature integral and the Levenberg–Marquardt method. The method has been successfully applied determining the kinetic parameters from two simulated TG curves. The results were compared with the values obtained by traditional methods. It can be concluded from this comparison that the nonlinear regression method appears to be the suitable solution for the evaluation of the kinetic parameters of solid-state heterogeneous reactions.

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