Dependence of the frequency factor on the temperature: a new integral method of nonisothermal kinetic analysis

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A new integral method of nonisothermal kinetic analysis has been developed with the dependence of the frequency factor on the temperature ($A = A_0 T^m$). The new integral method is obtained from the newly proposed approximation for the general temperature integral, which is more accurate than the other existed approximations. For applications, nonisothermal thermoanalytical data obtained by theoretical simulation have been processed. The results have shown that the newly proposed integral method is an ideal solution for the evaluation of kinetic parameters from nonisothermal thermoanalytical data with the frequency factor dependent the temperature.

KEY WORDS: Integral method, nonisothermal kinetic analysis, frequency factor, approximation

1. Introduction

Many technologically important processes and reactions occur under nonisothermal conditions and it is often desired to calculate or predict the progress of the reaction over time during transient heating [1]. Integral methods of nonisothermal kinetic analysis utilize cumulative values of a species concentration, heat of reaction, weight loss, etc., measured in temperature scanning experiments to extract the kinetic parameters of a reacting system [2].

Since the overwhelming majority of thermal analyses are conducted at constant heating rate and the frequency factor of some solid-state reactions are connected with the temperature [2], the present work seeks to develop a new integral method under experimental conditions of a linear temperature program and the dependence of the frequency factor on the temperature, and extend these results to more accurate determination of the Arrhenius kinetic parameters. It

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is hoped that the results of this work aid process development of nonisothermal kinetic analysis.

2.   Theory

Under nonisothermal conditions of a linear temperature program, the kinetic behavior of thermally stimulated solid-state reactions can be described by the following expression [3]:

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

where α represents the fractional conversion in the solid reactant; A the frequency factor, E the activation energy, R the gas constant, T the absolute temperature, β the heating rate and $f(\alpha)$ a so-called differential kinetic function that depends on the reaction mechanism.

It is noteworthy to point out that all existed integral methods of kinetic analysis generally used have been developed by assuming that the frequency factor can be considered as a constant all over the temperature range investigated. However, several authors [4–7] after extending the theory of the activated complex to the thermal decomposition of single solid-state reactions proposed that the frequency factor is connected with the temperature through the following relationship:

$$A = A_0 T^m, \tag{2}$$

where A_0 is a constant and values of the exponent m range from -1.5 to 2.5 for some solid-state reactions [8].

If equation (2) is fulfilled, equation (1) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A_0}{\beta}T^m\mathrm{e}^{-E/RT}f(\alpha). \tag{3}$$

Rearranging and integrating equation (3) results

$$g(\alpha) = \int\limits_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A_0}{\beta}\int\limits_0^T T^m\mathrm{e}^{-E/RT}\mathrm{d}T, \tag{4}$$

where $g(\alpha)$ is the integral kinetic function.

The integral $\int_0^T T^m\mathrm{e}^{-E/RT}\mathrm{d}T$ on the right-hand side of equation (4) does not have an exact analytical solution. For $m = 0$, the integral is named in the literature as the temperature integral or Arrhenius integral [9, 10]. Here we called $\int_0^T T^m\mathrm{e}^{-E/RT}\mathrm{d}T$ the general temperature integral. After doing the variable

change $x = E/RT$, the general temperature integral would be rearranged in the following way

$$\int_0^T T^m e^{-E/RT} \, dT = (E/R)^{m+1} \, p_m(x) = \frac{R}{E} T^{m+2} e^{-E/RT} h_m(x), \tag{5}$$

where

$$p_m(x) = \int_x^\infty e^{-x} x^{-m-2} \, dx, \tag{6}$$

$$h_m(x) = x^{m+2} e^x \int_x^\infty e^{-x} x^{-m-2} \, dx, \tag{7}$$

The $h_m(x)$ function does not have an exact analytical solution, but it can be numerically integrated by some numerical techniques. For this purpose, either general purposed mathematical software or a computer program developed in any programming language is used. In this work, the Mathematica software system has been employed for the numerical solution of the $h_m(x)$ function. The obtained numerical values of $h_m(x)$ as a function of the parameters x and m are plotted in figure 1.
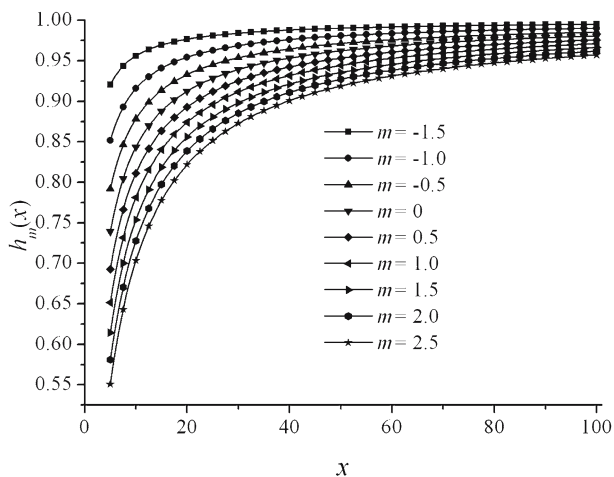

Figure 1. The numerical values of $h_m(x)$ as a function of the parameters x and m.

From figure 1, we use the following rational fraction to approximate the $h_m(x)$:

$$h_{1m}(x) = \frac{x + am + b}{x + cm + d}, \tag{8}$$

where a, b, c, and d are indeterminant parameters.

Since most thermally stimulated solid-state reactions take place in the range of $5 \leqslant x \leqslant 100$ [11], we consider this range in the determination of the values of a, b, c, and d. By using a multivariate nonlinear regression method at the Data-Fit software environment (detailed information about the DataFit software can be found in the web site: http://www.oakdaleengr.com/), the values of the parameters a, b, c, and d are established: $a = -0.054182$, $b = 0.65061$, $c = 0.93544$, and $d = 2.62993$. Thus the new approximations for $h_m(x)$, $p_m(x)$ and the general temperature integral are obtained and given below

$$h_{1m}(x) = \frac{x - 0.054182m + 0.65061}{x + 0.93544m + 2.62993}, \tag{9}$$

$$p_{1m}(x) = \frac{e^{-x}}{x^{m+2}} \frac{x - 0.054182m + 0.65061}{x + 0.93544m + 2.62993}, \tag{10}$$

$$\int_0^T T^m e^{-E/RT} dT = \frac{R}{E} T^{m+2} e^{-E/RT} \frac{E - 0.054182mRT + 0.65061RT}{E + 0.93544mRT + 2.62993RT}. \tag{11}$$

From equations (4) and (10), it follows:

$$g(\alpha) = \frac{A_0 R}{\beta E} T^{m+2} e^{-E/RT} \frac{E - 0.054182mRT + 0.65061RT}{E + 0.93544mRT + 2.62993RT}, \tag{12}$$

which is the starting equation for the new integral method of evaluating the kinetic parameters when the frequency factor depends on the temperature. Using a nonlinear regression method, the kinetic parameters can be determined from the above equation.

3.   Accuracy evaluation of the new approximation for $p_m(x)$

From the above section, we can obtain that the precision of the integral method depends on the precision of the approximation for the estimation of the general temperature integral. Since $p_m(x)$ is the variable transformation expression of the general temperature integral, the accuracy evaluation of the approximation for $p_m(x)$ is identical to that of the approximation for the general temperature integral.

Table 1
Relative error percentages of the newly proposed approximation for the estimation of $p_m(x)$.

x					m				
	-1.5	-1	-0.5	0	0.5	1	1.5	2	2.5
5	3.6213E-01	3.0587E-01	2.3453E-01	1.5406E-01	2.3453E-01	3.0587E-01	3.6213E-01	3.9951E-01	4.1572E-01
10	-8.4103E-02	-6.7653E-02	-5.5109E-02	-4.5424E-02	-5.5109E-02	-6.7653E-02	-8.4103E-02	-1.0524E-01	-1.3165E-01
15	-6.1800E-02	-4.6316E-02	-3.3589E-02	-2.3385E-02	-3.3589E-02	-4.6316E-02	-6.1800E-02	-8.0221E-02	-1.0172E-01
20	-2.9776E-02	-1.9387E-02	-1.1177E-02	-5.0954E-03	-1.1177E-02	-1.9387E-02	-2.9776E-02	-4.2379E-02	-5.7219E-02
25	-8.6289E-03	-2.2024E-03	2.4680E-03	5.3829E-03	2.4680E-03	-2.2024E-03	-8.6289E-03	-1.6807E-02	-2.6729E-02
30	4.4526E-03	8.1429E-03	1.0398E-02	1.1205E-02	1.0398E-02	8.1429E-03	4.4526E-03	-6.5848E-04	-7.1743E-03
35	1.2526E-02	1.4351E-02	1.4985E-02	1.4415E-02	1.4985E-02	1.4351E-02	1.2526E-02	9.5288E-03	5.3744E-03
40	1.7526E-02	1.8067E-02	1.7608E-02	1.6135E-02	1.7608E-02	1.8067E-02	1.7526E-02	1.6002E-02	1.3510E-02
45	2.0608E-02	2.0253E-02	1.9050E-02	1.6984E-02	1.9050E-02	2.0253E-02	2.0608E-02	2.0126E-02	1.8822E-02
50	2.2464E-02	2.1480E-02	1.9766E-02	1.7311E-02	1.9766E-02	2.1480E-02	2.2464E-02	2.2731E-02	2.2289E-02
55	2.3525E-02	2.2093E-02	2.0028E-02	1.7320E-02	2.0028E-02	2.2093E-02	2.3525E-02	2.4333E-02	2.4527E-02
60	2.4059E-02	2.2309E-02	2.0004E-02	1.7137E-02	2.0004E-02	2.2309E-02	2.4059E-02	2.5263E-02	2.5929E-02
65	2.4242E-02	2.2265E-02	1.9799E-02	1.6837E-02	1.9799E-02	2.2265E-02	2.4242E-02	2.5736E-02	2.6755E-02
70	2.4188E-02	2.2052E-02	1.9481E-02	1.6469E-02	1.9481E-02	2.2052E-02	2.4188E-02	2.5895E-02	2.7180E-02
75	2.3975E-02	2.1728E-02	1.9092E-02	1.6063E-02	1.9092E-02	2.1728E-02	2.3975E-02	2.5838E-02	2.7323E-02
80	2.3656E-02	2.1334E-02	1.8664E-02	1.5639E-02	1.8664E-02	2.1334E-02	2.3656E-02	2.5632E-02	2.7268E-02
85	2.3267E-02	2.0898E-02	1.8214E-02	1.5209E-02	1.8214E-02	2.0898E-02	2.3267E-02	2.5323E-02	2.7071E-02
90	2.2834E-02	2.0438E-02	1.7756E-02	1.4783E-02	1.7756E-02	2.0438E-02	2.2834E-02	2.4945E-02	2.6777E-02
95	2.2374E-02	1.9967E-02	1.7298E-02	1.4365E-02	1.7298E-02	1.9967E-02	2.2374E-02	2.4521E-02	2.6413E-02
100	2.1900E-02	1.9493E-02	1.6847E-02	1.3959E-02	1.6847E-02	1.9493E-02	2.1900E-02	2.4069E-02	2.6003E-02

Table 2
Relative error percentages of Wanjun approximation I for the estimation of $p_m(x)$.

x	m								
	-1.5	-1	-0.5	0	0.5	1	1.5	2	2.5
5	$-1.2700E+00$	$-2.2037E+00$	$-2.8931E+00$	$-3.4025E+00$	$-3.7774E+00$	$-4.0507E+00$	$-4.2467E+00$	$-4.3833E+00$	$-4.4740E+00$
10	$-3.8759E-01$	$-7.1453E-01$	$-9.9087E-01$	$-1.2248E+00$	$-1.4230E+00$	$-1.5910E+00$	$-1.7333E+00$	$-1.8537E+00$	$-1.9555E+00$
15	$-1.8600E-01$	$-3.5121E-01$	$-4.9813E-01$	$-6.2890E-01$	$-7.4540E-01$	$-8.4925E-01$	$-9.4184E-01$	$-1.0244E+00$	$-1.0981E+00$
20	$-1.0900E-01$	$-2.0851E-01$	$-2.9942E-01$	$-3.8253E-01$	$-4.5855E-01$	$-5.2812E-01$	$-5.9182E-01$	$-6.5016E-01$	$-7.0360E-01$
25	$-7.1568E-02$	$-1.3803E-01$	$-1.9977E-01$	$-2.5716E-01$	$-3.1054E-01$	$-3.6019E-01$	$-4.0639E-01$	$-4.4940E-01$	$-4.8945E-01$
30	$-5.0578E-02$	$-9.8094E-02$	$-1.4275E-01$	$-1.8474E-01$	$-2.2422E-01$	$-2.6137E-01$	$-2.9633E-01$	$-3.2923E-01$	$-3.6021E-01$
35	$-3.7635E-02$	$-7.3293E-02$	$-1.0709E-01$	$-1.3913E-01$	$-1.6951E-01$	$-1.9832E-01$	$-2.2566E-01$	$-2.5160E-01$	$-2.7622E-01$
40	$-2.9095E-02$	$-5.6840E-02$	$-8.3302E-02$	$-1.0855E-01$	$-1.3264E-01$	$-1.5563E-01$	$-1.7758E-01$	$-1.9853E-01$	$-2.1854E-01$
45	$-2.3164E-02$	$-4.5366E-02$	$-6.6648E-02$	$-8.7053E-02$	$-1.0662E-01$	$-1.2539E-01$	$-1.4339E-01$	$-1.6066E-01$	$-1.7723E-01$
50	$-1.8879E-02$	$-3.7047E-02$	$-5.4534E-02$	$-7.1367E-02$	$-8.7574E-02$	$-1.0318E-01$	$-1.1821E-01$	$-1.3269E-01$	$-1.4663E-01$
55	$-1.5682E-02$	$-3.0824E-02$	$-4.5447E-02$	$-5.9570E-02$	$-7.3213E-02$	$-8.6393E-02$	$-9.9128E-02$	$-1.1143E-01$	$-1.2333E-01$
60	$-1.3233E-02$	$-2.6047E-02$	$-3.8456E-02$	$-5.0475E-02$	$-6.2117E-02$	$-7.3395E-02$	$-8.4322E-02$	$-9.4909E-02$	$-1.0517E-01$
65	$-1.1316E-02$	$-2.2300E-02$	$-3.2963E-02$	$-4.3315E-02$	$-5.3366E-02$	$-6.3126E-02$	$-7.2603E-02$	$-8.1808E-02$	$-9.0748E-02$
70	$-9.7878E-03$	$-1.9308E-02$	$-2.8569E-02$	$-3.7578E-02$	$-4.6343E-02$	$-5.4871E-02$	$-6.3169E-02$	$-7.1244E-02$	$-7.9103E-02$
75	$-8.5494E-03$	$-1.6880E-02$	$-2.4998E-02$	$-3.2909E-02$	$-4.0620E-02$	$-4.8136E-02$	$-5.5462E-02$	$-6.2603E-02$	$-6.9565E-02$
80	$-7.5319E-03$	$-1.4883E-02$	$-2.2057E-02$	$-2.9060E-02$	$-3.5896E-02$	$-4.2569E-02$	$-4.9084E-02$	$-5.5444E-02$	$-6.1655E-02$
85	$-6.6859E-03$	$-1.3220E-02$	$-1.9607E-02$	$-2.5849E-02$	$-3.1951E-02$	$-3.7915E-02$	$-4.3747E-02$	$-4.9447E-02$	$-5.5021E-02$
90	$-5.9749E-03$	$-1.1821E-02$	$-1.7543E-02$	$-2.3142E-02$	$-2.8622E-02$	$-3.3985E-02$	$-3.9235E-02$	$-4.4373E-02$	$-4.9403E-02$
95	$-5.3715E-03$	$-1.0634E-02$	$-1.5789E-02$	$-2.0839E-02$	$-2.5788E-02$	$-3.0636E-02$	$-3.5387E-02$	$-4.0043E-02$	$-4.4605E-02$
100	$-4.8551E-03$	$-9.6162E-03$	$-1.4285E-02$	$-1.8864E-02$	$-2.3355E-02$	$-2.7759E-02$	$-3.2079E-02$	$-3.6316E-02$	$-4.0473E-02$

Table 3
Relative error percentages of Wanjun approximation II for the estimation of $p_m(x)$.

x					m				
	−1.5	−1	−0.5	0	0.5	1	1.5	2	2.5
5	−7.4604E-01	−1.2479E+00	−1.5741E+00	−1.7727E+00	−1.8781E+00	−1.9147E+00	−1.9009E+00	−1.8500E+00	−1.7720E+00
10	−1.3507E-01	−2.3292E-01	−3.0035E-01	−3.4284E-01	−3.6488E-01	−3.7014E-01	−3.6161E-01	−3.4178E-01	−3.1270E-01
15	−3.0794E-02	−5.0562E-02	−6.0867E-02	−6.3049E-02	−5.8262E-02	−4.7495E-02	−3.1605E-02	−1.1331E-02	1.2688E-02
20	−3.7472E-03	−3.0122E-03	1.6722E-03	9.8349E-03	2.1059E-02	3.4975E-02	5.1254E-02	6.9606E-02	8.9771E-02
25	3.3045E-03	8.8474E-03	1.6399E-02	2.5751E-02	3.6716E-02	4.9125E-02	6.2826E-02	7.7679E-02	9.3558E-02
30	3.8700E-03	9.0504E-03	1.5424E-02	2.2883E-02	3.1331E-02	4.0675E-02	5.0835E-02	6.1734E-02	7.3302E-02
35	2.1398E-03	5.1542E-03	8.9757E-03	1.3542E-02	1.8794E-02	2.4679E-02	3.1147E-02	3.8151E-02	4.5649E-02
40	−3.6964E-04	−8.9283E-05	7.9801E-04	2.2520E-03	4.2350E-03	6.7117E-03	9.6493E-03	1.3017E-02	1.6785E-02
45	−3.0600E-03	−5.5950E-03	−7.6346E-03	−9.2069E-03	−1.0338E-02	−1.1053E-02	−1.1376E-02	−1.1328E-02	−1.0930E-02
50	−5.6880E-03	−1.0925E-02	−1.5733E-02	−2.0133E-02	−2.4144E-02	−2.7785E-02	−3.1074E-02	−3.4027E-02	−3.6660E-02
55	−8.1584E-03	−1.5913E-02	−2.3280E-02	−3.0276E-02	−3.6916E-02	−4.3215E-02	−4.9187E-02	−5.4844E-02	−6.0201E-02
60	−1.0440E-02	−2.0508E-02	−3.0216E-02	−3.9578E-02	−4.8606E-02	−5.7312E-02	−6.5708E-02	−7.3804E-02	−8.1610E-02
65	−1.2532E-02	−2.4713E-02	−3.6554E-02	−4.8067E-02	−5.9261E-02	−7.0147E-02	−8.0734E-02	−9.1032E-02	−1.0105E-01
70	−1.4443E-02	−2.8551E-02	−4.2335E-02	−5.5803E-02	−6.8964E-02	−8.1827E-02	−9.4400E-02	−1.0669E-01	−1.1871E-01
75	−1.6188E-02	−3.2055E-02	−4.7608E-02	−6.2856E-02	−7.7806E-02	−9.2467E-02	−1.0684E-01	−1.2095E-01	−1.3478E-01
80	−1.7784E-02	−3.5257E-02	−5.2426E-02	−6.9298E-02	−8.5880E-02	−1.0218E-01	−1.1820E-01	−1.3395E-01	−1.4944E-01
85	−1.9245E-02	−3.8188E-02	−5.6835E-02	−7.5193E-02	−9.3267E-02	−1.1106E-01	−1.2859E-01	−1.4585E-01	−1.6285E-01
90	−2.0587E-02	−4.0879E-02	−6.0882E-02	−8.0602E-02	−1.0004E-01	−1.1922E-01	−1.3812E-01	−1.5676E-01	−1.7515E-01
95	−2.1821E-02	−4.3354E-02	−6.4604E-02	−8.5578E-02	−1.0628E-01	−1.2671E-01	−1.4689E-01	−1.6680E-01	−1.8646E-01
100	−2.2959E-02	−4.5636E-02	−6.8037E-02	−9.0166E-02	−1.1203E-01	−1.3363E-01	−1.5497E-01	−1.7606E-01	−1.9690E-01

Wanjun et al. proposed two approximations for $p_m(x)$ [12]:

$$\frac{e^{-x}}{x^{m+2}(1 + \frac{m+2}{x})},\tag{13}$$

$$\frac{e^{-x}}{x^{m+2}\left[1 + (m+2)\left(0.00099441 + \frac{0.93695599}{x}\right)\right]}.\tag{14}$$

Here, we call the above two expressions Wanjun approximation I and Wanjun approximation II, respectively. In this paper, we introduce the two $p_m(x)$ approximation for comparison.

Tables 1–3 list the relative error percentages of the three approximations for the estimation of the $p_m(x)$ function. The relative error has been defined by the following expression:

$$\varepsilon = \frac{p_{ma}(x) - p_m(x)}{p_m(x)} \cdot 100,\tag{15}$$

where $p_{ma}(x)$ is the value obtained by the approximation and $p_m(x)$ is the value obtained by numerical integration (in this study, the numerical integration is performed by means of the Mathematica software system, which is powerful for the numerical calculation and symbol computation [13]).

From tables 1–3, it can be obtained that the newly proposed approximation for the $p_m(x)$ function is more accurate than the other approximations, especially for low values of x.

4. Checking of the validity of the new integral method with theoretical nonisothermal data

For applications, nonisothermal thermoanalytical data obtained by the theoretical simulation have been used. The theoretical nonisothermal data was simulated by assuming a heating rate $\beta = 10$ K/min, a first order kinetic mechanism function (i.e., $f(\alpha) = 1 - \alpha$, $g(\alpha) = -\ln(1 - \alpha)$) and the following kinetic parameters: $A = 1.395T^2$, and $E = 90$ kJ/mol. According to equation (12), using a nonlinear regression method at the DataFit software environment, the values of the kinetic parameters have been established from the theoretical data: $E = 90.3297$ kJ/mol, $A = 1.4192T^{1.9323}$. The obtained value of E is about 0.3663% more than the true value. The relative error involved in the activation energy is very low. Figure 2 shows the simulated data points (α, T) and the α versus T curve generated with the obtained values of the kinetic parameters. It is seen that the curve fits the simulated data very well. Thus, the new integral method with the temperature dependent the frequency factor is available and accurate.
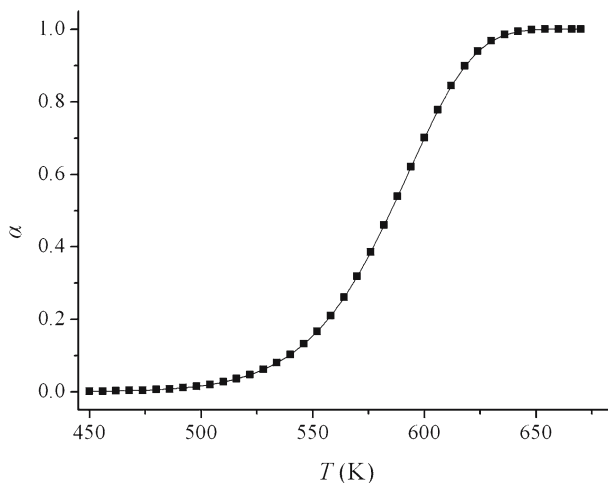
Figure 2. Simulated (α, T) data points $(\ldots)$ and the α versus T curve generated with the kinetic parameters evaluated by using equation (12).

5. Conclusions

(1) The general temperature integral is a special integral under nonisothermal conditions of a linear heating program and with the frequency factor dependent on the temperature ($A = A_0 T^m$). The general temperature integral does not have an exact analytical solution. Using some numerical techniques, we have proposed a new approximation for the general temperature integral:

$$\int\limits_0^T T^m \mathrm{e}^{-E/RT} \mathrm{d}T = \frac{R}{E} T^{m+2} \mathrm{e}^{-E/RT} \frac{E - 0.054182 m RT + 0.65061 RT}{E + 0.93544 m RT + 2.62993 RT}.$$

Compared with other existed approximations for the general temperature integral, the newly proposed approximation are more accurate than the other approximations as solutions of the general temperature integral.

(2) Considering the dependence of the frequency factor on the temperature, we have obtained a new integral method of nonisothermal kinetic analysis. The starting equation for evaluating the kinetic parameters is

$$g(\alpha) = \frac{A_0 R}{\beta E} T^{m+2} \mathrm{e}^{-E/RT} \frac{E - 0.054182 m RT + 0.65061 RT}{E + 0.93544 m RT + 2.62993 RT}.$$

(3) The new integral method of nonisothermal kinetic analysis has been applied successfully in the processing nonisothermal thermoanalytical data obtained by theoretical simulation.

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