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A new formula approximating the Arrhenius integral to perform the nonisothermal kinetics

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Abstract

A new approximating formula for the Arrhenius integral has been proposed using the Pattern Search Method, which is both reliable and accurate. Compared with several published Arrhenius integral approximations, the newly proposed formula is superior to the others and is an ideal solution for the estimation of kinetic parameters from nonisothermal thermogravimetric analysis data.

Keywords: Arrhenius integral; Nonisothermal kinetics; Kinetic parameters; Pattern Search Method

1. Introduction

The simplest experiment to determine the kinetics of a thermal decomposition is thermogravimetry under nonisothermal conditions. Since there are many inherent advantages, integral methods have been widely used to determine kinetic parameters from nonisothermal thermogravimetric analysis data [1]. Unfortunately, integral methods involve the integration of the Arrhenius function, so called 'Arrhenius integral', which has no exact analytical solution. A large number of approximate solutions for the Arrhenius integral, with varying complexity and precision, have been published [2]. However, many of these approximations are gross or even inaccurate and do not allow proper values for the kinetic parameters to be obtained [3]. In this work, a new Arrhenius integral approximate formula is obtained using the Pattern Search Method. It will be shown that the new approximation is reliable and accurate as a solution for the Arrhenius integral.

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2. Theory

The differential form of the nonisothermal rate of a solid reaction can be generally described by,

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

Upon integration, Eq. (1) gives,

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \mathrm{e}^{-(E/RT)}\,\mathrm{d}T \tag{2}$$

The integral of the right hand side of Eq. (2) is called the Arrhenius integral. If E/RT is replace by 'x' and the integration limits are transformed, the above equation becomes,

$$g(\alpha) = \frac{AE}{\beta R}\int_x^\infty \frac{\mathrm{e}^{-x}}{x^2}\,\mathrm{d}x \tag{3}$$

This is written as,

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

where $p(x)$ is the exponential integral.

The $p(x)$ function has no exact analytical solution and it is usually expressed as follows [4]:

$$p(x) = \frac{\mathrm{e}^{-x}}{x^2}h(x) \tag{5}$$

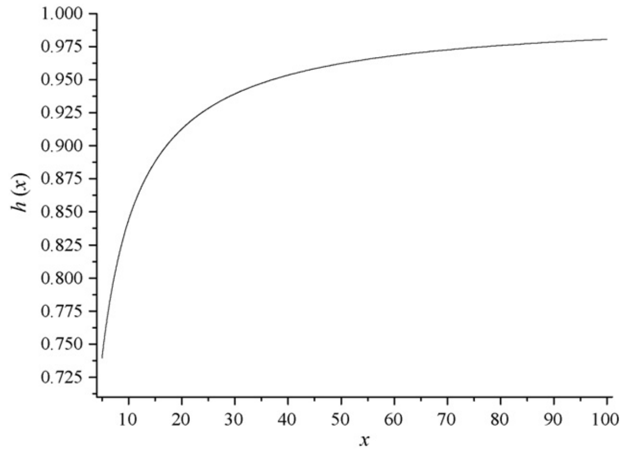

Fig. 1. The numerical results of $h(x)$ at various x.

where $h(x)$ is a function which changes slowly with x and is close to unity.

From Eqs. (3) to (5), one obtains

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

The $h(x)$ function has no exact analytical solution, but it can be solved by using numerical techniques. For this purpose, either general purposed mathematical software or a computer program developed in any programming language is used. In this study, the numerical calculations are performed by using the Mathematica software system [5]. Fig. 1 shows the numerical results of $h(x)$ at various x.

In this study, the following rational formula is used to approximate the $h(x)$ function:

$$h_1(x) = \frac{x + a\ \ln x + b}{x + c\ \ln x + d} \tag{7}$$

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

Most solid-state reactions take place in the range of $5 \leq x \leq 100$. To determine the values of a, b, c and d, the following objective function is established:

$$\text{O.F.} = \int_5^{100} [h(x) - h_1(x)]^2\, dx \tag{8}$$

Those values which minimize the objective function are the expected values. It is difficult to get information about concerning gradient or higher derivations of the objective function. Therefore, the optimization algorithm should be derivative-free, robust with respect to local optima. For this purpose, we propose the use of the Pattern Search Method, which is a derivative-free, direct search method and is superior to other direct search methods such as the Powell Method and Simplex Method in both robustness and number of function evaluations [6]. For more details of the Pattern Search Method, readers are referred to literature [7].

In order to perform the numerical calculations required by the minimization of the objective function, the 'Pattern Search Tool' in the 'Genetic Algorithm and Direct Search Toolbox' of the MATLAB software system has been employed [8]. The values of those parameters are established: $a = 0.25403$, $b = 0.36665$, $c = 0.24598$ and $d = 2.41457$. Then, the new exponential integral

Table 1
Expressions of some approximations for the Arrhenius integral

Author	$\int_0^T e^{-(E/RT)}\, dT$	$p(x)$
Coats and Redfern [9]	$\frac{RT^2}{E}\left(1 - \frac{2RT}{E}\right) e^{-(E/RT)}$	$\frac{e^{-x}}{x^2}\left(1 - \frac{2}{x}\right)$
Gorbachev [10] and Lee and Beck [11]	$\frac{RT^2}{E + 2RT}\, e^{-(E/RT)}$	$\frac{e^{-x}}{x}\, \frac{1}{x + 2}$
Li [12]	$\frac{RT^2}{E}\left[\frac{1 - 2(RT/E)}{1 - 6(RT/E)^2}\right] e^{-(E/RT)}$	$\frac{e^{-x}}{x^2}\, \frac{1 - (2/x)}{1 - (6/x^2)}$
Agrawal [13]	$\frac{RT^2}{E}\left[\frac{1 - 2(RT/E)}{1 - 5(RT/E)^2}\right] e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\, \frac{1 - (2/x)}{1 - (5/x^2)}$
Quanyin and Su [14]	$\frac{RT^2}{E}\left[\frac{1 - 2(RT/E)}{1 - 4.6(RT/E)^2}\right] e^{-(E/RT)}$	$\frac{e^{-x}}{x^2}\, \frac{1 - (2/x)}{1 - (4.6/x^2)}$
Zsakó [15]	$\frac{ET\, e^{-(E/RT)}}{(E + 2RT)[(E/RT) - (16(RT)^2/(E^2 - 4ERT + 84(RT)^2))]}$	$\frac{e^{-x}}{[x - (16/(x^2 - 4x + 84))](x + 2)}$
Wanjun et al. [16]	$\frac{RT^2}{1.00198882E + 1.87391198RT}\, e^{-(E/RT)}$	$\frac{e^{-x}}{x}\, \frac{1}{1.00198882x + 1.87391198}$
Junmeng et al. [17]	$\frac{RT^2}{E}\, \frac{E + 0.66691RT}{E + 2.64943RT}\, e^{-(E/RT)}$	$\frac{e^{-x}}{x^2}\, \frac{x + 0.66691}{x + 2.64943}$
New approximation	$\frac{RT^2}{E}\, \frac{E + 0.25403RT\ \ln(E/RT) + 0.36665RT}{E + 0.24598RT\ \ln(E/RT) + 2.41457RT}\, e^{-(E/RT)}$	$\frac{e^{-x}}{x^2}\, \frac{x + 0.25403\ \ln x + 0.36665}{x + 0.24598\ \ln x + 2.41457}$

Table 2
Relative errors of some Arrhenius integral approximations in percent

x	Coats–Redfern	Gorbachev–Lee–Beck	Li	Agrawal	Quanyin–Su	Zsakó	Wanjun et al.	Junmeng et al.	New approximation
5	−1.8858E+01	−3.4025E+00	6.7656E+00	1.4273E+00	−5.6143E−01	2.0017E−01	−1.7727E+00	1.8218E−01	1.4827E−03
10	−5.1758E+00	−1.2248E+00	8.7680E−01	−1.8507E−01	−6.0358E−01	−1.1497E−01	−3.4284E−01	−4.7663E−02	−2.4357E−04
15	−2.3955E+00	−6.2890E−01	2.7860E−01	−1.7722E−01	−3.5838E−01	−2.0139E−01	−6.3049E−02	−2.9961E−02	3.3156E−04
20	−1.3787E+00	−3.8253E−01	1.2314E−01	−1.3033E−01	−2.3137E−01	−1.8488E−01	9.8349E−03	−1.2219E−02	2.5837E−04
25	−8.9552E−01	−2.5717E−01	6.5106E−02	−9.6289E−02	−1.6070E−01	−1.5224E−01	2.5751E−02	−1.4517E−03	5.4371E−05
30	−6.2836E−01	−1.8474E−01	3.8563E−02	−7.3212E−02	−1.1785E−01	−1.2309E−01	2.2883E−02	4.8464E−03	−1.1300E−04
35	−4.6520E−01	−1.3913E−01	2.4715E−02	−5.7273E−02	−9.0030E−02	−1.0006E−01	1.3542E−02	8.5453E−03	−2.1605E−04
40	−3.5828E−01	−1.0855E−01	1.6786E−02	−4.5921E−02	−7.0981E−02	−8.2324E−02	2.2520E−03	1.0717E−02	−2.6339E−04
45	−2.8441E−01	−8.7053E−02	1.1920E−02	−3.7591E−02	−5.7382E−02	−6.8634E−02	−9.2069E−03	1.1969E−02	−2.6957E−04
50	−2.3125E−01	−7.1367E−02	8.7680E−03	−3.1316E−02	−4.7340E−02	−5.7952E−02	−2.0133E−02	1.2652E−02	−2.4738E−04
55	−1.9172E−01	−5.9570E−02	6.6373E−03	−2.6478E−02	−3.9717E−02	−4.9506E−02	−3.0276E−02	1.2976E−02	−2.0650E−04
60	−1.6153E−01	−5.0475E−02	5.1451E−03	−2.2673E−02	−3.3796E−02	−4.2736E−02	−3.9578E−02	1.3070E−02	−1.5390E−04
65	−1.3795E−01	−4.3315E−02	4.0689E−03	−1.9629E−02	−2.9105E−02	−3.7238E−02	−4.8067E−02	1.3016E−02	−9.4444E−05
70	−1.1918E−01	−3.7578E−02	3.2733E−03	−1.7156E−02	−2.5326E−02	−3.2720E−02	−5.5803E−02	1.2868E−02	−3.1486E−05
75	−1.0400E−01	−3.2909E−02	2.6724E−03	−1.5122E−02	−2.2238E−02	−2.8967E−02	−6.2856E−02	1.2658E−02	3.2682E−05
80	−9.1542E−02	−2.9060E−02	2.2101E−03	−1.3428E−02	−1.9681E−02	−2.5816E−02	−6.9298E−02	1.2411E−02	9.6517E−05
85	−8.1198E−02	−2.5849E−02	1.8486E−03	−1.2002E−02	−1.7541E−02	−2.3149E−02	−7.5193E−02	1.2141E−02	1.5900E−04
90	−7.2513E−02	−2.3142E−02	1.5618E−03	−1.0792E−02	−1.5732E−02	−2.0870E−02	−8.0602E−02	1.1860E−02	2.1947E−04
95	−6.5151E−02	−2.0839E−02	1.3314E−03	−9.7552E−03	−1.4189E−02	−1.8910E−02	−8.5578E−02	1.1575E−02	2.7753E−04
100	−5.8856E−02	−1.8864E−02	1.1443E−03	−8.8609E−03	−1.2862E−02	−1.7212E−02	−9.0166E−02	1.1290E−02	3.3294E−04

approximation is given below:

$$p_1(x) = \frac{e^{-x}}{x^2} h_1(x) = \frac{e^{-x}}{x^2} \frac{x + 0.25403 \ln x + 0.36665}{x + 0.24598 \ln x + 2.41457} \quad (9)$$

From Eqs. (2) to (4) and (9), the corresponding approximation for the Arrhenius integral is obtained:

$$\int_0^T e^{-(E/RT)} \, dT = \frac{RT^2}{E} \frac{E + 0.25403RT \ln(E/RT) + 0.36665RT}{E + 0.24598RT \ln(E/RT) + 2.41457RT} e^{-(E/RT)} \quad (10)$$

Substituting Eq. (10) to Eq. (2), rearranging Eq. (2) and logarithm on both sides of Eq. (2), one gets the equation for the evaluation of nonisothermal kinetic parameters:

$$\ln \left\{ \frac{g(\alpha)}{T^2} \frac{E + 0.24598RT \ln(E/RT) + 2.41457RT}{E + 0.25403RT \ln(E/RT) + 0.36665RT} \right\} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (12)$$

3. Results and discussion

The objective of this analysis is to evaluate the accuracy of the newly proposed Arrhenius integral approximation. For this purpose, several approximate formulas for the Arrhenius integral are introduced for comparison and listed in Table 1. The $p(x)$ approximations are also shown in Table 1.

Since $p(x)$ is the variable-transformed expression of the Arrhenius integral, the accuracy evaluation of the Arrhenius integral approximation is identical to that of the corresponding $p(x)$ approximation. The relative percent deviations associated with the use of the above $p(x)$ approximations for a physical realistic domain of x are shown in Table 2. The 'exact' values of $p(x)$ used for relative percent error calculations are obtained by double precision numerical integration using Simpson's 1/3 rule as coded for Mathematica.

As shown in Table 2, the newly proposed approximation for the Arrhenius integral is significantly more accurate than other approximate formulas in the range of $5 \le x \le 100$. The absolute value of relative deviation from the 'exact' value for the Arrhenius integral to the new approximate formula is less than $1.4827 \times 10^{-3}\%$. Furthermore, the newly proposed approximation is obtained directly from numerical results for the Arrhenius integral without derivation from any approximating infinite series, therefore it is reliable.

4. Conclusions

(1) By using the Pattern Search Method, a new approximation for the Arrhenius integral has been proposed, which is both reliable and accurate.
(2) Compared with several other published Arrhenius integral approximations, the newly proposed approximate formula is significantly more accurate than other approximations and is an ideal solution for the evaluation of kinetic parameters from nonisothermal thermogravimetric analysis data.
(3) The corresponding equation for the evaluation of the kinetic parameters is also presented, which can be put in the form:

$$\ln \left\{ \frac{g(\alpha)}{T^2} \frac{E + 0.24598RT \ln(E/RT) + 2.41457RT}{E + 0.25403RT \ln(E/RT) + 0.36665RT} \right\} = \ln \frac{AR}{\beta E} - \frac{E}{RT}.$$

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