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New Temperature Integral Approximation for Nonisothermal Kinetics

Junmeng Cai and Fusheng Yao
College of Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, P. R. China

Weiming Yi and Fang He
School of Light Industry and Agriculture Engineering, Shandong University of Technology, Zibo 255049, P. R. China

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A new approximation for the temperature integral has been obtained by using Pattern Search method. The corresponding equation for the evaluation of kinetic parameters is presented, which can be put in the form

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\frac{E + 0.66691RT}{E + 2.64943RT}\right] - \frac{E}{RT}$$

The validity of the new temperature integral approximation has been tested by numerical calculation. Its deviation from the values calculated by numerical integrating was discussed. Compared with several published approximate formulas, this new one is much superior to all other approximations, and is the most suitable solution for the evaluation of kinetic parameters from nonisothermal kinetic analysis. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 1554-1557, 2006
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Introduction

The temperature integral has played a somewhat enigmatic role in the development of thermal analysis reaction kinetics. That is, it has appeared to be a necessary disadvantage to be dealt with whenever the Arrhenius equation was integrated over time as a function of temperature. Many of the problems connected with its application have resulted from the inability to accurately approximate the temperature integral by a simple closed-form expression which is suitable for use in graphical form to determine the "Arrhenius Parameters".

A large number of solutions for the temperature integral, with varying complexity and precision, have been presented. A number of different approaches have been proposed in the literature during the last century as can be found in excellent reviews of Flynn.[1] How to evaluate an integral of the Arrhenius function had been reviewed.[2] Since the overwhelming majority of thermal analyses are conducted at constant heating rate, this work seeks to develop a more useful approximation for the temperature integral under experimental conditions of a linear temperature program. It is shown that the new approximation is simple, accurate, reliable, and suitable for the evaluation of kinetic parameters from nonisothermal kinetic analysis.

Theory

In nonisothermal kinetics, for the most usual case of a linear heating program corresponding to a constant heating rate (β), the dependence of the degree of conversion (α) on absolute

Correspondence concerning this article should be addressed to F. He at hefang_sdut@163.com

temperature (T) is describing by the well-known differential rate equation[3]

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

where A is the frequency factor, E is the activation energy, R is the universal gas constant and $f(\alpha)$ is the differential conversion function depending on the reaction mechanism.

Through variable separation and integration, Eq. 1 leads to

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

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

The integral on the righthand side of Eq. 2 has no exact analytical solution, but it can be approximated as follows[4–7]:

$$\int_0^T e^{-(E/RT)} dT = \frac{E}{R} P(u) \tag{3}$$

where $u=E/(RT)$ and

$$P(u) = \int_u^\infty \frac{e^{-u}}{u^2} du \tag{4}$$

An alternative way to express the temperature integral[8,9] is

$$\int_0^T e^{-(E/RT)} dT = \frac{RT^2}{E} e^{-(E/RT)} Q(u) \tag{5}$$

where $Q(u)$ is the function which changes slowly with u and is close to unity.

If Eq. 3 and 5 are taken into account, the following relationship between $P(u)$ and $Q(u)$ is obtained

$$P(u) = \frac{e^{-u}}{u^2} Q(u) \tag{6}$$

From Eq. 2 and 5, one obtains

$$g(\alpha) = \frac{AR}{\beta E} T^2 e^{-(E/RT)} Q(u) \tag{7}$$

which is the starting equation for many integral methods of evaluating nonisothermal kinetic parameters.

From Eq. 4 and 6, one obtains

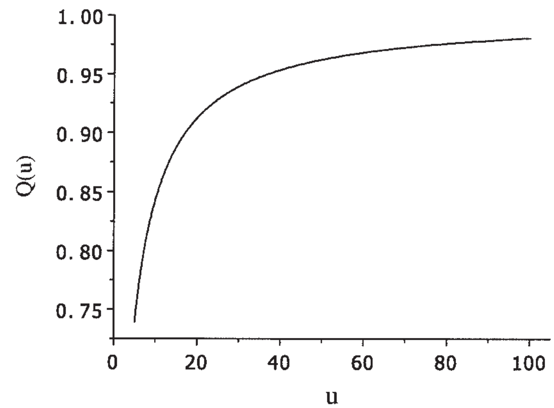

Figure 1. Numerical calculation results of *Q*(*u*).

$$Q(u) = \frac{\int_u^\infty \frac{e^{-u}}{u^2} du}{\frac{e^{-u}}{u^2}} \tag{8}$$

In this study, a Mathematica program has been written for the numerical calculation of the $Q(u)$ function. Numerical values of $Q(u)$ at various u are plotted in Figure 1.

We use the following one-degree rational formula to approximate the $Q(u)$ function

$$Q_1(u) = \frac{u+a}{u+b} \tag{9}$$

where a and b are undetermined parameters.

Most thermal decomposition reactions take place in the range of $5 \le u \le 100$. Therefore, the objective function to optimize parameters can be obtained

$$\min \int_5^{100} [Q(u) - Q_1(u)]^2 du \tag{10}$$

It is difficult to get the derivative information of the objective function without explicit expression. Therefore, the optimization algorithm should be derivative-free, robust with respect to local optima and should require as least function evaluations as possible to find the optimum. In this study, we propose the use of the Pattern Search method, a derivative-free, direct search method, which has advantages over the Powell method and the Simplex method in both robustness and function evaluations.[10]

In the Pattern Search method, a combination of an exploratory move and a pattern move is made iteratively to search out the optimum solution for the problem. An exploratory move is performed in the vicinity of the current point systematically, to find the best point around the current point. In the exploratory move, the current point is perturbed in positive and negative directions along each variable (weight here) one at a time and the best point is recorded. The current point is changed to the best point at the end of each variable perturbation. The exploratory move is a success if the perturbed point is different from

Table 1. Expressions for Some Proposed Approximations for the Temperature Integral

Author	$\int_0^T e^{-(E/RT)}dT$	$P(u)$
Coats-Redfern[11]	$\frac{RT^2}{E}\left(1-\frac{2RT}{E}\right)e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)$
Gorbachev-Lee-Beck[12,13]	$\frac{RT^2}{E+2RT}e^{-(E/RT)}$	$\frac{e^{-u}}{u}\frac{1}{u+2}$
Li Chung-Hsiung[14]	$\frac{RT^2}{E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-6\left(\frac{RT}{E}\right)^2}\right]e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)\Big/\left(1-\frac{6}{u^2}\right)$
Agrawal[15]	$\frac{RT^2}{E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-5\left(\frac{RT}{E}\right)^2}\right]e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)\Big/\left(1-\frac{5}{u^2}\right)$
Quanyin-Su[16]	$\frac{RT^2}{E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-4.6\left(\frac{RT}{E}\right)^2}\right]e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)\Big/\left(1-\frac{4.6}{u^2}\right)$
Wanjun-Yumen[17]	$\frac{RT^2}{1.000198882E+1.87391198RT}e^{-(E/RT)}$	$\frac{e^{-u}}{u}\frac{1}{1.00198882u+1.87391198}$
New equation	$\frac{RT^2}{E}\frac{E+0.66691RT}{E+2.64943RT}e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\frac{u+0.66691}{u+2.64943}$

the starting point, otherwise the exploratory move is a failure. In case, the exploratory move fails, then perturbation factor is reduced to continue the process. If the exploratory move is a success, then two successive best points are used to perform the pattern move. In case of better results, pattern move is repeated. This process is repeated till some termination criterion is met.

We use Pattern Search method as coded for MATLAB to compute the values of those parameters. The new approximations for the $Q(u)$ function and the $P(u)$ function are given below

$$Q_1(u) = \frac{u + 0.66691}{u + 2.64943} \tag{11}$$

$$P_1(u) = \frac{e^{-u}}{u^2}\frac{u + 0.66691}{u + 2.64943} \tag{12}$$

Inserting Eq. 11 into Eq. 5, the new approximation for the temperature integral is obtained

$$\int_0^T e^{-(E/RT)} = \frac{RT^2}{E}\frac{E + 0.66691RT}{E + 2.64943RT}e^{-(E/RT)} \tag{13}$$

Substituting Eq. 13 to Eq. 2, rearranging Eq. 2 and logarithm on both sides of Eq. 2, one gets the corresponding equation for the evaluation of nonisothermal kinetic parameters

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\frac{E + 0.66691RT}{E + 2.64943RT}\right] - \frac{E}{RT} \tag{14}$$

Results and discussion

The objective of this analysis is to compare the proposed approximation for the temperature integral with several known approximate formulas. The expressions of the Coats-Redfern,[11] Gorbachev-Lee-Beck,[12,13] Li Chung-Hsiung,[14] Agrawal,[15] Quanyin-Su,[16] and Wanjun-Yumen[17] equations, introduced for comparison, are listed in Table 1. The corresponding approximations of the $P(u)$ function are also listed in Table 1. The percentage of deviation from numerical results of the $P(u)$ function to those approximations at various u is shown in Table 2.

As shown in Table 2, Eq. 13, as a solution of the temperature integral, is significantly more accurate than other approximations in the range of $5 \leq u \leq 100$. The absolute deviation from the true value of the temperature integral to Eq. 13 is less than 0.187% within the range of $u \geq 5$.

Accuracy is one of the most significant characteristics to developed approximation formulas.[3] Equation 13 remains the simplicity of Coats-Redfern method, and has better accuracy

Table 2. Percentage Deviation from Numerical Result for Some Approximations at Various *u*

u	Coats-Redfern[11]	Gorbachev-Lee-Beck[12,13]	Li Chung-Hsiung[14]	Agrawal[15]	Quanyin-Su[16]	Wanjun-Yumen[17]	Eq. (13)
5	−18.858128	−3.402533	6.765622	1.427341	−0.561431	−1.644876	0.186918
10	−5.175813	−1.224805	0.876795	−0.185066	−0.603578	−0.192637	−0.046774
15	−2.395500	−0.628903	0.278596	−0.177216	−0.358382	0.095938	−0.029834
20	−1.378704	−0.382529	0.123143	−0.130333	−0.231365	0.173481	−0.012326
25	−0.895519	−0.257165	0.065106	−0.096289	−0.160702	0.192275	−0.001642
30	−0.628361	−0.184737	0.038563	−0.073212	−0.117852	0.191361	0.004627
35	−0.465202	−0.139126	0.024715	−0.057273	−0.090030	0.183430	0.008318
40	−0.358277	−0.108549	0.016786	−0.045921	−0.070981	0.173207	0.010492
45	−0.284412	−0.087053	0.011920	−0.037591	−0.057382	0.162582	0.011751
50	−0.231253	−0.071367	0.008768	−0.031316	−0.047340	0.152327	0.012442
55	−0.191723	−0.059570	0.006637	−0.026477	−0.039717	0.142735	0.012775
60	−0.161530	−0.050475	0.005145	−0.022673	−0.033796	0.133893	0.012878
65	−0.137949	−0.043315	0.004069	−0.019629	−0.029105	0.125794	0.012833
70	−0.119180	−0.037578	0.003273	−0.017156	−0.025326	0.118393	0.012692
75	−0.103997	−0.032909	0.002672	−0.015122	−0.022238	0.111631	0.012490
80	−0.091542	−0.029060	0.002210	−0.013428	−0.019681	0.105444	0.012250
85	−0.081198	−0.025849	0.001849	−0.012002	−0.017541	0.099774	0.011987
90	−0.072513	−0.023142	0.001562	−0.010792	−0.015732	0.094565	0.011713
95	−0.065151	−0.020839	0.001331	−0.009755	−0.014189	0.089769	0.011433
100	−0.058856	−0.018864	0.001144	−0.008861	−0.012862	0.085342	0.011153

than other methods mentioned previously. Furthermore, Eq. 13 is directly derived from numerical results of the temperature integral, so it is reliable.

Conclusion

(1) By using Pattern Search method, a new approximation for the temperature integral has been proposed, which is simple, accurate, and reliable.

(2) The validity of Eq. 13 has been tested by numerical calculation. Equation 13 gives more accurate values of the temperature integral than other approximations through numerical analyses. It can be concluded that this newly proposed approximation leads to reasonably good results and may be commonly used as integral methods of thermal analysis.

(3) The results also confirmed the availability of the mathematical approach using in this study for the derivation of Eq. 13.

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