New Procedure for Derivation of Approximations for Temperature Integral

Haixiang Chen and Naian Liu

State Key Laboratory of Fire Science, Univ. of Science and Technology of China, Hefei, Anhui 230026, P. R. China

A new procedure for the derivation of the approximations for temperature integral from its derivatives is presented. This procedure can produce a series of the approximations, including some published and some new ones. By combining the different order derivatives of temperature integral, a new approximation is proposed. The corresponding equation for the evaluation of kinetic parameters can be put in the form

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\frac{3(E/RT)^2 + 16(E/RT) + 4}{3(E/RT)^2 + 22(E/RT) + 30}\right] - \frac{E}{RT}$$

The validity of the new approximation has been tested with the true value of temperature integral from numerical calculation. Compared with several published approximations, the new one has the highest accuracy and at the same time retains simplicity, which indicates it is a good approximation for the evaluation of kinetic parameters from nonisothermal kinetic analysis. © 2006 American Institute of Chemical Engineers
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Introduction

Thermal analysis techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC) have been widely used to study the kinetics and mechanism of solid thermal decomposition reactions, generally carried out under a linear temperature program. The kinetic triplet (activation energy E, frequency factor A, and kinetic model) can be derived from the experimental data based on the kinetic equation of solid-gas phase decomposition as follows:

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

Correspondence concerning this article should be addressed to H. Chen at hxchen@ustc.edu.cn or N. Liu at liunai@ustc.edu.cn.

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where α ($0 < \alpha < 1$) is the fractional conversion, β (K/s) the heating rate, E (kJ/mol) the activation energy, A (S^{-1}) the pre-exponential factor, and R the gas constant. T (K) is the absolute temperature. The specific form of $f(\alpha)$ represents the hypothetical model of the reaction mechanism. The approaches to extract the kinetic triplet (E-A-$f(\alpha)$) from the above expression can be generally divided into two categories according to the kind of data used, that is, the *differential method* by using derivative thermogravimetric (DTG) data and the *integral method* by using TG data.

For the integral methods, integrating Eq. 1 and substituting $x = E/RT$ for T gives:

$$G(\alpha) = \frac{AE}{\beta R}\,p(x) \tag{2}$$

where

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}, \; p(x) = \int_\infty^x \frac{-e^{-x}}{x^2} dx$$

Here $p(x)$ is the Arrhenius temperature integral. Although the integral methods are believed to be more reliable and accurate than the differential methods,[1] the temperature integral has been a subject of much concern and controversy for a long time, since it cannot be analytically integrated. Many authors have proposed extensive approximations for the temperature integral $p(x)$ with different mathematical complexities and numerical precisions.[2–15] Flynn[16] provided a review of the various approximate expressions for the temperature integral, in which the solutions of the temperature integral are classified into three categories, that is, *series solution, complex approximations*, and *simple approximations*. In fact, most of the complex and simple approximations can be derived from one-term, two-term, or three-term truncations of different series solutions.[16] Besides, some simple approximations are obtained through the data-fitting process,[10–12] and another kind of approximations are proposed through integration over small temperature intervals to enhance the accuracy.[17]

In this work, we will present a new procedure to derive the approximations for the temperature integral. It is shown that this procedure not only can produce some published approximations, but also can yield new approximations with higher precision and simplicity.

Theoretical Background

It is known that besides $p(x)$, another function $h(x)$[9,11,18] can also be used to express the integral form Eq. 2 as follows:

$$G(\alpha) = \frac{AE}{\beta R} p(x) = \frac{AE}{\beta R} \frac{e^{-x}}{x^2} h(x), \text{ with } h(x) = p(x)x^2 e^x \quad (3)$$

The values of $p(x)$ and $h(x)$ are calculated versus x by numerical integral and shown in Figure 1. Compared with $p(x)$,
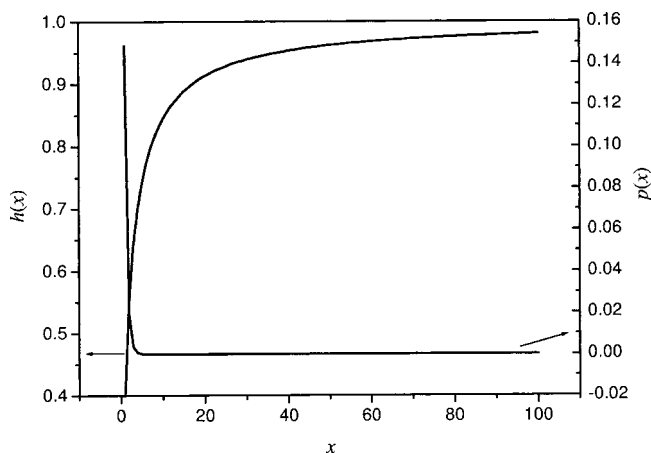

Figure 1. Values of *h(x)* and *p(x)* in the domain of $1 \leq x \leq 100$.
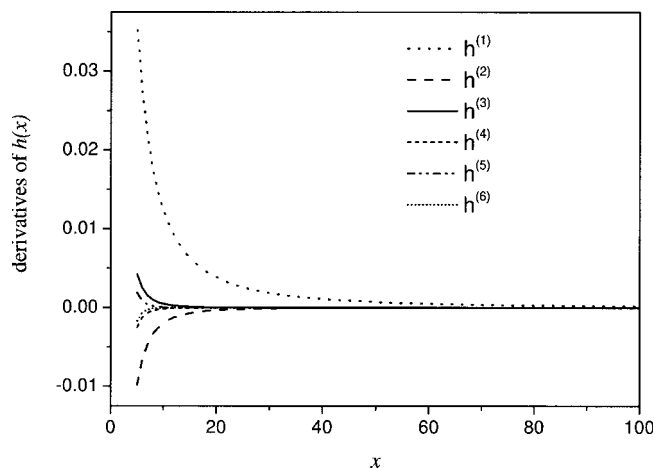

Figure 2. Values of the derivatives of *h(x)* in the domain of $5 \leq x \leq 100$.

$h(x)$ varies slowly and has an asymptotic value of 1 as x increases, and consequently it may be easier to explore reasonable approximations for $h(x)$. In the following text, $h(x)$ is used and named as the temperature integral, too.

New Procedure for the Derivation of the Approximations

By differentiating the equation $h(x)e^{-x}x^{-2} = p(x)$, we can obtain the 1st order derivative of the temperature integral $h(x)$:

$$h'(x) = h(x) \cdot \left(1 + \frac{2}{x}\right) - 1 \quad (4)$$

Some higher order derivatives of $h(x)$ are listed in the following:

$$h^{(2)}(x) = h(x) \cdot \left(1 + \frac{4}{x} + \frac{2}{x^2}\right) - \left(1 + \frac{2}{x}\right) \quad (5)$$

$$h^{(3)}(x) = h(x) \cdot \left(1 + \frac{6}{x} + \frac{6}{x^2}\right) - \left(1 + \frac{4}{x}\right) \quad (6)$$

$$h^{(4)}(x) = h(x) \cdot \left(1 + \frac{8}{x} + \frac{12}{x^2}\right) - \left(1 + \frac{6}{x} + \frac{2}{x^2}\right) \quad (7)$$

$$h^{(5)}(x) = h(x) \cdot \left(1 + \frac{10}{x} + \frac{20}{x^2}\right) - \left(1 + \frac{8}{x} + \frac{6}{x^2} - \frac{4}{x^3}\right) \quad (8)$$

$$h^{(6)}(x) = h(x) \cdot \left(1 + \frac{12}{x} + \frac{30}{x^2}\right) - \left(1 + \frac{10}{x} + \frac{12}{x^2} - \frac{12}{x^3} + \frac{12}{x^4}\right) \quad (9)$$

The values of these derivatives are presented in Figure 2 in the domain of $x \in [5,100]$, which are calculated from the values of $h(x)$ as presented in Figure 1. It is clear that the values of these derivatives are gradually close to zero as x increases, and compared with the values of $h(x)$, they are much lower. So, if they are assumed to be zero compared with the values of $h(x)$, we can obtain some approximations
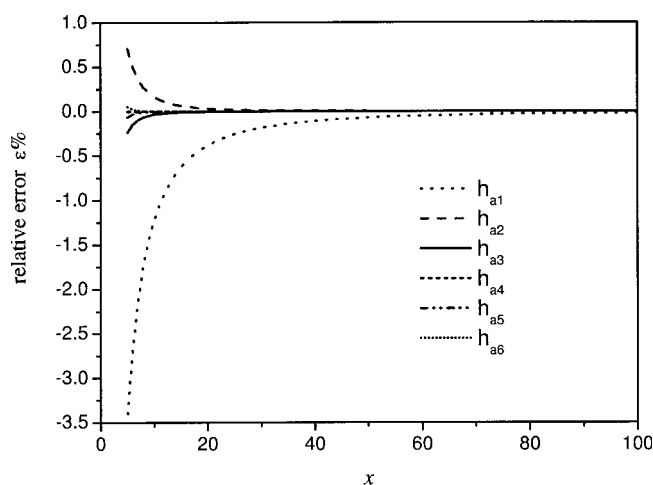
Figure 3. Relative error of the approximations $h_{ai}(I = 1,2,\ldots,6)$ in the domain of $5 \leq x \leq 100$.

of $h(x)$ from Eqs. 4–9:

$$h_{a1} = x/(x+2) \tag{10}$$

$$h_{a2} = x(x+2)/(x^2+4x+2) \tag{11}$$

$$h_{a3} = x(x+4)/(x^2+6x+6) \tag{12}$$

$$h_{a4} = (x^2+6x+2)/(x^2+8x+12) \tag{13}$$

$$h_{a5} = (x^2+8x+6-4/x)/(x^2+10x+20) \tag{14}$$

Here the subscript "a" means "approximation." Obviously, the approximation of $h_{a1} = x/(x+2)$(Eq. 10) is just the Gorbachev-Lee-Beck approximation,[4,5] and Eq. 12 is the 2nd degree rational approximation proposed by Senum and Yang.[9] The other three approximations (Eqs. 11, 13 and 14) seem to have appeared first.

If all the derivatives of $h(x)$ (Eqs. 4–9) are denoted as $h^{(i)} = hA_i - B_i$, $i = 1,2,3\ldots$, the relative error of the approximations can be expressed as follows:

$$\varepsilon_i\% = \frac{h_{ai}-h}{h} \cdot 100\% = \frac{-h^{(i)}}{A_i h} \cdot 100\% \tag{15}$$

Figure 3 presents the relative errors of these approximations. It can be seen that the approximation obtained from the higher order derivative of the temperature integral has lower errors, and the sign of relative errors changes continuously with the increase of the order of derivatives. The latter phenomenon indicates that we can combine the neighboring approximations or, equivalently, the neighboring derivatives of the temperature integral, to find more precise approximations.

The combination of Eqs. 4–9 with various coefficients can produce more approximations of the temperature integral. For example, from the expression of $h^{(3)} - h^{(2)}$, that is, Eq. 6 − Eq. 5, the Grobachev-Lee-Beck approximation is re-obtained; from $h^{(4)} - h^{(3)}$, the approximation of $(x+1)/(x+3)$ can be deduced, which is the two-term truncation of MKN expansion[7,14]; from $3h^{(3)} + h^{(2)}$, a new approximation of $x(2x+7)/(2x^2+11x+10)$ is produced. The following section will give a new and more accurate approximation from the combination of the derivatives.

A New Approximation for the Temperature Integral

From Eqs. 4–9 it can be seen that the expression of the derivatives becomes more complicated from the order of 5. Thus, the relatively simple derivatives are considered to be combined to obtain more accurate approximations here. From Figure 2, we can see that the values of $h^{(3)}$ and $h^{(4)}$ are very low and approximately accord with the relationship: $h^{(4)} = -h^{(3)}/2$. Therefore, if the two derivatives are combined as follows:

$$h^{(4)} + h^{(3)}/2 = h\left(\frac{3}{2}+\frac{11}{x}+\frac{15}{x^2}\right) - \left(\frac{3}{2}+\frac{8}{x}+\frac{2}{x^2}\right) \tag{16}$$

Table 1. Some Approximations for the Temperature Integral

Source	$h(x)$	$p(x)$
Coats-Redfern[2]	$1-\frac{2}{x}$	$\frac{e^{-x}}{x^2}\left(1-\frac{2}{x}\right)$
Gorbachev-Lee-Beck[4,5]	$\frac{x}{x+2}$	$\frac{e^{-x}}{x}\frac{1}{x+2}$
Li[6]	$\left(1-\frac{2}{x}\right)/\left(1-\frac{6}{x^2}\right)$	$\frac{e^{-x}}{x^2}\left(1-\frac{2}{x}\right)/\left(1-\frac{6}{x^2}\right)$
Agrawal[15]	$\left(1-\frac{2}{x}\right)/\left(1-\frac{5}{x^2}\right)$	$\frac{e^{-x}}{x^2}\left(1-\frac{2}{x}\right)/\left(1-\frac{5}{x^2}\right)$
Ran-Ye[13]	$\left(1-\frac{2}{x}\right)/\left(1-\frac{4.6}{x^2}\right)$	$\frac{e^{-x}}{x^2}\left(1-\frac{2}{x}\right)/\left(1-\frac{4.6}{x^2}\right)$
Wanjun-Yumen[12]	$\dfrac{x}{1.00198882x+1.87391198}$	$\dfrac{e^{-x}}{x}\dfrac{1}{1.00198882x+1.87391198}$
Cai[11]	$\dfrac{x+0.66691}{x+2.64943}$	$\dfrac{e^{-x}}{x^2}\dfrac{x+0.66691}{x+2.64943}$
Eq. 11	$\dfrac{x(x+2)}{x^2+4x+2}$	$\dfrac{e^{-x}}{x}\dfrac{x+2}{x^2+4x+2}$
Eq. 13	$\dfrac{x^2+6x+2}{x^2+8x+12}$	$\dfrac{e^{-x}}{x^2}\dfrac{x^2+6x+2}{x^2+8x+12}$
Eq. 14	$\dfrac{x^2+8x+6-4/x}{x^2+10x+20}$	$\dfrac{e^{-x}}{x^2}\dfrac{x^2+8x+6-4/x}{x^2+10x+20}$
Eq. 17	$\dfrac{3x^2+16x+4}{3x^2+22x+30}$	$\dfrac{e^{-x}}{x^2}\dfrac{3x^2+16x+4}{3x^2+22x+30}$

Table 2. Relative Error (%) from Numerical Computation for Some Approximations at Various x

x	Coats-Redfern	Gorbachev-Lee-Beck	Li	Agrawal	Ran-Ye	Wanjun-Yumen	Cai	Eq. 11	Eq. 13	Eq. 14	Eq. 17
5	−18.8581	−3.40253	6.76562	1.42734	−0.56143	−1.77275	0.18692	0.70800	0.11010	−0.06738	0.01207
10	−5.17581	−1.22481	0.87679	−0.18507	−0.60358	−0.34284	−0.04677	0.16639	0.00988	−0.00358	−0.00358
15	−2.39550	−0.62890	0.27860	−0.17722	−0.35838	−0.06305	−0.02983	0.06358	0.00203	−5.31E-04	−0.00163
20	−1.37870	−0.38253	0.12314	−0.13033	−0.23136	0.00983	−0.01233	0.03082	6.15E-04	−1.27E-04	−7.62E-04
25	−0.89552	−0.25716	0.06511	−0.09629	−0.16070	0.02575	−0.00164	0.01723	2.36E-04	−4.02E-05	−3.93E-04
30	−0.62836	−0.18474	0.03856	−0.07321	−0.11785	0.02288	0.00463	0.01060	1.06E-04	−1.54E-05	−2.21E-04
35	−0.46520	−0.13913	0.02471	−0.05727	−0.09003	0.01354	0.00832	0.00698	5.31E-05	−6.72E-06	−1.33E-04
40	−0.35828	−0.10855	0.01679	−0.04592	−0.07098	0.00225	0.01049	0.00484	2.90E-05	−3.26E-06	−8.51E-05
45	−0.28441	−0.08705	0.01192	−0.03759	−0.05738	−0.00921	0.01175	0.00349	1.69E-05	−1.71E-06	−5.67E-05
50	−0.23125	−0.07137	0.00877	−0.03132	−0.04734	−0.02013	0.01244	0.00260	1.04E-05	−9.55E-07	−3.92E-05
55	−0.19172	−0.05957	0.00664	−0.02648	−0.03972	−0.03028	0.01277	0.00199	6.67E-06	−5.62E-07	−2.80E-05
60	−0.16153	−0.05048	0.00515	−0.02267	−0.03380	−0.03958	0.01288	0.00155	4.44E-06	−3.46E-07	−2.05E-05
65	−0.13795	−0.04332	0.00407	−0.01963	−0.02910	−0.04807	0.01283	0.00124	3.05E-06	−2.21E-07	−1.53E-05
70	−0.11918	−0.03758	0.00327	−0.01716	−0.02533	−0.05580	0.01269	0.00100	2.15E-06	−1.46E-07	−1.17E-05
75	−0.10400	−0.03291	0.00267	−0.01512	−0.02224	−0.06286	0.01249	8.23E-04	1.55E-06	−9.95E-08	−9.09E-06
80	−0.09154	−0.02906	0.00221	−0.01343	−0.01968	−0.06930	0.01225	6.84E-04	1.14E-06	−6.94E-08	−7.17E-06
85	−0.08120	−0.02585	0.00185	−0.01200	−0.01754	−0.07519	0.01199	5.75E-04	8.52E-07	−4.95E-08	−5.73E-06
90	−0.07251	−0.02314	0.00156	−0.01079	−0.01573	−0.08060	0.01171	4.87E-04	6.48E-07	−3.61E-08	−4.63E-06
95	−0.06515	−0.02084	0.00133	−0.00976	−0.01419	−0.08558	0.01143	4.16E-04	−8.99E-07	−1.43E-08	−5.18E-06
100	−0.05886	−0.01887	0.00114	−0.00886	−0.01286	−0.09017	0.01115	3.58E-04	−9.03E-07	−1.31E-08	−4.42E-06

the corresponding approximation (see below) will hold high precision:

$$h_{ac} = \frac{3x^2 + 16x + 4}{3x^2 + 22x + 30} \tag{17}$$

Here the subscript "c" means "combined."

By substituting Eq. 17 and $x = E/RT$ into Eq. 3, the corresponding equation for the evaluation of kinetic parameters can be obtained:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E} \frac{3(E/RT)^2 + 16(E/RT) + 4}{3(E/RT)^2 + 22(E/RT) + 30}\right] - \frac{E}{RT} \tag{18}$$
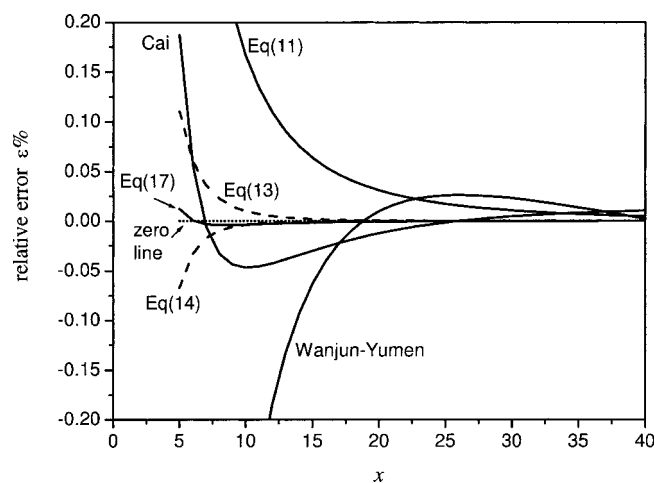

Figure 4. Relative error of some approximations at lower x.

The relative error of the above approximation is:

$$\varepsilon_c\% = \frac{h_{ac} - h}{h} \cdot 100\% = \frac{-(h^{(4)} + h^{(3)}/2)}{(3/2 + 11/x + 15/x^2)h} \cdot 100\% \tag{19}$$

By using this relative error, we can compare the new approximation, together with the approximations of Eqs. 10–14, with several known approximations. The expressions of Coats-Redfern,[2] Gorbachev-Lee-Beck,[4,5] Li,[6] Agrawal,[15] Ran-Ye,[13] Wanjun-Yumen,[12] and Cai[11] are listed in Table 1 for comparison. The corresponding approximations of $p(x)$ are also listed in Table 1. The percentage of deviation from numerical results of $h(x)$, that is, $p(x)$, to those approximations at various x is shown in Table 2.

As presented in Table 2, the new approximations, Eqs. 11, 13, 14, and 17, are significantly more accurate than other approximations in the domain of $5 \leq x \leq 100$. Especially, the absolute relative error of Eq. 17 is less than 0.003% when x begins to be higher than 10. As we know, the deviation from many approximations to the true value of the temperature integral is relatively higher when x is very low. So the performance of a new approximation at lower x is of high concern. Figure 4 compares the relative error of some approximations that appeared in Table 1 when x is low. It can be seen that the new approximation, Eq. 17, has the highest accuracy at lower x. Equations 11, 13, and 14 also have relatively high accuracy. At the same time, Eq. 17, together with Eqs. 11 and 13, retains the simplicity of the Li method, the Agrawal method, and the Ran-Ye method in calculation.

Conclusion

By using the derivatives of temperature integral, a new procedure for the derivation of the approximations for temperature integral is presented. This procedure has re-produced some published approximations and yielded some new ones.

Combining the different order derivatives of temperature integral, one can obtain more approximations, in which a new approximation with higher precision and simplicity has been tested in detail with the true value of temperature integral from numerical calculation. Compared with several published approximations, the new one has the highest accuracy and at the same time retains simplicity, which indicates it is a good approximation for the evaluation of kinetic parameters from nonisothermal kinetic analysis.

Acknowledgments

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