Science Journal of Applied Mathematics and Statistics
2026, Vol. 14, No. 3, pp. 71–78
https://doi.org/10.11648/j.sjams.20261403.11

Research Article

Evaluation of Some Approximations of the Temperature Integral Used in Kinetic Analysis of Solid-state Reactions

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Abstract

In general, thermal analysis is a very convenient way to study the kinetics of thermally activated solid reactions, and experiments involving thermally activated solid reactions typically occur under nonisothermal conditions. The experimental data analysis obtained under non-isothermal conditions includes a temperature integral, also called the Arrhenius integral, which is one of the integrals that belong to many interesting integrals that are important in engineering and have no analytical solution. There are many different approximations that can be applied to the processing of thermogravimetric analysis data, since there is no standard way to calculate the temperature integral. Many approximations of the temperature integral that are important to use determine the kinetic parameters, especially the activation energy, which are typically divided into two categories: exponential and rational approximations. In order to evaluate the accuracy of various approximations of the temperature integral, we consider several certain continuous intervals. When choosing an approximation of the temperature integral needed to analyze the experimental data, it is necessary to analyze the accuracy at different temperature intervals of the approximation and use the appropriate one. We present new rational, irrational and continued fractional approximations together with approximations of the temperature integral presented in several literatures and calculate the relative errors of their activation energies.

Keywords

Temperature Integral, Solid-state Reactions, Nonisothermal Conditions, Approximation, Activation Energy

1. Introduction

In general, thermal analysis is a convenient method to study the kinetics of thermally activated solid-state reactions. Experiments where these reactions occur are usually performed under nonisothermal conditions. Most of the part analysis of thermogravimetric data is an active research area and new methods have emerged after ICTAC publication [1]. In addition, some aspects of TGA data analysis, such as thermal inertia, are still under development and the use of logistic equations has been evaluated [2, 3]. Integral methods have the advantage of analyzing experimental kinetic data. Hence, nonisothermal calculations include the temperature integral, also called the Arrhenius function, which has no exact analytical solutions as integral exponential function. Mathematica technique is used for calculations for temperature integration [4]. Many approximations to the temperature integral have been proposed. In this paper, we consider new approximations while discussing the approximations presented in several literatures, which include rational, irrational and continued fractional approximations. In order to analyze the experimental data, when choosing an approximation, it is necessary to use a suitable one considering the accuracy in

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Received: 25 December 2025; **Accepted:** 15 January 2026; **Published:** 12 June 2026

different temperature intervals of approximations. Interesting approximation techniques related to special functions such as mathematical constants, including Napier constants, or gamma functions have been found [5-7]. In [8], deviations of approximations in several intervals or points in [5, 100] were considered. The evaluation method presented here does not indicate the overall behavior of approximations in the given interval. A general consideration is needed to evaluate the accuracy of various approximations of the temperature integral in different intervals. Starting from the classical kinetic equation of nonisothermal kinetics, many mathematical models have been developed to estimate the values of the kinetic triplet, that is, activation energy, pre-exponential factor and reaction mechanism, to fully describe the thermal activation process [9]. The procedure for kinematic analysis can be classified into differential and integral methods, and mathematical analysis can be done by model-free method and model fitting methods, and the model-free method is divided into the linear or nonlinear methods, and linear methods can be easily obtained from the log form of some approximations to temperature integration [10]. Some linear methods are obtained by some approximations, which result in high errors in certain temperature ranges, especially in special cases with low activation energies, whose range exceeds the application limit [11]. The model-free method is used to determine the value of activation energy, and the model fitting method can be used to determine the reaction mechanisms for solid reactions [12, 13]. The reaction mechanisms commonly used in nonisothermal reaction kinetics have been cited [14]. It is practical to find a mechanism corresponding to maximum R^2 to select the most probable reaction mechanism [15]. In this paper, we evaluate the approximations presented in the literature and new approximations using the relative errors of activation energies.

2. Theoretical Considerations Related to the Temperature Integration and Its Approximation

The mathematical model of the process of nonisothermal solid decomposition is given by the following differential equation:

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

where α ($0 < \alpha < 1$) is the fractional conversion, β (K/min) the heating rate, E (kJ/mol) the activation energy, A (min^{-1}) the preexponential factor, R the gas constant, T (K) the absolute temperature, specific form of $f\left(\alpha\right)$ represents the hypothesized model of the reaction mechanism.

In some works, the Simpson rule-based integral calculation method is used to generate the normalized temperature integral references [16].

Integrating after separating the variables to solve this differential equation, Eq. (1) becomes

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^{T}\exp\left(-\frac{E}{RT}\right)dT \tag{2}$$

The integral on the right-hand side in Eq. (2) is called the temperature integral or Arrhenius integral. Using the substitution $x=E/(RT)$, the temperature integral from the substitution integral formula is transformed as follows:

$$\int_0^{T}\exp\left(-\frac{E}{RT}\right)dT=\frac{E}{R}\int_x^{\infty}\frac{\exp\left(-\tau\right)}{\tau^2}d\tau=\frac{E}{R}f(x) \tag{3}$$

If $E/(RT)$ is very small, i.e., $E/(RT)<1$, then using power series expansion $\exp(-x)=\sum_{n=1}^{\infty}\frac{(-x)^n}{n!}$ and the formula

$$\lim_{m\to\infty}\left(\sum_{n=1}^{\infty}\frac{(-1)^n x^n}{n\cdot n!}+\ln m\right)=-\gamma$$

the Arrhenius integral can be expressed as

$$\int_0^{T}\exp\left(-\frac{E}{RT}\right)dT=\frac{E}{R}\left(\frac{\exp(-x)}{x}+\gamma+\sum_{n=1}^{\infty}\frac{(-1)^n x^n}{n\cdot n!}+\ln x\right) \tag{4}$$

where $\gamma=0.577215664\cdots$ is the Euler-Mascheroni constant.

The method using power series is not suitable for use in general cases because of the constraint on temperature.

Hence, several approximations other than the power series approximation are used.

In general, approximations to the temperature integral $f(x)$ are classified into two types: one is exponential approximation and the other is rational approximation.

The form of exponential approximation is

$$f_a(x)=\frac{\exp(-ax+b)}{x^k} \tag{5}$$

which is usually expressed as follows:

$$\ln(f_a(x))=b-k\ln x-ax \tag{6}$$

The form of rational approximation is

$$f(x)=\frac{\exp(-x)}{x^2}\cdot h(x) \tag{7}$$

Rational approximation is a method of approximating a function by a ratio of two algebraic polynomials, in which the degree of the rational approximation is defined as the degree of the highest degree polynomial. The rational approximation is often used since this can be used for any temperature. It is important to evaluate the accuracy of approximations of the temperature integral within a certain range. x in [9, 100] or [15, 60] is of practical significance. In practice, many reactions occur within this range.

To evaluate the accuracy of the approximation of the temperature integral, the following equations are used:

$$f_a(x)=\frac{\exp(-x)}{x^2}\cdot h_a(x) \tag{8}$$

$$\varepsilon_1=\int_5^{100}\left(\frac{f(x)-f_a(x)}{f(x)}\right)^2 dx=\int_5^{100}\left(\frac{h(x)-h_a(x)}{h(x)}\right)^2 dx \tag{9}$$

$$\varepsilon_2=\int_{15}^{60}\left(\frac{f(x)-f_a(x)}{f(x)}\right)^2 dx=\int_{15}^{60}\left(\frac{h(x)-h_a(x)}{h(x)}\right)^2 dx \tag{10}$$

where $f_a(x)$, $h_a(x)$ are approximations of the temperature integral from Eq. (7).

In [17], they evaluated the accuracy of two groups of approximations: exponential and rational approximations. [17] shows that exponential approximation has a worse approximation than rational approximation as a whole.

In the case of exponential approximation, when $x\in[5, 100]$, Cai-Liu's approximation ([18]) has excellent accuracy and Doyle's approximation has the worst accuracy. When $x\in[15, 60]$, the approximation of TLZW ([18]) has excellent accuracy.(see Table 1).

Table 1. Exponential approximations for the temperature integral.

Name	**ln$p_a(x)$**			**ε1**	**ε2**
	b	**K**	**a**		
Doyle	-5.3308	0	1.0516	15.39	0.91
TLZW	-0.37773896	1.8946610	1.00145033	$1.69\cdot10^{-2}$	$3.60\cdot10^{-5}$
Cai–Liu [7]	-0.460120828342246	1.86847901883656	1.00174866236974	$4.61\cdot10^{-3}$	$1.55\cdot10^{-3}$

In the case of rational approximation, the approximation ([19]) $h_a(x)=1$ has the worst accuracy, and the approximation of Coats and Redfern takes the next place.

Cai's approximation is of simple form ($N=2$, $n=1$), but has higher accuracy than the same complexity approximations ($N=2$, $n=1$ or $N=2$, $n=2$) ([17]).

Among the approximations with $N=3$, the best approximation for [5, 100] is Urbanovici–Segal's approximation and for [15, 60], the best approximation is Senum–Yang 's approximation. In the case of $N=4$, the best approximation is Ji's approximation.

Deng. et. al. [17] showed that the best approximation in [5, 100] is the Órfão′s approximation, and the best approximation in [15, 60] is the Senum-Yang's approximation.

We introduce here new rational approximations as follows:

$$f_5(x)=\frac{\exp(-x)}{x^2}h_5(x) \tag{11}$$

$$f_6(x)=\frac{\exp(-x)}{x^2}h_6(x) \tag{12}$$

$$f_7(x)=\frac{\exp(-x)}{x}h_7(x) \tag{13}$$

where

$$h_5(x)=\frac{x^5+28x^4+246x^3+756x^2+600x}{x^5+30x^4+300x^3+1200x^2+1800x+720}$$

$$h_6(x)=\frac{x^6+40x^5+552x^4+3168x^3+7092x^2+4320x}{x^6+42x^5+630x^4+4200x^3+12600x^2+15120x+5040}$$

$$h_7(x)=\frac{x^7+54x^6+1070x^5+9720x^4+41112x^3+71856x^2+35280x}{x^7+56x^6+1176x^5+11760x^4+58800x^3+141120x^2+141120x+40320}$$

The accuracies of Eqs.(11), (12) and (13) are evaluated in Table 2.

Table 2. Rational approximations for the temperature integral.

Name	**Approximation**	***N***	***n***	**ε1**	**ε2**
FJG [19]	1	0	0	0.65	0.19
Coats–Redfern	$\frac{x-2}{x}$	1	1	$6.51 \cdot 10^{-2}$	$2.96 \cdot 10^{-3}$
Cai	$\frac{x+0.66691}{x+2.64943}$	2	1	$3.92 \cdot 10^{-6}$	$6.17 \cdot 10^{-7}$
Urbanovici–Segal II	$\frac{x^2+3.5x}{x^2+5.5x+5}$	3	2	$1.60 \cdot 10^{-7}$	$2.71 \cdot 10^{-8}$
Senum–Yang I	$\frac{x^2+4x}{x^2+6x+6}$	3	2	$6.40 \cdot 10^{-6}$	$2.52 \cdot 10^{-8}$
Ji	$\frac{x^2+4.45239x+0.76927}{x^2+6.45218x+7.69430}$	4	2	$5.20 \cdot 10^{-11}$	$1.09 \cdot 10^{-11}$
Senum-Yang III	$\frac{x^4+18x^3+86x^2+96x}{x^4+20x^3+120x^2+240x+120}$	7	4	$5.94 \cdot 10^{-10}$	$1.22 \cdot 10^{-14}$
Órfão III	$\frac{0.9999936x^4+7.5739391x^3+12.4648922x^2+3.6907232x}{x^4+9.5733223x^3+25.6329561x^2+21.0996531x+3.9584969}$	8	4	$7.07 \cdot 10^{-11}$	$5.82 \cdot 10^{-12}$
h_5	$\frac{x^5+28x^4+246x^3+756x^2+600x}{x^5+30x^4+300x^3+1200x^2+180x+720}$	9	5	$1.21 \cdot 10^{-11}$	$2.38 \cdot 10^{-17}$
h_6	$\frac{x^6+40x^5+552x^4+3168x^3+7092x^2+4320x}{x^6+42x^5+630x^4+4200x^3+12600x^2+15120x+5040}$	11	6	$3.43 \cdot 10^{-13}$	$7.35 \cdot 10^{-20}$
h_7	$\frac{x^7+54x^6+1070x^5+9720x^4+41112x^3+71856x^2+35280x}{x^7+56x^6+1176x^5+11760x^4+58800x^3+141120x^2+141120x+40320}$	13	7	$1.25 \cdot 10^{-14}$	$3.29 \cdot 10^{-22}$

It can be seen from the Table 2 that the higher the order of the rational approximation, the higher the accuracy.

The newly proposed approximations h_5, h_6, and h_7 are much more accurate than the previous results for any x.

In addition, there are many approximations of the temperature integral. Table 3 shows some irrational approximations.

We compare here with the new irrational approximations.

Table 3. Irrational approximations for the temperature integral.

Name	**Approximation**	**ε1**	**ε2**
Balarin	$\sqrt{\frac{x}{x+4}}$	$9.07 \cdot 10^{-5}$	$1.57 \cdot 10^{-6}$
hr2	$\sqrt{\frac{x^2+6.5x-2}{x^2+10.5x+24}}$	$2.66 \cdot 10^{-9}$	$2.84 \cdot 10^{-11}$
hr5	$\sqrt{\frac{x^5+29.4265x^4+258.3529x^3+666.8235x^2}{x^5+33.4265x^4+376.0588x^3+1708.2353x^2+2850.7059x+920.6471}}$	$1.85 \cdot 10^{-11}$	$9.31 \cdot 10^{-17}$

As shown in Table 3, our new approximations have much higher accuracy compared to others.

In this paper, we introduce a new type of approximation, i.e., the approximations of the temperature integral by the continued fraction.

Table 4. Continued fractional approximations for the temperature integral.

Name	Approximation	ε1	ε2
hc1	$\frac{x+1}{x+2+\frac{x+3}{x+1}}$	$2.08 \cdot 10^{-3}$	$2.05 \cdot 10^{-4}$
hc2	$\frac{x^2+0.5x}{x^2+2.5x+\frac{x^2+0.5x}{x^2+1.5x}}$	$2.47 \cdot 10^{-3}$	$2.17 \cdot 10^{-4}$

3. Determination of Activation Energy Using the Approximations of Temperature Integrals

There are model fitting methods and model-free methods for determining activation energy. Generally, rational approximations can be used in both the methods, and exponential approximations are used in model-free methods.

The aforementioned approximations are used to calculate the activation energy. Equations for determining ε_E and ε_A are given by

$$\varepsilon_E = (\varepsilon_E + 1)\frac{h_a'((\varepsilon_E + 1)x)}{h_a((\varepsilon_E + 1)x)} - \frac{h'(x)}{h(x)}, \tag{14}$$

and

$$\varepsilon_A = \frac{(\varepsilon_E + 1)\exp(x\varepsilon_E)h(x)}{h_a((\varepsilon_E + 1)x)} - 1. \tag{15}$$

Obviously, ε_E and ε_A are dependent on the x and the approximation and not on the reaction model.

Table 5. The value of ε_E(%) of the approximations at different x.

x	FJG [19]	Coats–Redfern	Cai	Urbanovici–Segal II	Senum–Yang I	Ji	Senum-Yang III	Orfao III
0.5	$-1.28 \cdot 10^{2}$	$-2.69 \cdot 10^{2}$	$-7.81 \cdot 10^{2}$	$1.09 \cdot 10^{1}$	$1.31 \cdot 10^{1}$	$-3.15 \cdot 10^{1}$	4.74	$6.61 \cdot 10^{-2}$
2	$-1.97 \cdot 10^{1}$	$6.15 \cdot 10^{1}$	-3.62	$8.71 \cdot 10^{-1}$	1.34	$-3.66 \cdot 10^{-1}$	$1.39 \cdot 10^{-1}$	$-1.03 \cdot 10^{-5}$
5	-4.76	7.15	$-1.86 \cdot 10^{-1}$	$4.33 \cdot 10^{-2}$	$1.14 \cdot 10^{-1}$	$-2.40 \cdot 10^{-3}$	$2.71 \cdot 10^{-3}$	$1.49 \cdot 10^{-6}$
10	-1.47	$9.99 \cdot 10^{-1}$	$-4.70 \cdot 10^{-4}$	$1.40 \cdot 10^{-4}$	$1.03 \cdot 10^{-2}$	$4.68 \cdot 10^{-5}$	$5.39 \cdot 10^{-5}$	$-1.73 \cdot 10^{-6}$
15	$-1.73 \cdot 10^{-1}$	$3.09 \cdot 10^{-1}$	$4.19 \cdot 10^{-3}$	$-6.80 \cdot 10^{-4}$	$2.10 \cdot 10^{-3}$	$-2.97 \cdot 10^{-5}$	$3.83 \cdot 10^{-6}$	$7.00 \cdot 10^{-6}$
20	$-4.21 \cdot 10^{-1}$	$1.34 \cdot 10^{-1}$	$2.74 \cdot 10^{-3}$	$-4.13 \cdot 10^{-4}$	$6.35 \cdot 10^{-4}$	$-1.47 \cdot 10^{-5}$	$5.10 \cdot 10^{-7}$	$5.50 \cdot 10^{-6}$
25	$-2.78 \cdot 10^{-1}$	$6.98 \cdot 10^{-2}$	$1.61 \cdot 10^{-3}$	$-2.36 \cdot 10^{-4}$	$2.43 \cdot 10^{-4}$	$-3.30 \cdot 10^{-6}$	$9.93 \cdot 10^{-8}$	$2.19 \cdot 10^{-6}$
30	$-1.97 \cdot 10^{-1}$	$4.09 \cdot 10^{-2}$	$9.48 \cdot 10^{-4}$	$-1.40 \cdot 10^{-4}$	$1.09 \cdot 10^{-4}$	$1.70 \cdot 10^{-6}$	$2.50 \cdot 10^{-8}$	$-4.52 \cdot 10^{-7}$
40	$-1.14 \cdot 10^{-1}$	$1.76 \cdot 10^{-2}$	$3.28 \cdot 10^{-4}$	$-5.70 \cdot 10^{-5}$	$2.96 \cdot 10^{-5}$	$3.76 \cdot 10^{-6}$	$2.65 \cdot 10^{-9}$	$-3.24 \cdot 10^{-6}$
45	$-9.09 \cdot 10^{-2}$	$1.24 \cdot 10^{-2}$	$1.86 \cdot 10^{-4}$	$-3.90 \cdot 10^{-5}$	$1.72 \cdot 10^{-5}$	$3.51 \cdot 10^{-6}$	$1.03 \cdot 10^{-9}$	$-3.81 \cdot 10^{-6}$
50	$-7.42 \cdot 10^{-2}$	$9.10 \cdot 10^{-3}$	$9.70 \cdot 10^{-5}$	$-2.70 \cdot 10^{-5}$	$1.06 \cdot 10^{-5}$	$3.08 \cdot 10^{-6}$	$4.43 \cdot 10^{-10}$	$-4.08 \cdot 10^{-6}$
55	$-6.17 \cdot 10^{-2}$	$6.87 \cdot 10^{-3}$	$4.03 \cdot 10^{-5}$	$-1.95 \cdot 10^{-5}$	$6.78 \cdot 10^{-6}$	$2.61 \cdot 10^{-6}$	$2.04 \cdot 10^{-10}$	$-4.17 \cdot 10^{-6}$
60	$-5.22 \cdot 10^{-2}$	$5.31 \cdot 10^{-3}$	$3.70 \cdot 10^{-6}$	$-1.43 \cdot 10^{-5}$	$4.51 \cdot 10^{-6}$	$2.18 \cdot 10^{-6}$	$9.99 \cdot 10^{-11}$	$-4.13 \cdot 10^{-6}$
80	$-2.98 \cdot 10^{-2}$	$2.26 \cdot 10^{-3}$	$-5.06 \cdot 10^{-5}$	$-5.12 \cdot 10^{-6}$	$1.15 \cdot 10^{-6}$	$9.87 \cdot 10^{-7}$	$9.11 \cdot 10^{-12}$	$-3.54 \cdot 10^{-6}$
100	$-1.92 \cdot 10^{-2}$	$1.67 \cdot 10^{-3}$	$-5.57 \cdot 10^{-5}$	$-2.25 \cdot 10^{-6}$	$3.96 \cdot 10^{-8}$	$4.09 \cdot 10^{-7}$	$1.38 \cdot 10^{-12}$	$-2.86 \cdot 10^{-6}$

Table 6. The value of $\varepsilon_E(\%)$ *of the approximations at different x.*

x	Balarin	h_5	h_6	h_7	hr_2	hr_5	hc_1	hc_2
0.5	$-3.60 \cdot 10^{1}$	$1.35 \cdot 10^{1}$	1.96	1.30	$3.38 \cdot 10^{1}$	2.39		$-1.52 \cdot 10^{1}$
2	-2.89	$-1.45 \cdot 10^{-1}$	$1.88 \cdot 10^{-2}$	$7.53 \cdot 10^{-3}$	$4.39 \cdot 10^{-1}$	$4.33 \cdot 10^{-2}$	$-1.06 \cdot 10^{-1}$	2.34
5	$-3.11 \cdot 10^{-1}$	-3.14	$-1.06 \cdot 10^{-4}$	$2.41 \cdot 10^{-5}$	$2.71 \cdot 10^{-3}$	$5.67 \cdot 10^{-4}$	$5.52 \cdot 10^{-1}$	$7.32 \cdot 10^{-1}$
10	$-4.08 \cdot 10^{-2}$	$-4.74 \cdot 10^{-1}$	$5.70 \cdot 10^{-7}$	$7.13 \cdot 10^{-8}$	$-3.71 \cdot 10^{-4}$	$7.51 \cdot 10^{-4}$	$1.58 \cdot 10^{-1}$	$1.76 \cdot 10^{-1}$
15	$-1.09 \cdot 10^{-2}$	$-1.25 \cdot 10^{-1}$	$1.59 \cdot 10^{-8}$	$1.29 \cdot 10^{-9}$	$-7.78 \cdot 10^{-5}$	$2.84 \cdot 10^{-7}$	$6.27 \cdot 10^{-2}$	$6.69 \cdot 10^{-2}$
20	$-4.10 \cdot 10^{-3}$	$-4.42 \cdot 10^{-3}$	$1.02 \cdot 10^{-9}$	$5.84 \cdot 10^{-11}$	$-2.29 \cdot 10^{-5}$	$-7.11 \cdot 10^{-8}$	$3.07 \cdot 10^{-2}$	$3.22 \cdot 10^{-2}$
25	$-1.87 \cdot 10^{-3}$	$-1.88 \cdot 10^{-2}$	$1.07 \cdot 10^{-10}$	$4.61 \cdot 10^{-12}$	$-8.14 \cdot 10^{-6}$	$-8.59 \cdot 10^{-8}$	$1.73 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$
30	$-9.23 \cdot 10^{-4}$	$-9.07 \cdot 10^{-3}$	$1.59 \cdot 10^{-11}$	$5.33 \cdot 10^{-13}$	$-3.35 \cdot 10^{-6}$	$-7.16 \cdot 10^{-8}$	$1.06 \cdot 10^{-2}$	$1.09 \cdot 10^{-2}$
40	$-3.39 \cdot 10^{-4}$	$-2.74 \cdot 10^{-3}$	$7.01 \cdot 10^{-13}$	$1.55 \cdot 10^{-14}$	$-7.79 \cdot 10^{-7}$	$-4.53 \cdot 10^{-8}$	$4.86 \cdot 10^{-3}$	$4.96 \cdot 10^{-3}$
45	$-2.19 \cdot 10^{-4}$	$-1.66 \cdot 10^{-3}$	$1.89 \cdot 10^{-13}$	$3.48 \cdot 10^{-15}$	$-4.20 \cdot 10^{-7}$	$-3.63 \cdot 10^{-8}$	$3.51 \cdot 10^{-3}$	$3.57 \cdot 10^{-3}$
50	$-1.47 \cdot 10^{-4}$	$-1.05 \cdot 10^{-3}$	$5.73 \cdot 10^{-14}$	$8.98 \cdot 10^{-16}$	$-2.40 \cdot 10^{-7}$	$-2.94 \cdot 10^{-8}$	$2.62 \cdot 10^{-3}$	$2.66 \cdot 10^{-3}$
55	$-1.03 \cdot 10^{-4}$	$-6.89 \cdot 10^{-4}$	$1.93 \cdot 10^{-14}$	$2.60 \cdot 10^{-16}$	$-1.44 \cdot 10^{-7}$	$-2.41 \cdot 10^{-8}$	$2.0 \cdot 10^{-3}$	$2.03 \cdot 10^{-3}$
60	$-7.43 \cdot 10^{-5}$	$-4.68 \cdot 10^{-4}$	$7.05 \cdot 10^{-15}$	$8.26 \cdot 10^{-17}$	$-9.0 \cdot 10^{-8}$	$-2.0 \cdot 10^{-8}$	$1.56 \cdot 10^{-3}$	$1.58 \cdot 10^{-3}$
80	$-2.48 \cdot 10^{-5}$	$-1.27 \cdot 10^{-4}$	$2.40 \cdot 10^{-16}$	$1.74 \cdot 10^{-18}$	$-1.84 \cdot 10^{-8}$	$-1.03 \cdot 10^{-8}$	$6.87 \cdot 10^{-4}$	$6.94 \cdot 10^{-4}$
100	$-1.05 \cdot 10^{-5}$	$-4.53 \cdot 10^{-5}$	$1.65 \cdot 10^{-17}$	$8.15 \cdot 10^{-20}$	$-5.26 \cdot 10^{-9}$	$-5.98 \cdot 10^{-9}$	$3.61 \cdot 10^{-4}$	$3.64 \cdot 10^{-4}$

Table 7. The value of $\varepsilon_A(\%)$ *of the approximations at different x.*

x	FJG [19]	Coats–Redfern	Cai	Urbanovici–Segal II	Senum–Yang I	Ji	Senum-Yang III	Orfao III
0.5	$-1.04 \cdot 10^{2}$	$-1.04 \cdot 10^{2}$	$-1.01 \cdot 10^{2}$	$1.73 \cdot 10^{1}$	$2.23 \cdot 10^{1}$	$-3.45 \cdot 10^{1}$	6.26	$6.47 \cdot 10^{-2}$
2	$-7.0 \cdot 10^{1}$	$7.05 \cdot 10^{2}$	$-1.22 \cdot 10^{1}$	3.14	5.3	-1.17	$4.6 \cdot 10^{-1}$	$-3.05 \cdot 10^{-5}$
5	$-4.45 \cdot 10^{1}$	$8.08 \cdot 10^{1}$	-1.25	$2.92 \cdot 10^{-1}$	$8.98 \cdot 10^{-1}$	$-1.46 \cdot 10^{-2}$	$1.87 \cdot 10^{-2}$	$-2.37 \cdot 10^{-6}$
10	$-2.82 \cdot 10^{1}$	$1.74 \cdot 10^{1}$	$4.17 \cdot 10^{-2}$	$-8.37 \cdot 10^{-3}$	$1.47 \cdot 10^{-1}$	$3.72 \cdot 10^{-4}$	$6.85 \cdot 10^{-4}$	$-3.07 \cdot 10^{-6}$
15	$-2.08 \cdot 10^{1}$	7.60	$9.65 \cdot 10^{-2}$	$-1.79 \cdot 10^{-2}$	$4.32 \cdot 10^{-2}$	$-5.53 \cdot 10^{-4}$	$7.05 \cdot 10^{-5}$	$1.13 \cdot 10^{-4}$
20	$-1.64 \cdot 10^{1}$	4.28	$6.96 \cdot 10^{-2}$	$-1.30 \cdot 10^{-2}$	$1.70 \cdot 10^{-2}$	$-2.73 \cdot 10^{-4}$	$1.23 \cdot 10^{-5}$	$8.32 \cdot 10^{-5}$
25	$-1.36 \cdot 10^{1}$	2.75	$4.35 \cdot 10^{-2}$	$-8.87 \cdot 10^{-3}$	$8.03 \cdot 10^{-3}$	$-9.07 \cdot 10^{-6}$	$2.95 \cdot 10^{-6}$	$6.11 \cdot 10^{-6}$
30	$-1.16 \cdot 10^{1}$	1.91	$2.47 \cdot 10^{-2}$	$-6.17 \cdot 10^{-3}$	$4.27 \cdot 10^{-3}$	$1.31 \cdot 10^{-4}$	$8.85 \cdot 10^{-7}$	$-6.84 \cdot 10^{-5}$
40	-9.01	1.08	$2.94 \cdot 10^{-3}$	$-3.25 \cdot 10^{-3}$	$1.54 \cdot 10^{-3}$	$2.00 \cdot 10^{-4}$	$1.24 \cdot 10^{-7}$	$-1.66 \cdot 10^{-4}$
45	-8.10	$8.59 \cdot 10^{-1}$	$-3.20 \cdot 10^{-3}$	$-2.46 \cdot 10^{-3}$	$1.00 \cdot 10^{-3}$	$1.90 \cdot 10^{-4}$	$5.42 \cdot 10^{-8}$	$-1.91 \cdot 10^{-4}$
50	-7.35	$6.98 \cdot 10^{-1}$	$-7.50 \cdot 10^{-3}$	$-1.90 \cdot 10^{-3}$	$6.81 \cdot 10^{-4}$	$1.68 \cdot 10^{-4}$	$2.57 \cdot 10^{-8}$	$-2.04 \cdot 10^{-4}$
55	-6.73	$5.78 \cdot 10^{-1}$	$-1.05 \cdot 10^{-2}$	$-1.50 \cdot 10^{-3}$	$4.79 \cdot 10^{-4}$	$1.44 \cdot 10^{-4}$	$1.30 \cdot 10^{-8}$	$-2.08 \cdot 10^{-4}$
60	-6.21	$4.87 \cdot 10^{-1}$	$-1.27 \cdot 10^{-2}$	$-1.20 \cdot 10^{-3}$	$3.47 \cdot 10^{-4}$	$1.84 \cdot 10^{-4}$	$6.91 \cdot 10^{-9}$	$-2.06 \cdot 10^{-4}$
80	-4.74	$2.75 \cdot 10^{-1}$	$-1.64 \cdot 10^{-2}$	$-5.64 \cdot 10^{-4}$	$1.18 \cdot 10^{-4}$	$3.50 \cdot 10^{-5}$	$8.37 \cdot 10^{-10}$	$-1.63 \cdot 10^{-4}$
100	-3.83	$1.77 \cdot 10^{-1}$	$-1.68 \cdot 10^{-2}$	$-3.08 \cdot 10^{-4}$	$5.02 \cdot 10^{-5}$	$-1.68 \cdot 10^{-5}$	$1.62 \cdot 10^{-10}$	$-1.02 \cdot 10^{-4}$

Table 8. The value of $\varepsilon_A(\%)$ *of the approximations at different x.*

x	Balarin	h_5	h_6	h_7	hr_2	hr_5	hc_1	hc_2
0.5	$-4.71 \cdot 10^{1}$	$-3.44 \cdot 10^{1}$	2.33	1.49	$4.31 \cdot 10^{1}$	2.98		$-7.12 \cdot 10^{1}$
2	$-1.11 \cdot 10^{1}$	$-5.25 \cdot 10^{1}$	$5.89 \cdot 10^{-2}$	$2.31 \cdot 10^{-2}$	1.40	$1.40 \cdot 10^{-1}$	4.49	$1.44 \cdot 10^{1}$
5	-2.56	$-2.38 \cdot 10^{1}$	$7.0 \cdot 10^{-4}$	$1.57 \cdot 10^{-4}$	$1.40 \cdot 10^{-2}$	$3.85 \cdot 10^{-3}$	6.0	7.52
10	$-6.17 \cdot 10^{-1}$	-6.87	$2.82 \cdot 10^{-7}$	$8.57 \cdot 10^{-7}$	$-4.64 \cdot 10^{-3}$	$8.99 \cdot 10^{-5}$	2.85	3.12
15	$-2.40 \cdot 10^{-1}$	-2.63	$2.35 \cdot 10^{-8}$	$2.26 \cdot 10^{-8}$	$-1.58 \cdot 10^{-3}$	$1.87 \cdot 10^{-6}$	1.59	1.64
20	$-1.17 \cdot 10^{-1}$	-1.21	$3.06 \cdot 10^{-9}$	$1.33 \cdot 10^{-9}$	$-6.0 \cdot 10^{-4}$	$-4.29 \cdot 10^{-6}$	1.01	1.05
25	$-6.61 \cdot 10^{-2}$	$-6.35 \cdot 10^{-1}$	$5.42 \cdot 10^{-10}$	$1.30 \cdot 10^{-10}$	$-2.62 \cdot 10^{-4}$	$-4.62 \cdot 10^{-6}$	$6.97 \cdot 10^{-1}$	$7.18 \cdot 10^{-1}$
30	$-4.09 \cdot 10^{-2}$	$-3.64 \cdot 10^{-1}$	$3.15 \cdot 10^{-11}$	$1.89 \cdot 10^{-11}$	$-1.28 \cdot 10^{-4}$	$-4.20 \cdot 10^{-6}$	$5.09 \cdot 10^{-1}$	$5.22 \cdot 10^{-1}$
40	$-1.88 \cdot 10^{-2}$	$-1.45 \cdot 10^{-1}$	$1.10 \cdot 10^{-11}$	$1.13 \cdot 10^{-12}$	$-3.91 \cdot 10^{-5}$	$-3.27 \cdot 10^{-6}$	$3.05 \cdot 10^{-1}$	$3.11 \cdot 10^{-1}$
45	$-1.36 \cdot 10^{-2}$	$-9.77 \cdot 10^{-2}$	$2.91 \cdot 10^{-12}$	$1.47 \cdot 10^{-12}$	$-2.36 \cdot 10^{-5}$	$-2.88 \cdot 10^{-6}$	$2.47 \cdot 10^{-1}$	$2.51 \cdot 10^{-1}$
50	$-1.01 \cdot 10^{-2}$	$-6.83 \cdot 10^{-2}$	$2.22 \cdot 10^{-13}$	$-2.89 \cdot 10^{-13}$	$-1.49 \cdot 10^{-5}$	$-2.54 \cdot 10^{-6}$	$2.03 \cdot 10^{-1}$	$2.06 \cdot 10^{-1}$
55	$-7.78 \cdot 10^{-3}$	$-4.92 \cdot 10^{-2}$	$-3.42 \cdot 10^{-12}$	$-6.22 \cdot 10^{-13}$	$-9.82 \cdot 10^{-6}$	$-2.26 \cdot 10^{-6}$	$1.70 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$
60	$-6.09 \cdot 10^{-3}$	$-3.64 \cdot 10^{-2}$	$-3.64 \cdot 10^{-2}$	$-4.17 \cdot 10^{-12}$	$-6.67 \cdot 10^{-6}$	$-2.02 \cdot 10^{-6}$	$1.45 \cdot 10^{-1}$	$1.47 \cdot 10^{-1}$
80	$-2.69 \cdot 10^{-3}$	$-1.31 \cdot 10^{-2}$	$1.80 \cdot 10^{-12}$	$1.80 \cdot 10^{-12}$	$-1.81 \cdot 10^{-7}$	$-1.35 \cdot 10^{-6}$	$8.44 \cdot 10^{-2}$	$8.51 \cdot 10^{-2}$
100	$-1.42 \cdot 10^{-3}$	$-5.80 \cdot 10^{-3}$	$4.09 \cdot 10^{-12}$	$4.09 \cdot 10^{-12}$	$-6.43 \cdot 10^{-7}$	$-9.61 \cdot 10^{-7}$	$5.51 \cdot 10^{-2}$	$5.55 \cdot 10^{-2}$

Among the approximations presented in the previous works, the approximations of E and A determined by Senum-Yang have the best accuracy. Also, given x for each approximation, we can see that the value of ε_A is greater than that of ε_E.

4. Conclusions

By numerical methods with rapidly increasing computational capabilities, temperature integration can be determined, but when enough accuracy is required, the importance of approximations cannot be neglected.

Using efficient approximations, the analytical procedure may be simplified. In addition, suitable approximations may reduce computation time.

We have considered approximations of known or newly constructed temperature integrals.

In general, the rational approximation has better accuracy than the exponential approximation. Rational approximations have better accuracy as the order increases. Efficient selection of approximations requires detailed consideration, such as its complexity, accuracy, and the range of *x*.

Abbreviations

TGA	Thermogravimetric Analysis

Acknowledgments

It is also the result of collaborative research with State Academy of Sciences.

Author Contributions

Kim Hyon Chol: Conceptualization, Investigation, Visualization, Writing – original draft, Writing – review & editing

Ri Kwang Il: Conceptualization, Validation, Writing – review & editing, Supervision

Funding

This work was partially supported by State Academy of Sciences.

Conflicts of Interest

The authors declare no conflicts of interest.

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