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## Research Article

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# The 3-D Image of the Temperature Integral and Its Self-similarity

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## Abstract:

How to derive the accurate value of temperature integral is a vital problem for the non-isothermal kinetic analysis. In the past six decades, researchers provided various methods to solve above problem, but the error usually becomes divergent when the value of  $x$  ( $x=E_a/RT$ ) is too small or too large, no matter whether it is a numerical method or an approximation method. In this paper, we present a new series method and elaborately design a computer program to calculate the value of temperature integral. Finally, we reveal the mysterious relationship between the integral, the temperature and the activation energy, and we find an extremely interesting phenomenon that the 3-D image of the temperature integral is of self-similarity according to the fractal theory.

**Keywords** temperature integral; 3-D image; self-similar

## Introduction

The non-isothermal chemical kinetics is extensively introduced in chemical engineering [1,2], mineral technology [3], metallurgical technology [4], materials science [5], biomass energy [6,7], and other relevant disciplines. The reaction rate of a solid-involved reaction is now generally accepted as

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where  $\alpha$  denotes the conversion ratio of the concerned substance at time  $t$ ,  $f(\alpha)$  is the mechanism function, and  $k$  is the rate constant expressed by Arrhenius equation:

$$k = A\exp(-E_a/RT) \quad (2)$$

where  $A$ ,  $T$ ,  $E_a$  is pre-exponential factor, temperature, and activation energy of the reaction, respectively.

For a linear heating process, the heating rate  $\beta$  is usually a function of time,

$$\beta = \frac{dT}{dt} \quad (3)$$

Combining all above equations, re-arranging and integrating Equation (1), we obtain

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (4)$$

where  $T_0$  is the initial reaction temperature, and the initial reaction extent  $\alpha_0$  usually equals zero.

Then the integral of Boltzmann factor  $\Psi(T)$  is derived from Equation (4),

$$\Psi(T) = \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (5)$$

The integral of Boltzmann factor is a transcendental function and any attempts to give the analytical solution failed finally[8]. It was encountered by scientists in the early thermogravimetric analyses[9–13]. Reich and Levi [14] made mistakes since they didn't recognize it is a transcendental function. Although different efforts have been made for solving this puzzle during the past six decades [15–28], troubles still exist occasionally since ‘there is no true value for the integral’[27]. The temperature integral has been playing an ‘enigmatic’ role in the kinetic analysis. That is, it has appeared to be a necessary evil to be dealt with [25].

Flynn [25] and Órfão [17] provided excellent reviews on the temperature integral. According to Flynn's categorization, these solutions of the temperature integral are classified into three categories: series solutions, complex approximations[29,30], and simple approximations. The series solutions listed by Flynn all have some drawbacks [25] and are inapplicable because of unbearable errors under some particular occasions. On the other hand, the complex and simple approximations were preferred and truncated from these series solutions. Besides the truncations, some modified approximations were also proposed [17–20,26–28,31].

The numerical calculation based on quadrature method was occasionally mentioned in previous papers [24,28]. However, the residual error usually increases with the rise of upper limit temperature of the integration, or increases with the decrease of  $x$  (denotes  $E_a / (RT)$ ). As a disquieting situation, even the published paper [24] misled readers and gave the wrong quadrature results as standard integral values. All in all, the

accurate value of the temperature integral is always attractive in the kinetic analysis.

## Theory

All approximations to the temperature integral makes a detour, errors and troubles cannot be eradicated. The only way to get the exact numerical solution of the integral is to develop an appropriate series solution which is easy to reach convergence. Assuming  $T$  is not much larger than  $T_0$ , here we provide a new series solution based on Taylor's expansion,

$$\Psi(T_0 + \Delta T) \stackrel{n \rightarrow \infty}{=} \Psi(T_0) + \Psi'(T_0) \cdot \Delta T + \frac{1}{2!} \Psi''(T_0) \cdot \Delta T^2 + \dots + \frac{1}{n!} \Psi^{(n)}(T_0) \cdot \Delta T^n \quad (6)$$

Where  $\Delta T$  is the difference between  $T$  and  $T_0$ ,  $T = T_0 + \Delta T$ , and  $n$  denotes the order of Taylor expansion.

Then the exact derivative value at temperature  $T_0$  could be calculated using Equations (7) - (9).

$$(n = 1) \quad \Psi'(T) = \exp\left(-\frac{E_a}{RT}\right) = g(T) \quad (7)$$

$$(n = 2) \quad \Psi''(T) = \frac{E_a}{R} \times T^{-2} \cdot g(T) \quad (8)$$

$$(n > 2) \quad \Psi^{(n)}(T) = \frac{E_a}{R} \times \sum_{i=0}^{n-1} C_{n-1}^i g^{(i)}(T) \cdot (T^{-2})^{n-i-1} \quad (9)$$

The  $n$ -th-order derivative expression shown as Equation (9) is established according to Leibniz formula [32]. With the help of the general form of  $n$ -th-order derivative equation, we designed a computer program to calculate the integral of Boltzmann factor with Equation (6). The numerical value can converge within a sufficiently small

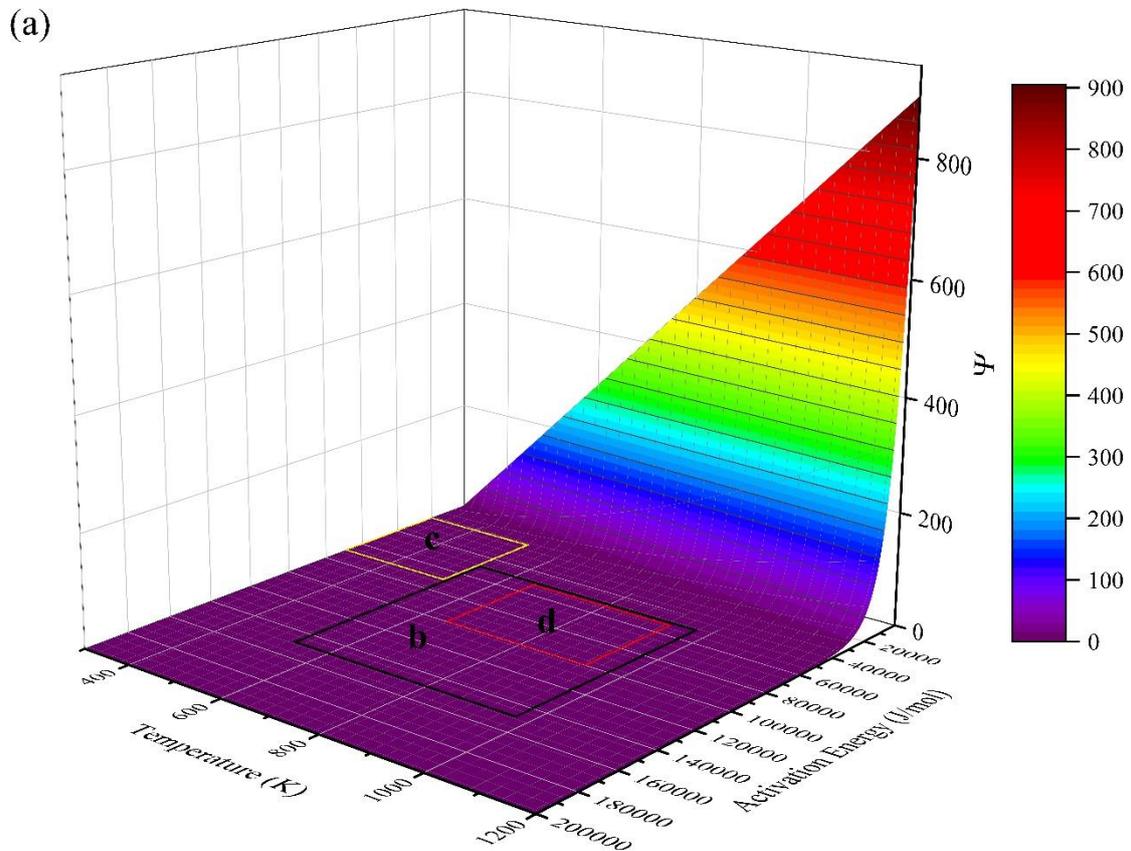
residual error when the derivative order  $n$  is large enough and  $\Delta T$  is small enough. Computing results show that the value usually converges in a reasonably little error when  $n$  is more than 4 and  $\Delta T$  is no more than 50 K. Consequently, a multi-step integral method is applied to compute the integral value when the difference between upper and lower limit temperature is larger than 50 K. The corresponding error analysis of present calculation method is also provided in the supplemental material.

## Results

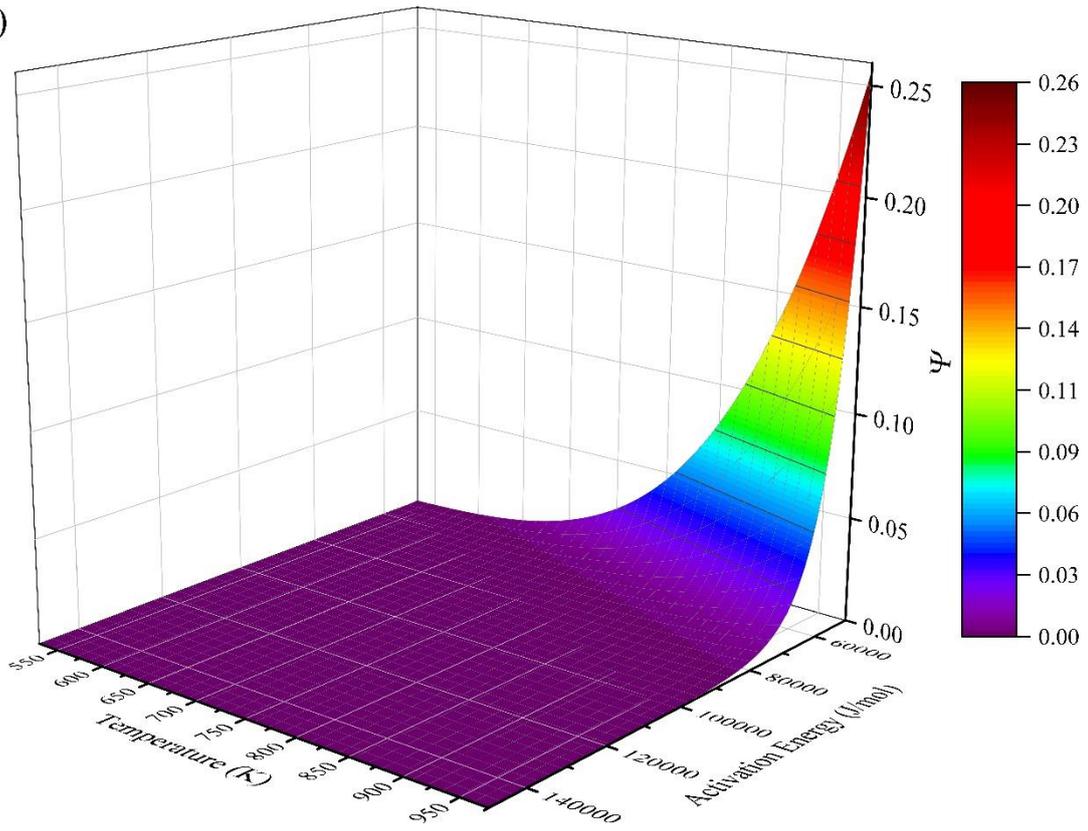
The dependence of integral value on  $E_a$  and  $T$  has always kept as mysterious relationships. Here we show the true value of the integral in Fig.1 a. This image is drawn based on  $200 \times 200$  calculation nodes, and each node is computed with the Taylor order of 20 to ensure the numerical value is accurate enough. It can be seen that the integral value declines in order of magnitude with the multiple growth of the activation energy, which proves the integral value is extremely sensitive to the activation energy. Therefore, the approximation method often provides an inaccurate value and fails to predict the kinetic process. The integral value tends to be equivalent to the value of  $\Delta T$  when  $E_a$  is nearby 0 kJ/mol, while the integral value declines in order of magnitude and tends to be 0 when  $E_a$  is larger than 75 kJ/mol.

There is also an interesting phenomenon that the profile of the 3D-surface remains a similar one if the independent variables (temperature, activation energy) are arbitrarily truncated such as images (b), (c) and (d). Image (a) is drawn based on  $200 \times 200$  node network, and each node is computed with the Taylor order of 20 to ensure the numerical

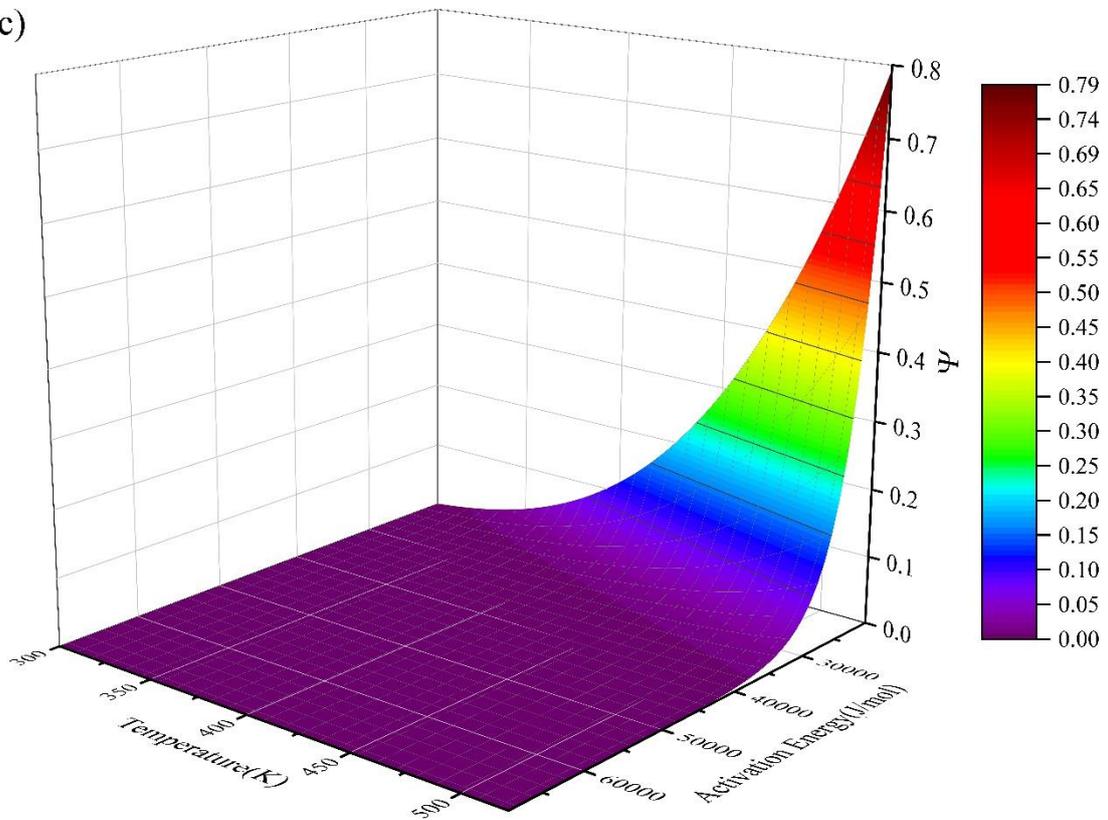
value is accurate enough. Independent variables,  $E_a$  and  $T$ , vary from 2 to 200002 J/mol and 300 to 1200 K, respectively. In the aforementioned node network (200×200), mid nodes ( $E_a$  varies from 50002 to 149002 J/mol, and  $T$  varies from 529.5 to 975 K) are chosen to form new node network (100×100), then image (b) can be drawn. The node network of image (c) is 50×50, and its values of  $E_a$  and  $T$  change from 20002 to 69002 J/mol and 300 to 520.5 K, respectively. As for image (d), its node network is 49×63 and corresponding ranges of  $E_a$  and  $T$  are 52002 to 100002 J/mol and 651 to 930 K, respectively. As we can see, the four images are similar with each other. This phenomenon indicates the self-similarity property of the figure according to the fractal theory[33].



(b)



(c)



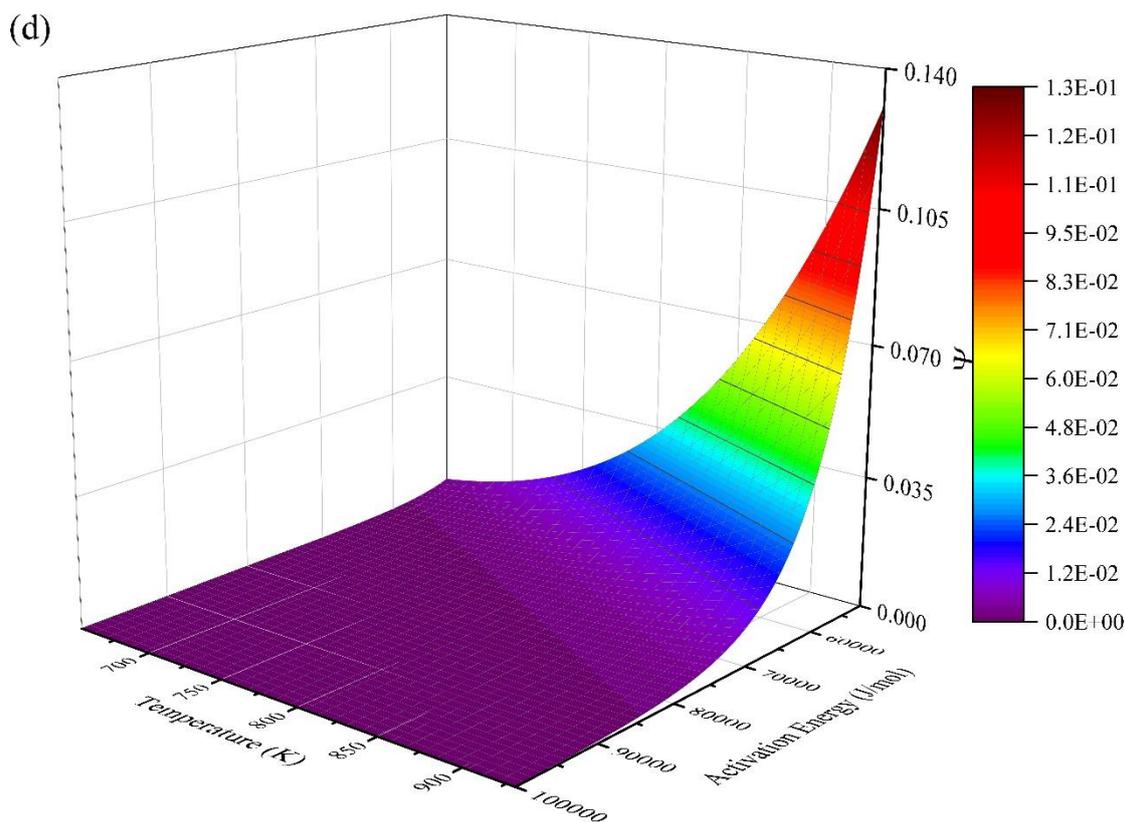


Fig.1 Three-dimensional image for the integral function of Boltzmann factor

## Conclusions

A new method is proposed to obtain the accurate value of temperature integral. Taylor series is expanded to 20th for each node to ensure the high accuracy of result calculated by new method. The temperature integral function actually is very sensitive to the activation energy according to the 3-D image of temperature integral. This is why the previous approximation or truncated series methods occasionally cause huge errors. What is more exciting, we find the 3-D image of the temperature integral performs self-similarity according to the fractal theory. This new finding presents a hybrid research interest of Chemistry, Physics and Mathematics, which deserves further investigation.

## Statements

Author contributions: Conceptualization: Wei Zhang; Writing original draft: Wei Zhang and Kui Li; Resources: Zhangliang Xue and Guangqiang Li; Editing: Juhua Zhang and Chengzhi li.

Competing Interests: There are no conflicts of interest to declare.

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