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NEW APPROXIMATIONS OF THE TEMPERATURE INTEGRAL FOR NONISOTHERMAL KINETICS

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Abstract

The accuracy and scope of application of previously reported approximations of the temperature integral were evaluated. The exact solution was obtained independently by solving the temperature integral numerically be Simpson's rule, the trapezoidal rule and the Gaussian rule.

Two new approximations have been proposed:

$$P(X) = e^{-x}(1/X^2)(1-2/X)/(1-5.2/X^2)$$

$$P(X) = e^{-x}(1/X^2)(1-2/X)/(1-4.6/X^2)$$

where $X = E/RT$. The first equation gives higher accuracy, with a deviation of less than 1% and 0.1% from the exact solution for $X \geq 7$ and $X \geq 10$, respectively. The second equation has a wider scope of application, with a deviation of less than 1% for $X \geq 4$ and of less than 0.1% for $X \geq 35$.

Keywords: kinetics, thermal analysis

Introduction

By means of nonisothermal thermoanalytical techniques, changes in mass and concentration or enthalpy changes of a substance can be recorded automatically and continuously as a function of temperature. In the course of programmed heating, the changes in mass of a sample can be automatically recorded by thermogravimetry (TG). The volatile products formed during the heating process are usually recorded by either evolved gas detection (EGD) or evolved gas analysis (EGA) techniques. The enthalpy changes are recorded by differential scanning calorimetry (DSC) or differential thermal analysis (DTA). The modern thermoanalytical instrument universally incorporates a computer for the control and data processing. Consequently, it ensures accurate data recording on processing and is therefore less prone to error, data processing be-

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coming very rapid and convenient. As a wealth of valuable information can be obtained from a single measurement, the nonisothermal methods are more and more popular, and the number of their applications is on the increase. In recent years these techniques have been widely employed to investigate various kinetic problems, e.g. the kinetics of chemical reactions such as decomposition, oxidation, dehydration, polymerization, crosslinking and degradation; the kinetics of physical changes such as crystallization and crystalline transition; and the kinetics of surface reactions such as adsorption. A difficulty in nonisothermal kinetic methods is that there is no exact analytical solution of the temperature integral. In order to express the integral, Doyle in 1961 suggested an approximation in logarithmic form [1]. Subsequently, a number of approximations were proposed in succession, notably those suggested by Coats and Redfern in 1964 [2], Gorbachev in 1975 [3], Li in 1985 [4], and Agrawal in 1987 [5]. Their methods successively improved the accuracy of the approximate solutions and thereby enlarged the scope.

The object of the present study was to compare the accuracy and scope of these approximations so as to correctly select and use them in kinetic studies involving thermal analysis; simultaneously, an attempt was made to seek approximations which are more accurate, simple and easily applied. Two new approximations have been developed, one is more accurate, while the other may be used over a wide range of values of E/RT.

New temperature integral approximations

The rate of reaction of a substance is generally expressed as

$$d\alpha/dt = Kf(\alpha) \tag{1}$$

where α represents the fraction of substance reacted at time t, $f(\alpha)$ is a function of α depending on the reaction mechanism, and K is the specific rate constant given by the Arrhenius equation:

$$K = A\exp(-E/RT) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature. For a nonisothermal system, a constant heating rate is often used:

$$dT/dt = \beta \tag{3}$$

Substituting Eqs (2) and (3) into Eq. (1) and separating variables, we get

$$d\alpha/f(\alpha) = A/\beta \exp(-E/RT)dT \tag{4}$$

Ordinarily, the rate of the reaction at low temperatures is low enough to be neglected, and thus the left and right-hand sides of Eq. (4) may be integrated from 0 to α and from 0 to T, respectively:

$$\int_0^\alpha d\alpha/f(\alpha) = A / \beta \int_0^T \exp(-E/RT)dT \tag{5}$$

$\int_0^T \exp(E/RT)dT$ on the right-hand side of Eq. (5) is known as the temperature integral and is not analytically integrable.

Let $X = E/RT$. Then

$$\int_0^T \exp(-E/RT)dT = E/R \int_X^\infty e^{-X}/X^2 dX = E/RP(X) \tag{6}$$

Since E/R is a constant, solving the temperature integral involves finding an expression for the function $P(X)$.

$P(X)$ can be solved by various methods, and the final solution for $P(X)$ is an infinite series.

Two series developments often used are as follows:

$$P(X) = e^{-X}/X^2[1 - 2!/X + 3!/X^2 - \ldots\ldots] \tag{7}$$

$$P(X) = [e^{-X}/X(X + 1)][1 - 1/(X + 2) + 2/(X + 2)(X + 3) - \ldots\ldots] \tag{8}$$

For X in a definite range, the logarithmic values of $P(X)$ have been tabulated [1]. Since plots of log $P(X)$ *vs.* X reveal an approximately linear relation, Doyle obtained a simple approximation by regression analysis:

$$\log P(X) = -2.315 - 0.4567X \quad (20 < X < 60) \tag{9}$$

Coats and Redfern [2] used the first two terms of the asymptotic series in Eq. (7) as an approximation of $P(X)$:

$$P(X) = e^{-X}(1/X^2)(1 - 2/X) \tag{10}$$

From the first two terms of the asymptotic series in Eq. (8), Gorbachev [3] suggested the following equation:

$$P(X) = e^{-X}(1 / X)[1/(X + 2)] \qquad (11)$$

The approximation later derived by Lee and Beck [6] is actually the same as the Gorbachev equation. On multiplication of the numerator and denominator by (1–2/*X*), Eq. (11) can be transformed into

$$P(X) = e^{-X}(1/X^2)(1 - 2/X)/(1 - 4/X^2) \qquad (12)$$

Li [4] integrated the temperature integral by parts twice to arrive at the equation

$$P(X) = e^{-X}(1/X^2)(1 - 2/X)/(1 - 6/X^2) \qquad (13)$$

As Eqs (12) and (13) lead to positive and negative derivations, respectively, from the exact solution, Li developed two methods to obtain a more precise solution of *P*(*X*) by use of their average or weighted average:

$$P(X) = 1/2(Q1 + Q2) \qquad (14)$$

$$P(X) = 1/3(Q1 + Q2) \qquad (15)$$

where $Q1$ and $Q2$ represent the right-hand sides of Eqs (12) and (13), respectively. Li's methods require the calculation of $Q1$ and $Q2$, and are therefore inconvenient.

Table 1 Scope of application and accuracy for various approximations

Approximation	Absolute value of percentage deviation		
	Less than 1%	Less than 0.1%	Note
Agrawal Eq. (16)	$X \geq 6$	$X \geq 24$	When $X \geq 7$, the deviation is within 0.2%
Li Eq. (13)	$X \geq 10$	$X \geq 22$	
Gorbachev Eq. (11)	$X \geq 12$	$X \geq 42$	
Coats and Redfern Eq. (10)	$X \geq 24$	–	
Doyle Eq. (9)	–	–	When $28 \leq X \leq 50$, the deviation is within 5%
This work Eq. (17)	$X \geq 7$	$X \geq 10$	
This work Eq. (18)	$X \geq 4$	$X \geq 35$	

By comparing Eqs (12) and (13), Agrawal [5] found that the only difference is the coefficient of the term X^2 in the denominator. The former is the integer 4,

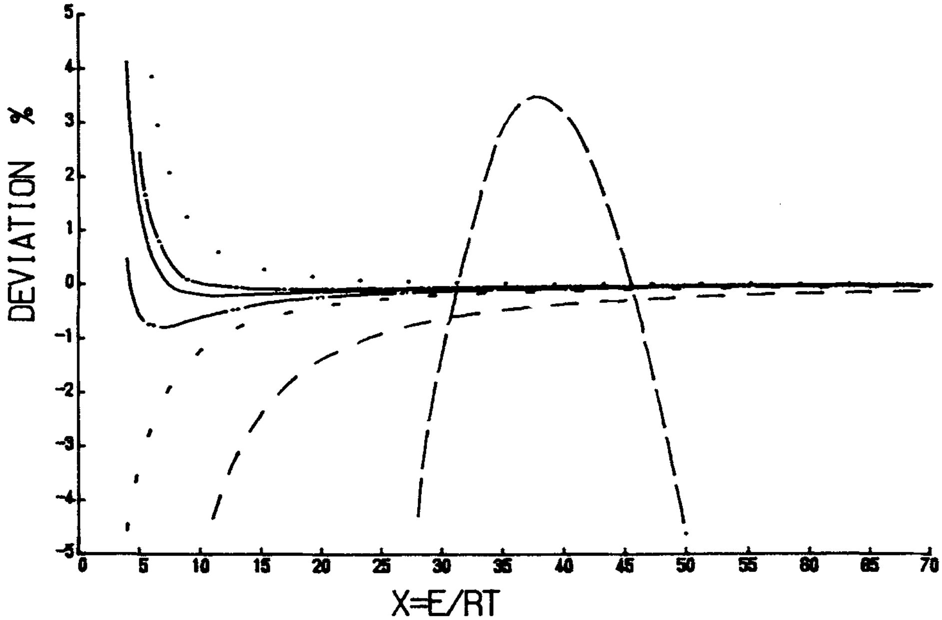

Fig. 1 Deviation of various approximations from Simpson's 1/3 rule: (—) Agraval, (---) Gorbachev, (— — —) Doyle, (—··—) This work Eq.(18), (···) Li, (– – –) Coats and Redfern and (—·—) This work Eq.(17)

and results in a negative deviation, whereas the latter is the integer 6 and results in a positive deviation. Hence, by replacing the integer by 5, Agrawal proposed a simpler and more precise approximation:

$$P(X) = e^{-X}(1/X^2)(1 - 2/X)/(1 - 5/X^2) \tag{16}$$

In order to improve the preciseness of the approximation further, we studied how the coefficient of the term X^2 in the denominator affects the deviation. The results of our calculations lead us to propose that the following two new approximations of the temperature integral are superior:

$$P(X) = e^{-X}(1/X^2)(1 - 2/X)/(1 - 5.2/X^2) \tag{17}$$

$$P(X) = e^{-X}(1/X^2)(1 - 2/X)/(1 - 4.6/X^2) \tag{18}$$

Their form is the same as that of Eqs (12), (13) and (16) but the coefficient of the term X^2 in the denominator is 5.2 and 4.6, respectively. Equation (17) gives the higher accuracy, whereas Eq. (18) has a wider applicability.

Evaluation of accuracy of various approximations

The reference value of the temperature integral was obtained independently by numerically integrating the integral, using the 1/3rd Simpson's rule, the trapezoidal rule and the Gaussian rule. The values from these methods are in excellent accordance. Total agreement between the calculated values and the mathematical tables of Abramowitz and Stegun [7], and between its logarithm and the log $P(X)$ table given by Doyle proved the preciseness of the reference values. The calculated percentage absolute deviations of various approximations from the 1/3rd Simpson's rule agreed with Table 2 in reference [5], further confirming the accuracy of the reference values.

Table 2 Comparison of the deviation for various approximations

$X = E / RT$	This work Eq. (17)	Agrawal Eq. (16)	This work Eq. (18)
3	23.12	16.96	6.33
4	6.06	4.13	0.47
5	2.46	1.43	–0.56
6	1.15	0.50	–0.78
7	0.57	0.11	–0.79
8	0.28	–0.06	–0.74
9	0.12	–0.14	–0.67
10	0.03	–0.18	–0.60
15	–0.08	–0.17	–0.35
20	–0.08	–0.13	–0.23
25	–0.06	–0.09	–0.16
30	–0.05	–0.07	–0.11
40	–0.03	–0.04	–0.07
50	–0.02	–0.03	–0.04
60	–0.01	–0.02	–0.03
70	–0.008	–0.01	–0.02

Figure 1 shows the effects of variation of X on the percentage deviations of various approximations from the exact solution.

Table 1 summarizes their scope of application and accuracy. From these, it can be clearly seen that in the previously reported approximations of the temperature integral the Agrawal equation is the most superior, followed in turn by the Li, Gorbachev, Coats and Redfern, and Doyle equations.

Table 2 presents data on the deviations of the proposed Eqs (17) and (18) and the Agrawal equation (16) from the exact solution. The results indicate that when $X \geq 9$ Eq. (17) is superior to Eq. (16). Equation (16) deviates by less than 0.1% for $X \geq 24$, whereas Eq. (17) deviates by less than 0.1% for $X \geq 10$. The increase in accuracy is very obvious. However, when $X > 9$, Eq. (17) is somewhat inferior to Eq. (16). For values of X below 6, the deviations for both equations increase rapidly and exceed 1%. In this case, Eq. (18) is more suitable. Its deviation is less than 1% for $X \geq 4$, which is small by comparison with that for the other equations.

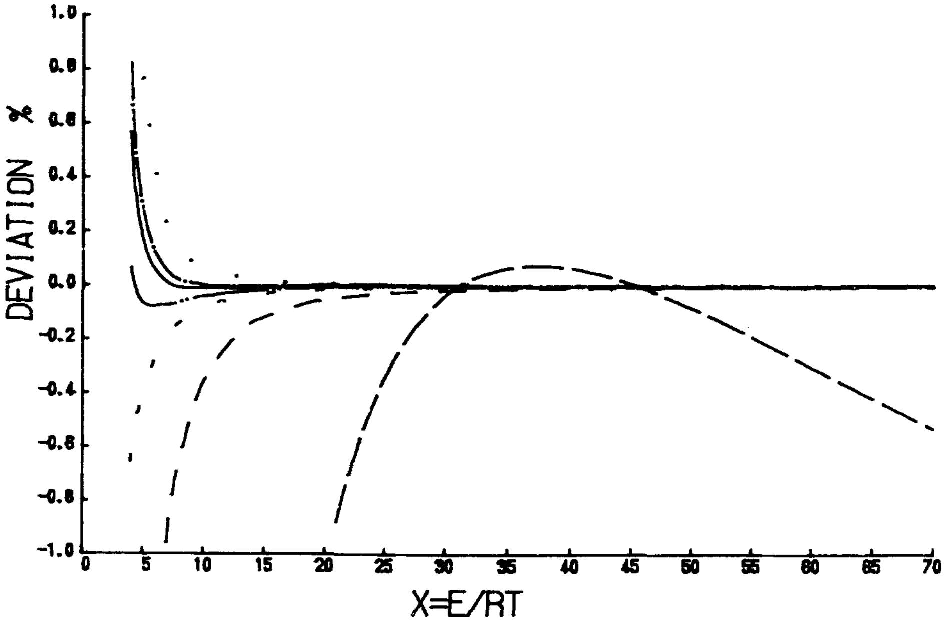

Fig. 2 Deviation of the logarithm of various approximations from the logarithm of the exact solution: (—) Agraval, (---) Gorbachev, (— — —) Doyle, (—··—) This work Eq.(18), (···) Li, (– – –) Coats and Redfern and (—·—) This work Eq.(17)

Table 3 Scope of a application and accuracy for the logarithm various approximations

Approximation	Absolute value of percentage deviation	
	Less than 1%	Less than 0.1%
Agrawal Eq. (16)	$X \geq 4$	$X \geq 7$
Li Eq. (13)	$X \geq 5$	$X \geq 9$
Gorbachev Eq. (11)	$X \geq 4$	$X \geq 10$
Coats and Redfern Eq. (10)	$X \geq 7$	$X \geq 17$
Doyle Eq. (9)	$21 \leq X \leq 80$	$29 \leq X \leq 50$
This work Eq. (17)	$X \geq 4$	$X \geq 7$
This work Eq. (18)	$X \geq 3$	$X \geq 4$

As described above, $X = E/RT$, i.e. X is a function of the activation energy E and the temperature T. Therefore, the approximations can be used appropriately according to the characteristic of each reaction. If $X \geq 7$, Eq. (17) is recommended, while if $4 \leq 7$, Eq. (18) would be best. However, for $X > 4$ the deviations of the above equations from the reference values are still large, and it is necessary to search for even more accurate approximation.

Figure 2 presents the relations of the percentage deviation of log $P(X)$ for various approximations from the logarithm of the exact solution. The range of accuracy of various approximations in the logarithmic case is shown in Table 3. It appears that the deviations become smaller. This is because taking logarithms leads to a decrease in the sensitivity of these equations, and therefore care must be taken when using the approximations in logarithmic form.

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Zusammenfassung — Es erfolgt eine Abschätzung der Genauigkeit und der Möglichkeiten der Anwendung von zuvor beschriebenen Annäherungen des Temperaturintegrales. Die exakte Lösung wurde durch numerisches Lösen des Temperaturintegral mittels der Simpson'schen Regel, der Trapezregel und der Gauß'schen Regel erhalten.

Es werden zwei neue Näherungen vorgeschlagen:

$$P(X) = e^{-x}(1/X^2)(1-2/X)/(1-5.2/X^2)$$

$$P(X) = e^{-x}(1/X^2)(1-2/X)/(1-4.6/X^2)$$

wobei $X = E/RT$ bedeutet. Die erste Gleichung ergibt eine größere Genauigkeit mit einer Deviation von weniger als 1 % bzw. 0,1% bei der exakten Lösung für $X \geq 7$ bzw. $X \geq 10$. Die zweite Gleichung bietet breitere Einsatzmöglichkeiten mit einer Deviation von weniger als 1 % für $X \geq 4$ und von weniger als 0.1% für $X \geq 35$.