A NEW EQUATION FOR MODELING NONISOTHERMAL REACTIONS

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Based on previously reported approximations of the temperature integral, a new approximation

$$\int \exp\left(-E/RT\right) dT = \frac{RT^2}{E} \left[\frac{1 - 2(RT/E)}{1 - 5(RT/E)^2} \right] \exp\left(-E/RT\right)$$

has been proposed for modeling nonisothermal reactions. It has been found that the equation of Coats and Redfern deviates by less than 1% from the exact solution for E/RT ratio greater than 23 and by less than 10% for E/RT ratio greater than 6. The exact solution was obtained independently by solving the exponential temperature integral numerically by the Simpson's rule and the Trapezoidal rule. The Gorbachev equation deviates by less than 0.1% for E/RT ratio greater than 41 and by less than 1% for E/RT ratio greater than 11. The Li equation deviates by less than 0.1% for E/RT ratio greater than 21 and by less than 1% for E/RT ratio greater than 9. The proposed equation deviates by less than 0.1% for E/RT greater than 7.

Nonisothermal techniques are being extensively used in studying various reactions (example: chemical reactions, surface reactions, diffusion controlled reactions, and other physical decompositions reactions such as phase transformation and nucleation) [1–6]. Nonisothermal methods of analyzing reactions usually involve heating the reactants at a constant rate from ambient temperature to a temperature sufficiently high that the reactant undergoes a transformation. To study the mechanism and kinetics of the reactions, changes in parameters such as weight loss, or concentration, or enthalpy changes are continuously recorded as a function of time or temperature. The physical changes in weight can be recorded by either thermogravimetry (TG) or thermal volatilization techniques. The enthalpy changes are usually recorded by differential thermal analysis (DTA) or differential scanning calorimetry (DSC) devices. These instruments are highly automated,

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simple to operate and yield rapid results. These factors have greatly contributed to the acceptance and thus popularity of the non-isothermal techniques.

The importance of the nonisothermal methods are also due to the fact that a large amount of information can be obtained from a single measurement. However, these devices have certain limitations. The first group of limitations may be classified as instrumental limitation which include: inability to provide an accurate measure of the sample temperature, inability to minimize temperature gradients across the sample and other factors include bouyancy and aerodynamic effects which contribute to the drift in the baseline. The second complication is in the mathematical analysis of the data since there is no closed form solution of the temperature integral.

The purpose of this communication is to report on a new approximate solution of the temperature integral which is more accurate than previously known approximations. A comparison of the proposed approximation is also made with the popular approximations available in the literature. It has been shown that the proposed approximation is accurate to within 0.2% of the exact solution for an E/RT ratio as low as 6.

Nonisothermal kinetics

The rate of reaction of a substrate is generally expressed by the relation:

$$\frac{d\alpha}{dt} = k f(\alpha) \tag{1}$$

where α represents the fraction of the reactant at time t, $f(\alpha)$ is the conversion factor of α and k is the rate constant. In chemical reaction studies the temperature dependence of the rate constant is given by the Arrhenius equation:

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

where A is the frequency factor and E the activation energy. The tremendous success of the Arrhenius equation in explaining the temperature dependence of the rate constant in most chemical reactions has resulted in a similar definition of k in physical decomposition theories. For a nonisothermal system where the temperature is linearly increased at a heating rate of β, (dT/dt), Eq. (1) combined with Eq. (2) can be written as

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp(-E/RT) \, dT \tag{3}$$

Integrating Eq. (3) between the initial temperature T_0, and any final temperature T, and the reactant fraction between 1 and α, we have

$$\int_1^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp(-E/RT)\,dT \tag{4}$$

If the initial temperature T_0 is low enough such that no reaction occurs, then the lower limit may be neglected. The left hand side of Eq. (3) can be analytically integrated provided a mathematical definition of $f(\alpha)$ is available. Table 1 summarizes some well known integrated expressions for both chemical and physical decomposition models. The category of grouping various equations are similar to that used by Brown et al. [1]. If a chosen equation fits the data, then it does not necessarily imply that the mechanism described by the equation is correct. This is because some equations in Table 1 contain enough parameters and logarithmic terms, that the equation becomes insensitive. Therefore, the equation can fit the

Table 1 Various integrated expressions of $\int d\alpha/f(\alpha)$ popular in decomposition studies

1 Chemical decomposition process	
n^{th} order chemical reaction	$\dfrac{\alpha^{1-n}-1}{1-n}$ $(n \neq 1)$
First order chemical reaction	$\ln \alpha$ $(n=1)$
2 Acceleratory rate equations	
Power law	$\alpha^{1/n}$
Exponential law	$\ln \alpha$
3 Sigmoid rate equation	
Avrami–Erofe'ev Nuclei growth	$[-\ln(1-\alpha)]^{1/n}$ $(n=2, 3 \text{ and } 4)$
Prout–Tompkins Branching nucleation	$\ln[\alpha/(1-\alpha)]$
4 Deceleratory rate equations	
4.1 Based on diffusion mechanisms	
One dimensional diffusion	
(Parabolic law)	α^2
Two dimensional diffusion	
(Valensi equation)	$\alpha + (1-\alpha)\ln(1-\alpha)$
Three dimensional diffusion	
(Cylindrical geometry ot Ginstling–Brounshtein equation)	$[1-(2\alpha/3)]-(1-\alpha)^{2/3}$
Three dimensional diffusion	
(Spherical geometry or Jander equation)	$[1-(1-\alpha)^{1/3}]^2$
4.2 Based on geometric symmetry	
Contracting area (or cylindrical symmetry)	$1-(1-\alpha)^{1/2}$
Contracting volume (or spherical symmetry)	$1-(1-\alpha)^{1/3}$

data to within the experimental error even though the reaction mechanism does not obey the equation. In such a case care must be taken to insure the uniqueness of the results. In case of reactions with enthalpy changes, the results may be extended to DTA and DSC through the assumption that the rate is proportional to $\Delta T/A_r$ or dH/dT. Where ΔT is the observed temperature difference between the sample and reference substance temperature, A_r is the area under the thermal trace and H is the enthalpy of the reaction.

Accuracy of the integral approximations

The right-hand side of Eq. (4) is known as the temperature integral or the exponential integral and is not analytically integrable. For large values of E/RT, Coats and Redfern [7] approximated the integral by the relation

$$\int_0^T \exp\left(-E/RT\right) dT = \frac{RT^2}{E}\left(1 - \frac{2RT}{E}\right)\exp\left(-E/RT\right) \tag{5}$$

Coats and Redfern [7] obtained this solution for the temperature integral by approximating the sum of the first three terms of asymptotic series. Figure 1 com-
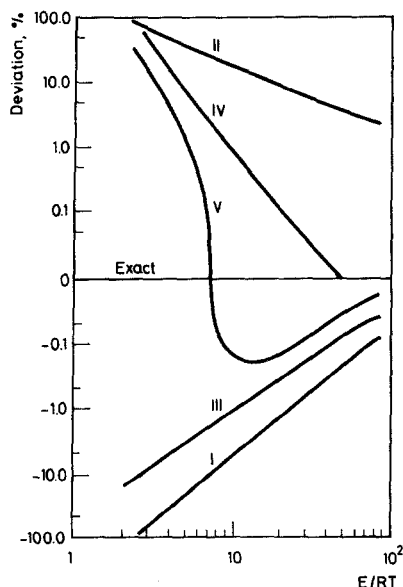

Fig. 1 Logarithm of % deviation of various temperature integral approximations versus logarithm of the E/Rt ratio. Symbols: I – Coats and Redfern (Eq. (5)), II – preliminary approximation (Eq. (7)), III – Gorbachev or first approximation (Eq. (8)), IV – Li or second approximation (Eq. (9)), and V – this work (Eq. (11))

pares the deviations of the Coats and Redfern approximation [7] from the exact solution for various values of E/RT. Figure 1 compares the logarithm of % deviation from the exact solution versus logarithm of the E/RT ratio because it is more sensitive and brings out more details than a plot of % deviation versus the E/RT ratio. The exact value of the temperature integral was independently obtained by numerically integrating the integral using the $1/3^{rd}$ Simpsons rule and the $1/4^{th}$ Trapezoidal rule. Agreement between the Simpson, Trapezoidal and the mathematical tables of Abramowitz and Stegun [8] proved the preciseness of the reference values. The results summarized in Fig. 1 indicates that the Coats and Redfern approximation underpredicts the value of the temperature integral for all values of E/RT. For E/RT ratio of over 80, Coats and Redfern equation deviates from the exact solution by less than 0.1%. However, the deviation is greater than 1% for E/RT ratio less than 23 and greater than 10% for E/RT ratio less than 6.

Alternatively, the temperature integral can be expanded and integrated by parts to yield the following equation

$$\int \left(1 + \frac{2RT}{E}\right) \exp\left(-E/RT\right) = \frac{RT^2}{E} \exp\left(-E/RT\right) \tag{6}$$

If as a preliminary approximation, it is assumed that $2RT/E$ is much less than unity and hence neglected, than Eq. (6) can be written as:

$$\int \exp\left(-E/RT\right) = \frac{RT^2}{E} \exp\left(-E/RT\right) \tag{7}$$

A comparison of deviations of the preliminary approximation from the exact solution indicates that Eq. (7) overestimates the value of the temperature integral and is a very poor approximation with a deviation of over 2% for an E/RT ratio of 80. At lower values of the E/RT ratio the deviations are significantly higher. Hence, this equation is not suited for modeling nonisothermal reactions. In order to improve the approximation, if it is assumed that the ratio $2RT/E$ is very much less than unity and, that the value of $(1 + 2RT/E)$ to be in the neighbourhood of unity such that it can be assumed to be constant. With these assumptions the term $(1 + 2RT/E)$ can be taken out of the integral and Eq. (6) may be approximated as

$$\int \exp\left(-E/RT\right) dT = \frac{RT^2}{E} \left[\frac{1}{1 + 2RT/E}\right] \exp\left(-E/RT\right) \tag{8}$$

This equation was suggested by Gorbachev [9] to be more accurate than the equation of Coats and Redfern [7]. Figure 1 summarizes the deviations of the Gorbachev approximation from the exact solution and reaffirms the findigs of Gorbachev [9]. The Gorbachev equation underestimates the value of the

temperature integral for all values of the E/RT ratio. The deviation is less than 0.1% for E/RT ratio greater than 41 and less than 1% for E/RT ratio greater than 11.

Li [10], in order to improve the approximation integrated the temperature integral twice to arrive at the equation:

$$\int \exp\left(-E/RT\right) dT = \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-6(RT/E)^2}\right]\exp\left(-E/RT\right) \qquad (9)$$

Figure 1 indicates that this second approximation of Li overestimates the values of the temperature integral. For this equation the deviation is less than 0.1% for E/RT ratio greater than 21 and less than 1% for E/RT ratio greater than 9.

Multiplying the numerator and denominator of Eq. (8) by $(1-2RT/E)$ we obtain

$$\int \exp\left(-E/RT\right) dT = \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-4(RT/E)^2}\right]\exp\left(-E/RT\right) \qquad (10)$$

A comparison of Eqs (9) and (10) indicates a striking resemblence. The only difference being the integers of the term $(RT/E)^2$ in the denominator. The integer 4 in the denominator of Eq. (10) results in an under prediction of the temperature integral, whereas the integer 6 results in an over prediction of the temperature integral. Hence, to minimize these deviations we replaced the integer by 5. The temperature integral can now be approximated as

$$\int \exp\left(-E/RT\right) dT = \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-5(RT/E)^2}\right]\exp\left(-E/RT\right) \qquad (11)$$

From Fig. 1 it can be seen that the proposed approximation yields a deviation of less than 0.1% for E/RT ratio greater than 7. For E/RT ratio less greater than 5. For E/RT ratio less than 5, the best value of the number multiplying the term $(RT/E)^2$ in the denominator of equation (11) is between 4 and 5. For high values of E/RT, the approximations of Coats and Redfern, Gorbachev, Li and this work yield comparable results.

Table 2 Percent absolute deviations of various approximations

Equation	Value of E/RT ratio			
	5	10	25	50
Preliminary approximation (Eq. (7))	34.8	18.0	7.6	3.9
Coats and Redfern (Eq. (5))	18.5	5.0	0.9	0.23
Gorbachef (Eq. (8))	3.4	1.2	0.25	0.07
Li (Eq. (9))	6.5	0.8	0.06	0.007
This work (Eq. (11))	1.3	0.18	0.09	0.03

Table 2 summarizes the results of various proposed approximations of the temperature integral. Our studies indicate that the proposed equation is more accurate than the previously proposed equations. Since the proposed approximation is accurate to within 0.2% for E/RT ratio greater than 6, it may be used in combination with various equations summarized in Table 1 for modeling nonisothermal reactions.

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Zusammenfassung — Basierend auf früher mitgeteilten Näherungslösungen für das Temperaturintegral wird eine neue Näherung

$$\int \exp(-E/RT)\,dT = \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-5(RT/RT/E)^2}\right]\exp(-E/RT)$$

zur Modellierung nicht-isothermer Reaktionen vorgeschlagen. Es wurde festgestellt, daß die Gleichung von Coats und Redfern für E/RT-Verhältnisse größer als 23 um weniger als 1%, für E/RT-Verhältnisse größer als 6 dagegen um weniger als 10% von der exakten Lösung abweicht. Die exakte Lösung wurde unabhängig durch Lösung des exponentiellen Temperaturintegrals auf numerischem Wege nach der Simpson-Regel und der Trapezoid-Regel erhalten. Die Gorbachev-Gleichung weicht bei E/RT-Verhältnissen größer als 41 um weniger als 0.1%, bei E/RT-Verhältnissen größer als 11 um weniger als 1% ab. Die Li-Gleichung weight bei E/RT-Verhältnissen größer als 21 um weniger als 0.1%, bei E/RT-Verhältnissen größer als 9 um weniger als 1% ab. Die vorgeschlagene Gleichung weicht bei E/RT-Verhältnissen größer als 7 um weniger als 0.1%.

Резюме — На основе ранее сообщенных приближений для интеграла температуры, для модельных неизотермических реакций предложено́ новое уравнение:

$$\int \exp(-E/RT)\, dT = \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-5(RT/E)^2}\right]\exp(-E/RT)$$

Найдено, что уравнение Коутса–Рэдферна отклоняется менее, чем на 1% от точного решения числового отношения E/RT более 23 и менее 10% при численном отношении E/RT более 6. Точное решение температурного интеграла было получено двумя независимыми числовыми методами: по правилу Симпсона и правилу трапезоиды. Уравнение Горбачева отклоняется менее 0,1% при E/RT больше 41 и менее 1% — при E/RT больше 11. Уравнение Ли отклоняется менее 0,1% при E/RT больше 21 и менне 1% — для E/RT больше 9. Предложенное новое уравнение отклоняется менее 0,1% при E/RT равным 7.