R & D NOTES

An Integral Approximation Formula for Kinetic Analysis of Nonisothermal TGA Data

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INTRODUCTION

The main objective of this study is to present a precise integral approximation formula for kinetic analysis of nonisothermal thermogravimetric analysis (TGA) data. Three basic approaches to the analysis of nonisothermal TGA data have been discussed in the literature, although the integral method seems to be best (Lee and Beck, 1984). The Coats and Redfern (1964) equation has been used as an approximation formula for the integral method but is not as precise as desired. A new integral approximation formula was derived by Lee and Beck (1984) that was more precise than the Coats and Redfern equation. Comparisons shown in Figures 1 to 4 of the paper by Lee and Beck (1984) show that their equation is superior to the Coats and Redfern equation for all cases. Results also showed that both approximations reflect negative deviations in all cases. Integral approximation methods in this note were derived in order to reduce the negative deviations and to improve the preciseness of the approximation. They are also simple and easily applied. For easy comparison, the notation and the procedures used to derive the formulas in this note are the same as those of Lee and Beck (1984).

Thermogravimetric analysis provides a semiquantitative understanding of pyrolysis by the use of fine particles and small sample size. The thermal behavior of coal, wood, and related biomass is frequently studied by measuring the rate of weight loss of the material as a function of time and temperature. The knowledge of kinetic behavior is essential for understanding and predicting the thermal conversion processes. A proposed reaction mechanism is used to estimate activation energies and frequency factors for Arrhenius type reaction rate expressions with measured data. The ranges of parameters to be used from previous pyrolysis studies can be found in Table 1 of the paper by Lee and Beck (1984).

DERIVATION OF APPROXIMATION FORMULAS

Pyrolysis of a solid is a typical irreversible chemical reaction. The stoichiometric equation for such a reaction can be described as

$$sS_{(s)} \rightarrow rR_{(s)} + vV_{(g)}$$

where S, R, and V are the original solid, final solid residue, and

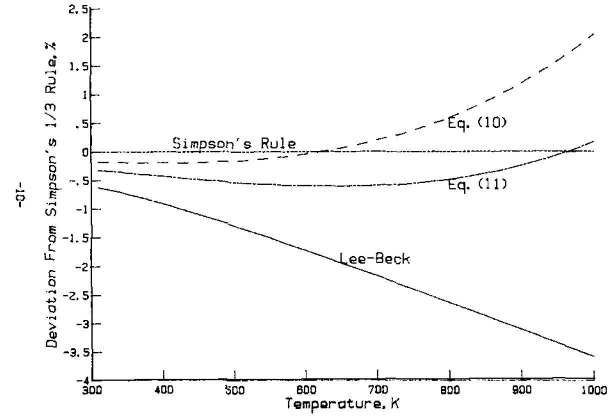

Figure 1. Comparison of approximation methods (E = 40 kJ/mol).

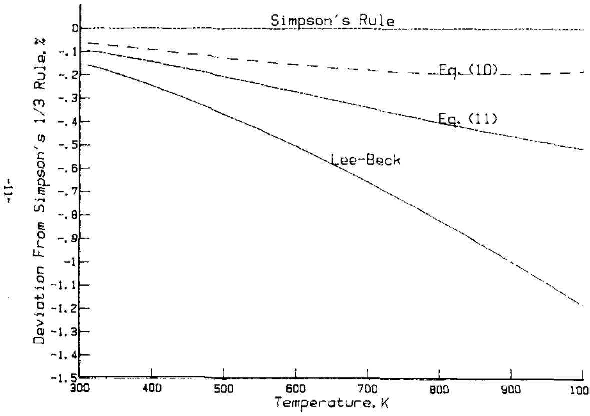

Figure 2. Comparison of approximation methods (E = 85 kJ/mol).

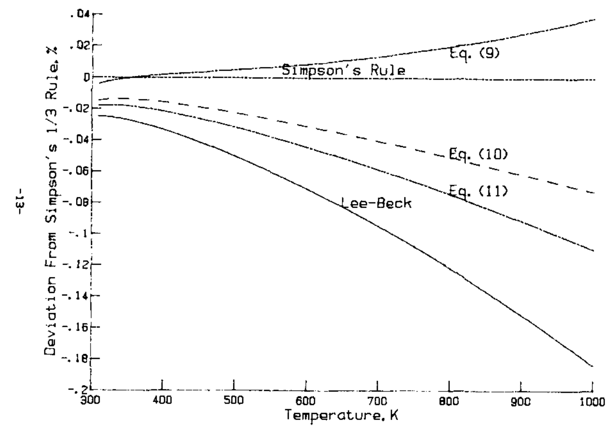

Figure 3. Comparison of approximation methods (E = 170 kJ/mol).

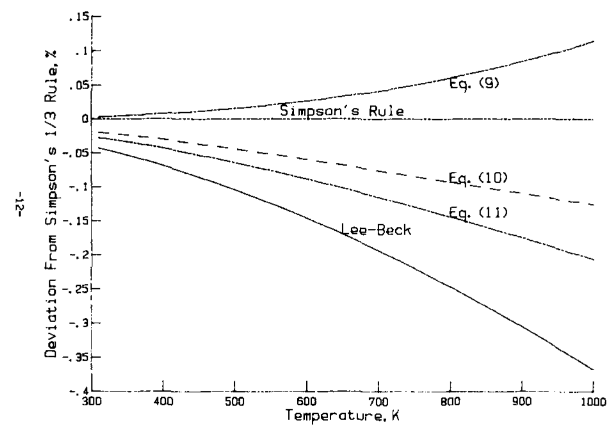

Figure 4. Comparison of approximation methods (E = 250 kJ/mol).

volatile matter, and s, r, and v are the coefficients of the stoichiometric equation, respectively.

The decomposition rate of a solid can be represented by the general rate expression as

$$\frac{d\omega}{dt} = kf(\omega) \qquad (1)$$

where ω is the decomposed fraction of solid at time t, $f(\omega)$ is a function of ω depending on the reaction mechanism, and k is the rate constant given by the Arrhenius equation for nonisothermal chemical reaction as

$$k = A\exp(-E/RT) \qquad (2)$$

where A = frequency factor, E is activation energy, R is the universal gas constant (8.314 J/mol·K), and T is the absolute temperature.

For a linear heating rate, say β K/s, the following relationship is valid:

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

Combining Eqs. 1, 2 and 3 and integrating between the initial temperature T_o and any final temperature T, and conversion between ω_o and ω respectively, the result can be stated as

$$\int_{\omega_0}^{\omega}\frac{d\omega}{f(\omega)} = \frac{A}{\beta}\int_{T_0}^{T}\exp(-E/RT)dT \qquad (4)$$

As with Lee and Beck (1984), the main objective of this study is to find the precise approximation solution for the right-hand side integral form of Eq. 4. To obtain the solution of the integral on the left-hand side, one can refer to the mechanisms given in chemical reaction engineering textbooks such as by Levenspiel (1972).

The right-hand side of Eq. 4 is not analytically integrable. From integration by parts, one can arrive at

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

Since $2RT/E$ is much less than unity at moderate temperatures and high activation energies, the value of $(1 + 2RT/E)$ is in the neighborhood of unity. Therefore, $(1 + 2RT/E)$ in the left-hand side of Eq. 5 can be assumed a constant. From Eq. 5 one can arrive at the approximate integral solution as

$$\int\exp(-E/RT)dT \approx \frac{\frac{RT^2}{E}\exp(-E/RT)}{1+\frac{2RT}{E}} \qquad (6)$$

From Eq. 6, Lee and Beck obtained their final approximate solution as

$$\int_{T_0}^{T}\exp(-E/RT)dT \approx \frac{\frac{RT^2}{E}\exp(-E/RT)}{1+\frac{2RT}{E}} - \frac{\frac{RT_0^2}{E}\exp(-E/RT_0)}{1+\frac{2RT_0}{E}} \qquad (7)$$

But it should be noted that their solution yields a negative deviation from the numerical solution for all cases in their paper. The analysis presented in this note is intended to improve preciseness by reducing the negative deviations of the Lee and Beck equation. From the righthand side of Eq. 4, applying integration by parts twice, one can arrive at

$$\int\left[1 - 3!\left(\frac{RT}{E}\right)^2\right]\exp(-E/RT)dt = T\left[\frac{RT}{E} - 2!\left(\frac{RT}{E}\right)^2\right]\exp(-E/RT) \qquad (8)$$

Using the same procedure used to obtain Eq. 7, Eq. 8 can be rewritten as

$$\int_{T_0}^{T}\exp(-E/RT)dT \approx \frac{\frac{RT}{E} - 2\left(\frac{RT}{E}\right)^2}{1-6\left(\frac{RT}{E}\right)^2}T\exp\left(-\frac{E}{RT}\right) - \frac{\frac{RT_0}{E} - 2\left(\frac{RT_0}{E}\right)^2}{1-6\left(\frac{RT_0}{E}\right)^2}T_0\exp\left(-\frac{E}{RT_0}\right). \qquad (9)$$

Q_1 and Q_2 are used to represent the right-hand sides of Eqs. 7 and 9, respectively.

Two methods are developed to obtain a more precise solution of $\int_{T_0}^{T}\exp(-E/RT)dT$ in this note. The first method makes use

TABLE 1. EFFECT OF ACTIVATION ENERGY AND TEMPERATURE ON APPROXIMATION METHODS

Apparent Activation Energy, kJ/mol	Deviation from Simpson's ⅓ Rule, % 700 K Lee-Beck	Eq. 9	Eq. 10	Eq. 11	900 K Lee-Beck	Eq. 9	Eq. 10	Eq. 11
40	−2.17		0.20	−0.59	−3.11		1.19	−0.25
85	−0.66		−0.18	−0.34	−1.00		−0.19	−0.46
170	−0.19	0.04	−0.08	−0.12	−0.31	0.09	−0.11	−0.18
250	−0.10	0.01	−0.04	−0.06	−0.15	0.03	−0.06	−0.09

of the fact that the asymptotic series solutions for Q_1 and Q_2 are, respectively, smaller and larger than the true solutions, because the terms in the asymptotic series alternate between positive and negative values. Therefore, the average of Q_1 and Q_2 is probably closer to the true solution than either Q_1 or Q_2. Thus we can say that

$$\int_{T_0}^{T} \exp(-E/RT)dT \approx \frac{1}{2}(Q_1 + Q_2) \qquad (10)$$

The solution of Eq. 10 will reduce the negative deviation of Eq. 7.

The second method is similar to the first, except that Q_1 is weighted more heavily than Q_2 in arriving at the solution. Thus, for method 2 we can write

$$\int_{T_0}^{T} \exp(-E/RT)dT \approx (2Q_1 + Q_2)/3 \qquad (11)$$

to reduce the negative deviation of the Lee-Beck equation.

RESULTS AND DISCUSSION

The objective of this analysis is to compare the proposed methods shown in Eqs. 10 and 11 with Lee and Becks' integral approximation formula as shown in Eq. 7. As in Lee and Beck's paper, four different activation energies (40, 85, 170, and 250 KJ/mole) of realistic kinetic parameters are chosen for comparison. The temperature ranges from 300 to 1,000 K. Figures 1 to 4 show the comparison between the Lee-Beck approximation (Eq. 7) and the present approximations (Eqs. 10 and 11). Simpson's ⅓ rule is used to calculate the reference value with a finite interval of 1 K. The numerical integration is computed by every ten intervals (i.e., 10 K) for making the comparison graphs. All numerical values were computed on an HP-86 microcomputer and plotted on an HP-7470A plotter as shown in Figures 1 to 4. For all cases, both proposed methods are superior to the Lee-Beck formula.

A low activation energy or a high temperature will result in a large value of $(2RT/E)$, which will lead to a larger deviation from the reference value. Table 1 illustrates how the activation energy and temperature affect the approximations.

The maximum absolute deviation is 3.6% for the Lee and Beck formula (Eq. 7), and 2.0% for the proposed method 1 (Eq. 10), and 0.6% for the proposed method 2 (Eq. 11). An increase in accuracy is the greatest advantage of these newly developed approximations. In addition, these equations retain simplicity in calculation and formulation. It is also found that Eq. 11 is superior at lower activity energy and Eq. 10 is superior at higher activation energy in terms of percentage deviation.

It should be noted that the approximation solution given by Eq. 9 is superior to the solution of Eqs. 10 and 11 at high activation energies and is poor at low activation energies. This is because the asymptotic series Q_2 converges to the true solution very rapidly for high activation energies but not for low activation energies. Comparisons of different methods for high activation energies are shown in Figures 3 and 4.

NOTATION

A = Arrhenius frequency factor
E = apparent activation energy, kJ/mol
k = reaction rate constant, s^{-1}
Q_1 = dummy, used to represent the right-hand side of Eq. 7
Q_2 = dummy, used to represent the right-hand side of Eq. 9
r = stochiometric coefficient of char residue
$R_{(s)}$ = char residue
R = gas constant, 8.314 J/mol·K
s = stoichiometric coefficient of unreacted solid
$S_{(s)}$ = unreacted solid
t = time, s
T = absolute temperature, K
v = stoichiometric coefficient of volatile pyrolysis products
$V_{(g)}$ = volatile pyrolysis products

Greek Letters

β = heating rate, K/s
ω = fraction of solid pyrolyzed

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