Integral Approximations for Nonisothermal Kinetics

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In the past decade there has been an accelerated use of thermal analysis techniques to investigate the kinetics of various carbonaceous materials (Antal, 1983; Dickens and Flynn, 1983; Howard, 1981; Johnson, 1979; Milne, 1981; Wendlandt, 1974) and inorganic materials (Brown et al., 1980). One of the most popular thermal analysis techniques is probably thermogravimetry (TG). In most reported TG studies the temperature of the sample is linearly increased. A knowledge of the activation energy and the frequency factor can then be obtained from various approximations of the temperature integral. The integral approximation of the temperature integral is generally believed to be convenient, reliable, and more accurate than either the differential method or the series expansion method (Flynn and Wall, 1966). Consequently, extensive efforts have been devoted to yield better integral approximations of the temperature integral (Balarin, 1977; Gyulai and Greenhow, 1973, 1974; Gorbachev, 1975, 1976, 1977; Norwisz and Hajduk, 1978; Senum and Yang, 1977; Zsako, 1975). Recently two interesting articles have addressed the problem of the temperature integral (Lee and Beck, 1984; Li, 1985). Unfortunately the studies of Lee and Beck and Li have overlooked some previous developments in this area. The "new" approximation of the temperature integral proposed by Lee and Beck was in fact suggested earlier by Gorbachev (1975). The aim of this note is to report on the development of a better approximation of the temperature integral based on the earlier studies.

Integral Approximations

The temperature integral, $\int \exp(-E/RT)\,dT$, is obtained when the temperature is increased at a constant rate (Flynn and Wall, 1966; Li, 1985). The temperature integral is not analytically integrable. For high values of E (>250 kJ/mol), the integral can be approximated as

$$\int_0^T \exp(-E/RT)\,dT = \frac{RT^2}{E}\exp(-E/RT) \qquad (1)$$

This integral approximation yields poor results for low-value E reactions. Coats and Redfern (1964) improved the approximation by replacing the integral by the relation:

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

Coats and Redfern obtained this solution for the temperature integral by approximating the sum of the first three terms of the asymptotic series. In 1975, Gorbachev suggested that the first approximation of the temperature integral is

$$\int_0^T \exp(-E/RT)\,dT = \frac{RT^2}{E}\left(\frac{1}{1+2RT/E}\right)\exp(-E/RT) \qquad (3)$$

The first approximation, Eq. 3, has been reported to be more accurate than the equation of Coats and Redfern (Balarin, 1977; Gorbachev, 1975, 1977; Senum and Yang, 1977). In a recent article Lee and Beck (1984) integrated $\int \exp(-E/RT)\,dT$ and showed the first approximation to be Eq. 3. The results of Lee and Beck indicates that Eq. 3 is a better approximation than Eq. 2 for E ranging from 40 to 250 kJ/mol over the temperature range 300–1,000 K. Lee and Beck also reported that both Eq. 2 and Eq. 3 reflected negative deviations from the

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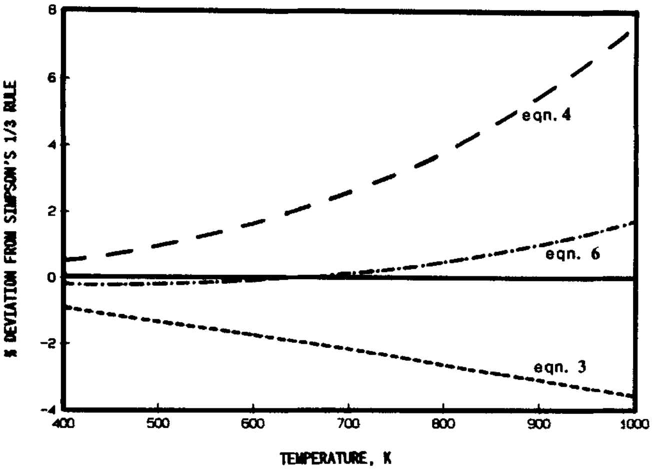

Figure 1. Comparison of approximation methods, $E = 40$ kJ/mol.

exact solution. Following up on this finding, Li (1985) reported that the second approximation is

$$\int_0^T \exp(-E/RT)\,dT = \frac{RT^2}{E}\left[\frac{1 - 2(RT/E)}{1 - 6(RT/E)^2}\right]\exp(-E/RT) \quad (4)$$

The results of Li indicate that the second approximation yields positive deviations. Since the first approximation yields negative deviations and the second positive, Li suggested that the average and weighted average of Eqs. 3 and 4 could yield better results. The ideal weight factor was however reported to be dependent on the value of E. Since in pyrolysis studies the value of E may not always be available, this application could be limited. Further it is not an elegant way to use results from two independent equations. Therefore, we investigated further to understand the reason for both negative and positive deviations. In our study we found that by multiplying the numerator and denominator of Eq. 3 by $(1 - 2RT/E)$ we obtain

$$\int_0^T \exp(-E/RT)\,dT = \frac{RT^2}{E}\left[\frac{1 - 2(RT/E)}{1 - 4(RT/E)^2}\right]\exp(-E/RT) \quad (5)$$

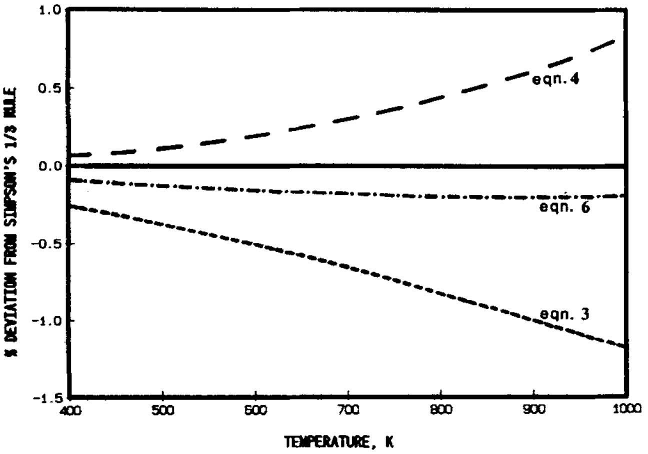

Figure 2. Comparison of approximation methods, $E = 85$ kJ/mol.

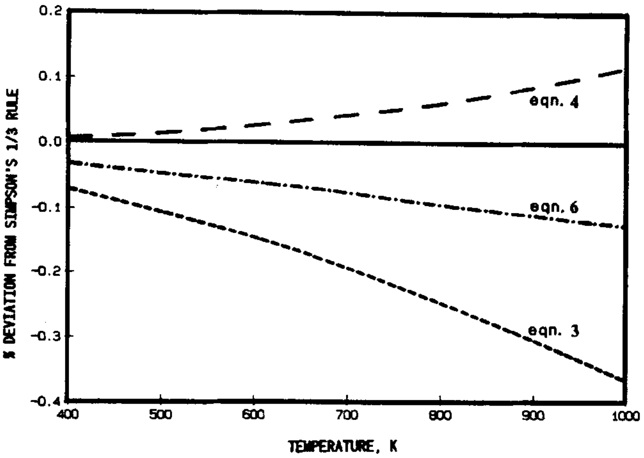

Figure 3. Comparison of approximation methods, $E = 170$ kJ/mol.

A comparison of Eqs. 4 and 5 indicates a striking resemblance, the only difference being the integers of the term $(RT/E)^2$ in the denominator. The integer 4 in the denominator of Eq. 5 yields negative deviations, whereas the integer 6 yields positive deviations. Hence to minimize these deviations we replaced the integer by 5. The temperature integral can now be written as

$$\int_0^T \exp(-E/RT)\,dT = \frac{RT^2}{E}\left[\frac{1 - 2(RT/E)}{1 - 5(RT/E)^2}\right]\exp(-E/RT) \quad (6)$$

In the following section a comparison of Eqs. 3, 4, and 6 to the exact solution is made.

Results and Discussion

For comparison purposes, we examined four values of E(40, 85, 170, and 250 kJ/mol) over the temperature range 300–1,000 K. This range of parameters has been studied previously by Lee and Beck (1984) and Li (1985) and probably covers the extreme values of reported experimental conditions. Figures 1 through 4 show comparisons for the first approximation, Eq. 3, second approximation, Eq. 4, and the proposed approximation, Eq. 6. Simpson's one-third rule was used to calculate the reference values of the temperature integral. For all cases the proposed Eq. 6 is superior to both the first and the second approximations. The maximum absolute deviation for the range examined in this study is 3.6% for the first approximation, 7.7% for the second approximation, and 1.7% for the proposed approximation. To match with the exact solution, we found that multiplication factors of 5.0, 5.3, 5.6, and 5.7 best represented the reactions with E's of 40, 85, 170, and 250 kJ/mol, respectively. However if the

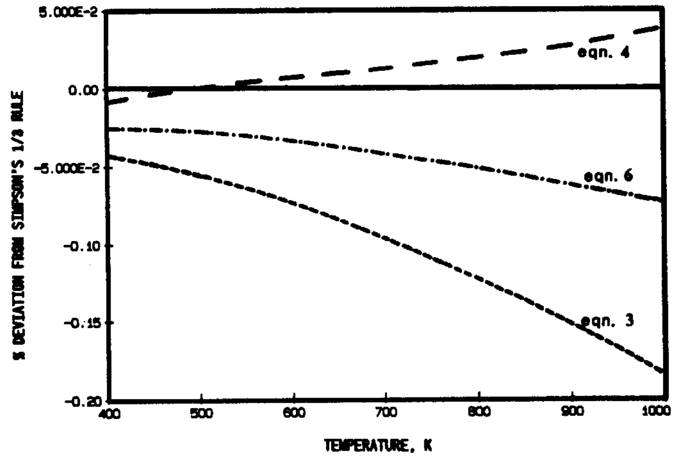

Figure 4. Comparison of approximation methods, E = 250 kJ/mol.

value of E is not known *a priori*, then the use of a multiplication factor of 5 is recommended since it yields deviations of less than 0.2% for higher E reactions.

A comparison of the average and weighted averages of Eqs. 4 and 5 suggested by Li (1985) was also found to be inferior to the proposed approximation in the range studied. However, the weighted average was found to yield slightly better results at high temperatures for the low-E reaction. For the high-E reaction the results of the first, second, and proposed approximations were less than 0.15%. Hence for a high-E reaction any of these three approximations will yield reasonable results.

Notation

E = activation or apparent activation energy, kJ/mol
R = gas constant, 8.314 kJ/mol
T = absolute temperature, K

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