LETTERS TO THE EDITOR

Editor's Note:

The following letter also pertains to the R&D Note in this issue by R. K. Agrawal and M. S. Sivasubramanian. Dr. Agrawal has informed me that the reduction to the exponential integral was also demonstrated by Doyle (1961) and by Zsako (1968), as well as by earlier authors. This point regarding the equivalence to an easily-obtained tabulated function, with well-known asymptotic properties, has not been made in the recent literature on the subject that has appeared in *AIChE Journal;* hence it was decided to publish this letter.

Literature cited

Doyle, C. D., "Kinetic Analysis of Thermogravimetric Data," *J. Applied Poly. Sci.*, **5**, 285 (1961).

Zsako, J., "Kinetic Analysis of Thermogravimetric Data," J. Physical Chemistry, **72**, 2406 (1968).

To The Editor:

Lee and Beck (**30** (3), p. 517, 1984) and Li (**31**(6), p. 1036, 1985), in their papers, presented a new integral approximation formula for kinetic analysis of nonisothermal TGA data and compared their results with the more previous Coats-Redfern approximation formula (1964). The two new integral approximation formulas have been shown to be superior to the Coats-Redfern approximation, but they still suffer deviations from the exact solutions. The integral that Lee and Beck and Li claim "not analytically integrable" can be solved by the generalized *n*th-order exponential integral technique.

The nonisothermal TGA kinetics, coupled with Arrhenius equation and linear heating rate, leads to the following equation:

$$\int_{\omega_o}^{\omega} \frac{d\omega}{f(\omega)} = \frac{A}{\beta} \int_{T_o}^{T} \exp(-E/RT)\, dT \quad (1)$$

The integral in the righthand side of Eq. 1 is solved by letting

$$\alpha = E/RT \quad \text{and} \quad \alpha_o = E/RT_o \quad (2)$$

Then

$$T = ER\alpha \quad \text{and} \quad dT = -(E/R)(d\alpha/\alpha^2) \quad (3)$$

Consequently, Eq. 1 becomes

$$\int_{\omega_o}^{\omega} \frac{d\omega}{f(\omega)} = -\frac{A}{\beta}\frac{E}{R} \int_{\alpha_o}^{\alpha} \exp(-\alpha)/\alpha^2\, d\alpha \quad (4)$$

It should be noted that Coats and Redfern did use this change of variable to arrive at Eq. 4, but they evidently did not realize that they thus had obtained a tabulated function. This is achieved by further noting that the *n*th-order exponential integral is defined by:

$$E_n(x) = x^{n-1} \int_x^{\infty} \exp(-t/t^n\, dt \quad \text{for} \quad n = 1, 2, 3, \ldots \quad (5)$$

Therefore, we obtain the second-order exponential integral

$$E_2(x/x = \int_x^{\infty} \exp(-t/t^2\, dt) \quad (6)$$

As a result, we have the analytical solution and Eq. 4 becomes

$$\int_{\omega_o}^{\omega} \frac{d\omega}{f(\omega)} = \frac{A}{\beta}[TE_2(\alpha) - T_oE_2(\alpha_o)] \quad (7)$$

It must be recognized that the second-order exponential integral is a well documented and tabulated function and, therefore, no numerical integration is required (e.g., Abramowitz and Stegun, 1965). In addition, the function can be calculated by digital computers. Accuracy to at least nine decimal points can be obtained through efficient computational algorithm. It takes only about 25 lines in a language such as FORTRAN. Using exact solution as the reference values, the approximate solutions obtained separately by Coats-Redfern, Lee-Beck, and Li are compared. A portion of the results is shown in Table 1.

Notation

A = Arrhenius frequency factor
E = apparent activation energy, kJ/mol
$E_n(x)$ = *n*th-order exponential integral
$E_2(x)$ = second-order exponential integral
$f(\omega)$ = a function of ω depending on reaction mechanism
R = gas constant, 8.314 J/mol · K
T_o = initial temperature, K
T = final temperature, K

Greek letters

α = dummy variable, defined by Eq. 2
α_o = dummy variable, defined by Eq. 2
β = heating rate, K/s
ω = fraction of solid pyrolyzed

Literature cited

Coats, A. W., and J. P. Redfern, "Kinetic Parameters from Thermogravimetric Data," *Nature*, **201**, 68 (Jan. 4, 1964).

Abramowitz, M., and I. A. Stegun, Eds., *Handbook of Mathematical Functions*, Dover (1965).

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Table 1. Effect of Activation Energy and Temperature on Approximation Methods

Apparent Activation Energy, kJ/mol	Deviation from Exact Solution, %					
	700 K			900 K		
	Coats-Redfern	Lee-Beck	Li	Coats-Redfern	Lee-Beck	Li
40	−10.5	−2.17	2.57	−16.7	−3.11	5.48
85	−2.52	−0.66	0.30	−4.07	−1.00	0.61
170	−0.66	−0.19	0.04	−1.08	−0.31	0.09
250	−0.31	−0.10	0.01	−0.51	−0.15	0.03