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A RATIONAL FRACTION APPROXIMATION TO THE TEMPERATURE INTEGRAL IN NON-ISOTHERMAL KINETICS *

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ABSTRACT

A new method for deriving the Arrhenius activation energy from dynamic thermal analysis measurements is described. The method utilizes a rational fraction approximation for the temperature integral and is especially suitable for use when the activation energy has a small value. When used iteratively, the approximation converges quickly and gives essentially the exact result. The approximation can also be further simplified to permit the activation energy to be obtained from the experimental data as the solution to a quadratic equation. The method is illustrated by deriving the activation energies, from dynamic differential scanning calorimetry data, for the cures of an epoxy resin and a commercial epoxy film adhesive.

Non-isothermal methods of thermal analysis have been used increasingly to obtain the kinetic parameters for reacting systems. A recent review [1] has summarized many of the techniques employed in this pursuit. The goal of non-isothermal kinetics is to derive a rate law that describes the time development of the extent of a reaction as a function of temperature. Assuming Arrhenius behavior, the general form of this rate law is

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \tag{1}$$

where A and E are the Arrhenius pre-exponential factor and activation energy, respectively, α is the extent of reaction and $f(\alpha)$ is a function of α alone that depends on the reaction mechanism. In many cases of practical interest, for example time–temperature shifting of experimental data, only the activation energy is required. Thus, the determination of E will be the major focus of this report.

The method for abstracting E from the dependence of a reaction's thermal behavior on heating rate has been previously detailed [2]. Briefly, if a reactive system is subjected to a linear temperature program of heating rate

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ϕ, then temperature is related to time by $T = \phi t$ and

$$\frac{d\alpha}{dT} = \frac{A}{\phi} e^{-E/RT} f(\alpha) \tag{2}$$

Separating the variables and integrating to a fixed conversion α yields

$$\int_0^{\alpha} \frac{d\alpha'}{f(\alpha')} = C = \frac{A}{\phi} \int_0^T e^{-E/RT} dT \tag{3}$$

where C is a constant independent of heating rate and it is assumed that no reaction occurs prior to the onset of the exotherm. The activation energy is obtained from the variation of the temperature to a constant α as a function of ϕ. The main difficulty arises in evaluating the temperature integral in eqn. (3). Approximation schemes such as continued fraction representations [3] and asymptotic expansions [4] as well as numerical integration have been used to analyze non-isothermal kinetic data. One widely used approximation technique is Doyle's method [5] which approximates the logarithm of the temperature integral by a straight line. Corrections for nonlinearity have been provided by Flynn [6] and this method serves as the basis of the ASTM E-693 standard for determining E. Doyle's method as well as the series approximations are adequate when $x = E/RT$ is fairly large: $20 \leqslant x \leqslant 60$. For smaller values of x, however, these methods become more cumbersome as more terms in the series representations or more iterations in their evaluation are required. This report describes a rational fraction approximation to the temperature integral that is easily implemented and is particularly useful for small values of x.

Consider the expression in eqn. (3). Making a change in variables $x = E/RT$ and integrating by parts gives

$$C = \frac{AE}{\phi R}\left[\frac{e^{-x}}{x} - \int_x^{\infty} \frac{e^{-x}}{x} dx\right] = \frac{AE}{\phi R}\left[\frac{e^{-x}}{x} - E_1(x)\right] \tag{4}$$

where $E_1(x)$ is the exponential integral function. A rational approximation for $E_1(x)$ is given by [7]

$$E_1(x) = \frac{e^{-x}}{x} g(x) = \frac{e^{-x}}{x}\left[\frac{x^2 + 4.03640x + 1.15198}{x^2 + 5.03637x + 4.19160} + \epsilon(x)\right] \tag{5}$$

For $10 \leqslant x \leqslant \infty$, $|\epsilon(x)| < 10^{-7}$ and since $g(x)$ is typically of the order of unity, the error term is completely negligible. With this approximation, eqn. (4) becomes

$$C = \frac{AT}{\phi} e^{-E/RT}[1 - g(E/RT)] \tag{6}$$

or rearranging and taking logs

$$\ln\left\{\frac{\phi}{T[1 - g(E/RT)]}\right\} = \frac{-E}{RT} + \ln\frac{A}{C} \tag{7}$$

For all practical purposes, eqn. (7) can be considered exact within the domain of the rational approximation. If $1 \leqslant x \leqslant 10$, a higher order rational expression [7] can be employed which will yield the same accuracy. Clearly, eqn. (7) can be used in an iterative manner to determine E. The approximation may be extended, however, to give E as the solution to a quadratic equation. Applying the binomial expansion to the denominator of $g(x)$ and evaluating the resulting expression gives

$$1 - g(x) \approx \frac{1}{x}\left[1 - \frac{2}{x} + \dots\right] \tag{8}$$

and

$$\ln\left[\frac{\phi}{T^2}\right] = \ln\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} + \ln\frac{AR}{CE} \tag{9}$$

which is recognized as the Coats–Redfern approximation [8]. Representing $\ln(1 - 2/x)$ by a Taylor series about $x = x_0$, where T_0 is the midpoint of the experimental temperature range, gives

$$\ln\left[1 - \frac{2}{x}\right] \approx \frac{-4}{x_0} + \frac{2x}{x_0^2} + \dots \tag{10}$$

and eqn. (9) becomes

$$\ln\left[\frac{\phi}{T^2}\right] = \left[\ln\left(\frac{CR}{AE}\right) - \frac{4RT_0}{E}\right] - \frac{E}{RT}\left[1 - 2\left(\frac{RT_0}{E}\right)^2\right] \tag{11}$$

Thus, for an experiment where the temperature to a fixed conversion is measured as a function of heating rate, the slope m of a $\ln(\phi/T^2)$ vs. $1/T$ plot is given by

$$m = -\frac{E}{R}\left[1 - 2\left(\frac{RT_0}{E}\right)^2\right] \tag{12}$$

The activation energy is then determined by solving the quadratic equation

$$E^2 + mRE - 2R^2T_0^2 = 0 \tag{13}$$

While this approximation will be quite good, in general, an alternative method that yields the exact result involves estimating E as $E = -mR$, using this value to compute $g(x)$ and refitting the data according to eqn. (7). This procedure converges very quickly and typically requires only a single iteration.

The above techniques are illustrated by determining E for the cure of two epoxy systems from dynamic differential scanning calorimetry (DSC) measurements. In the first case, a Bisphenol A type epoxy resin (Epirez 510) is cured with diethyltoluenediamine (DETDA, Ethacure 100) and the second system is a nitrile modified-dicyandiamide cured epoxy film adhesive (American Cyanamide FM123-5). All data were recorded with a Perkin-Elmer

TABLE 1

Heating rate dependence of the DSC exotherm peak position for Epirez 510 epoxy cured with diethyltoluenediamine and for FM123-5 film adhesive

Heating rate ($K\ min^{-1}$)	Peak position (K)	
	Epirez 510	FM123-5
2.5	426.8	396.8
5	445.1	405.9
10	463.6	416.0
20	485.3	427.2

DSC-2 that was interfaced to an LSI 11/23 microcomputer for data acquisition and analysis. The exotherm peak temperatures as a function of heating rate for Epirez 510 cured with DETDA and for FM123-5 are shown in Table 1 where it has been assumed that the conversion at the peak of a dynamic DSC scan is independent of heating rate [9]. Plots of $\ln(\phi/T^2)$ vs. $1/T$ were linear with correlation coefficients of -0.9999 and -0.9996, respectively. The activation energies for curing were obtained from the quadratic equation as well as from the exact iterative method and by use of Doyle's approximation with Flynn's corrections. In the latter case, correction factors were obtained by linear interpolation from the tables of Flynn [6]. The results for Epirez 510/Ethacure 100 and FM123-5 are shown in Tables 2 and 3, respectively, and cover the range of E/RT from 14 to 26. It is seen that the solution to eqn. (13) yields sensibly exact results over this range and requires neither iteration nor correction tables for its use.

In summary, a simple rational fraction approximation to the temperature integral in non-isothermal kinetics has been described. This expression gives essentially exact results and can be further expanded to give the Coats–Redfern approximation. From there, a quadratic equation is derived that permits the activation energy to be obtained from the heating-rate dependence of

TABLE 2

Determination of the activation energy ($kcal\ mol^{-1}$) for the cure of Epirez 510 epoxy resin with diethyltoluenediamine. The exact results are obtained from eqn. (7) and the quadratic equation results from eqn. (13)

Iteration	Doyle approximation	Exact	Quadratic equation
1	13.97	12.89	13.01
2	13.09	12.99	
3	12.99	12.99	
4	12.98		
5	12.98		

TABLE 3

Activation energy (kcal mol $^{-1}$) for the cure of FM123-5 epoxy film adhesive

Iteration	Doyle approximation	Exact	Quadratic equation
1	21.88	21.39	21.45
2	21.47	21.44	
3	21.44	21.44	
4	21.44		

dynamic thermal measurements. The method gives excellent results and is especially useful for small values of E/RT. For the case of Epirez 510 epoxy cured with Ethacure 100, $E/RT_0 \approx 14$ and the solution to the quadratic equation agrees with the exact value to within 0.2% which is well within experimental error. It is concluded that the proposed quadratic equation presents a simple yet reliable method for the rapid determination of the activation energy from non-isothermal kinetic measurements.

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