Analysis of non-isothermal reaction kinetics.
Part 1. Simple reactions

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Abstract

Owing to the compensation effect, multiple sets of Arrhenius parameters can be obtained from non-isothermal data. This leads to non-unique results and, hence, to criticisms of the non-isothermal methods. In this paper, procedures used to analyze non-isothermal data in order to obtain reliable Arrhenius parameters for simple reactions are discussed. The integral method has been found to yield reliable Arrhenius parameters from non-isothermal data. Concurrent use of the integral and the multiple heating-rate methods has been found to be a powerful tool for obtaining reliable results for both the order of reaction and the Arrhenius parameters.

INTRODUCTION

I am honored to participate in an issue dedicated to Joe Flynn. It was Flynn's publications [1] and the late Professor H.H.G. Jellinek's course on polymer degradation at Clarkson University that triggered my interest in non-isothermal reaction kinetics. Flynn has worked extensively on the kinetics of non-isothermal reactions (both simple and complex reactions) and was one of the first researchers to identify the problems of uniqueness with kinetic parameters obtained from non-isothermal analysis. Unfortunately, the problem of uniqueness has generally been ignored, resulting in an accumulation of unreliable results. In this paper the reliability of non-isothermal kinetics (in the light of the uniqueness problem) and its application in understanding the behavior of simple reactions are discussed. The non-isothermal kinetics of complex reactions is discussed in the companion paper.

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

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Non-isothermal methods generally involve heating the reactant at a constant rate from ambient temperature to a temperature sufficiently high so that the reactant undergoes transformation. In theory, all experiments conducted to measure the Arrhenius parameters are non-isothermal because they generally involve a change in temperature as a function of time, at least during the initial heating and cooling periods. Non-isothermal techniques are becoming extremely popular in the study of reaction kinetics. The popularity of non-isothermal methods is due to the fact that both analytical and kinetic data can be obtained simultaneously from a single experiment, and in a relatively short period of time. Unfortunately, the ease with which such data can be obtained has resulted in an increased volume of data and confusion, rather than an increase in the quality of research in thermal analysis [1]. Non-isothermal kinetic equations are mathematically more involved and, consequently, are not without problems. Several reviews have been published on the techniques used to obtain Arrhenius parameters from non-isothermal experiments [1–10].

The studies of Flynn and Wall [1] have indicated a problem of uniqueness with kinetic parameters from non-isothermal analysis. Unfortunately, the problem of uniqueness has generally been ignored resulting in unreliable results and in criticisms of non-isothermal methods [11–15]. For example, the reported values of the activation energy for the decomposition of the simple substance $CaCO_3$ range from about 20 to over 300 kcal mol^{-1}, and the calculated value of the rate constant varies by over three orders of magnitude [16]. Hence it is not surprising that the usefulness of Arrhenius parameters obtained from non-isothermal techniques is questioned. Recently, Boldyreva [12] criticized most of the non-isothermal kinetic information available in the literature and suggested that such kinetic information may be meaningless. Although this criticism may be strong (but not necessarily wrong), it does imply the need to establish a standard procedure to assure the reliability of kinetic data obtained from non-isothermal methods.

In this paper, the limitations of thermoanalytical devices will be discussed briefly, followed by a review of the reliability of non-isothermal kinetics (in the light of the uniqueness problem) and its application in understanding the behavior of simple reactions. The applications of non-isothermal techniques to complex reactions such as competitive, multiple and successive reactions will be dealt with elsewhere [17].

EXPERIMENTAL LIMITATIONS

Experimental techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC) are being used increasingly as analytical tools for the identification and characterization of solid materials, and also for determining kinetic parameters. To determine reliable kinetic parameters

from non-isothermal data, variables such as weight (or enthalpy), time and temperature need to be measured precisely. Although the weight (or enthalpy) and time can be measured with reasonable accuracy using modern thermal analysis devices, temperature measurement remains a serious problem in the case of TG balances [3,18–22]. This is because the measurement of the actual sample temperature in TG is difficult because it hinders the weighing mechanism. Therefore the thermocouple is not generally in contact with the sample and careful attention must be given to temperature measurement. The difference between the measured and the correct sample temperature may be as high as 45 K (if not more) depending on the experimental conditions. Although errors due to temperature measurement may be minimized by increasing the reaction temperature range and/or by placing the thermocouple close to the sample, calibration of the system under identical experimental conditions is a prerequisite for reliable results. Agrawal [19] has suggested that a temperature range of at least 70 K is desirable for reducing errors in estimating the Arrhenius parameters. For a reaction occurring over a temperature range of less than 70 K, errors due to uncertainties in temperature measurement can be significant. In such a case, detailed analysis of errors is desirable to reduce the uncertainty in estimated values of the Arrhenius parameters. In most modern devices, instrumental limitations are "believed" to have been minimized to yield acceptable data.

KINETIC ANALYSIS OF SIMPLE REACTIONS

For a well-defined set of experimental conditions, the shape of the non-isothermal curve obtained from thermoanalytical devices reveals the kinetic nature of the reaction being studied. A simple reaction is represented as

a → products

Because the reaction rate is proportional to the amount of reactant a at any time t, the reaction rate is assumed to be represented by the relation

$$d\alpha/dt = kf(\alpha) \tag{1}$$

where α represents the conversion of the reactant at time t, $f(\alpha)$ is the conversion factor of α, and k the rate constant. For a true reacting system, $f(\alpha)$ is a function of time and k is a function of temperature. In condensed phase studies, α is generally defined by the relation

$$\alpha = (W_0 - W)/(W_0 - W_f) \tag{2}$$

where W is the weight of the sample and the subscripts 0 and f refer to the values at the beginning and at the end of the weight-loss reaction. α varies

from 0 to 1 as the reaction proceeds to completion. The temperature dependence of the rate constant k is assumed to have the Arrhenius form

$$k = A \exp(-E/RT) \tag{3}$$

where A is the pre-exponential factor, E the activation energy and R the gas constant. The application of the Arrhenius equation to solid-state reactions has often been criticized in the literature. The misconceptions in the use of the Arrhenius equation have been referred to in detail by Flynn [23] and Agrawal [19,24,25]. For a simple reaction, the Arrhenius equation is appropriate provided $E > 2RT$ or $k < A \, e^{-2}$. Despite criticism of the use of the Arrhenius equation, it is perhaps the most widely used equation and is satisfactory in explaining the temperature dependence of the rate constant in solid-state decomposition kinetics.

Identifying the form of f(α) *and the order of reaction*

Identifying the correct form of $f(\alpha)$ to be used for kinetic analysis is not trivial; and identifying the true form of $f(\alpha)$ is critical for obtaining unique results. The simplest and the most frequently used model for $f(\alpha)$ in the analysis of non-isothermal data is

$$f(\alpha) = (1 - \alpha)^n \tag{4}$$

where n, in analogy to homogeneous chemical kinetics, is referred to as the order of reaction. Numerous forms of $f(\alpha)$ have been reported in the literature for the decomposition of solids [5,26–28]. These rate equations include processes such as chemical decomposition, nuclei growth and diffusion. The applicability of $f(\alpha)$ expressions used in nuclei growth and diffusion processes to non-isothermal reactions will be discussed in a subsequent publication [26]. Rate equations involving multiple use of α in the $f(\alpha)$ expression result in non-unique estimates of the kinetic parameters and should be avoided.

Although the data can be fitted by more than one form of $f(\alpha)$, the aim should be to select a model which uses the minimum number of parameters to fit the data with reasonable accuracy. Some forms of $f(\alpha)$ recommended for determining Arrhenius parameters involve using of reaction of (in order of preferred sequence) 0, 1, 2 or fractional orders, 1/2 or 2/3. Although other orders of reaction are possible, by using these orders of reactions the data can be linearized in most cases. For uniqueness of the results, no more than two parameters should be estimated from a single curve. Extraction of more parameters may lead to non-unique results which are meaningless. However if the decomposition products are measured, then additional parameters may be considered, depending on the accuracy of the data.
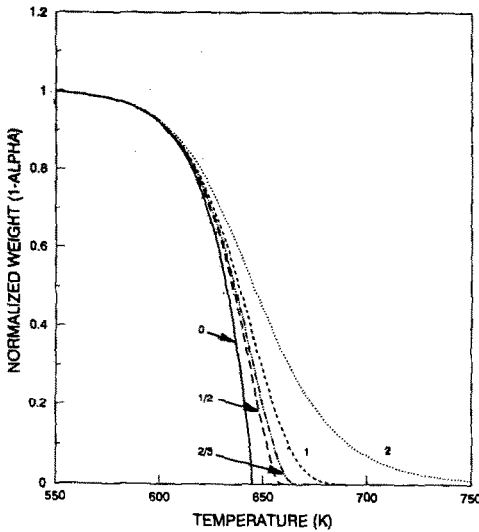
Fig. 1. Normalized weight fraction $(1 - \alpha)$ as a function of temperature for various orders of reaction ($A = 3.6 \times 10^{13}$ min^{-1}, $E = 40.0$ kcal mol^{-1} and $\beta = 20$ K min^{-1}).

Figure 1 summarizes the normalized residual weight as a function of temperature for various orders of reaction. This is the form of data obtained from thermal analysis devices and it is difficult to pin down the reaction order based on this limited information. However, the shape of the curve may be used to obtain preliminary information on the order of reaction. As the order of reaction increases from 0 to 2, the tail of the curve increases. Flynn [1] has shown that the peak width of a plot of $d\alpha/dT$ against temperature increases with an increase in the order of reaction (see Fig. 2). Also the amplitude of the peak decreases with an increase in the reaction order. However, because the maxima (in Fig. 2) of these reactions (with the same Arrhenius parameters) occur in a narrow temperature range it is difficult to identify uniquely the order of reaction. A plot of $d\alpha/dT$ versus conversion (α) or $(1 - \alpha)$ shows a clear difference in the order of reaction (Fig. 3).

The conversion at the maximum $d\alpha/dT$ is unique for a given order of reaction. However, at the maximum rate, owing to the fast reaction together with instrumental limitations, the errors in determining the temperature and conversion may be high. Analyzing the results of Kissinger [29], Flynn [1] has shown that at the maximum rate, expressions can be summarized as

$$n(1 - \alpha)^{n-1} \text{ at max rate} = 1 + (n - 1)2RT_{\text{max}}/E \qquad \text{for } n > 0 \text{ and } \neq 1$$

$$\tag{5}$$

$$-\ln(1 - \alpha) \text{ at max rate} = (1 - 2RT_{\text{max}}/E) \qquad \text{for } n = 1 \tag{6}$$
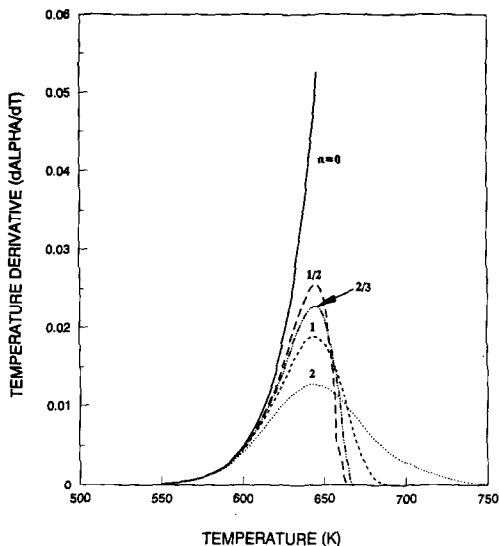
Fig. 2. Temperature derivative $(d\alpha/dT)$ as a function of temperature; data are shown in Fig. 1.

Based on these approximations, Table 1 summarizes the value of $(1-\alpha)_{max}$ as a function of various orders of reactions and E/RT ratio.

Figure 4 summarizes the order of reaction as a function of normalized weight at maximum rate $(1-\alpha)_{max}$ and E/RT ratio. At low values of
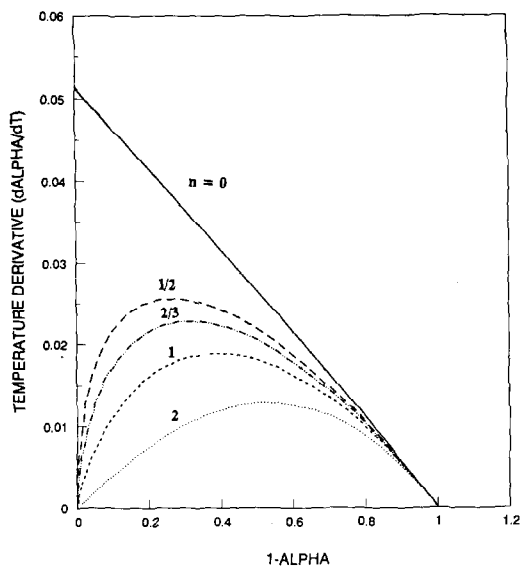

Fig. 3. Temperature derivative $(d\alpha/dT)$ as a function of normalized weight $(1-\alpha)$; data are shown in Fig. 1.

TABLE 1

Value of $(1 - \alpha)_{max}$ as a function of order of reaction and E/RT

Reaction order	$(1 - \alpha)$ at maximum rate					
	$E/RT = 10$	20	30	40	50	∞
1/2	0.3086	0.2770	0.2675	0.2630	0.2603	0.2505
1	0.4493	0.4066	0.3932	0.3867	0.3829	0.3686
3/2	0.5378	0.4900	0.4746	0.4669	0.4624	0.4453
2	0.6000	0.5500	0.5333	0.5250	0.5200	0.5010
3	0.6831	0.6325	0.6146	0.6055	0.6000	0.5785
4	0.7368	0.6875	0.6694	0.6600	0.6542	0.6312
5	0.7746	0.7274	0.7095	0.6999	0.6940	0.6701

reaction order, $(1 - \alpha)_{max}$ is slightly dependent on the E/RT ratio. However at high orders, $(1 - \alpha)_{max}$ becomes a strong function of the E/RT ratio. Because E/RT is not known *a priori*, this implies that the higher order of reaction determined by this method may not be very accurate. To estimate a preliminary value for the reaction order based on the conversion at the maximum rate, the following expression has been developed

$$n = i \exp[j(1 - \alpha)_{max}] \tag{7}$$

where i and j are the constants obtained by fitting the data in Table 1 to the equation and are summarized in Table 2. As a first guess, $E/RT = 20$ appears reasonable to estimate the order of reaction based on the maxi-
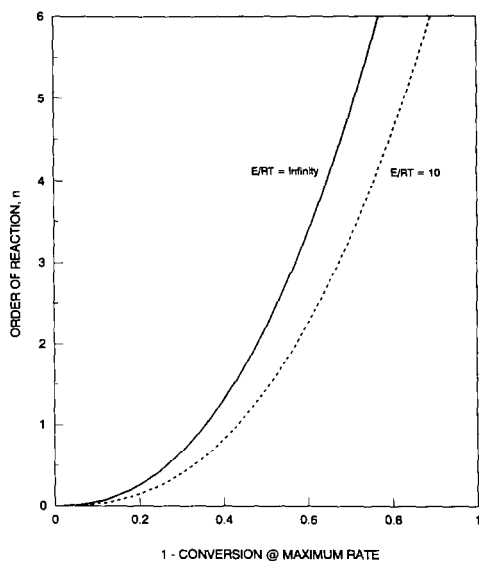

Fig. 4. Order of reaction as a function of $(1 - \alpha)_{max}$ and E/RT.

TABLE 2

Parameters for eqn. (7)

E/RT	i	j
10	0.1099	4.8789
20	0.1253	5.0486
30	0.1288	5.1457
40	0.1301	5.2053
∞	0.1319	5.4213

mum rate. The final result can be updated by iterations and using more accurate equations.

Arrhenius parameters from non-isothermal data

Depending on the Arrhenius parameters, the nature of the non-isothermal curve can be significantly different. Figure 5 summarizes the results of the normalized weight $(1 - \alpha)$ as a function of temperature. As the activation energy increases, the reaction temperature range decreases. As the activation energy decreases, the reaction becomes less sensitive to temperature and the reaction occurs over a broad temperature range. The Arrhenius parameters (summarized in Fig. 5) were chosen such that the tempera-
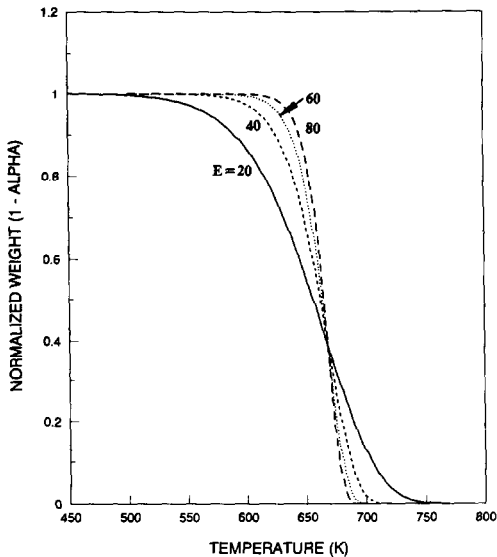

Fig. 5. Normalized weight fraction for a first-order reaction as a function of temperature for various activation energies: $A_1 = 5.9 \times 10^6$ min^{-1}, $E_1 = 20.0$ kcal mol^{-1}; $A_2 = 3.8 \times 10^{13}$ min^{-1}, $E_2 = 40.0$ kcal mol^{-1}; $A_3 = 2.0 \times 10^{20}$ min^{-1}, $E_3 = 60.0$ kcal mol^{-1}; and, $A_4 = 9.0 \times 10^{26}$ min^{-1}, $E = 80.0$ kcal mol^{-1}. $\beta = 70$ k min^{-1}, $T_{max} = 668$ K, and $T_{iso} = 649$ K.
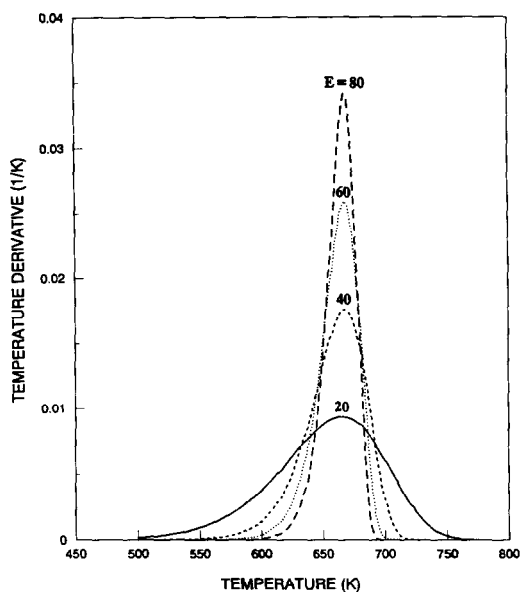
Fig. 6. Temperature derivative as a function of temperature and activation energy; data given in Fig. 5.

ture at the maximum of all four reactions coincide. The temperature derivative as a function of temperature is shown in Fig. 6. The peak width of the temperature derivative curve decreases with an increase in E, indicating that the reaction occurs in a narrower temperature range. The temperature derivative peak-amplitude increases with an increase in A/β. Owing to the compensation effect (discussed later), an increase in E is generally accompanied by an increase in A; therefore, with an increase in E, the peak width decreases. Comparison of the curves in Figs. 2 and 6 indicates that an increase in activation energy is similar to a decrease in the order of reaction. Thus identification of the order of reaction and the activation energy could be difficult without further analysis. To separate the effects of reaction order and activation energy, the temperature derivative should be plotted against normalized weight fraction or conversion (see Fig. 7). Figure 7 indicates that the peak occurs at the same conversion for the same order of reaction, almost independent of the activation energy. By comparing Figs. 3 and 7 it becomes relatively easy to identify differences due to reaction orders and the activation energy. However, the value of the Arrhenius parameters cannot be obtained from these figures. Reliable methods to obtain Arrhenius parameters are discussed briefly below.

If the temperature of an nth order system is linearly increased, eqn. (1) can be rewritten as

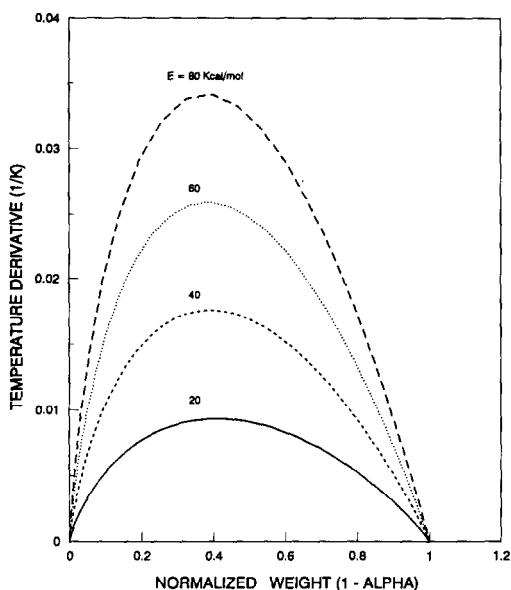$$\mathrm{d}\alpha/\mathrm{d}T = (A/\beta)\exp(-E/RT)(1-\alpha)^{n} \qquad (8)$$

Fig. 7. Temperature derivative as a function of normalized weight and activation energy; data given in Fig. 5.

where β, $= dT/dt$, represents the heating rate; $d\alpha/dT$ is the temperature derivative of the extent of non-isothermal conversion and is also referred to as the rate. Over the years numerous methods have been proposed to obtain Arrhenius parameters from eqn. (8). During the fifties and early sixties, owing to the lack of computing techniques, Arrhenius parameters were obtained from eqn. (8) by linearizing it to the form

$$\ln(d\alpha/dT) = n \ln(1 - \alpha) + \ln(A/\beta) - E/RT \tag{9}$$

or

$$\ln(\beta \, d\alpha/dT) = \ln\left[A(1 - \alpha)^n \right] - E/RT \tag{10}$$

From these equations, A, E and n were obtained. The use of $d\alpha/dT$ for studying the behavior of reactions or for comparing results is acceptable; however, the use of $d\alpha/dt$ (or $d\alpha/dT$) along with α to obtain results is controversial. This is because $d\alpha/dt$ (or $d\alpha/dT$) is obtained from α (even from highly sophisticated thermal analysis devices) and can result in errors due to auto-correlation. Manipulating eqn. (9) and (10) to obtain the three parameters, n, E and A, from a single curve results in non-unique results and is not recommended. It is stressed that no more than two parameters should be extracted from a single curve. Flynn and Wall [1] have analyzed the non-isothermal data and have shown that the differential method (involving utilization of the rate) and the difference differential method (involving difference in rate) results in magnification of experimental

scatter, thereby yielding erroneous results. Therefore, further use of differential methods and difference-differential methods should be discouraged.

Ozawa [30] and Flynn and Wall [31] have shown independently that eqn. (9) with Doyle's approximation [32] can be reduced to the form

$$\ln f(\alpha) = \ln(AE/R) - \ln \beta - 5.33 - 1.05E/RT \tag{11}$$

At a constant conversion level, a plot of $\ln \beta$ versus $1/T$ will yield a slope of $1.05E/R$. This method is popularly referred to as the Ozawa–Flynn–Wall (OFW) method, the isoconversion method, or the multiple heating-rate method. Maximum rate methods such as the Kissinger [29] could be considered to be a special case of the OFW equation. Friedman [33] had earlier proposed the use of rate $(d\alpha/dt)$ rather than $f(\alpha)$ for determining the kinetic parameters. Because the experimental accuracy of $f(\alpha)$ is greater than $d\alpha/dt$, the OFW equation is superior to the Friedman equation. Theoretically, the OFW equation is powerful and independent of the choice of the form of $f(\alpha)$. It also allows for the examination of E as a function of conversion. There are some experimental limitations, and calculations of the constant conversion factor can be troublesome [34]. Conducting experiments at different heating rates can result in variation of temperature gradients with the sample leading to erroneous results.

Another popular method for obtaining the Arrhenius parameters from non-isothermal data is the integral method, perhaps the most reliable method for determining the Arrhenius parameters from non-isothermal data. The integral method involves integrating eqn. (8) to obtain

$$g(\alpha) = \int d\alpha/f(\alpha) = A/\beta \int \exp(-E/RT) \, dT \tag{12}$$

and then approximating the temperature integral (also known as the exponential integral) $\int \exp(-E/RT) \, dT$ to obtain [1]

$$\int \exp(-E/RT) \, dT = E/R \int x^{-2} e^{-x} \, dx = (E/R)p(x) \tag{13}$$

where $x = E/RT$ and $p(x)$ is a function which includes the temperature integral. Equation (12) now reduces to the form

$$g(\alpha) = (AE/\beta R)p(x) \tag{14}$$

For large values of x (> 50), the errors due to approximation are negligible. However for lower values of x (5–40) of interest in thermal analysis, errors resulting from approximations may not be negligible. A significant amount of information in the literature is based on poor approximations. The results from these studies are misleading and this is the reason for most criticism of non-isothermal methods. Several series expressions and semi-empirical approximations of $p(x)$ are available in the literature [1–4].
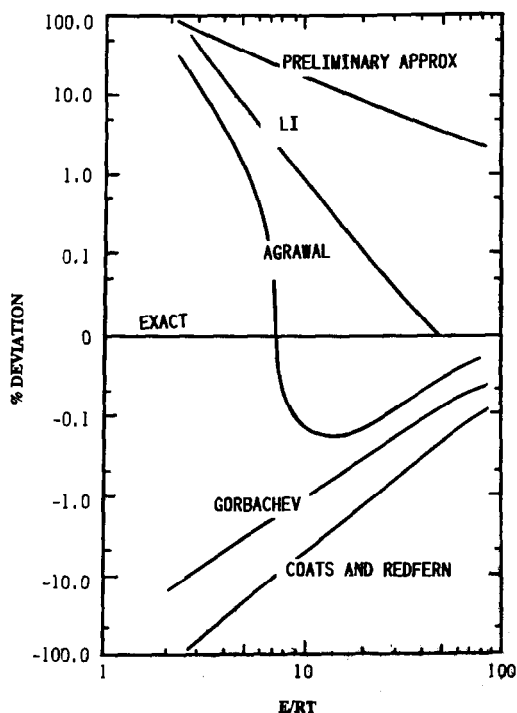
Fig. 8. Accuracy of various temperature integral approximations.

Agrawal [35,36] has shown that most of the temperature integral approximations can be generalized to the form

$$p(x) = \frac{e^{-x}}{x^2} \left[\frac{1 - 2/x}{1 - m(1/x)^2} \right] \tag{15}$$

where $m = 0$ for the Coats and Redfern equation, $m = 4$ for the Gorbachev equation, $m = 5$ for the Agrawal equation and $m = 6$ for the Li equation. For low values of x the ideal value of m varies from 4.6 to 5. Although the condition $m = 0$ is popularly referred to as the Coats–Redfern equation, the form of the equation is available in earlier literature [29,37,38]. The term in the right-hand-side bracket of eqn. (15) is the generalized correction factor (CF). For reactions of interest in thermal analysis, deviation from the exact solution by less than 0.1% is desirable, although deviations of less than 1% may be acceptable. Figure 8 indicates the accuracies of some of the integral forms. For the preliminary approximation $CF = 1$. The preliminary approximation (still used in many studies) is a very poor approximation with deviations of over 2% for $x = 80$. At lower values of x the deviations are significantly higher and therefore the use of the preliminary approximation should be avoided. The deviations of the Coats–Redfern equation are greater than 1% for x values less than 23. The

deviations of the Gorbachev equation are less than 0.1% for x values greater than 41 and less than 1% for x values greater than 11. The Li equation deviates by less than 0.1% for x values greater than 21 and by less than 1% for x values greater than 9. The Agrawal equation deviates by less than 0.1% of x values greater than 7. Thus depending on the value of x, any of the equations should be acceptable for non-isothermal kinetic analysis.

The Arrhenius parameters can then be obtained by linearizing the generalized integral equation to obtain

$$\ln\left[g(\alpha)/T^2\right] = \ln\left[(AR/\beta E)CF\right] - E/RT \tag{16}$$

A plot of $\ln[g(\alpha)/T^2]$ versus $1/T$ will yield a slope of $-E/R$ and an intercept of $\ln[(AR/\beta E)CF]$. Equation (16) indicates that the use of the CF does not influence the estimation of E, but influences the value of the pre-exponential factor and thus the rate constant. So although E values may be comparable from various approximations, the value of the rate constant will be significantly different. Therefore, more accurate equations should be used to obtain reliable Arrhenius parameters.

For a simple reaction, both the multiple heating-rate and integral methods should yield identical values of the Arrhenius parameters. To obtain the Arrhenius parameters, the integral method requires fewer experiments when compared to the multiple heating-rate method. If data are available, a combination of integral and multiple heating-rate methods provides a powerful tool with which to study non-isothermal reactions. Differences in the Arrhenius parameters from these two methods, if any, should be helpful in identifying experimental errors and/or the nature of the reaction. It is stressed that reporting the value of E alone is not sufficient: reporting and comparing the value of the rate constant is more appropriate.

The kinetic analysis discussed in this paper is limited to chemical reactions and is, therefore, independent of sample size, heating rate, particle size and geometry of the sample holder. Simon [39] has shown the influence of such physical factors on the weight-loss curve. These physical parameters complicate the study of chemical reactions and should be avoided. Flynn [40] has recently proposed some ground rules to be applied to avoid problems in gathering TG data.

RESOLUTION OF UNIQUENESS PROBLEMS

Although the non-isothermal curve indicates the nature of the solid state reaction being studied, analyzing the data to obtain unique kinetic parameters can be problematic due to the compensation effect. The compensation effect [16,19,41] causes the kinetic parameters A and E to be linked (see Fig. 9). An increase in slope (E/R) causes an increase in the intercept
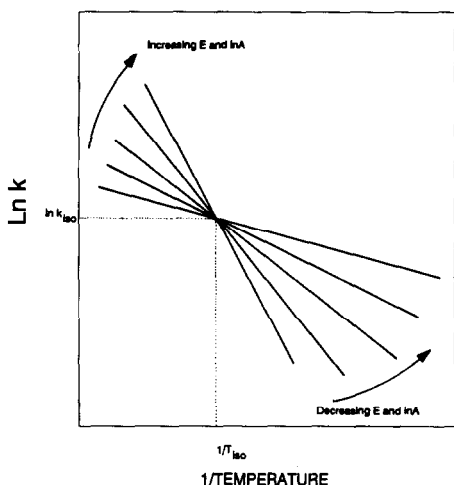
Fig. 9. Arrhenius plot displaying a natural link between ln A and E due to the compensation effect.

(ln A) and a decrease in the slope causes a decrease in the intercept. Owing to this relationship, numerous values of E may fit the data. For example, a reaction with a rate constant of 0.015 min^{-1} at 300°C can be reasonably well represented by an Arrhenius equation with an E of either 20 or 60 kcal mol^{-1} in the narrow temperature region around 300°C, depending on the value of A [25]. Thus obtaining Arrhenius parameters from both isothermal and non-isothermal data could become difficult owing to the compensation effect.

Many researchers show a plot of conversion versus temperature to compare their model with experimental data. However, this is not a convincing method of testing the model. The results of Flynn and Wall [1] indicate the closeness of the normalized residual weight $(1 - \alpha)$ curves for different activation energies. They showed that for E values of 35, 40 and 80 kcal mol^{-1} (maximum rate at $\alpha = 0.5$), the conversion data look very similar. Figure 10 is a similar plot of normalized weight as a function of temperature for E values of 40 and 60 kcal mol^{-1}. The pre-exponential factors were chosen such that the rate constant is equal to 573 K and is summarized in Fig. 10. Thus depending on the accuracy of the data, it appears that both sets of Arrhenius parameters may fit the data. Therefore comparison of model to experimental data by plots of conversion versus temperature is unreliable. In order to resolve the issue, a plot of temperature derivative $(d\alpha/dT)$ as a function of temperature (or conversion) may be plotted (Fig. 11). The higher E reaction has a sharper peak and the lower E reaction has a broader peak. However if the errors at the maximum rate are not negligible, it becomes difficult to identify the magnitude of E based on Fig. 11. The magnitude of E can be identified by
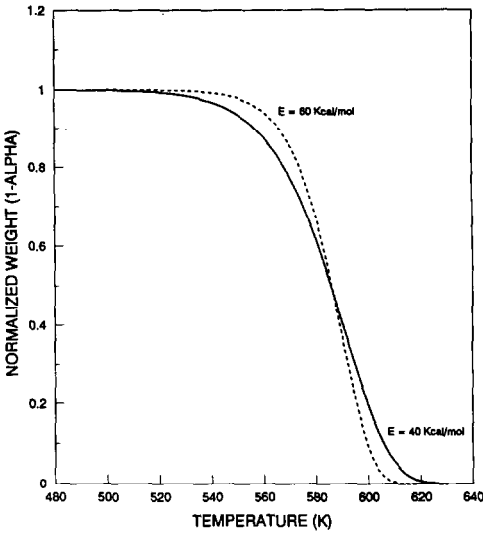
Fig. 10. Normalized weight fraction for a first-order reaction as a function of temperature. Set 1: $A = 3.6 \times 10^{13}$ min^{-1} and $E = 40$ kcal mol^{-1}; Set 2: $A = 1.5 \times 10^{21}$ min^{-1} and $E = 60$ kcal mol^{-1}. $\beta = 1$ K min^{-1}.

varying the heating rate as shown in Fig.12. The higher E reaction will be more sensitive to temperature resulting in separation of the data. However this requires additional experimentation. As suggested by integral methods, a plot of $\ln\{[-\ln(1-\alpha)]/T^2\}$ versus $1/T$ may be plotted (Fig. 13). Figure 13 indicates that by plotting the data, one can be successful in identifying
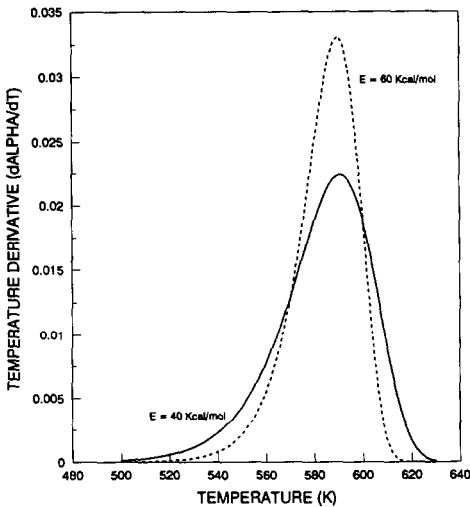

Fig. 11. Rate as a function of temperature. The Arrhenius parameters and the heating rate are given in Fig. 10.
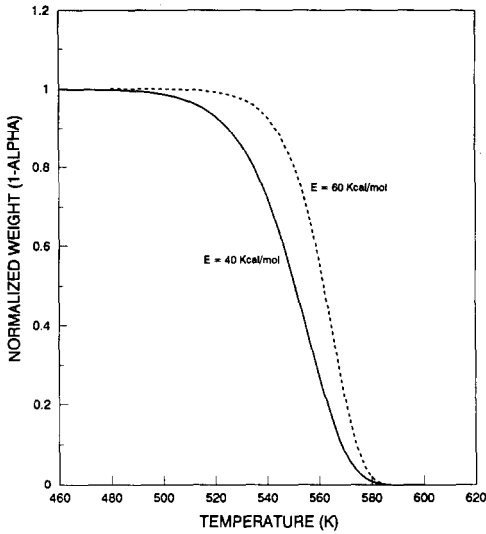
Fig. 12. Normalized weight fraction for a first-order reaction as a function of temperature. Set 1: $A = 3.6 \times 10^{13}$ min^{-1} and $E = 40$ kcal mol^{-1}. Set 2: $A = 1.5 \times 10^{21}$ min^{-1} and $E = 60$ kcal mol^{-1}. $\beta = 0.1$ K min^{-1}.

the values of A and E. The value of E is obtained from the slope, and A can be obtained from the intercept. However, the temperature range is again critical. If the temperature range is limited to ± 15 K around 573 K (the temperature at which the rates are equal), then it can be extremely difficult to obtain the correct value of E. Therefore, the reaction tempera-
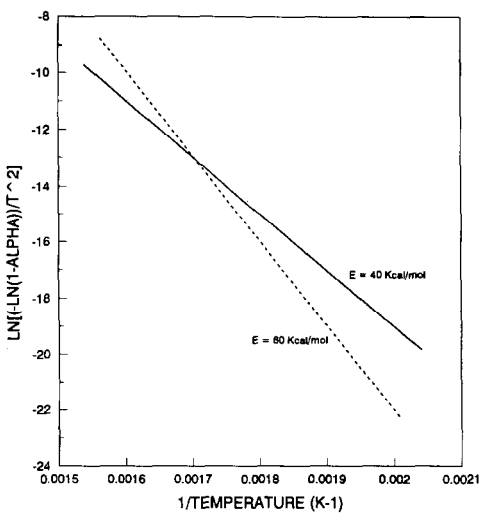

Fig. 13. Arrhenius plot as suggested by the integral method; data are shown in Fig. 10.

ture range should be large enough (at least 70 K) to avoid complications due to the compensation effect.

CONCLUSIONS

Experiments conducted to obtain kinetic parameters should be designed such that complications due to temperature measurement and due to physical factors, such as particle size, sample size, geometry of the sample holder etc. are minimized. Physical factors tend to make the reaction diffusion-limited and lead to complications while analyzing the data. Identifying the correct form of $f(\alpha)$ is critical. Although more than one model of $f(\alpha)$ may fit the data, the aim should be to select a model which requires the minimum number of parameters to fit the data within reasonable accuracy. Maximum rate equations are helpful to pin down the order of reaction. Both the multiple heating-rate method (OFW equation) and the integral method (generalized equation proposed by Agrawal) are recommended to obtain the kinetic parameters. For a simple reaction, both methods yield identical results. Because E can be estimated from the OFW equation without a knowledge of $f(\alpha)$, differences, if any, in the two recommended methods should be helpful in identifying the correct form of $f(\alpha)$ and should reveal the true nature of the reaction. Due to the compensation effect, A and E (either or both) should not be assumed a priori, but should be estimated from the data.

In brief, data gathering has become easy due to modern thermoanalytical devices; however, analysis of the data to obtain unique and reliable Arrhenius parameters remains a challenge.

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