Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 407 (2003) 93–103

thermochimica acta

www.elsevier.com/locate/tca

Perennial problems and promising prospects in the kinetic analysis of nonisothermal rate data

Andrew K. Galwey

18, Viewfort Park, Dunmurry, Belfast BT17 9JY, Northern Ireland, UK

Received 23 July 2002; received in revised form 4 January 2003; accepted 16 May 2003

Abstract

A critical examination is made of the mathematical principles that are used for the kinetic interpretation of nonisothermal thermoanalytical rate measurement by a representative approximate method, the widely applied Coats–Redfern (CR) equation. It is concluded that the dominant feature in the identification of that isothermal kinetic equation, which most satisfactorily expresses the rate characteristics, is the (effective) exponent in the set of equations comparatively considered. Consequently, the form of the CR equation possesses only limited ability to distinguish between 'fits' to alternative kinetic models. This is entirely consistent with literature conclusions expressing the view that data from a single nonisothermal experiment is insufficient to identify the three kinetic parameters: kinetic model, $g(\alpha) = kt$, and both Arrhenius terms, A and E.

An usual first step in kinetic analysis by the CR (and other related) equations is to incorporate the kinetic model ($g(\alpha) = kt$) into the expression used to calculate A and E. Because the rate equation (effective) exponent is a dominant and, without supporting observations, is an unknown parameter, this introduces the well-known ambiguity that alternative kinetic parameters are obtained by the uncritical use of this method.

Accordingly, the following replacement calculation sequence is recommended as being more trustworthy. At least two, preferably several, nonisothermal experiments are undertaken, each at a different (usually constant) rate of temperature increase. For a comprehensive range of constant increments of reaction, $\Delta\alpha_i$, the different rates ($\mathrm{d}\alpha/\mathrm{d}t$) at different reaction temperatures, T_i, are determined from the several experiments and the activation energy, E_i, for each successive reaction interval can be calculated. The constancy, or otherwise, of E_i with α_i throughout the reaction is thus established. From these data, the rate constant for each α_i value can be extrapolated to a selected representative temperature T_R, perhaps at the mid-point of a reaction ($\alpha = 0.5$). From these data a pseudoisothermal α–t (T_R constant) curve can be constructed, suitable for analysis by the usual methods. Various advantages from this approach are perceived. The unfortunate role of the (effective) kinetic model exponent in combination with the logarithmic form of the CR equation in analyzing the data, which inhibits recognition of the kinetic model, is avoided. The laborious calculations will not be a problem for modern high-speed computers, unlike the situation existing when the CR equation was first introduced in 1964. Suitable programs may be used to maximize the accuracy of the method, through the use of several nonisothermal experiments and small $\Delta\alpha$ increments in the analysis. Kinetic comparisons can be extended to a wider range of kinetic models than the limited selection that often restrict the possibilities for nonisothermal rate data interpretation by the most widely used approximate methods.

Keywords: Kinetic analysis; Coats–Redfern equation; Nonisothermal kinetics; Rate equation; Arrhenius parameters

E-mail address: andrew@galwey.freeserve.co.uk (A.K. Galwey).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00307-1

1. Introduction

The greatest contributions towards advancing *chemical* knowledge should, perhaps, be expected to result from the use of *chemical* methods to investigate *chemical* reactions. This assertion might be regarded as self-evident, obvious, even a truism. Nevertheless, the statement is not universally accepted or applied. For example, thermal analysis kinetics, TAK, studies of the (chemical) reactions that occur on heating solids, and/or liquids, are most usually investigated from measured changes of a physical parameter (mass, enthalpy, etc.). Currently and conventionally such observations are kinetically interpreted by ever-more sophisticated methods of mathematical analyses. The direct chemical and physical inputs into such TAK investigations have become limited because the computational procedures used to analyze the measured rate data tend to be stereotyped in form, by the use of accepted methods whereby observations are comparatively tested for 'best fit' to only a limited range of possible reaction types. Conclusions obtained from such studies usually include identification, for the reaction of interest, of the kinetic model [1] (the isothermal rate equation, $g(\alpha) = kt$, often referred to as the 'reaction mechanism') together with the Arrhenius parameters (A, pre-exponential term and E, activation energy). These three characteristics will be referred to here as the 'kinetic parameters' for any reactions considered and are generally accepted as providing a convenient summary of thermal reactivity characteristics. Such results are sometimes interpreted to identify the chemical change occurring and/or the reaction mechanism.

Thermal analysis, TAK, data measurement, collection and interpretation are readily performed by modern, computer-controlled, experimental equipment in which automated computational programs for data analysis can be incorporated. For suitable reactants, this approach often yields kinetic parameters that are easily prepared for publication. However, although the collection of new TAK data has been facilitated, little (if any) attention is directed towards finding systematic order within the wider literature, which has already accumulated through many application of this approach and which is now composed of a very large number of individual contributions. Consequently, the subject proliferates rather than progresses, because there is a lack of scientific theory to correlate the available observations; recent TAK observations have resulted in no ordered growth of a coherent body of systematic chemical knowledge. A contributory factor, exacerbating this unsatisfactory situation, is that the significances of the most widely used chemical terms in the standardized data analysis procedures, have become modified from the concepts originally proposed and as accepted throughout the wider subject. This inhibits theory development and isolates TAK results, interpreted and correlated through alternative theoretical concepts, from other branches of chemistry. A general review of the TAK literature, considering these problems, has been submitted for publication [2].

This article comments on some of the inadequacies, mentioned above, in the currently accepted methods of kinetic analysis and interpretation of TAK measurements, most particularly the uncertainties that arise in attempting to calculate the (three) 'kinetic parameters' [$g(\alpha) = kt$, A and E] from a single set of nonisothermal rate measurements. It is now widely agreed that this is not possible, and that a full kinetic analysis cannot be based on data from a single rising temperature experiment; early hopes that this might be achievable have been shown to be overoptimistic. Criado et al. [3] state: "It has been proved previously [refs] that the actual kinetics of solid-state reactions cannot be discerned by means of kinetic analysis of a single thermogravimetric (TG) curve". Similar statements are made in other published papers [3–8] which confirm that the computational procedures conventionally most widely used lack discrimination in identifying the 'best fit' kinetic model. A single set of nonisothermal (α, t, T) data have been shown [5] give similarly satisfactory fits (as measured by a correlation coefficient, r, close, often very close, to unity) to most (even all) of the many equations that comprise the set of rate expressions usually comparatively tested in TAK data analyses. This set is conventionally taken as the group of kinetic models that are characteristic of decomposition reactions of solids (Table 3.3. of [1]; see also [3,5,8,9]). The apparent magnitudes of the Arrhenius parameters, however, vary significantly with each alternative kinetic model compared [5]. To obtain the kinetic parameters from a single nonisothermal data set, it is necessary to have additional information giving either the rate equation or E [8]. Without such independent evidence, there are no adequate criteria for distinguishing the ‘best’ set of kinetic parameters; this is important where very small differences in r (or other term) can result in changes of apparent E values by a factor ×2 (or more) [10].

This lack of discrimination in nonisothermal TAK studies contrasts with the facility with which the kinetic model can often be determined from a single isothermal experiment (reliable kinetic analysis can, of course, be based on observations of both types). Inspection of isothermal curve shapes enables the three main classes of crystolysis [1] reactions to be readily distinguished: (i) sigmoid shaped yield–time curves, often identified as nucleation and growth processes; (ii) deceleratory reactions that may alternatively be identified as contracting envelope or first order (perhaps alternatively homogeneous) rate processes; (iii) strongly deceleratory reactions that are attributable to diffusion controlled (and sometimes second, even possibly third order) rate processes. Distinguishability in kinetic analysis of isothermal rate measurements has been discussed [11]. However, and perhaps surprisingly, these quite distinct kinetic characteristics become effectively indistinguishable by some widely used methods of nonisothermal kinetic analysis, based on a single set of rate measurements [5].

2. Objectives

The literature contains many articles that discuss TAK methods of mathematical analysis [3–8], in particular the use of interpretive calculations to extract the maximum number of kinetic parameters from a minimum number of (usually nonisothermal) rate measurements [6–8]. However, much less interest has been directed towards characterizing the limitations inherent in the theoretical principles underlying the methods and towards establishing any computational reasons for the uncertainties (ambiguities, inconsistencies) found in the kinetic parameters calculated by these methods.

2.1. Significance of the term ‘activation energy’

One response to the recognition that alternative analyses of a single nonisothermal data set yields several distinct E values, usually different for each kinetic model used [5], has been the proposed acceptance of the concept of the ‘variable activation energy’, whereby several (many) E values may be reported for a single reaction. (‘Multiple-value activation energy’ would appear to be a more realistic descriptive term in the several triads of different kinetic parameters: E, A and kinetic model.) The concept of ‘variable E’ has been particularly advocated by Vyazovkin [12] and is now quite widely accepted. An alternative approach, apparently not in current favor, is to retain the original idea that activation energy is an invariable quantity identified with a rate-controlling process and characteristic of a particular reaction; this cannot, therefore, be either ‘variable’ or exhibit multiple values. Activation energy is a generally accepted theoretical concept, successfully applied throughout chemistry [13], and there appears to be no compelling reason why E should be given a different meaning when employed in TAK studies. The discussion below argues the view that it is more useful to examine the reasons why some calculations yield multiple values of E rather than to change its definition. It is unacceptable to regard the definition of E as ‘wrong’, without exploring the alternative possibilities that the calculation methods might be based on inadequate theoretical foundations and/or that an alternative computational approach is required.

2.2. Analysis of multiple sets of kinetic data

Kinetic parameters derived from a single nonisothermal experiment are regarded as unsatisfactory because data apparently adequately fit several different kinetic models [5]. One (often unstated) implication is that multiple experiments are more reliable in leading to the recognition of a single, dominant, preferred, ‘best’ fit, from which the kinetic parameters can be regarded as applicable to the reaction of interest. This is not, however, obvious, or confirmed in the literature. Two recent comparative studies demonstrate conclusively that kinetic analyses of the same, or similar, sets of data, which included several alternative nonisothermal conditions, gave a range of widely different kinetic parameters [14–16].

The interpretation of nonisothermal kinetic data most frequently proceeds through the use of one (or more) equation from the set of approximate relationships [1] originally proposed to simplify the calculations. These enabled the kinetic parameters to be extracted manually from data sets in a reasonable time. The approach was the best available pragmatic compromise in the precomputer era and the methods, with some additions and modifications, have endured substantially in their early forms to the present day. The essential feature is that approximations are required because no general integral connects the three equations [$g(\alpha) = kt$, Arrhenius equation and the (often constant) rate of heating] for the three (measured) variables, α, t, T. Accordingly, many alternative computational methods, based on the different characteristics and widely used equations, are to be found in the literature [1,17,18], usually each is associated with the name of the originating author(s). There appears to be no critical, comparative survey of the relative merits of these alternative formulae (unlike the discussions of distinguishability for isothermal equations [11]). Different workers select different methods, from the many available, without explanations for their choice; sometimes results from more than a single method are reported and each may give a different triad of kinetic parameters. A particular choice of equation for use in an analysis requires no justification, because every one of the 'popular' equations has been so widely employed as to be generally acceptable without support. More recently, Flynn [19] has drawn attention to the specific errors that may arise in such kinetic analyses through the approximate forms of the 'temperature integral' used in these calculations. He concludes that the inaccuracies introduced should no longer be tolerated because advances and availability of computer capacity have increased the precision now generally achievable. His comments on current attitudes should perhaps be extended to consider the necessity for a general reappraisal of the continued applicability of older methods of kinetic analysis of nonisothermal data. It is now opportune to implement a comprehensive replacement of the original, dated and obsolete, approximate formulae by accurate (modern) computational programs [20,21].

Problems inherent in the use of these older approximate formulae are discussed in the next section with reference to the Coats–Redfern (CR) equation [22]. This method has been selected, for this examination, as a representative example of the approximate approach to the kinetic analysis of nonisothermal rate measurements, based on a single data set [1,17,18]. The relationships of the component terms in this equation are discussed in the context of their overall ability to compute meaningful kinetic parameters. The conclusions are probably applicable to other comparable approximate methods of analysis of nonisothermal rate measurements.

3. The CR equation

One form of the CR equation [22], widely used for the kinetic analyses of single sets of nonisothermal rate measurements, e.g., [23,24], is

$$\ln[g(\alpha)] - 2\ln T = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \qquad (1)$$

where T is the temperature, R the gas constant and β the (constant) rate of reactant temperature increase during the nonisothermal reaction. Consider the terms individually:

(i) The first term is the logarithm of the numerical value for kinetic model. Comparisons undertaken during such kinetic analyses, from which the 'best fit' is identified, are almost invariably based on kinetic models selected from the set that are applicable to decompositions of solids [3,23,24] and Table 3.3. of [1]. The preferred result from this comparison, yielding kinetic parameters that are then reported to be characteristic of the reaction, may be identified as that triad [$g(\alpha) = kt$, A, E] for which the correlation coefficient, r, is the closest to unity. (By definition, α, the fractional reaction, varies from zero to unity across the completed reaction. The logarithm of this term, $g(\alpha)$, undergoes its maximum relative variation during the most rapid reaction interval (mid-reaction for sigmoid shaped α–t curves or during the early stages extending to mid-reaction for deceleratory curves). This inevitably represents a large proportion of the rate process of interest, though in any comparative statistical analysis of the data, contributions from the initial and final stages of reaction may become significant. Thus the overall behavior, and the value of r, will be influenced, to greater or lesser extent, by the range of α incorporated into the comparative analysis. Contributions from small amounts of early and/or late reaction sometimes exert a disproportionate influence in determining apparent overall ‘excellence of fit’ (r value). Furthermore, use of the logarithmic form can diminish the sensitivity of kinetic discrimination.)

(ii) The term $2\ln T$ undergoes systematic changes with the temperature rise during reaction; this may be relatively small across the ranges considered in many kinetic investigations. The variations will depart only slightly from a linear dependence on temperature across most of the intervals relevant to kinetic studies of the types considered here. For example, for a representative rate process studied between 500 and 550 K, the change $\Delta 2\ln T = 0.1906$ and for the intervals 500–501 K and 549–550 K the (Δ1 K) changes are 0.003996 and 0.003640, respectively. Thus across the 50 K interval, the change for each Δ1 K varies by only (0.000356), or about 10%.

(iii) The term $\ln(AR/\beta E)$ is constant during reaction and independent of temperature.

(iv) The relationship between first and last terms is the same as that in the Arrhenius equation and, from a suitable graph, the (apparent) activation energy will be obtained.

The feature to be considered here is that the calculated *apparent* value of E varies considerably with the various alternative kinetic models introduced in Eq. (1).

To compare the fit of a data set to the alternative power law equations, through variations of n in $[g(\alpha) \rightarrow \alpha^{1/n}(= kt)]$ [1], the CR equation (1) becomes

$$\left(\frac{1}{n}\right) \ln(a) - 2\ln T = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{2}$$

The kinetic model (first) term is diminished by the factor, n^{-1}, representing the exponent in the kinetic model and so, if n is not known, the apparent magnitude of E cannot be determined from one set of measured data points. The form of this equation exhibits little ability to distinguish between curve shapes for the kinetic models most usually of interest in such kinetic analyses. Across temperature ranges usually of interest, the second term changes relatively less than the first and its variation with temperature is almost linear. Consequently, it is apparent that the CR equation possesses little capacity for distinguishability [11] (here the fit, and r, varies only marginally with change of n). This conclusion is also evident in the literature [3,5–8] where the same result has been obtained through unsuccessful specific applications of this approach and the result is consistent with the above demonstration of the inability of CR equation to perform adequate kinetic analyses. The reasons are apparent from a direct examination of the properties of Eq. (2) through the following quantitative considerations:

Table 1
Variation of magnitudes of the term $\Delta[g(\alpha)]$ with changes of α between 0.1 and 0.9 and 0.05 and 0.95 for power law and AE kinetic models [1]

Equation [1]	Exponent n	Range of α 0.1–0.9	Range of α 0.05–0.97
Power law	1	2.198	2.965
	2	1.099	1.483
	4	0.549	0.741
AE	1	3.084	4.225
	2	1.542	2.112
	4	0.771	1.056

(i) Relative magnitudes of the first two terms in Eq. (2): Table 1 shows the overall changes of magnitude of $\Delta[g(\alpha)]$, corresponding to the differences of $\Delta\alpha$ between 0.1 and 0.9 and between 0.05 and 0.97, for the two sets of kinetic models: power law and the Avrami–Erofeev (AE) equation [1] (the AE equation is as Eq. (2), except that the term (α) is replaced by ($-\ln(1-\alpha)$), for the nucleation and growth models).

These (first term) magnitude changes tend to be significantly larger than the second term $\Delta[2\ln T]$ in Eq. (2), which was 0.1906 for the illustrative example given. The contribution from the temperature term appears, therefore, to be secondary and often a relatively minor influence and, because it undergoes approximately linear changes as reaction progresses, can only exert limited accommodation for the α–t curve shape.

(ii) Variation of E with power law equation exponent n: examination of Eq. (2) shows that incorporation of the $2\ln T$ term means that the variation of E with n is not linear. Plots of published values of these variables (e.g., from [23,24] and other similar analyses) show that E is zero when n is about 10, which corresponds approximately to when the second term (0.1906) is similar value to the first (Table 1).

(iii) α-Range of kinetic fit: this is an aspect of TAK analysis that is rarely discussed. The range of α-applicability of a particular kinetic model to the data set under analysis is important in describing rate characteristics, but few such value ranges are reported. The aspect requiring consideration here is that variations of the first term, $\Delta \ln[g(\alpha)]$, change markedly from zero to a maximum value and later return to zero as α increases from 0 to 1.0, whereas the $\Delta[2\ln T]$ term falls at an almost constant rate. The relative contributions from the composite term $[(1/n)\ln(\alpha) - 2\ln T]$ in an Arrhenius plot will, therefore, vary appreciably across the range of variations of α and influence the magnitude of the correlation coefficient, r, or other statistical parameter expressing degree of fit. This is the reason for the (sometimes small) variations of r between those kinetic models which differ only in the exponent, n. The term is important where r values are used to distinguish the kinetic model giving the 'best' fit, an unsatisfactory criterion because these variations are not sensitive to changes of the mathematical relationships which are to be compared. However, more significantly, calculations for model systems show that r values also change with α range, the largest influences appear at the limiting α values, corresponding to onset and completion of reaction, which was unexpected, some calculations of this type are given in Table 2 of [21].

(iv) Other kinetic models: the above considerations account for the variations of E with kinetic model for the range of equations normally represented with exponents, n, between 1 and 4 (power law and AE) [1]. To extend the comparisons to the range normally incorporated in solid-state kinetic analyses, two other group reaction types must be discussed:

  (a) Contracting envelope: the shapes of these deceleratory curves are approximately similar to first order (AE with $n = 1.0$, Table 1) and values of E calculated from the same data sets for these three kinetic models (F1, R2, R3) tend to be close to the same value, ±about 10% [10,12,23,24]. While the differences remain perceptible, the pattern of results identify the exponent (here n being regarded as effectively unity) as the dominant feature in determining the apparent magnitude of E.

  (b) Diffusion control: rate control through a diffusion limitation is a dominant influence on rate characteristics and, whether or not a geometric factor is incorporated, all such rate processes are strongly deceleratory [1,11,17]. The magnitudes of E calculated using the several alternative diffusion controlled kinetic models approximate to a similar value which is close to twice that found for the ($n = 1.0$) set (F1, R2, R3) and is ascribed to the dominant influence of the characteristic diffusion exponent, $n = 0.5$.

The overall conclusion from this comparative appraisal of the characteristics of the CR approach to kinetic analysis of TAK data is that the form of Eq. (1) is generally unsuitable for the determination of the kinetic parameters. The interrelationship between the exponent n and the activation energy is effectively unable to separate the individual contributions to the composite function, nE, given by the Arrhenius type plots based on Eq. (1). This is, of course, simply one of the many possible ways of saying (in the various relevant contexts): "The problem can be solved, however, if the true activation energy is known" [6] or "For uniqueness of the results, no more than two parameters should be estimated from a single curve" [7] or "A knowledge of both α as a function of temperature and activation energy is required to construct the experimental master plots" [8]. Recognition of the dominant role of the exponent in all those forms of kinetic models that are most usually of interest in these analyses, identifies this parameter as the overriding determining factor of the magnitude of the apparent activation energy. The pattern of variation of E and A with kinetic model is constant (compare tabulated values for different reactions reported in [23,24]) and appears as a computational artifact. The results of kinetic analysis of data are curtailed by the limitations of Eq. (1). (Distinguishability [11] is probably effectively diminished by the logarithmic form of the kinetic model and variations of the contribution from the $2\ln T$

term between different reactions, together with influences from data error scatter, range of α considered, etc.)

Comment. Results of the above analysis may be summarized as follows. Differences between the several diffusion equations (D1–D4, and others) are minor compared with the role of the exponent ($n = 0.5$). The deceleratory curves of the contracting interface models (R2 and R3) are sufficiently similar in shape to the first order equation to regard $n = 1.0$ for all three. For power law and AE equations (Pn and An) the kinetic model term varies with exponent (Eq. (2)): $n = 1$ or 2 to $n = 4$. The (effective) exponent is recognized as dominating the kinetic curve characteristics. However, calculated values of E are not directly proportional to n because of the contribution from the term $2\ln T$, which becomes relatively greater for the larger values of n. Other, lesser variations arise from the different forms of the specific and different kinetic model (equations) compared. There is a constant and exact pattern of variation of relative E values with equations from the usual set of expressions, $g(\alpha) = kt$, used, as can be recognized through collation of the several literature reports, including, for example, [10,12,23,24]. This (E/kinetic model) constant pattern is identified, therefore, to be an artefact from which the magnitude of E that relates to the rate of the chemical reaction is not readily deduced without additional information.

Prolonged use of this CR method of kinetic analysis has lead to the recognition [3–8] that either the method is ineffectual or additional information [E or $g(\alpha) = kt$] is required to obtain the three kinetic parameters. Despite the extensive literature demonstrating the inability of this approach in kinetic analysis to obtain reliable results from a single set of nonisothermal rate measurements, conclusions based on this method continue to be published. What appears (to me) even more surprising is that the CR equation ever attained the pre-eminence that it has and that it retained its importance so long, when a critical examination of its form and function, such as that given above, reveals its profound inadequacies. It is unexpected (again, to me) that, during several decades of active use, no one appears to have recognized the essential mathematical weaknesses and inadequacies inherent in the CR and some other computational approaches.

4. Aspects of kinetic analysis

4.1. Rate constants

It is a feature of many approximate approaches to the kinetic analysis of nonisothermal TAK rate measurements that the rate constants (k) are by-passed in the calculation procedure. However, there is an interesting parallel between the above recognition of an effective controlling influence on the (apparent) magnitude of E by the exponential term in the kinetic model and the different values of E that are found from the following alternative definitions of the rate constants, k, e.g., for the power law (see [1, p. 121]):

$$\alpha = \begin{cases} k^n t^n & \text{for which the units of } k \text{ are (time)}^{-1}, \\ Kt^n & \text{for which the units of } K \text{ are (time)}^{-n} \end{cases}$$

Arrhenius parameters (E and $\ln A$) calculated from these alternative rate constants are scaled by the factor $\times n$. This differs from the CR pattern in that the $2\ln T$ term does not contribute, but it is worth pointing out that a similar general trend of inconsistency of E values which vary with the effective exponent, n, is found. Moreover, both derive ultimately from a lack of precise definitions of the terminology used and the acceptance of the convention that activation energies, described as ‘variable’ [12] can take multiple values for the same reaction. This practice is not profitable for the development of TAK theory because the results cannot be directly related to other aspects of chemistry so that more precise definitions and consistent use of terms are essential [20,21].

In an early discussion of the limitations of the CR equation, Criado and Morales [4] define the rate constant for the AE equation as $[-\ln(1-\alpha) = kt^m]$ (their Eq. (3)). Later, in considering a hypothetical reaction, it is assumed in the calculations that $m = 3$ and the rate constant is determined, reported (with reciprocal time units) as $k^{1/m} = 0.118\,\text{min}^{-1}$. The only reason given for this choice of $m = 3$ is “the most usual in the kinetic data reported in the literature”. The problems in any kinetic analysis are to determine E and n.

4.2. Experimental measurements of rate data

The sophisticated equipment now widely available to measure changes of physical parameters (mass, enthalpy, etc.) enables large numbers of data points

(α, t, T) to be efficiently collected and stored. The computer-controlled equipment can then, at least partially, interpret data by completing routine calculations to obtain results in a form that can be readily incorporated into publishable reports. As Agrawal has stated [7] “data gathering has become easy due to modern thermochemical devices”. (He goes on to say, in agreement with a main conclusion from the present paper, however, analysis of the data to obtain unique and reliable Arrhenius parameters remains a challenge.)

It is important to remember that, while much of the laboratory labor has been removed from the collection of TAK data by instrumental advances, results from any investigation can only be as reliable as the observations upon which these are based. In the recent TAK literature, there is a lack of critical consideration of the significance of experimental data and an absence of examination of the influences of conditions within the reaction vessel in determining kinetic characteristics. Much of the greatest interest in this field has been directed towards reactions that are both reversible and endothermic in which the rates may be influenced by the movement of a volatile product from the reaction zone and by self-cooling. These effects appear through the significant, often large, variations of kinetic characteristics that result from changes of the procedural variables [25] (sample mass, heating rate, particle size, etc.). L’vov [26], in discussing the factors controlling this type of reaction, distinguishes two types of kinetic behavior: *equimolar*, where there is an absence of reaction products in the reactor atmosphere, and *isobaric*, where the pressure of a gaseous product present is constant during reaction. In a later study [27], the same author shows that the influence of self-cooling, resulting from endothermic reactions, has been seriously underestimated in many discussions of the kinetics of carbonate dissociations. These representative examples draw attention to the necessity to identify all the factors controlling the rate characteristics of the observations as part of any kinetic analysis directed towards identification of the chemical factors that determine reactivity.

4.3. The compensation effect

A consequence of the influence of procedural variables [25] on kinetic behavior is that the temperature coefficient of the rate of a particular reaction varies with conditions within the reaction zone due to secondary controls through changing contributions from the influences of heat and mass transfer. Consequently, different apparent values of E (and A) may be calculated for the same chemical change when it takes place within an approximately constant temperature interval. This is (at least approximately) *isokinetic behavior* [28]; it is a characteristic property of rate processes, within a set exhibiting this feature, that the Arrhenius parameters exhibit a *compensation effect* (CE):

$$\ln A = bE + c$$

A CE that appears in data for the same reaction studied under a range of different conditions has been referred to [16] as a type 2 CE, for example, the decomposition of calcium carbonate [29]. A type 3 CE is [16] found where alternative calculation methods (e.g., the incorporation of different kinetic models into the formula, as in Eq. (1) above) yield different $\ln A$ and E values [23,24]. Calculations based on a single data set (i.e., using different kinetic models in the CR equation which each yield a different magnitude of Arrhenius parameters) are necessarily isokinetic and so a CE effect is mathematically inevitable. Unlike the Arrhenius equation [13], the (empirical) interrelationship between the Arrhenius parameters in the CE is based on no theoretical model and, although widely reported in the TAK literature, has provided no new concepts of value in the interpretation of chemical kinetic characteristics. A type 2 CE represents the variable consequences of usually unknown differences of conditions within a reacting mass and a type 3 CE is a mathematical artefact, as concluded above (see also [14–16,20,21]).

4.4. Further examples of problems in kinetic data analysis

The limitations of the CR equation discussed in Section 3 exemplify specific problems in kinetic analysis mainly through illustrations from the detailed rate data reported in [23,24]. The conclusions are, however, equally applicable to a much wider range of comparable kinetic studies for diverse reactants (and probably also apply equally to other equations used in nonisothermal kinetic analysis [1,17,18]). Further relevant examples are given in articles concerned with the significance of the term 'variable activation energy' [20], the use of correlation coefficients in distinguishing 'best kinetic fit' [21] (see, also the pattern of kinetic results reported in [30]), and in divergences of quantitative conclusions obtained by different workers from studies of the same reactions [14] and, even, from interpretations of the same data [15], discussed in [16]. These articles mention, through consideration of a wider range of reactions that are different from those cited here, the necessity to improve generally the interpretation of rate data. There also remains the requirement to reappraise (as above) possible inherent limitations of the other approximate mathematical methods and equations [1,17,18] used to obtain kinetic parameters from nonisothermal rate data.

5. An alternative approach to the kinetic analysis of nonisothermal rate data

The development of computational procedures suitable for the kinetic analyses of nonisothermal TAK data might reasonably seek to exploit the techniques that have been demonstrably successful in the past, while excluding those shown to be inadequate. We note that single sets of *isothermal* α–t data can discriminate reliably between kinetic models [11] to identify the best fit, $g(\alpha) = kt$ [8]. Isoconversional methods to determine E have been successfully applied to diverse systems for several years and modern sensitive equipment, coupled with high-speed computing systems, has enabled apparent E values to be obtained readily from nonisothermal experiments, see, e.g., [10,12]. However, this emphasis has not always extended to kinetic model identification. (Moreover, the influences of mass and heat diffusion on kinetic characteristics tend to be ignored [25].)

The present proposal, intended to exploit the established strengths of kinetic analyses methods, is that the accepted computation procedure inherent in present practices should be inverted. Hitherto, the usual first step has been to select the kinetic model and subsequently to obtain the Arrhenius parameters following its incorporation in Eq. (1). The alternative calculation program now suggested is based on the use of at least two, but preferably several, complementary sets of nonisothermal measurements from experiments using different (perhaps constant) rates of temperature increase. (These represent the minimum experimental observations, often mentioned as desirable [6–8], but, of course, accuracy and reliability is expected to be increased by additional observations.) Values of α are calculated for each experiment and each data set is divided into stepwise small increments, $\Delta\alpha_i$. The time, Δt_i, required to complete each equal, incremental step of reaction is then individually calculated at the mean temperature, T_i, for each progressive addition and these are recorded. Assuming a linear rate of reaction within each (small) reaction interval, the (zero order) rate constant, k_i at T_i is given by $\Delta\alpha_i = k_i \times \Delta t_i$. From each pair of k_i values (or, preferably, a set of several) one from each experiment and representing the same interval, $\Delta\alpha_i$, the activation energy, E_i, applicable to that restricted α interval can be calculated. A comparison of E_i values, corresponding to each sequential step that contributes to the completed reaction, identifies any variation with α, a result alternatively obtained by isoconversional kinetic analysis, e.g., [10,12]. By increasing the number of experiments, each at a different heating rate, the accuracy of the E_i values, and any systematic changes with α may be increased. The α-range of applicability for any reported activation energy should always be specified.

These data may then be analyzed to identify the kinetic model. A representative temperature, T_R, is selected, $T_{0.5}$, arbitrarily, perhaps corresponding to $\alpha = 0.5$, or alternatively the mean temperature across which the kinetic data have been collected. Rate constants, k_R, for each reaction interval, $\Delta\alpha_i$, can be calculated for T_R using values of k_i and the calculated activation energy. Summation of the time intervals required to complete each successive reaction step then enables a set of α–t values that represent a *pseudoisothermal* reaction at T_R to be obtained. The usual methods of kinetic analysis can then be applied to consider the relative excellence (or otherwise) of fit of this set of α–t values to each of the isothermal equations normally tested [11]. Moreover, these data may additionally be considered for applicability to a wider range of mechanisms, such as melt formation, the intervention of transient intermediates, the influences of secondary controls and/or any other model or mechanistic explanation of behavior that seems suitable. Complementary (nonkinetic) observations may be useful in providing confirmation of all mechanistic conclusions formulated.

The proposed method (summarized in Appendix A) requires extensive computational capacity [21] and was clearly unlikely to have been practicable, or welcomed, at the time of inception of the CR equation and its variants. However, no such laborious mathematical procedure need now be regarded as a deterrent, once the necessary programs have been written. This reappraisal of traditionally accepted kinetic analysis methods proposes that a novel and alternative calculation routine is necessary to avoid the pitfalls of the past, which have so often yielded ambiguous and unreliable kinetic conclusions. The principal result from the present comparative analysis is that the logarithmic form of the approximate rate equation was unable to discriminate kinetic models in which the dominant feature is the effective exponent, n. This can, however, be circumvented through the use of the calculated pseudoisothermal α–t curve as the preferred route to identification of the kinetic model. This isoconversional approach, *first* based on zero order kinetic small steps (rate constant units $(\text{time})^{-1}$) contrasts with the alternative proposals in [10,12].

6. Conclusions

The purpose of this critical appraisal of the selected, but representative and widely used, approximate equation (CR) [21] for the kinetic analysis of nonisothermal TAK measurements has been to identify reasons for the inconsistencies in published kinetic results (kinetic model, A, E) obtained through this and other related computational approaches. Various aspects of the limitations and unreliability of conclusions obtained by the generally used methods have already been discussed [3–10]. However, the present review appears to be the first recognition of the fundamental inadequacies of the mathematical foundations widely applied together with the demonstration that the method is unsuitable for its intended purposes. One alternative procedure, advocated here, is to calculate the pseudoisothermal rate data, which can then be used to characterize the kinetic model. This avoids the irresolvable problems that arise in attempting to base kinetic distinctions [10] between equations dominated by an exponential term through the use of logarithmic equations. Taken with uncertainties in the significance of many rate measurements (due to contributions from secondary controls), the (suggested) alternative concept of activation energy [12], together with other inconsistencies in kinetic terminology and the above explanations for the appearance of CEs, it has to be concluded that the theory, methods and conclusions of TAK research are overdue for a general and critical reappraisal [2].

Current TAK theory is severely limited in its ability to characterize kinetic parameters for any specific reaction by confining comparative considerations to a restricted range of possibilities (e.g., reactions involving melting, perhaps temporary or partial, or which proceed with the participation of transient intermediates are effectively excluded from consideration). It appears that a much more chemical approach is required to replace the present preoccupation with the use of mathematical methods to extract the maximum information from a minimum number of experiments [6–8]. Chemical reactions can be complicated and mechanisms vary much more widely [2] than is adequately recognized within current TAK theory and practices. The new concepts proposed by L'vov [26,27] offer a way forward to the greater understanding of crystolysis reactions that merits wider application and extension. In marked contrast with the ideas in current use in TAK studies, this theory has identified chemically and physically explained correlations between kinetic results for different reactions. This is a welcome start towards finding order in a subject which, at present, appears to be a proliferation of individual contributions that share no chemical foundations but are related only through common data collection methods and formulae used in the kinetic analyses.

The analysis presented above shows that the mathematical foundations of kinetic analyses are unsuitable and ineffectual, a conclusion already accepted to some extent [3–10]. Further work is obviously required to establish a replacement method of kinetic analysis, which must be based on reliable and meaningful measurements in which secondary controls are characterized quantitatively and each α value determined is shown to be directly controlled by the rate of the (fully characterized) reaction of interest. The difficulties in kinetic analysis of TAK observations are not restricted to the single, nonisothermal data sets discussed here but also include multiple complementary experiments, as shown by the inconsistencies between results obtained in comparative surveys [14–16,20,21]. Clearly progress is required to establish reliable methods for

TAK rate data analysis to obtain kinetic parameters that are scientifically valid, so that the factors controlling reactivity can enable reaction mechanisms to be discussed with reference to the wider subject of chemistry. Before order can be found in the large numbers of published kinetic results obtained by TAK methods, and so advance the understanding of thermal chemistry, the validity of these observations and conclusions must first be established. Further progress to identify acceptable and realistic theoretical foundations is essential before scientific order is fully introduced into TAK studies.

Appendix A. Summary of mathematical steps in the proposed method for kinetic analysis of nonisothermal rate measurements

(i) Yield–time measurements are obtained by TAK methods for at least two (preferably several) nonisothermal reaction experiments at different (usually, but not necessarily, constant) rates of temperature increase. The results for each experiment are then expressed in the form of a set of (α, t, T) values.

(ii) A representative temperature, T_R, is identified, preferably within the range of the collected data, perhaps a value for $\alpha = 0.5$, or the mean reaction range temperature.

(iii) Each reaction is divided into a large number of small steps, $\Delta\alpha_i$, and the time required to complete each such step recorded ($\Delta\alpha_{i1}$, $t_b - t_a$:$\Delta\alpha_{i2}$, $t_c - t_b$:...:$\Delta\alpha_{ix}$, $t_y - t_z$). From these values the individual rate constants, k_i ($=\Delta\alpha_i/(t_n - t_{n-1})$), are calculated. For each pair of (or preferably several) rate constants, the magnitude of E_i is obtained together with the rate constant at the representative temperature, T_R.

(iv) The magnitudes of E during each step, $\Delta\alpha_i$, in the progress of reaction are calculated and compared, to determine whether E varies systematically with α.

(v) From the rate constants at T_R the time required to complete each step, $\Delta\alpha_i$, is found and a pseudoisothermal set of (α, t) values at constant T_R is obtained.

(vi) The calculated pseudoisothermal set of (α, t) values at T_R are kinetically analyzed by the usual methods [1,11] for relative excellence (or otherwise) of 'fit' to all appropriate rate expressions, which may be extended beyond the often restricting set considered in many nonisothermal kinetic analyses.

(vii) The calculations are applied with maximum accuracy [19] by computer programs.

References

[1] A.K. Galwey, M.E. Brown, Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam, 1999.
[2] A.K. Galwey, submitted for publication.
[3] J.M. Criado, A. Ortega, F. Gotor, Thermochim. Acta 157 (1990) 171.
[4] J.M. Criado, J. Morales, Thermochim. Acta 16 (1976) 382.
[5] J.M. Criado, A. Ortega, J. Therm. Anal. 29 (1984) 1225.
[6] J. Malek, Thermochim. Acta 200 (1992) 257.
[7] R.K. Agrawal, Thermochim. Acta 203 (1992) 93.
[8] F.J. Gotor, J.M. Criado, J. Malek, N. Koga, J. Phys. Chem. A 104 (2000) 10777.
[9] J. Malek, J.M. Criado, Thermochim. Acta 175 (1991) 305.
[10] S. Vyazovkin, J. Therm. Anal. Calorim. 64 (2001) 829.
[11] M.E. Brown, A.K. Galwey, Thermochim. Acta 29 (1979) 129; M.E. Brown, A.K. Galwey, Thermochim. Acta 269/270 (1995) 1.
[12] S. Vyazovkin, Int. Rev. Phys. Chem. 19 (2000) 45.
[13] J.K. Laidler, J. Chem. Educ. 61 (1984) 494.
[14] H.L. Anderson, A. Kemmler, G.W.H. Hohne, K. Heldt, R. Strey, Thermochim. Acta 332 (1997) 33, 55.
[15] M.E. Brown, et al., Thermochim. Acta 355 (2000) 125.
[16] M.E. Brown, A.K. Galwey, Thermochim. Acta 387 (2002) 173.
[17] M.E. Brown, D. Dollimore, A.K. Galwey, Comprehensive Chemical Kinetics, vol. 22, Elsevier, Amsterdam, 1980.
[18] M.E. Brown, Introduction to Thermal Analysis, Chapman & Hall, London, 1988;
M.E. Brown, Introduction to Thermal Analysis, 2nd ed., Kluwer Academic Publishers, Dordrecht, 2001.
[19] J.H. Flynn, Thermochim. Acta 300 (1997) 83.
[20] A.K. Galwey, Thermochim. Acta 397 (2003) 249.
[21] A.K. Galwey, Thermochim. Acta 399 (2003) 1.
[22] A.W. Coats, J.P. Redfern, Nature (London) 201 (1964) 68; A.W. Coats, J.P. Redfern, Polym. Lett. 3 (1965) 917.
[23] S.-L. Li, D.-X. Liu, S.Q. Zhang, H. Wang, Z.-H. Yang, Thermochim. Acta 275 (1996) 215.
[24] P. Mu, R.F. Wang, L. Zhao, Thermochim. Acta 296 (1997) 129.
[25] F.W. Wilburn, J.H. Sharp, D.M. Tinsley, R.M. McIntosh, J. Therm. Anal. 37 (1991) 2003, 2021.
[26] B.V. L'vov, Thermochim. Acta 373 (2001) 97.
[27] B.V. L'vov, Thermochim. Acta 386 (2002) 1.
[28] A.K. Galwey, Adv. Catal. 26 (1977) 247.
[29] A.K. Galwey, M.E. Brown, Thermochim. Acta 300 (1997) 107.
[30] J.J.M. Orfao, F.G. Martins, Thermochim. Acta 390 (2002) 195.