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Eradicating erroneous Arrhenius arithmetic

Andrew K. Galwey

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

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Abstract

A general and critical analysis is made of theories used to interpret those thermochemical rate measurements that are directed towards investigations of the mechanisms of chemical changes that result from the heating of initially solid reactants. It is concluded that the concepts and reaction models in current usage are inadequate and that the assumptions conventionally made in the interpretation of this type of experimental data are in urgent need of radical reappraisal. The present article specifically identifies several shortcomings in results obtained from the Coats–Redfern equation, which is widely used to calculate Arrhenius parameters for reactions that are regarded as capable of representation by rate equations characteristic of decompositions of solids. The view that activation energy values can vary with the kinetic model used in their calculation is regarded as unacceptable for reasons that are discussed in detail.

Introduction. An appraisal is made of the limitations of the various theories available for the interpretation of rate data obtained from thermal analytical measurements. *Literature survey*. From an examination of research reports, mainly published in the last decade, a common pattern of variation of magnitudes of Arrhenius parameters with rate expression (kinetic model), calculated using the Coats–Redfern equation, is identified as a set of Trends. This pattern of rate parameters is shown to occur widely. *Reappraisal of methods of analysis of thermochemical rate data*. It is shown that the Trends identified in calculated Arrhenius parameters are mathematical artefacts that arise through identified inadequacies in the assumptions underlying the approximate computational method. *Discussion*. It is concluded that the concept of the ‘variable activation energy’, which has recently become approved through its use in considering nonisothermal kinetic data, is unacceptable. If the theory of thermal analysis is to remain consistent with other branches of chemistry, and if scientific order is to be developed within the thermoanalytical literature, the definitions of all terms must remain common and constant. The shortcomings, which have been identified here in the approximate mathematical methods of thermal rate data interpretation, introduce doubt into the significance of many published Arrhenius parameters. Some consequences of these uncertainties for the future development of the theory of the subject and our progress towards understanding the controls and mechanisms of crystolysis reactions are examined. Meaningful kinetic data must be obtained if thermal analysis results are to be considered in the context of the recent general theoretical models developed by L’vov, which are based on a physical approach to thermal reactions. This theory offers insights into the controls and mechanisms of thermal reactions involving solids and introduces the possibility of promoting scientific order in this literature, which is not currently obvious.

Keywords: Activation energy; Coats–Redfern method; Kinetic analysis; Thermal analysis

1. Introduction

This critical literature review identifies important shortcomings that have been recognized in the science of thermoanalytical kinetics. Numerous recently published articles in this subject report the magnitudes of countless activation energies, and other kinetic conclusions, based on measurements by thermal analysis

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methods. However, critical examinations of the experimental data and of the experimental methods used in such studies show that of many reported magnitudes of kinetic parameters, and conclusions drawn therefrom, are not supported by an adequate theoretical justification. As emphasized throughout this survey, usage of the term ‘activation energy’ by thermal analysts differs significantly from its meaning as originally defined and as generally accepted throughout other branches of the literature concerned with chemical kinetics. This terminological modification is demonstrated here to occur within an extensive and representative range of published results and engenders doubts about the value and significance of kinetic conclusions across an even wider range of rate studies by thermal methods. In the absence of critical scrutiny of the observations and of their interpretations, kinetic conclusions based on thermoanalytical investigations should not be accepted as possessing mechanistic significance and may not be capable of providing a measure of absolute reactivity. These generalizations represent a most serious criticism of practices that are currently widely regarded as acceptable in kinetic analysis investigations of condensed phase reactions studied by various thermal experimental methods and interpreted through reaction models that originated from the theory of solid state decompositions (crystolysis reactions) [1]. This considered expression of my profound lack of confidence in the reliability of many published conclusions, throughout an important subject area, is not made lightly. It is forcefully expressed here and now in the expectation of initiating an overdue debate directed towards reappraising generally the objectives, methods and theory of thermal analysis.

The above assertions introduce a literature analysis that identifies specific inconsistencies that are inherent in computational programs widely used to interpret kinetic measurements for decomposition reactions proceeding in a condensed phase. It is argued below that conclusions reached in recent discussions have resulted in unrecognized modifications to the subject theory now used throughout the thermal analysis literature that is concerned with reaction rates, reaction mechanisms and reactant reactivities [1,2]. It is argued that the problems identified in this review must be comprehensively addressed if the methods and practices routinely used in kinetic investigations of many thermal rate processes are to progress the subject as a comprehensible and systematic science. Urgent and critical reassessments of the significances of many recent published results are now overdue and a comprehensive new approach to the mathematical analysis of rate data obtained by thermoanalytical measurements is essential. The theoretical understanding of chemical behaviour must derive from, and always include, the rigorous application of chemical principles, methods and models. The excessive reliance placed, in many recent thermoanalytical reports, on ever more sophisticated mathematical manipulations of rate measurement data can have only limited ability to support proposed kinetic interpretations, even when correctly used. The present article is directed towards identifying reasons for the incorrect or unreliable conclusions that have arisen through the use of methods of kinetic analysis that are incapable of realizing the chemical objectives being addressed. The consequences of such errors, which appear to have had unexpectedly harmful influences in investigating mechanisms of thermal reactions, must be addressed and corrected before the scientific foundations for kinetic interpretation of thermoanalytical data can be restored and the subject can again prosper. Identification of some of the problems, the extents of their implications and the remedial action required for their removal, are discussed here in what is intended to be an optimistic appraisal of a potentially and ultimately bright future for thermoanalytical chemistry. However, realization of this promise is only possible if the limitations inherent in many aspects of recent researches are identified and removed.

Historical background. Motivations for undertaking a rigorous survey of the field, at this time, include my belief that thermoanalytical chemistry has effectively replaced the study of thermal decompositions of solids, while selectively retaining limited aspects of the theory developed by the former discipline. Thermal analysis has profitably exploited the mathematical and computational advantages of the advances in instrumentation that have characterized the formative phase of this subject. However, these developments have not been accompanied by the adequate provision of a suitable theoretical framework for data interpretation or comparable progress (or much obvious interest) in investigating and recognizing the chemical and physical characteristics of the reactions concerned. The continuing apparent progress of the subject is maintained despite the insufficient foundations in theory. There is the uncritical acceptance of important kinetic terms for which the definitions have undergone subtle, but apparently insufficiently appreciated, or even unrecognized, modifications for use in discussions of thermoanalytical observations. There are also uncertainties in the reliability of many experimental measurements where the sensitivity of rate data to prevailing reaction conditions has not, apparently, been considered in the interpretations of rate measurements. The cumulative consequence of these unappreciated shortcomings in theory, and inherent in some experimental practices, has been to make many reported conclusions increasingly empirical.

The thermoanalytical literature. Thermal analysis is now characterized by an ability to obtain and to interpret kinetic results rapidly and with a minimum of effort. This has generated an extensive but fragmented literature in which systematic order, together with an ability to predict behaviour by induction, essential characteristics of a science, are now absent or, at least (to me), far from obvious. The superficially attractive advantages of collecting rate data (that may be empirical) easily has now replaced the former appreciation [1] of the difficulties that arise in the characterization of reactivity controls and of the mechanisms of chemical changes that occur on heating initially solid reactants. The present motivation towards contributing to an ever expanding report accumulation, within which order is evidently absent, continues. However, little current effort appears to be directed towards the recognition of trends that may be identifiable in the literature, through provision of reviews of the extensive information that is already available. Moreover, article introductions are frequently selective, by including relatively few citations for systems which might reasonably be related to (or may be inconsistent with) the new research being published. Thermal analysis is a subject that contains remarkably few comparative discussions, either as dedicated comparative reviews or within the many contributed articles. One probable consequence is the absence of theory development and the recognition of few systematic trends or patterns in behaviour. Consequently, there is a progression towards a literature composed of isolated or individual contributions and there is no organic, systematic growth of a coherent science.

The above criticisms, drawing attention to the uncertain significance of some recent experimental measurements, are based on selected valuable, often older, literature sources which contain important, fundamental contributions to the subject that remain insufficiently recognized. These include reports that emphasize the specific experimental difficulties which arise when attempting to measure kinetic data that may be positively used to identify a chemically controlling (rate determining) step, particularly for reactions involving solids. It has been conclusively demonstrated that, for many crystolysis reactions [1], self-heating/cooling [3–6] and/or reaction reversibility [7–9] exert significant, sometimes dominant, controls on the reaction rates observed. Nevertheless, kinetic investigations ignoring these realities continue to be reported, and, consequently, the rate measurements often determined are specifically applicable (only) to some particular reaction conditions. Such data are, therefore, empirical, but are all too frequently interpreted through theory relevant to and originally formulated to explain homogeneous rate processes, where a single, dominant controlling step operates. Recognizing the limitations of current methods and practices, L’vov [10,11] has recently developed a general theoretical model, discussed further below, applicable to solid state decompositions and accounting for the various essential characteristic features of these reactions. However, the useful application of this approach, and its further development, depends on obtaining suitable, reliable kinetic data, values of the activation energy in particular, that are related to the rate of the controlling process in the reaction.

The present paper demonstrates important, but apparently unappreciated, limitations in some conventional methods of kinetic interpretation of measured reaction rates. An appraisal is made of one of the most widely accepted techniques used for the computation of activation energies from nonisothermal thermoanalytical measurements. A critical reexamination of the assumptions and mathematical steps in the Coats–Redfern equation [12], CR, used to determine Arrhenius parameters from rising temperature experiments, is given below. Important shortcomings in this well-known computation are revealed, which have been present, apparently undetected, in the numerous literature reports concerned with the uncritical application of this equation. The consequences are now discussed in the context of their probable wider implications. A second and complementary review, now in active preparation, considers a range of other related problems besetting aspects of thermal kinetics generally. This includes uncertainties in the definitions of terms, together with the units applicable, and limitations inherent within those theoretical models which are most frequently applied in reports of thermoanalytical work. The absence of critical appraisal of thermoanalytical results, through reviews and articles, is regarded as constituting a retarding influence on progress in the field. Together the present and the forthcoming articles pose the question, in a literature not noted for its ability to respond to unwelcome contributions: is it preferable to continue the accumulation of unrelated largely empirical results or is it timely (overdue) to return to the scientific method? I unreservedly regard the latter course as preferable. I wonder if other authors will recognize, or condescend to respond to, the criticisms of thermal analysis, methods and practices, that I publicize here. I suspect that my unwelcome and critical analysis will be consigned to the 'Great Repository' of the unrecognized and uncited literature. Nonetheless, the fact remains that thermal analysis is not fulfilling its potential because progress is no longer based on chemical and physical principles and (equally importantly) on adequate theoretical scientific foundations.

Personal note. This survey is presented in direct terms because I believe that kinetic studies by thermal analysis is in a state of considerable disarray, even crisis, that has not been the subject of the concern that it so richly merits. I am not a thermal analyst myself, but am familiar with the literature through related interests [1,2]. Because this unsatisfactory situation continues to remain apparently unrecognized, certainly hitherto unaddressed, I consider that it is timely to present my views (as an 'outsider') in the hope that the subject overall might eventually benefit from a forthright critical comment.

1.1. The application of kinetic analysis in the interpretation of thermoanalytical data

The concept of activation energy (E), as developed, accepted and used generally throughout almost all chemical kinetics, identifies the energy with the barrier to the bond redistribution processes for the rate determining step in a single reaction [13]. It is a physicochemical parameter determined by the magnitudes of the interatomic interactions that are activated and modified during the changes occurring. For each particular reaction it has a characteristic and constant value. An exception to this generally agreed nomenclature is found in the field of thermal analysis, in which many workers hold or accept a different view: "the acceptance of a variable activation energy. . . " has been suggested [14], though no precise definition for this replacement term was given. However, one possible alternative definition for this 'variable E' might be: "For any reaction, the magnitude of 'variable E' is found by (uncritically) applying the Arrhenius equation to any rate constants (k) determined from diverse kinetic expressions [1] of the form $g(\alpha) = kt$ or $f(\alpha) = (1/k)(\mathrm{d}\alpha/\mathrm{d}t)$ (where α is the fractional reaction)". This type of meaning appears to be the, currently fashionable, preferred choice by many, perhaps even a majority, of researchers who have recently published in the field of thermoanalytical kinetic studies. It follows that many E values reported, for nominally the same reaction, show wide variation and/or different E values are found through the use of alternative rate equations to analyse the same data (examples are given below). Consequently, the magnitude of this parameter must be regarded as having no recognizable (or intended?) mechanistic significance. Such values of E are, therefore, empirical and should not be cited as evidence for the identification of a rate determining step or other mechanistic inference. Why this 'variable' term should retain the descriptive label, 'activation energy', associated with a precise chemical concept, is not explained [14]. (It also seems that E, used in this sense, is not correctly regarded as a 'variable', but could be more suitably described as a 'multivalue' parameter.)

Many recent articles report wide differences in apparent magnitudes of 'variable' E with change of the rate equation used in the calculations. This means that either the chemical concept of E, as originally defined and conventionally accepted, is inapplicable or the method of calculating E is incorrect. If the former is believed, then the 'activation energies' considered are empirical (multivalue) quantities, which, nevertheless, may be capable of useful extrapolation, under suitable circumstances, to estimate reactivities or reaction rates outside the range for which experimental data are available. Alternatively, and to maintain consistency with other branches of chemistry, E can be regarded as a property of a controlling step and for any reaction must have a constant value (which may or may not be experimentally determinable). It follows then that changes in the apparent value of E with the kinetic model [$g(\alpha) = kt$], on which the calculations have been based, must arise as a consequence of unsuitable computational procedures or inappropriate assumptions in those calculations. I unhesitatingly express my preference for the latter of these alternative views. To support this opinion, and to identify the mathematical reasons for the apparent variability of E, I have made a careful reappraisal of the steps involved in the calculation routine use for the Coats–Redfern equation [12]. It is concluded that this method does not provide an acceptable method of kinetic analysis and identifies a considerable uncertainty about the reliability of many reported values of Arrhenius parameters in numerous published articles. This outstanding concern remains to be resolved and raises important questions concerning the reliability of kinetic results obtained by other similar methods of calculation.

1.2. *Objectives of kinetic studies*

Kinetic studies of crystolysis [1] reactions most frequently appear to be motivated by an interest in reporting magnitudes of Arrhenius parameters (E and the frequency factor, A) together with identification of the rate equation, kinetic model, [$g(\alpha) = kt$] that most satisfactorily provides the ‘best fit’ to the yield–time data. Reasons for addressing these objectives are not always satisfactorily explained but the reporting of E (etc.) appears to be widely regarded as providing self-evident justification for many published research reports. However, these achievements may often be adjudged to add relatively little of substance to our understanding of the chemistry and physics of the specific reactions selected as being of interest for several reasons, some of which are outlined below. (More than one reason may apply to the results from any particular research program.)

1. *Mechanism determination*. Kinetic investigations of homogeneous rate processes are often directed towards the elucidation of the reaction mechanisms. The sequence of participating chemical changes, including the rate limiting step, through which reactants are converted into products can often be characterized for rate processes proceeding in solution or in the gas phase. However, much less is known about the controls and conditions that exist within an active reaction interface during crystolysis reactions (solid state decompositions [1]) and papers concerned with the kinetics of such rate processes do not elucidate the detailed mechanism of the chemical changes considered. Comparisons of kinetic conclusions with similar results for related systems are infrequently made. Moreover, there appears to be little interest in identifying systematic order and trends of behaviour within groups of comparable reactions, which is a primary objective of the scientific method. The literature contains remarkably few reported attempts to classify the thermal reactions of solids on the basis of the large numbers of kinetic results (magnitudes of A, E and rate equation applicable) that are available for the thermal observations already reported for numerous and diverse reactants. Many recent thermoanalytical kinetic studies cannot be regarded as contributing to the elucidation of reaction mechanisms.
2. *Kinetic characteristics may be complex*. More than a single rate-influencing factor may contribute to determining the rate characteristics of many crystolysis reactions and the relative influences and effects of the complementary, but different controls are not always readily distinguished. Consequently, the calculated values of A and of E for the overall reaction cannot be assumed to provide a measure of the frequency of occurrence of, or the energy barrier to, a single, dominant rate controlling chemical step (as may occur in many homogeneous rate processes). The kinetics of many reactions of solids are significantly influenced by rates of various diffusion or mobility (physical) controls, including the movement of heat to (or from) the active reaction zone (interface) [3–6] and/or removal of volatile product from the sites of reversible dissociation steps [7–9]. Such effects are clearly demonstrated by the well-known influences on rates of many reactions that result from changes of the procedural variables [15,16]. These modifications of conditions cause changes within the reaction zone which may be inhomogeneous within the reactant mass and undergo systematic variations with time during progress of the chemical change of interest. The significance of rates

measured for such reactions must be interpreted with quantitative consideration of all possible participating rate controls. It cannot be assumed, as sometimes appears, that there is a rate determining (single, chemical, dominating) step, comparable with the concept familiar from homogeneous kinetics.

3. *Errors may arise in the calculations used in kinetic interpretation*. The mathematical procedures used to calculate Arrhenius parameters and to identify the 'best fit' of measured rate data to appropriate kinetic models [1], may yield results of uncertain relevance or reliability. The present paper is primarily concerned this aspect of kinetic analysis: it is concluded that calculation methods based on approximate formulae techniques do not always yield the results sought.

2. Literature survey

2.1. Variable activation energies

A principal objective of this critical survey is to explain a characteristic pattern, discerned between relative magnitudes of E and the kinetic models, $g(\alpha) = kt$, used in their calculation, that has been identified in published articles, for example [14]. These variations are inconsistent with the theory of reaction kinetics and no satisfactory explanation appears to have been provided. Representative instances of these trends are described below. This is not intended to constitute a comprehensive review or an attempt to locate and list every traceable example of this particular pattern that can be found in thermal analysis data. However, the selection of examples cited here shows the generality of this behaviour pattern which has been reported for studies of thermal decompositions involving numerous and diverse reactants by many researches from geographically dispersed laboratories, including observations based on different experimental measurement methods. The constant pattern of trends and correlations, identified within the reported combinations of E (also A) with $[g(\alpha) = kt]$, are explained (in the subsequent section) by shortcomings and inconsistencies inherent in the calculation methods used. The pattern identified is, therefore, a mathematical artefact.

2.2. Identification of a representative set of kinetic data for use in this comparative literature survey (StdSet)

To discuss the characteristic pattern of variations of E with kinetic model, $g(\alpha) = kt$, identified, it was convenient to select a suitable and representative set of results, with which the other kinetic reports found in the literature could be compared quantitatively. The data set that were selected (perhaps arbitrarily), as the most appropriate and comprehensive reference available for comparisons, were the kinetic parameters, E, A and $[g(\alpha) = kt]$ (together with the linear correlation coefficients, r) calculated by the Integral method and listed in Table 4 of [17]. This is referred to below as the StdSet. The reaction involved was Stage 1 of the thermal decomposition of the complex of europium *p*-methylbenzoate with 2,2′-dipyridine. Results reported in this paper [17] included the original rate measurements used in the calculations, the fit of measured rate data to 19 different kinetic models by both Integral and Differential methods (38 values of Arrhenius parameters in all) and r values, correlation coefficients, that are predominantly close to unity. It should be emphasized that any one of the many sets of results mentioned in the papers cited below could equally well have been selected as the basis for the comparisons. However, this most extensive range of 'good fit' observations [17], with r values close to unity, was taken as a the preferred benchmark against which other variations of E with $[g(\alpha) = kt]$ could be most usefully and suitably examined.

In the StdSet, only three of the 19 values of r reported for the calculated Arrhenius parameters (0.661, 0.932, 0.973) are less than 0.980 and six are 0.995 or greater. (One immediate conclusion, possible from this comparison, is that the analytical method used exhibits a marked inability to discriminate [18,19] between the alternative kinetic models to which the fit of data has been tested.) Values of $\ln A$ and E show closely comparable patterns of considerable variation with kinetic model used in their calculation. These values give two strong compensation relationships [20,21] (discussed further below) for the two data sets in Table 4 of [17] which represent the Integral and Differential calculation methods. Both lines pass through (or very close to) the origin of the graph (0,0). The isokinetic temperatures [20] are 510 and 481 K, respectively: as expected, these are within the range of temperatures, 443 to 511 K, of the kinetic measurements used to calculate the Arrhenius parameters.

2.3. *Trends in magnitudes of kinetic parameters in the StdSet*

The following Trends were found in the StdSet [17] which enable comparisons to be made with other published results (equations are numbered as in [17]).

*Trend A*1. Calculated magnitudes of E, also $\ln A$, decreased (irregularly) in the sequence: Eqs. (6), (4), (3), (2), (1), (5), (18), (7), (13), (12), (14), (8), (9), (15), (10), (19), (16), (11), (17). The range of variations of E magnitudes was considerable, decreasing from 365 to 26 kJ mol^{-1}. It is noted qualitatively that the highest relative values of E are found for diffusion controlled reaction models [1].

*Trend A*2. Values of E decreased markedly and linearly with reduction of the exponent n for both the power law (Eqs. (1), (14)–(17)) and the Avrami–Erofeev AE (Eqs. (8)–(11)) equations [1], Fig. 1. However, both plots intercepted the axis at a small positive value of n ($n = 0.05$–0.10, approximately) so that magnitudes of E/n show small progressive diminutions as E and n decrease.

*Trend A*3. The value of E for Eq. (4) (diffusion controlled equation, D3 [1]) was just more than twice that for Eq. (13), the contracting volume equation, R3 [1], and this was about 5% greater than that of Eq. (12), the contracting area rate expression, R2 [1].

*Trend A*4. There was a pronounced compensation effect [20], all points on a plot of $\ln A$ against E were close to a straight line, that passed close to the origin (0, 0).

The relationships between E values obtained from the Integral and Differential methods (StdSet) from Table 4 in [17], are conveniently illustrated by the unconventional plot, comparing these quantities, Fig. 2.

The following Trends were found for E values from the Differential method, Table 4 of [17].

*Trend B*1. The sequence of decrease in E values was: Eqs. (6), (4), (3), (18), (2), (1), (19), (5), (7), (13), (12), (8), (9), (14), (10), (11), (15), (16), (17). The Trend is generally similar to, but not identical with, that in the StdSet and, interestingly does not represent the closely comparable values of E that should have been anticipated from application of the different forms of the same rate expressions to the same data, Fig. 2.

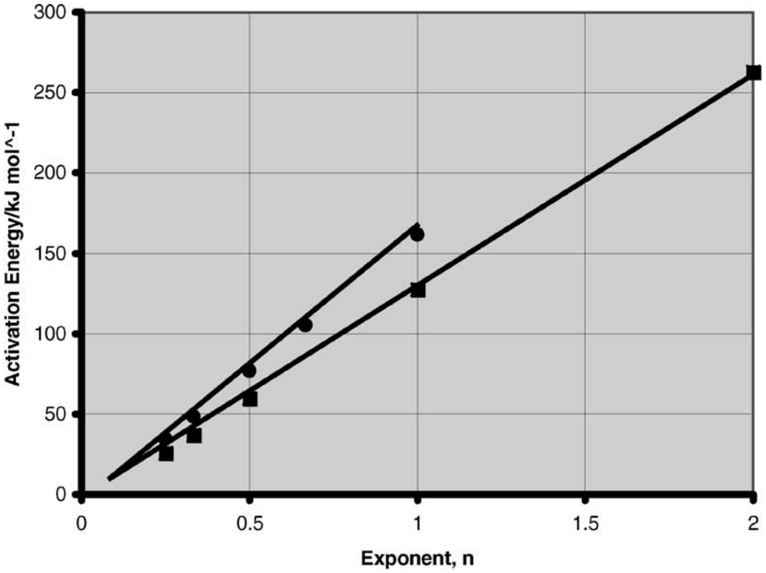

Fig. 1. Plot of exponent, n, in power law (●) and Avrami–Erofeev (AE) (■) kinetic models [1] against E for data calculated by the Integral method from Table 4 in [17]. The extrapolated straight lines, through each set of points, intersect the axis at small positive values of n, between about 0.05–0.10.

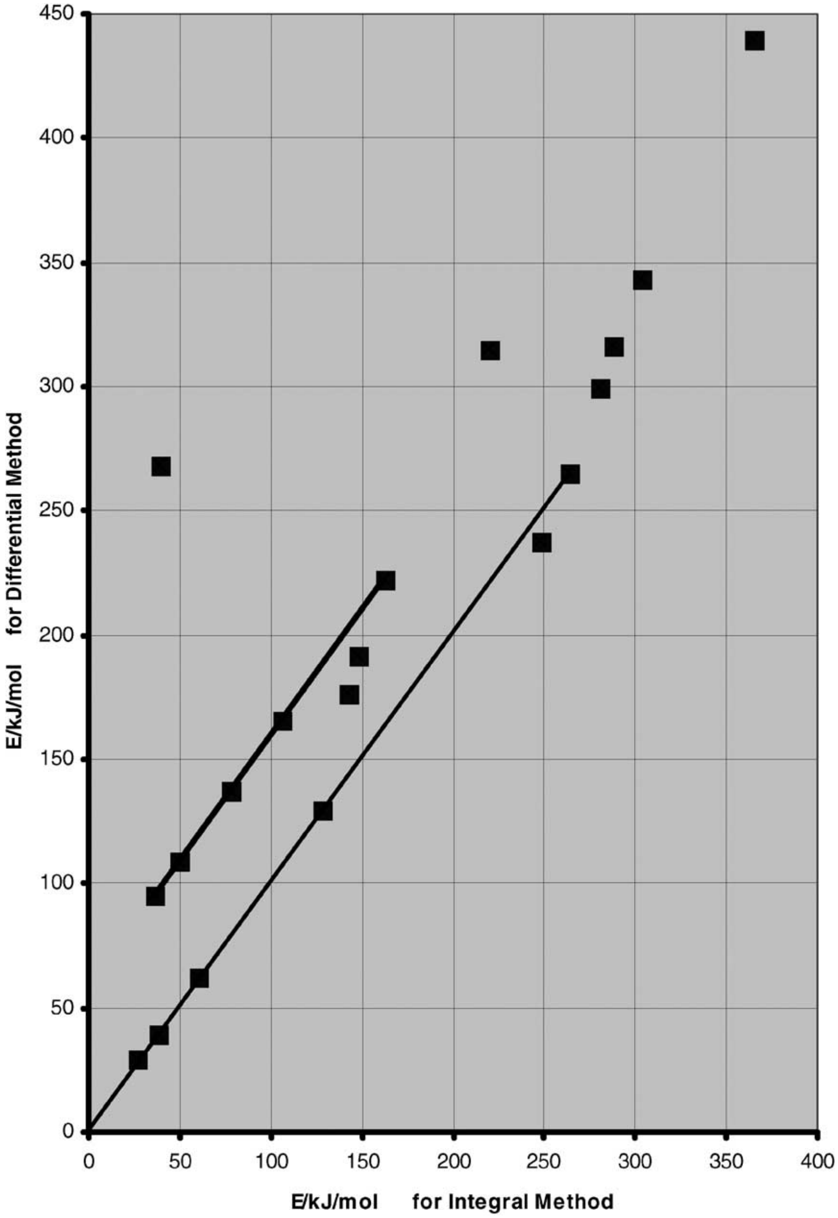

Fig. 2. Plot of values of E calculated by Integral method (StdSet) against those calculated by Differential method from Table 4 in [17]. The (upper) stronger line connects five points for the Avrami–Erofeev equation with $n = 1.0, 0.667, 0.5, 0.333$ and 0.25: the lower line, passing through the origin, connects the five points for the power law with $n = 2.0, 1.0, 0.5, 0.333$ and 0.25. The contracting geometry equation points ($n = 0.5$ and 0.333) are between the two lines and all the high apparent values of E resulted from the kinetic models characteristic of diffusion controlled rate processes [1].

Moreover, it might reasonably have been expected [19] that the Differential method would have provided a more discriminating method for identification of the kinetic model giving the ‘best fit’. There were some examples of considerable differences between the alternatively calculated Arrhenius parameters, most notably Eq. (19), for which E changed sevenfold. There was also a significant (50%) change for Eq. (18), together with a few other, smaller variations.

Trend B2. Values from the Differential method showed general similarities with those described for Trend A2. It was further noticed that the differences between the alternatively calculated E values for the power law were remarkably constant (2,908 cal mol^{-1}) for the five values of n. The same accuracy, but different difference (61,100 cal mol^{-1}), was apparent between each pair of values for the five AE equations, Fig. 2.

Trend B3. As Trend A3.

Trend B4. A compensation effect was again found.

2.4. Comparisons of the StdSet data with results obtained by comparable methods

Similar sets of detailed results from the kinetic analysis of rate data for Stage 3 of the thermal decomposition of the same reactant are given in Table 5 of [17]. Magnitudes of E, and $\ln A$, are generally smaller than those in Table 4 but a closely comparable pattern of relative values appears, though with some small quantitative variations. Results from Integral methods exhibit almost the same sequence as in Trend A1, but values of E from Eqs. (18) and (19) are relatively larger and some minor changes in sequence are found in Trend B1. Trend B3 was less obviously applicable, exceptionally Arrhenius parameters from Eq. (12) were relatively smaller. The pattern of differences in E calculated alternatively by Integral and Differential methods was identical with that illustrated in Fig. 2 (Trend A2) but absolute values were different from those in Table 4. Again two lines are found on the compensation plot (Trends A4 and B4), from the two data sets, but here the lines are almost parallel, giving the isokinetic temperature [20] 824 K, within the interval of the kinetic measurements.

These patterns of kinetic parameters [17] are readily and comprehensively compared with results obtained by almost identical kinetic studies reported [22] for decompositions of two copper and two nickel complexes of Schiff bases. The presentations in both articles are closely similar, including the same range of equations tested comparatively and the information reported. (The close relationships of these two complementary studies provided another reason for selection of the StdSet. This unusually similar correspondence occurs even though the investigations were completed in different universities with no common authors.) The data reported in Tables 7–10 of [22] are readily compared with the results in Tables 4 and 5 of [17], discussed above. While the absolute magnitudes of the Arrhenius parameters vary for the several different reactants, and many r values are much lower than the high values characteristic of the StdSet, the patterns of variation are remarkably similar. The following generalizations can be made.

1. Values of E reported for each of the data sets from [17,22] extended across a wide range of magnitudes. While some exceptions were found, the relative values of E calculated for the different reactants frequently followed virtually identical patterns of relative change with the kinetic model used in the calculations: Trends A1 and B1. Negative values of E were reported for some equations using the Differential method. In most tables some values of E, alternatively calculated from Integral and Differential methods, were approximately similar while others exhibited significant differences: reasons for these variations were not established.
2. Every set of Arrhenius parameters recorded in all six tables of kinetic results [17,22] exhibited marked compensation effects, Trends A4 and B4. For all data from Integral methods, the six lines passed through, or near, the graph origin (0, 0). Isokinetic temperatures calculated from the slopes were always within the temperature ranges of the rate measurements (close to 600 and 660 K for both of pairs of copper and nickel salts [22], respectively). Each of the compensation [20] lines for kinetic parameters obtained by the Differential method (Trend B4) were close to, but not coincident with, the lines obtained from Integral method values (Trend A4) for the same reaction.
3. E magnitudes calculated by the Integral method varied linearly with the exponent, n, for both power

law (Eqs. (1), (14)–(17)) and AE (Eqs. (7)–(11)) equations [1]. However, extrapolation to $E = 0$ gave a small positive intercept at $n = 0.05$–0.10 (approximately) for all six data sets. Thus, E varies linearly with n, but the magnitude of E/n decreases with diminution of both parameters.

4. Within each group of related rate equations (power law or AE [1]), the magnitude of the difference (E(Integral) $-$ E(Differential)) was precisely constant for each of the two groups of five equations. However, the magnitude of this difference varied widely and apparently randomly, from small values up to about 110 kJ mol^{-1} within each of the six data sets. No pattern in the magnitudes or explanation for these variations could be advanced. Calculated sets of E values for all these reactants showed the relative distribution pattern illustrated on Fig. 2.

It seems probable that this characteristic, and generally constant, pattern of variations in the magnitudes of calculated Arrhenius parameters arises through common features, present within the mathematical procedure. The Trends appear, therefore, as a computational artefact. We first consider the generality of these Trends, then discuss the mathematical treatment because different patterns of variation appear in the different data sets, for example, the unexplained differences in point 4 of the previous paragraph. Reasons for the overall pattern described are considered in the subsequent section, including a brief discussion of some aspects of the background theory that may be applicable to enable the problems of analysis to be placed in a wider context. First, however, the above pattern of Trends is compared with other relevant literature reports. This comparison is inevitably incomplete, because most of the relevant articles contain less detailed information.

Identification of ‘best fit’ rate equation. Recognition of the kinetic model that most satisfactorily represents a rate process of interest, from amongst the several, or many, possibilities included in the consideration, is often based on the equation giving the relatively largest value of the correlation coefficient (r). However, as pointed out by Vyazovkin [23], this can be unsatisfactory where two or more values of r are close and represent very different magnitudes of E and kinetic models. This might alternatively be expressed as ‘uncertainty is introduced by the uncertainty in the uncertainty’. This approach to kinetic analysis must be regarded as unsatisfactory because it provides poor ability to discriminate ‘best fit’ between alternative possible kinetic models. Identifying the appropriate (‘correct’) rate equation can be difficult and aspects of the problems encountered have been discussed [18,19,24,25]. One proposed solution [23] to this conundrum is the use of the ‘advanced isoconversional method’, using multiple heating rates to calculate E values. Temperature coefficients are measured for the zero order reaction rate, $\mathrm{d}\alpha/\mathrm{d}t$, applicable over small α intervals. This method of rate data analysis does not appear to characterize the kinetic model. A comprehensive kinetic analysis should be capable of accounting for all rate characteristics. This includes distinguishing between the three main types of solid state reactions [1]: sigmoid (nucleation and growth), deceleratory (contracting volume or area), strongly deceleratory (diffusion control). Where this is not achieved, as in some examples mentioned above and also below, a principal objective of the kinetic analysis has not been realized.

Compensation effect. The compensation effect is a linear relationship between $\ln A$ and E: any increase in the magnitude of one parameter is offset, or compensated, by an appropriate increase of the other [20,21]. Instances of this pattern of behaviour are reported widely in the kinetic literature, representing patterns of relative rate variations with temperature. The effect has been widely observed to occur within a group of reactions related by one or more common chemical features or for a single reaction investigated under a range of different experimental conditions. It is a property of the compensation relationship [20] that at the isokinetic temperature rate constants for all reactions within the group exhibiting the effect have the same value. It follows that if the same, perhaps even a single set of rate data, which necessarily apply within the same temperature interval, are alternatively analysed to give a range of Arrhenius parameters, their magnitudes must exhibit compensation. Thus, although compensation parameters b and c ([20] from $\ln A = bE + c$) are often reported in articles of the type surveyed here, these terms can have no chemical significance because they arise (as explained below) as an artefact inherent in the mathematical procedures used.

2.5. Comparisons with other representative published studies

The other literature reports of multiple kinetic analyses were found to be much less comprehensive than those in [17,22] above. Most included only a relatively small number of pairs of Arrhenius parameters calculated for a range of kinetic models by the Integral method. For most of the comparable examples cited below, it is argued here that all of the (sometimes limited) evidence available apparently presented the same relationships, Trends, as those described above for the data in [17,22].

Decomposition of copper ammonium chromate. Although the range of kinetic data reported in [26] was limited to Arrhenius parameters calculated for nine Integral forms of the rate equations, close parallels were found with those of the StdSet. Reported variations of E with rate equation were relatively larger ($\times 1.57 \pm 0.06$) than in Trend A1, but all values followed the same sequence. A plot of E against n, for three AE equations, intersected the axis at $n = 0.05$ (Trend A2) and data exhibited a compensation effect (Trend A4). Values of r reported for the nine equations were all 0.9920 or greater, despite the quite different forms of the rate/time curves represented: again evidence of poor discrimination.

Decomposition of bis(*dialkyldithiocarbamate*) *complexes of palladium*. Relative magnitudes of E and A varied considerably between the five reactants studied [27] and were approximately comparable with the StdSet. Extrapolations from the calculated two AE values of E for each of the five reactants intercepted the axis between $n = 0.05$ and 0.10 (Trend A2). A pronounced compensation effect was found (Trend A4) for reactions that occurred within similar temperature intervals.

Ammonium dinitramide, HMX and ammonium nitrate. Three kinetic studies, for the thermal decompositions of ammonium dinitramide [28], of HMX [14] and of ammonium nitrate [23], have been reported by Vyazovkin and with Wight [28] reporting values of E calculated for 12 equations by the Integral method. The Trend (A1) of E values with rate equation were as for the StdSet. From each rate equation, the ratios of calculated magnitudes of E were almost a constant value (all E values for ammonium dinitramide/HMX were 1.83 ± 0.12 and for ammonium dinitramide/ammonium nitrate were 1.11 ± 0.11), evidence of a closely similar pattern of variation between the calculated results for all three reactants. Trend A2 was found: plots for E calculated from both power law (five points each) and AE equation (four points each) against exponent, n, gave separate lines but all six lines extrapolated to intercept the axis close to the same value of $n = 0.05$ (Trend A2). Trends A3 and A4 were also observed. Values of A were not recorded for ammonium nitrate but the slopes of the compensation plots for ammonium dinitramide and HMX gave isokinetic temperatures of 457 and 502 K, respectively, both within the ranges of the kinetic measurements. Overall these patterns of kinetic parameters show a close resemblance to that of the StdSet.

Ortho-palladated complexes with pyridine. Activation energies were reported [29] from nonisothermal kinetic studies for the thermal decompositions of five reactants analysed through 10 alternative kinetic models. The sequences of E magnitudes for the nine comparable equations were as the StdSet (Trend A1). Values of E found from four forms of the AE equation ($n = 1.0, 0.667, 0.5, 0.333$) extrapolated to intercept the axis close to $n = 0.05$ (Trend A2). Results also exhibited Trend A3. Values of A were not reported so that the existence of a compensation effect could not be tested. Arrhenius parameters reported for isothermal rate measurements using the same five reactants showed values of r all greater than 0.9948 for the fit of each data set to three different rate expressions (A1.5, A2, R2 [1]): again the apparently close representation of data by the different rate equations is evidence of poor kinetic model discrimination [18,19].

Areneruthenium(*II*) *derivatives*. Sanchez et al. [30] have reported kinetic (rising temperature) studies for the first step in the thermal decompositions of areneruthenium(II) chloride complexes with five different ligands. The various ligands were eliminated between 424 and 487 K in air to give residual binuclear complexes. Rate data were analysed by three different equations, conventionally used in kinetic analysis (Coats–Redfern (CR), MacCallum–Tanner (MT) and Horowitz–Metzger (HM)), to investigate the comparative fits of data to a range of Integral rate expressions including most of those listed in [17]. For each of the 10 reactants studied, three values of E and $\log A$ calculated by three of the expressions given above are recorded, apparently selected to give

r values closest to unity. For the 90 pairs of Arrhenius parameters listed, r values for two are 0.99999, a further 21 are 0.99990 or above, 46 are between 0.99900 and 0.99990, 15 are between 0.99800 and 0.99900, the remaining six were above 0.99600. These are remarkably high correlation coefficients and demonstrate that the approach does not satisfactorily discriminate between the fit of data to alternative possible rate expressions [18,19]. Twenty-nine from the 30 fits found by the CR method were to diffusion or contracting geometry kinetic models, while the alternative analyses (MT and HM) of the same data included some fits to the AE equations [1]. The sets of results gave evidence that the Arrhenius parameters showed variations for the different salts studied. However, within each set, the magnitudes of E followed the same sequence as the StdSet, Trend A1. There were some trends of decrease of E with AE exponent, suggesting Trend A2, but the limited evidence available was insufficient to provide confirmation. Trend A3 was found in many instances. There was a strong compensation trend overall, Trend A4, and some of the slight scatter of points was attributable to lines of different slopes given by each of the ten different reactants considered in the composite plot.

Dehydrations of sodium lanthanum sulphate monohydrates. Kolcu and Zumreoglu-Karan [31] have made nonisothermal kinetic studies of the dehydrations of double sulphate monohydrates of sodium with four light lanthanides. The pattern of variations of Arrhenius parameter magnitudes with kinetic model was again closely similar to that of the StdSet. The sequence of E values, for the eight Integral method equations that could be compared, conformed with Trend A1. Extrapolations of the plots of E against the three values of n (1.0, 0.5, 0.333) for the AE equation intercepted the axis close to $n = 0.1$ for all four salts (Trend A2). Values of E from the diffusion controlled/interface equation were about twice those for the contracting volume and contracting area expressions (Trend A3). There were some indications that the activation parameters calculated by the Differential method showed approximate fits to Trends B1 and B3, but the behaviour pattern showed appreciable variations from those described above. Again compensation effects were found, Trends A4 and B4: points for Integral method and for Differential method values were close to two parallel lines.

Other examples. Further reports that exhibit some of the behaviour patterns described above include [32,33].

Dehydration of transition metal sulphate hydrates. A further set of kinetic reports, see [34,35] and references therein, contain features similar to those described above. Magnitudes of E, calculated using the AE equation for several values of n, intercepted the ($E = 0$) axis close to $n = 0.05$ for the four reactions distinguished in the stepwise dehydration of $NiSO_4{\cdot}6H_2O$: however, see [36] for a discussion of aspects of the stoichiometry of these reactions. Compensation behaviour was found in which, surprisingly, the Arrhenius parameters for the four dehydration steps distinguished as occurring in different temperature intervals, between the limits 416 and 631 K, were all close to a single line (apparent evidence of Trend A4). However, reservations must be expressed about incorporating these results into the present comparisons because it appears that α values used in the kinetic analyses of the individual and distinct consecutive rate processes are referred to the overall reaction ($-6H_2O$), instead of being calculated individually for each dehydration step.

Comparative studies. In a recent comparative project [37], "Computational aspects of kinetic analysis" initiated and coordinated by ICTAC, different groups of workers compared results of their kinetic analyses of the same eight sets of measured rate data supplied. A principal outcome was that there were very significant variations in the magnitudes of Arrhenius parameters reported by the different participants, all calculated from the identical data. Aspects of these variations and the patterns of kinetic parameter distributions have been discussed [38] in the context of the compensation trends identified. It is considered impossible to make a definitive comparison of the extensive tabulated data in [37] with the Trends identified above, because procedures in the computational methods used by the several participating laboratories are not available in sufficient detail. However, the recognition of compensation trends in [38] suggests the possibility that some, at least, of the spread of reported E values in [37] may arise for similar reasons to those underlying the variation of E with rate equation, [$g(\alpha) = kt$], found in [17] and in the other systems listed above as exhibiting comparable behaviour.

Similar considerations may (or may not) apply to results obtained in the “Round robin test in the kinetic evaluation of a complex solid state reaction from 13 European laboratories” [39]. This study differed from the ICTAC project [37] in that each of the participating laboratories made their own kinetic measurements, using samples from the same reactant preparation, and the data obtained were kinetically analysed using a common computer program. Again the spread of calculated kinetic parameters, for each of the three distinct reactions investigated, was considerable and compensation trends were identified. These results are said (Abstracts of [39]) to “allow an optimistic assessment for the application of kinetic procedures to solid state reactions with well-known chemical course investigated by TG (Part 1)... by DSC (Part 2).” It is not clear to me exactly what aspect of this work is regarded as providing the evidence for such optimism, because the kinetic conclusions and magnitudes of the calculated Arrhenius parameters show considerable scatter for reasons that have not been established. It could be that a method capable of resolving the inconsistencies demonstrated in [39] may ultimately emerge from the shortcomings identified here as present in the kinetic analysis methods widely used. (It should also be pointed out that the first of the reactions in this study does not follow a ‘well-known chemical course’, as stated, because the dehydration of calcium oxalate monohydrate has been shown to proceed as two concurrent of overlapping reactions [40]. This mechanistic consideration, probably influencing the kinetic interpretation, is not discussed in [39]. The initial dehydration rate process is, therefore, complex. Consequently, the comparisons consider the kinetic analyses of three distinct reactions, of which two may be single or simple, but these certainly do not constitute a ‘complex’ solid state reaction, as described in the article title.)

Additional related kinetic patterns. The pattern of variation of E with kinetic model, $g(\alpha) = kt$, reported in [41], includes significant differences from those described above, though the specific forms of the rate equations used here for the data interpretation are not specified. Similarities include an approximate Trend A3 and compensation effects (Trends 4) for the thermal decompositions of the three reactants studied: cadmium, manganese and lead carbonates. However, although the magnitudes of E diminished in the sequence Eqs. (7), (12), (13) [17] (apparent Trend 2), the diminutions were small and the E values reported for each reactant might (just?) be regarded as approximating to a constant value. Many of the E magnitudes from the Integral and Differential equations compared were similar, though there were also instances of significant differences. Of the 60 regression coefficient values reported (two alternative methods of kinetic analysis comparing fits to 10 rate equations for three reactants), 10 were greater than 0.9990 (all for $CdCO_3$), and 32 were between 0.9900 and 0.9990. This is evidence of apparently satisfactory fit of sets of measured data to alternative rate equations so that again the analysis method gives a low level of distinguishability [18,19].

Arrhenius parameters were calculated from rate data [42] for the first step in the decomposition of $(CH_3NH_3)_2MnCl_4$, by a range of different mathematical approximate approaches to nonisothermal kinetic analysis [1]. These results again showed considerable variation and also exhibited a compensation effect. Reasons will not be discussed here, because alternative analytical expressions were used, whereas the present survey is mainly concerned with the CR method [12].

2.6. Comment

Kinetic results from [17,22] were compared and contrasted here to exemplify the particular characteristic and systematic pattern of variations of calculated magnitudes of Arrhenius parameters with changes of the rate equation used in the analysis. While the absolute apparent magnitudes of E change between different reactants, there is an almost constant pattern of relative variations of E with $g(\alpha) = kt$ within each of the series of Trends recognized above. It appears that, with minor variations and within less extensive ranges of data than those given in [17,22], the same Trends are to be found in the many other sets of kinetic data cited above. I suggest that the most probable explanation for these variations is that the calculated (apparent) magnitude of E for any reactant (expected to be constant [13]) changes as a direct consequence of alternative steps constituting the mathematical procedures used when applied through the different kinetic models. In consequence, the Trends observed are identified as computational artefacts. This means that the value of (the correctly defined, constant) E for any reaction might be determined by a method other than through the unsatisfactory [23] criterion of comparing r values. Identification of the reasons for the (apparently) variable E would eliminate a considerable uncertainty in the kinetic analyses of many thermochemical investigations. This problem is explored below.

Linear correlation coefficients (r) *and coefficients of determination* (r^2). These statistical parameters, that provide a measure of the excellence of fit (or otherwise) of data to a kinetic expression, appear to be regarded by researchers as being increasingly welcome, acceptable or significant as their magnitude approaches unity. Values of r or r^2 provides a measure of the closeness of fit of data to a perfect representation by the kinetic model considered. Such criteria are to be regarded as valuable in kinetic analysis, as in other scientific fields, and the sources cited above report many high values of r or r^2. However, when attempting to identify the 'best kinetic fit' between alternative rate equations, the appearance of two, or more, high values of r or r^2 should no longer be welcomed because this then becomes evidence of poor ability to discriminate [18,19] between these alternatives. Ideally, in kinetic analysis, one equation should appear to be much 'better' (i.e., r or r^2 close to unity) than all others and so that expression can be recognized as being uniquely applicable. The demonstration that alternative rate expressions, representing nucleation and growth, deceleratory or strongly deceleratory α–time (t) relationships [1], when applied to the same data, give values of r or r^2 close to unity demonstrates that the method is unsuitable for identification of the 'best fit'. This is clearly evident in many thermoanalytical publications, including several discussed above.

3. Reappraisal of methods of analysis of thermochemical rate data

The experimental techniques now exploited to obtain kinetic measurements, using thermoanalytical methods, enable large numbers of accurate data points to be collected rapidly and efficiently. The application of integrated (or associated) computer equipment, using analytical programs or spread-sheet methods of computation, permits almost effortless data interpretation (partial). The results so obtained are printed in a convenient, and apparently authoritative, format which is readily prepared for publication. The kinetic conclusions arising as a consequence of this approach include (as in the papers cited above) multiple values of the Arrhenius parameters derived from single, or sometimes from multiple, data sets. (Kinetic interpretations reported, proposed or formulated are often limited to the identification of the kinetic model giving the 'best fit' to the data. This kinetic model is then frequently (and incorrectly) described as the 'reaction mechanism', thereby conveniently disregarding the more difficult objectives of elucidating the chemical steps and controls of the participating reactions. These are recognized as essential features of a reaction *mechanism* in other areas of chemistry.) The outcome of the widespread acceptance (toleration) of these conventions and practices is a literature consisting of individual reports, largely composed of empirical observations, in which the descriptive scientific terms (mechanism, activation energy) used may, or may not, have been applied in a form intended to maintain consistency with other branches of chemistry. What is abundantly clear is that this collection of separate and distinct information fragments does not constitute a coherent scientific discipline within which the contributions are linked by unifying concepts or theoretical models [13]. Consideration of these practices is essential to recognize the shortcomings inherent in current kinetic analysis methods which might then lead to methods whereby errors in published work could be corrected. Some of the literature data might yet yield valuable results on critical reappraisal and reanalysis.

As in other branches of chemistry, those contributions to the thermoanalytical literature, which are concerned with kinetic measurements, appear to be motivated by the intention to elucidate reaction mechanisms. However, the published literature lacks coherence, results are without an adequate theoretical framework and a proportion of the conclusions are based on unsuitable experimental measurements (only capable of yielding empirical, conditions-sensitive rate information [3–9]). The problem, not always addressed in published articles, is how to formulate the theoretical framework essential to introduce order into the extensive published material available and encourage future growth of the subject in a systematic manner. The absence of critical reviews has undoubtedly contributed towards the apparent absence of interest in theory development.

I suggest that two complementary problems must be recognized as existing within the accepted customs and practices of thermal analysis and both now require urgent recognition and reappraisal. One is the necessity for a critical examination of the computational methods that are currently employed in the kinetic analysis of thermochemical data and, in particular, the necessity to ensure that all scientific terms and data units are correctly used. The present article commences this appraisal by critically examining the mathematical procedures (apparently) used for kinetic analyses, based on the applications of the CR equation in the citations given above. This is essential because progress can be expected only if the data used are reliable and the meanings, and limitations, of all conclusions are fully understood (which, at present, is not always obvious). The second action required is the systematization of results, of proven reliability, which requires a unifying theoretical model [13], to which the individual systems may be related and classified. This is found in recent proposals by L'vov [10,11] which provide a rigorous and self-consistent explanation for the exponential dependence of the rate of crystolysis reactions [1] on temperature. This physical approach replaces earlier theoretical (chemical) treatments and has already been successfully applied (see [10,11] and references therein) to several groups of thermal reactions in which systematic order for sets of rate processes has now been identified where none had previously been perceived. This reaction model, based on published thermochemical data, can only be successful in correlating reliable experimental observations that are related to completely characterized chemical changes.

The aspect of kinetic analysis addressed here is that, for a literature which includes many recommended approximate calculation methods for the determination of kinetic information (including A, E and $g(\alpha) = kt$) from nonisothermal measurements [1], the relative strengths and weaknesses of the diverse and various alternative expressions available [1,2] have never been established nor agreed. Reports exploiting these methods almost invariably choose one or other expression, or several, without explaining the reasons or providing any justification for the particular calculation method selected. In the absence of critical and comparative reviews, the choice of approximate program for kinetic analysis becomes arbitrary. (Various approximations were proposed in developing the alternative equations [1] which were originally formulated to enable kinetic calculations to be completed in a reasonable time. This was necessary in the era before high speed computing facilities became widely available. The same well-established procedures have, however, continued to remain as preferred methods of data analysis. No comparative tests, designed to identify sensitivity in distinguishability or ranges of applicability of fit to different kinetic models (such as [18,19]) appear to have been reported. Even now, decades after their introduction, there are few suggestions that these computational methods should be replaced by the more sophisticated computer programs, now available, that must be capable of increasing the accuracy and reliability of calculated parameters and kinetic modelling, as pointed out by Flynn [43].)

The present paper is specifically concerned with an examination of the properties of the widely used approximate method of kinetic analysis usually referred to as the Coats–Redfern (CR) equation [12] used in [17], see also [22,23,26,29–32,37,41]. In the absence of quantitative characterization of the properties of this equation, including tests of its efficacy in distinguishing the fit of experimentally measured data to alternative kinetic models [18,19], significant, indeed fundamental, shortcomings present in this analytical method appear not to have been appreciated. However, in addition to their ability to interpret kinetic observations, computers are equally capable of checking the methods and results from such data analysis. This is initiated here. A principal consequence should be the introduction of improved calculation methods throughout this subject area, exploiting the power of the computer [43] to replace the obsolete, now demonstrably redundant, older approximate methods of kinetic analysis. Results obtained by improved analysis methods may then contribute to the development of a subject ordered within the theoretical framework recently proposed and developed [10,11].

Conclusions from my critical reappraisal of the CR equation are reported below. This analysis is based on the results in [17] because the kinetic information is given in detail, is relevant to the wider literature and is in a form suitable for reconsideration by a kineticist who now does not have access to suitable equipment to enable me to make my own kinetic measurements. Similar investigations of the reliability of calculations using the several other equations mentioned in [1] would certainly be worthwhile. Alvarez et al. [42], for example, have shown that apparent magnitudes of Arrhenius parameters vary with the approximate analytical expression used in their calculations. The motivation for the present comparative survey was to show that (so-called [14]) 'variable activation energies' can arise through limitations and shortcomings of the programs and mathematical methods used to calculate Arrhenius parameters. This is demonstrated here for the CR method when applied to solid state type kinetic models, $g(\alpha) = kt$ [1], and the conclusions are probably equally applicable to other approximate methods.

3.1. Properties of the Coats–Redfern (CR) equation [12]

The CR equation is often applied in the form [17]:

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

where the symbols have their usual meanings. This expression omits the necessity to define a specific rate constant for reaction, and, significantly, any obligation to consider units. This is a fundamental, and potentially damaging, flaw in this approach to rate data analysis which is capable of accounting for features of the Trends described above. The isothermal kinetic equation [1] is usually expressed in the form $g(\alpha) = kt$ where the rate constant, k, has the units $(\text{time})^{-1}$. It would appear that the use of Eq. (1) introduces units of an implied rate constant. The units of temperature, at constant heating rate, include $(\text{time})^{-1}$, whereas the overall contribution from the temperature change through the (T^{-2}) term is much smaller. Where there are other terms, such as rate constants introduced to interpret rate data, the Arrhenius parameters may become scaled accordingly, for example, the magnitude of the conventional E can be changed by a factor n ([1], p. 121), as shown in Section 3.2.

In discussing the analysis of data below, we refer to the kinetic models (from Table 3 of [17]) as FI1 to FI19 for the Integral method and FD1 to FD19 for the Differential method, and data points D1 to D17 refer to the reported α values. Representative plots of $\ln[g(\alpha)/T^2]$ against T^{-1} are shown in Fig. 3 for equations FI7 (upper steep slope), FI13 (lower steep slope) for which the values of E are not widely different (161.550 and 147.661 kJ mol^{-1} [17]) and FI16 for which E was much less (37.195 kJ mol^{-1}). Representative repeat calculations from the data given in Tables 2 and 3 of [17] confirmed and were entirely in accordance with values reported in Table 4 [17].

3.2. Power law equations

For the power law equations FI1, FI14 to FI17 [17], we can write Eq. (1) in the following form:

$$n\ln(\alpha) - 2\ln T = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$
$$\left(n = 2.0, 1.0, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}\right) \tag{2}$$

The significant feature of this expression is that the various forms of the power law differ only by the magnitude of the exponent, n [44]. Dividing through by n, it is immediately apparent that the form of Eq. (2) is incapable of distinguishing between these kinetic models and that the apparent Arrhenius parameters are scaled by the exponent.

Distinguishability. The first term in Eq. (2) is significantly larger than the second. Specifically, for data from [17] these values range from ×29 to ×2.8 when n decreases from 2.0 to 0.25. The range of magnitudes of $n\ln\alpha$ between points D1 and D17 (i.e., $\Delta(n\ln\alpha)/T^{-2} = n\ln \text{D17}(0.9948)/T^{-2} - n\ln \text{D1}(0.013)/T^{-2}$) are listed in Table 1, together with comparable data for the other equations from Fig. 3, similarly correlated here. For the power law expressions, in the first row, these changes are much larger than the change in $2\ln T$ (which is $12.471 - 12.188 = 0.284$). Moreover, these CR function increments reduce progressively from 0.0045 to 0.0039 for each degree (K) rise across the particular temperature interval studied [17]. It follows that the form of the first two terms in Eq. (2) is incapable of distinguishing [18,19] the fit of data varying between the deceleratory process (FI1), the constant rate of reaction (FI14) and the three acceleratory processes (FI15 to 17). Consequently, this method of kinetic analysis is shown to possess almost no ability to detect any change in shape of the α–t relationships so that distinguishability is poor (indeed, almost nonexistent) except the effect arising from the small contribution through the constant systematic variation of the $2\ln T$ term. This is confirmed by the small changes in the

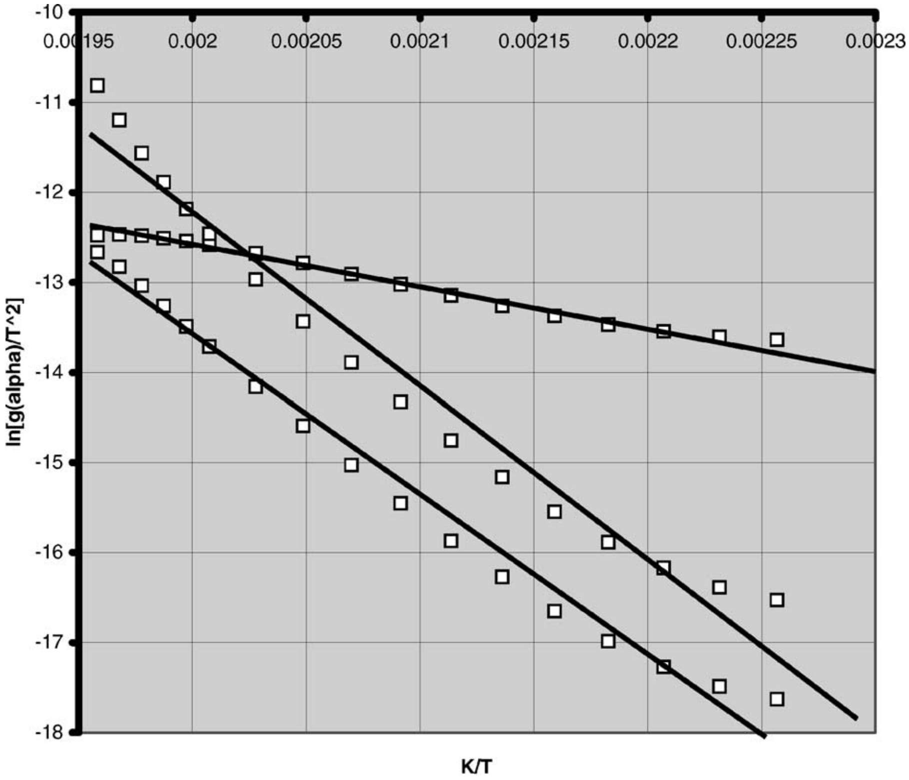

Fig. 3. Representative plots of $\ln[g(\alpha)/T^2]$ against $1/T$ for three equations from data listed in [17]: FI7 (first order equation, upper steep line), FI13 (contracting volume equation, lower steep line) and FI16 (power law, cube root equation, lower slope).

Table 1
Range of magnitudes of the term $\ln[g(\alpha)/T^2]$, for the different kinetic models considered in Fig. 3, across the temperature interval (443.14–520.64 K) for data recorded in Tables 3 and 4 of [17], and including calculated magnitudes of E[a,b]

Exponent, n	2.0	1.0	0.6667	0.5	0.3333	0.25
Power law FI1, 14–17	8.392	4.054	–	1.885	1.162	0.801
r^2	0.9910	0.9905	–	0.9893	0.9879	0.9861
E (kJ mol^{-1})	262.84	127.46	–	59.76	37.19	25.92
Avrami–Erofeev equation FI7–11	–	5.713	3.714	2.714	1.715	1.215
r^2	–	0.9707	0.9694	0.9680	0.9649	0.9613
E (kJ mol^{-1})	–	161.56	105.08	76.82	48.57	34.44
Contracting volume FI4, 13	10.210	4.963	–	–	–	–
r^2	0.9952	0.9845	–	–	–	–
E (kJ mol^{-1})	303.29	147.68	–	–	–	–

[a] The r^2 values are the ‘coefficient of determination’, and are lower than r, the ‘correlation coefficients’ given in [17]: overall the values agree well.

[b] The values of E given are recorded to a greater number of significant figures than I consider appropriate to confirm the close agreement with the results in [17].

coefficient of determination, r^2 (values 0.9910–0.9861: this variation arises from the systematically changing contribution from the $2\ln T$ term), listed in Table 1 for the set of power law expressions considered. Effectively, the comparative 'fitting' process is almost independent of n and the kinetic analysis is totally unsatisfactory in this respect.

Arrhenius parameters. The slope of the linear plot between the CR exponential term and $(T/\text{K})^{-1}$ is multiplied by the factor n between the different power law expressions and the overall influence of the second term ($-2\ln T$) remains small. Accordingly, the magnitudes of both apparent E and $\ln A$ values are scaled by the factor n, as found in Trend A2 (Fig. 1) and the compensation effect (Trend A4).

3.3. Avrami–Erofeev equations

For equations FI7 to FI11 we can rewrite Eq. (1) in the form:

$$n\ln[-\ln(1-\alpha)] - 2\ln T = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$
$$\left(\text{AE equation with } n = 1.0, \frac{2}{3}, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}\right) \quad (3)$$

The factor n multiplies (or scales) the magnitude of the logarithm of the deceleratory first order (FI7) expression which is modified only very slightly by the relatively much smaller contribution from $-2\ln T$. Again, the forms of these terms are incapable of distinguishing [18,19] between the deceleratory character of Eq. (FI7) and the progressively increasingly acceleratory character of Eqs. (FI8) through (FI11). The pattern of behaviour given by the CR analysis using the AE equations is identical with that described above for the power law, explaining the Trends A2 and 4. There is no adequate test of distinguishability.

3.4. Contracting volume equation

Only two other equations, identical in form but differing in exponent, FI4 and FI13, were available for this comparison [17] and have been included in Table 1, where the conclusions described in the two previous paragraphs again apply. The differences between the similar rate expressions FI12 and FI13 were small, Trend 3, the range of the first term, for Eq. (FI12) in the CR equation, was 4.674, r^2: 0.9980 and E: 141.79 kJ mol^{-1}.

3.5. Variation of activation energy with α range of data

The above analysis represents selected (Fig. 3) results of kinetic and statistical analyses in which the complete range of data points recorded in [17] were included (i.e., D1–D17). In this section, the consequences of systematic deletion of the initial data points are examined. Under the rising temperature regime, used in these experiments, at the mid-point of the temperature range from which data were collected, only some 12% reaction had occurred. Apparent E values calculated, with selective deletion of different numbers of points from the lower end of the temperature interval of the kinetic measurements, are shown in Table 2. The trend of variation of E values with range of α included [17] in the CR calculations is illustrated for the first order equation in Fig. 4.

The data in Table 2 (again) demonstrate that apparent magnitudes of E vary substantially with the rate equation used (Table 4 of [17]). Here, the calculated E values usually, but not invariably, increase with the selective deletion of low α values (by amounts between approximately 10 to 70%, for the equations compared). The values of r^2, which approach unity, are usually accepted as the measure of good kinetic 'fit'. However, the above variations demonstrate the existence of a further uncertainty that requires consideration when basing kinetic interpretations exclusively on this kinetic criterion [23]. The α range across which the kinetic model is applicable must be considered in any complete description of rate characteristics, but is not always mentioned or reported.

3.6. Trends

The above discussion of the mathematical steps in analyses of the same data by alternative rate functions in the CR equation, shows that this approach yields apparent E values that vary widely with both kinetic model (Trend A1) and range of α considered. (There may well be additional controlling influences from factors other than those considered here, including physical and chemical controls such as the dependence of rate measurements on reaction conditions, the procedural variables [3–9,15,16].) The systematic

Table 2
Apparent activation energy values calculated from selected kinetic measurements in Table 2 of [17] with selective deletion of measurements at low α values

	Range α	Eq. FI7	FI9	FI11	FI4	FI13	FI12
E (kJ mol^{-1})	0.013–0.9948	161.56	76.82	34.45	303.29	147.68	141.79
r^2		0.9707	0.9680	0.9613	0.9852	0.9845	0.9880
E (kJ mol^{-1})	0.0194–0.9948	177.79	84.88	38.44	328.05	160.02	152.52
r^2		0.9825	0.9810	0.9774	0.9949	0.9947	0.9968
E (kJ mol^{-1})	0.0374–0.9948	192.06	91.98	41.94	345.42	168.66	158.87
r^2		0.9867	0.9856	0.9831	0.9983	0.9982	0.9990
E (kJ mol^{-1})	0.0839–0.9948	206.68	99.25	45.54	357.35	174.59	161.35
r^2		0.9875	0.9865	0.9843	0.9993	0.9993	0.9987
E (kJ mol^{-1})	0.195–0.9948	225.90	108.82	50.28	366.46	179.10	160.25
r^2		0.9875	0.9866	0.9845	0.9996	0.9996	0.9970
E (kJ mol^{-1})	0.4339–0.9948	257.12	124.38	58.02	371.82	181.73	152.80
r^2		0.9904	0.9897	0.9883	0.9991	0.9991	0.9927

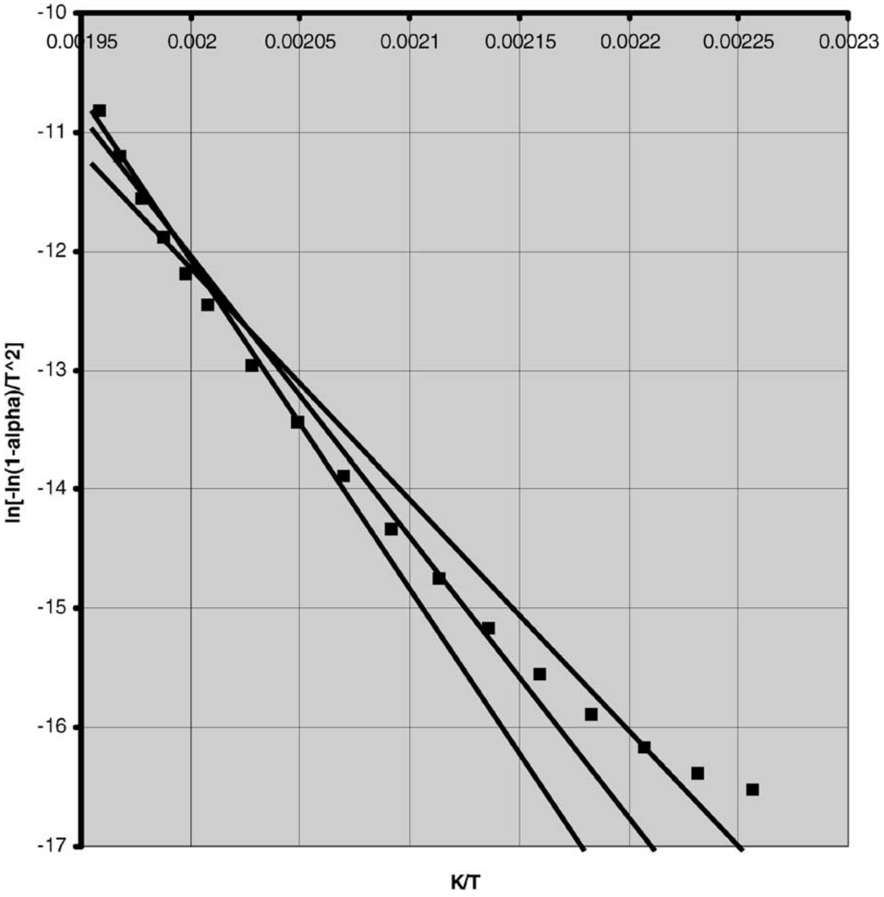

Fig. 4. Plots of the Coats–Redfern term with $g(\alpha) = kt$ as the first order equation for the StdSet data [17] with regression lines, in order of increasing slope, representing 'best fit' to data for α ranges extending from 0.013, 0.0374 and 0.195 to 0.9948, respectively (these graphs represent the first, third and fifth entries of the FI7 column in Table 2). There are significant changes in apparent E values with range of α data considered; calculated values, in the same sequence, were: 162, 192 and 226 kJ mol^{-1}.

changes of E with n (Trends A2 and A3) are shown to arise from the form of the Integral equations (Eqs. (2) and (3)) used in the kinetic analyses. The compensation effect (Trend A4) appears because the alternative rate equations are applied to the (identical) rate data measured within the same temperature interval (isokinetic behaviour) and both E and $\ln A$ are scaled by n. Plots of E against n (Fig. 1) do not pass through the origin but $E = 0$ at a small value of n, usually between 0.05 and 0.10. The magnitude of $\Delta(-2\ln T)$, across the temperature interval for the data used in this comparison, 0.284, corresponds to 0.05 to 0.10 of the range of variation of the term $\ln[g(\alpha)/T^2]$ (4–6 in Table 1), thus this term contributes to the intercept on the n axis.

The CR equation forms used in the present analysis omit all consideration of rate constants and the units of time do not explicitly appear in the treatment. However, the above observations suggest an interesting analogy between the role of the rate expression exponent, n, here and an inconsistency that appears during isothermal analysis using the AE equation. In the latter analyses, the incorrect definition of rate constant units as $(\text{time})^{-n}$ gives a value of E which is similarly modified by the factor n (see [1], p. 121). Consequently, term definitions and rigorous consistency of units must be regarded as essential features of kinetic analysis. This is currently being given insufficient attention.

3.7. Comparison of E values alternatively calculated by Coats–Redfern and isoconversional methods

Vyazovkin [14,23] and Vyazovkin and Wight [28] have reported magnitudes of E calculated alternatively by the Coats–Redfern equation and by the isoconversional method for the thermal decompositions of HMX, ammonium nitrate and ammonium dinitramide. Attention was principally concerned with the calculated magnitudes of E because Vyazovkin [23] finds "... the preexponential factor is a dependent and, therefore, an inferior parameter". (Why A should be considered 'inferior' to E in consideration of two complementary and potentially equivalent parameters connected by a compensation relationship is not explained. The essential significance of A, as one of the factors that provides an overall measure of absolute reactivity, is apparently disregarded.)

A comparison of these results, based on alternative interpretative calculations from [14,23,28] and summarized in Table 3, are of interest here in examining the above shortcomings of the Coats–Redfern equation. "Corrected" E refers to the values from Eq. (FI14) (estimated from the linear relationship between E and n) and FI7, to which the intercept ($-E$) at $n = 0$ has been added (for both the zero and first order equations the units of k are $(\text{time})^{-1}$). No explanation for the omission of E values for the zero order equation is given, but magnitudes are easily estimated from plots of E against n.

It was expected that the zero order equation would provide the most reliable values of E for comparison with those found by the isoconversional approach, which is based on consideration of successive reaction intervals of constant rate (i.e., the same kinetic model). However, the values in Table 3 identify an additional uncertainty, responsible for a difference of around 10% (compare columns three and five) between values obtained by the two calculation methods. The reasons are not identified here but could be a further conse-

Table 3
Comparison of activation energies calculated by Coats–Redfern method ("Corrected" as described in the text) and by the isoconversional method from data in [14,23,28][a]

	Kinetic order	"Corrected" E (see text)	Isoconversional E (approximate range of values)	Isoconversional E (approximate mean value)
Ammonium nitrate	Zero	76	85–95	92
	First	88.5		
Ammonium dinitramide	Zero	127	75–175	130
	First	147		
HMX	Zero	118	122–152	142
	First	134		

[a] All activation energy values E (kJ mol^{-1}) and rate equation units were $(\text{time})^{-1}$.

Table 4
Kinetic analysis of model data sets calculated for power law with $n = 2.0$, 1.0 and 0.5[a,b,c,d]

Model data set from power law, n	Test equation exponent, n					
	2	1	2/3	1/2	1/3	1/4
Fit of data to power law						
0.5	**103.72** (0.99819)	48.92 (0.99784)	–	21.52 (0.99684)	12.38 (0.99524)	7.82 (0.99247)
1.0	206.58 (0.99999)	**100.20** (0.99999)	–	47.01 (0.99997)	29.27 (0.99996)	20.41 (0.99993)
2.0	409.39 (0.99994)	201.49 (0.99994)	–	**97.54** (0.99994)	62.89 (0.99994)	45.57 (0.99994)
Fit of data to Avrami–Erofeev equation						
0.5	–	57.94 (0.9855)	36.68 (0.9842)	26.04 (0.9826)	15.39 (0.9787)	10.08 (0.9730)
1.0	–	115.44 (0.9864)	74.90 (0.9858)	54.63 (0.9851)	34.35 (0.9835)	24.22 (0.9815)
2.0	–	231.83 (0.9845)	152.43 (0.9841)	112.71 (0.9837)	73.00 (0.9828)	53.15 (0.9818)

[a] Apparent magnitudes of activation energy (E, kJ mol^{-1}) (and r^2 values) for fit of model data sets to power law ($n = 2.0$, 1.0, 1/2, 1/3, 1/4) and Avrami–Erofeev ($n = 1.0$, 2/3, 1/2, 1/3, 1/4) equations.

[b] Model rate data (α, T values) calculated for power law ($n = 0.5$, 1.0 and 2.0) from: $\log_{10} k = 12.00–100{,}000/RT$ for rising temperature (1 K min^{-1}) reaction across the approximate temperature range 320–400 K.

[c] Calculated activation energy values (kJ mol^{-1}) listed, together with (coefficients of determination, r^2), across range from $\alpha = 0.01$ to completion of reaction.

[d] Bold values refer to kinetic analysis of data by the 'correct' equation.

quence of the unreliability of the CR approximate approach in estimation of the ‘temperature integral’, see [43].

3.8. *Kinetic analysis of calculated model data by other rate equations*

Aspects of the pattern of results of kinetic analyses identified above were confirmed by comparative analysis of simulated (calculated) rate data. Three sets of α–T values were computed for fit to the power law equations, $\alpha^{1/n} = kt$, with n values, 0.5, 1.0 and 2.0, representing deceleratory, constant rate and acceleratory reactions. Rate constants for a typical reaction were taken as $\log_{10} k = 12.00–100{,}000/RT$, during heating at $1\,\mathrm{K\,min^{-1}}$ between about 320 and 400 K and kinetic analyses were made for α in the range 0.01 to virtual completion, $\alpha = 1.00$. Equations tested were from the series considered throughout this survey, the power law with $n = 2.0$, 1.0, 1/2, 1/3, 1/4 and AE with $n = 1.0$, 2/3, 1/2, 1/3, 1/4. The calculated values of E and r^2 are given in Table 4, ‘bold’ entries refer to analysis by the ‘correct’ expression, that used to obtain the data.

Plots of E against n were linear for both equations, all AE values were about 15% larger than the power law values (Fig. 1). All six lines extrapolated to coincide at an apparent $E = -6$ to $7\,\mathrm{kJ\,mol^{-1}}$ when $n = 0$ and the intercepts for $E = 0$ were between $n = 0.03$ and 0.11. An important limitation of the CR analysis is that some magnitudes of calculated E were significantly different from values used in the expression from which the simulated rate data were obtained. (The divergence was even greater from similar computations for the $n = 3$ power law, 93 instead of the expected $100\,\mathrm{kJ\,mol^{-1}}$.)

The values of r^2 in Table 4 show that the excellence of data fit changes only marginally with n, particularly for tests to the power law when values are close to unity. This cannot, therefore, be used as a criterion for kinetic distinguishability. The values recorded refer to the main reaction interval, in the range of data points between 1 and 100% completion. Tests were extended to lower α ranges, but these were characterized by lower r^2 values and magnitudes of E that changed with extent of α included and diverged even further from magnitudes associated with the high r^2 values listed in Table 4. This is readily explained through consideration of Eq. (1). The terms $-2\ln T$ and E/RT change systematically with the temperature rise, by relatively constant increments. The magnitude of the CR term $g(\alpha)$, in contrast, is determined by two parameters: the mathematical form of α and the exponential temperature dependency of the (usually unconsidered) rate constant that determines the magnitude of α and its incremental increases. Thus, the magnitude of the values of this term and the increments $\Delta(g(\alpha))$ vary relatively to the others as reaction progresses and no linear relationship can be maintained between $\ln[g(\alpha)/T^2]$ and T^{-1}. Thus the form of the CR function is most suitable for calculation of apparent E values over limited α intervals and the comparative data given in Table 4 refer to the range that is often of greatest interest in kinetic investigations. The CR approximation may be inapplicable at low α.

4. Discussion

The principal result from the above critical analysis of some methods of kinetic interpretation of thermal measurements is unambiguous. The Coats–Redfern equation, Eq. (1) [12], cannot be regarded as an acceptable method for the kinetic analyses of thermochemical rate data which are capable of representation through those kinetic models that are derived through geometric models applicable to crystolysis reactions [1]. The apparent magnitudes of CR-calculated Arrhenius parameters are scaled by the exponential term, n, present in many of the rate expressions. Moreover, the methods of testing the ‘fit’ of yield–time data to kinetic models, by the usual statistical criteria, are incapable of distinguishing between the alternative equations that contain different exponents. Arrhenius parameters are scaled by an undetermined factor, kinetic distinguishability is unsatisfactory: the CR equation is totally incapable of achieving its intended objectives, through its characteristic approach to kinetic analysis. While specific limitations of the method have been mentioned in previous publications [23,44], it appears that this is the first appraisal that has recognized the full extent, and reasons for, its general unsuitability. Reported conclusions based on the method, and interpretations derived therefrom, must not be regarded as reliable and these now require fundamental reconsideration.

The next obvious problem, for the subject overall, is to establish whether the other approximate approaches to analysis of nonisothermal kinetic data [1,2] are more reliable or suffer from similar unconsidered faults in the calculation methods and/or the underlying assumptions. Critical reappraisal of the consequences of the shortcomings now recognized should also be extended to reconsider all recently published kinetic conclusions. This might usefully include reports where only a single magnitude of E (perhaps accompanied by A) appears as the principal result from a kinetic study: possible limitations in the kinetic analysis method used may not be so readily perceived. Indeed, it is now obvious that the approximate methods of kinetic analysis have outlived their use and are due for replacement. A good starting place is the final sentence of the paper by Flynn, who considered the applications of the 'Temperature Integral' ("Its use and abuse") [43], and who states that: "... in this age of vast computational capabilities, there is no reason not to use precise values for the temperature integral when calculating kinetic parameters". Surely, by now, the practice of using the older (highly) approximate formulae in kinetic analysis might be regarded as redundant. It is unacceptable (mindful of current, and continuing, conventional practices) that the advantages and the untapped potential of the powerful computing facilities, that are now so widely available, should remain inadequately applied in this field. A more fundamental approach to the kinetic interpretation of thermoanalytical data is now overdue.

For the future prosperity of thermochemical rate studies, the reintroduction of the fundamental assumptions of chemical kinetics is essential, indeed overdue. Methods used to interpret programmed temperature rate data now require radical reassessment. The potential of the computing methods that are so widely available [43] should be applied in a constructive and critical manner through the use of programs that are soundly based on and capable of being related to chemically acceptable reaction models [10,11,13]. A new start, this proposed renaissance, must incorporate the essential chemical assumptions and definitions, rather than proceeding through mathematical manipulations which, in recent times, have eclipsed the realities of the subject. It is particularly surprising to me that the errors introduced into the CR equation during its initial development, through its applications to these types of reactions, were not immediately recognized. It is strange that these shortcomings have been disregarded for so long and that this, and other comparable, calculation methods still maintain pride of place in the forefront of modern thermokinetics. This cannot and should not be tolerated or sustained any longer. However, only when a full appreciation of the hopelessness of the present situation has been generally accepted can a new generation of data interpretation methods be implemented. The present discussion of the weaknesses exposed in the present criticism of the CR approach is intended to enable these faults to be comprehensively recognized, fully appreciated and avoided in the future. The hope now is for the restoration of acceptable scientific foundations that will provide an optimistic base for the regeneration of this branch of chemical kinetics.

Nonisothermal kinetic studies of rates of reactions in solution. Alibrandi [45] has drawn attention to the advantages of applying nonisothemal methods to the determination of activation parameters for reactions in solution, with reference to the earlier source [46]. Kinetic data can be collected in a shorter time, by spectrometric methods described, and with greater accuracy than with the usual isothermal technique. However, the approach to data analysis explained [45] bypasses the pitfalls that have substantially devalued the interpretation of kinetic observations in the field of thermal analysis. First, approximate calculation formulae are not introduced into the characterization of the separate influences of first order rate processes and of the Arrhenius equation through the use of curve fitting methods. Second, the analysis is directed towards distinguishing the relatively few homogeneous rate expressions and the complexity arising from the larger number of kinetic models associated with reactions of solids is avoided. For the examples mentioned, the rate constant units are $(\text{time})^{-1}$. Third, the potentially rate-influencing effects of self-heating and of diffusion control are inapplicable in the homogeneous reaction medium. Thermal analysis could perhaps learn from the simpler, more direct approach to rate interpretation in this treatment.

4.1. Identification of the kinetic model

Historically, the first step in data interpretation was often characterization of the kinetic model, though perhaps this has become less usual in more recent work. The form of the CR equation, Eq. (1), however, makes it incapable of distinguishing [18,19], by r^2 values or other criteria, the kinetic model that 'best' describes the data from that group of rate expressions which constitute the set [1] most usually considered and compared in the interpretation of rate data from thermoanalytical measurements. A generally similar conclusion was previously discussed by House et al. [24,25] when comparing kinetic results obtained from successive identical experiments. They pointed out that a 'good fit' may be found for an incorrect rate law. In most of the recent investigations, kinetic analyses take no account of the extent of reaction across which the fit is tested. As shown above, apparent magnitudes of E can vary with the α interval of the data included in the CR calculations applied during the kinetic analysis. Moreover, some reports do not mention rate behaviour during the early or the late stages of reaction where, for many kinetic relationships, distinguishability [18,19] is most reliably tested.

4.2. Determination of the activation energy

Uncertainties in values of E calculated by the CR method include the following, from which no obvious means of identifying the 'correct' value appears to be available.

(i) The slope of the plot of $\ln[g(\alpha)/T^2]$ against T^{-1}, for many rate expressions, includes the exponent n and is, therefore, $-E/nR$: Figs. 1 and 3 and Tables 1 and 4.

(ii) E magnitudes can vary significantly with the range of α included in the calculations: Fig. 4 and Table 2.

(iii) After allowance for n values, (i) above, E values were not reconciled with magnitudes from the isoconversional calculations: Table 3.

(iv) E values determined for standard model calculated data varied with the α range included in the analysis: Section 3.7 above, also Table 4.

The scaling of E by the factor n, (i) above, is an inconsistency that parallels the variations that arise through incorrect definition of k, to units $(\text{time})^{-1}$, in isothermal kinetics (see p. 121 of [1]). Even when E is corrected for the exponential factor, n, to nominal units $(\text{time})^{-1}$, the CR-calculated values vary with kinetic model and also differ from those found by the isoconversional method, (iii) above. Reasons probably include limitations inherent in the CR equation, which does not suitably accommodate the kinetic model and is also based on an approximate form of 'temperature integral' [43].

4.3. Arrhenius parameter trends

The above explanations for the systematic variations of E and $\ln A$ values with kinetic models confirms that the Trends identified above are mathematical artefacts. These are implicit within the calculation programs and are, therefore, without chemical significance. Their appearance in the several reports mentioned demonstrates their generality. The similar behaviour patterns recognized in the many diverse publications cited means that the reservations expressed here concerning the significance of kinetic and mechanistic conclusions are, in all probability, equally applicable to all the sources mentioned.

4.4. The significance of activation energies

The convention, apparently accepted throughout this literature, is that virtually every parameter computed can be regarded as reliable and, in particular, that E should be identified as a variable quantity [14]. This appears to me to be an unreasonable and unscientific approach to the resolution of the uncertainty concerning the significance of calculated apparent E values. It is the computed values and not the definition of E that are without meaning and, as shown here for the CR method, this arises through shortcomings in the calculation and/or the experimental methods. Accordingly, it is recommended that, in thermal analysis, E should retain its original defined meaning and continue to be regarded as a property of the reaction chemical step [13], the model accepted throughout other branches of the subject. It may be difficult, even virtually impossible, experimentally to determine E and other kinetic parameters, including A and $g(\alpha) = kt$, but this does not justify a change of the definition and the concept of a term that is of inestimable importance throughout reaction rate studies. Correctly calculated E values may be used in correlations between different chemical changes and be used in the formulation of reaction mechanisms.

All kinetic terms, including E, must be meaningfully defined before such quantities may be interpreted to provide insights into the reactivities of different substances through concepts capable of providing a theoretical framework for the subject and into reaction chemistry, see L'vov [10,11]. Chemical objectivity is always to be preferred over mathematical expediency.

The applicability of the theory of the single (identifiable) activation step model to reactions of solids remains incompletely established [47], and is regarded by many practitioners as being of doubtful value, or even impossible to confirm. We have little agreement concerning the factors that determine absolute reactivities of solids and the mechanisms of chemical changes including their controls (see, however [10,11]). The experimental measurement of E, in its correctly defined meaning, is undoubtedly difficult for many reactions [3,4,7–9] and may, in practice, be impossible for some. However, the benefits arising from the alternative view that E can be usefully regarded as a function of $g(\alpha) = kt$ have yet to be demonstrated. In my view this approach devalues an accepted theoretical model without substituting a demonstrably useful or adequately defined replacement. An essential reason for maintaining a clearly understood and significant meaning for E is that this parameter is potentially capable of being used as a criterion for the classification of observations (which seems unlikely for a 'variable' E). The recent contributions by L'vov [10,11] identify the physical significance of E, which is a fixed (emphatically not variable) property for each specific chemical reaction.

4.5. One view of the future of thermal analysis

Mindful of these limitations and fundamental problems inherent within current practices concerning thermal analytical kinetic studies, it seems to me that there are two alternative directions in which the subject can now progress. One view of the future is to maintain the 'status quo'. (The alternative view is discussed in Section 4.6. which follows.) We can continue to apply thermoanalytical methods to collect even more rate data for already well-studied thermal systems and/or to extend similar investigations to include additional novel reactants. This approach appears to have dominated the recent literature in which reports continue to appear giving further values of Arrhenius parameters and kinetic models for reactants both familiar and unfamiliar. Investigations are relatively easily completed by largely automated computer programs, that rapidly undertake most of the labour of data interpretation. All desired significant rate parameters appear, almost effortlessly, machine-presented in an apparently authoritative printed format. The recent outcome of such research has been the generation of a subject literature that is characterized by the accumulation of large numbers of individual reports which remain generally, or entirely, unrelated to each other and do not contribute to the organic growth of a coherent body of scientific knowledge. Mechanistic and chemical interpretation of much of the kinetic data so obtained has remained incomplete for many, if not most, of the thermal decompositions studied. Such reactions are often indicated, or implied through kinetic properties, to occur in the solid state, though usually without direct or adequate confirmation. It must also be remembered that measured rate data do not necessarily, and frequently do not, yield a magnitude of E that is characteristic of any identified rate limiting step. Such measured reaction rates are all too often subject to multiple controls, due to the influences of procedural variables [3–9,15]. Many reported observations are empirical because, in addition to the (uncharacterized) chemical controlling step, there are significant, even dominant, contributions from self-cooling/heating and reaction reversibility, which may be inhomogeneous within the reactant mass and change with time. Reaction conditions must be designed to eliminate or to minimize secondary controls [3–9] if chemically significant observations are to be obtained.

It has become increasingly evident, from the practices and conventions that characterize the recent literature, that the principal conclusions obtained in most kinetic studies of crystolysis reactions (A, E and $g(\alpha) = kt$) do not provide criteria whereby the properties of the reactants investigated can be systematized or correlated to establish the general features which control reactivities, mechanisms or reaction rates. This is a consequence of the absence of theoretical models capable of ordering the results available and permitting predictions, by induction, of the behaviour of hitherto untested reactants. These are principal objectives of the scientific method and, in the absence of an adequate theory, order may not be found [13]. Moreover, the theoretical models inherited from the precursor subject, thermal decompositions of solids, have found progressively fewer positive applications in the interpretation of thermoanalytical data. The absence of principles, theories and models, capable of ordering information, reduces the scientific achievements of such studies. Based on a prediction from recent history, the further accumulation of observations, of types that are already available in large quantities, is unlikely either to introduce scientific order or to provide general insights capable of identifying the controls of reactivity, thermal properties or reaction mechanisms. The alternative view for the future is to review radically the principles and practices of thermal analysis with the intention of restoring scientific methods based on chemical and physical concepts which gives an optimistic view for theory development.

4.6. A more optimistic view for theory and subject development

The recognition that current data interpretation practices are unacceptable and should be discontinued represents both an advance and a challenge. A more attractive option than continuing the unsatisfactory, even hopeless, scenario outlined above is to reappraise fundamentally and comprehensively the existing and alternative methods that are capable of achieving the intended objectives of the subject. The removal of the present impasse, arising from the excessive preoccupation with unsuitable mathematical analysis methods, and the doubtful significances of results calculated therefrom, reveals an apparently considerable gap in theory. Throughout chemistry, kinetic studies are the accepted approach to the elucidation of reaction mechanisms, including the controls of reactivity and comprehensively understanding the dynamics of chemical change. Thermochemical methods offer one particularly suitable approach for addressing such problems. However, the changes of emphasis within this subject, during its development and effective eclipse of studies of thermal decompositions of solids, have, in practice, effectively weakened any motivation towards obtaining information of chemical significance. The greatest investments of effort in thermal analysis have been directed towards extending instrumental convenience and in promoting the mathematical interpretation of data (largely using the kinetic models derived through solid state rate equations). This is excellent progress but is insufficient by itself to characterize all features of chemical reactions. The limitation to the advances possible by thermal methods alone arises because of the accompanying (but not necessarily consequent) reduced interest in reaction chemistry generally. Relatively less effort has been directed towards investigating reaction stoichiometries, structural features and bonding properties of reactants, textural changes accompanying reactions, etc., which has inevitably restricted the total amount of chemical information that can be derived from such work.

4.7. Other problems in thermal analysis

Uncertainties, inconsistencies and calculation errors are not the only problems limiting the advance of thermochemical kinetics. Other limitations and shortcomings of the subject, as now practised, that have become apparent and are identified as being significant, will the subject of a forthcoming review, now in preparation, including the aspects mentioned below. It is not intended to imply, however, that each and every feature mentioned here is to be found in every thermoanalytical paper, but rather that these limitations are sufficiently frequently found in the literature to be generally regarded as acceptable to a majority of the contributing researchers, and, significantly, to the journal referees, active in the field. Overall it is argued that much greater attention should be directed, through the complementary studies usually necessary, to the chemical features of the chemical reactions that are the subject of thermochemical investigations.

1. *Stoichiometry*. Kinetic data must be related to an identified chemical change or changes. Many thermoanalytical investigations do not completely characterize and confirm reaction stoichiometry. Each A, E or kinetic model, rate expression, reported must be identified with a single, fully characterized rate process.
2. *Single reaction*. Interpretation of rate data to determine Arrhenius parameters must be unambiguously identified with, and based on, data for a single rate process, unless methods capable of resolving complex data are used. This is not always adequately demonstrated. The extent, α range of fit, for each kinetic model identified as applicable should be stated.

3. *Absolute reactivities*. Rate measurements obtained to determine an absolute reaction rate, or absolute reactivity, for an interface process must show that the contributions from concurrent and/or overlapping consecutive rate processes and effects of reversibility and/or heat flow have all been considered or eliminated [3–9].
4. *State in which reaction proceeds*. To provide a satisfactory description of any rate process, the phase in which the chemical changes of interest take place must always be characterized. The possibility of melting before or during reaction is not always mentioned. Alternatively, an initially solid reactant may undergo precursor changes such as a polymorphic crystal transition or dehydration. The term 'crystolysis' may be used to confirm that the reaction occurs in the solid state [1].
5. All computational methods used to calculate kinetic parameters must be fully understood, appropriate and reliable, including term definitions and their units.
6. Kinetic evidence alone is almost invariably insufficient to characterize a reaction mechanism, particularly when solids participate, and support for mechanistic interpretation must be sought through complementary observations. Information of all relevant types, microscopic investigations of textures, chemical analysis, crystallographic information including topotactic [1] relationships (if any), spectroscopic data, etc., may be expected to increase the reliability of conclusions. The most dependable deductions are most usually based on investigations that include the widest range of relevant complementary measurements.
7. Conclusions should, where possible, be discussed in the context of related reactions and the chemical similarities considered. Many reports are not integrated into the context of all relevant literature, often neglecting discussions for results that are inconsistent with the deductions being presented. There are remarkably few critical reviews or comparative surveys in this subject area.

4.8. Comment

The point of the above, highly critical and general, comments on the thermoanalytical literature is to advocate a general reappraisal of all accepted but inappropriate practices. The realistic interpretation of chemical measurements by chemical methods in the context of chemical theory should always be used, together with the support of complementary observations (physical and chemical). This approach might be expected to introduce scientific order into a topic currently composed of random and unrelated investigations. The way forward, towards developing a coherent scientific subject, requires the recognition of two complementary principles. First, the introduction and application of revised methods for kinetic measurements and for data interpretations to yield reliable E values, and all related features of kinetic analysis, that are fully consistent with the accepted (defined) meanings (and units) of the terms used. The present paper demonstrates the catastrophic weaknesses of current practices in a subject that appears to have stagnated [48], lacks critical input and apparently has ceased to be based on recognizable scientific principles. Second, the kinetic parameters, most notably E (and not its 'variable' replacement) obtained for representative systems by the revised methods can then be compared with the unifying theoretical concepts developed by L'vov [10,11]. A revitalized attitude, intent on introducing coherence and order based on theoretical models, should be welcomed as offering an optimistic future. The importance of a theoretical model, capable of providing a central feature in ordering results, has been stressed by Laidler [13]. Let us all adopt a scientific stance for the optimistic development of a subject that is experimentally and theoretically difficult. L'vov [11] has stated "It is difficult to imagine how much effort, time and money have been spent in vain in the investigations of kinetics of solid decompositions because of neglecting this method" (i.e., the third-law method for the calculation of E). Perhaps now, at last, we can cease to contribute to this unnecessary and unproductive waste by initiating a renaissance in which the principles of the scientific method are restored to thermal analysis.

My optimism for an impending regeneration of the initial promise offered by thermal analysis (so many years ago) is based on the possibility that we might now replace outdated calculation programs by eliminating inappropriate approximate methods. This was powerfully advocated by Flynn [43] and significant additional faults in the currently popular methods are identified above. Second, the formulation of a reaction model, by L'vov [10,11], capable of accounting for absolute reactivities and enabling systematic comparisons of thermochemical properties, provides the essential theoretical foundation for scientific progress that has hitherto been missing. We should now anticipate a much improved future for the science of thermal analysis, a veritable renaissance.

Appendix A. Before describing a quantity as an activation energy, make sure that it involves activation and that it is an energy

This heading is my response to the prefatory quotation by Vyazovkin in his paper "Two types of uncertainty in the values of activation energy" [23], attributed to Daniil Kharms: "When you're buying a bird, make sure it hasn't got teeth. If it's got teeth, it isn't a bird". My dissimilar sentiment expresses my complete inability and unwillingness to accept the reasons for regarding activation energies as 'variable' [14] quantities or, more usually, the explanations given for their apparent property of being able to adopt several different values for the same reaction. (Is a multivalue term correctly described as a 'variable'?) However, this should not license the (chameleon-like) use of the term to represent any and every change of magnitude of reaction rate with temperature under different, and frequently incompletely described, reaction conditions or results obtained from the same data by alternative, approximate calculation methods.

Why, within the current thermoanalytical kinetic literature, are these quantities described as 'activation energies', when they are obviously no such thing, see [13]? The activation energy is a well-established concept, it has a constant value, it is a characteristic property within the rate limiting step of the particular chemical change being considered. It is widely and conventionally accepted as perhaps the most important and successful concept that is applicable throughout chemical kinetics [13]: being "... an energy E which can be related to the height of an energy barrier for the reaction." Notwithstanding the well-founded credentials of this term, the convention in thermal analysis now appears to be that any product ($R \times \ln$(temperature coefficient of reaction rate)) is to be regarded as an 'activation energy'. However, there are (at least) two obvious disadvantages to this effective (and local) change of terminology.

(i) It confers a spurious authority to those reported empirical magnitudes of E, which frequently have no identifiable theoretical pedigree or chemical significance.

(ii) It undermines and cheapens a term that, elsewhere throughout chemical kinetics, has inestimable value. (Should we not use a different term for the quantities calculated by this method (i.e., $R \times \ln$(temperature coefficient of reaction rate)) to introduce realism into kinetic reports and acknowledge the limitations and empiricism of the new quantity?)

The continued interests in promoting the use of this term (apparent E values are so easily (automatically, machine) calculated from thermoanalytical data) confers a veneer of respectability on a (modified) parameter that, to be realistic, at present lacks any theoretical support and which introduces no concepts that might be capable of unifying the subject. The 'variable' E is related to no activation process and is not identified with a particular energy. However, it provides a measure of the Apparent Exponential Dependence of Rate On Temperature and could, therefore, be more realistically distinguished from E by being referred to as the 'AEDROT' Factor, G. No useful purpose is served by including the gas constant in its calculation, so that it can be determined as a recognized empirical term from any 'rate constants' by: $\ln k = \ln F - G/T$.

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