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Review Paper

WHAT THEORETICAL AND/OR CHEMICAL SIGNIFICANCE IS TO BE ATTACHED TO THE MAGNITUDE OF AN ACTIVATION ENERGY DETERMINED FOR A SOLID-STATE DECOMPOSITION?

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This critical survey argues that the theory, conventionally used to interpret kinetic data measured for thermal reactions of initially solid reactants, is not always suitable for elucidating reaction chemistry and mechanisms or for identifying reactivity controls. Studies of solid-state decompositions published before the 1960s usually portrayed the reaction rate as determined by Arrhenius type models closely related to those formulated for homogeneous rate processes, though scientific justifications for these parallels remained incompletely established. Since the 1960s, when thermal analysis techniques were developed, studies of solid-state decompositions contributed to establishment of the new experimental techniques, but research interest became redirected towards increasing the capabilities of automated equipment to collect, to store and later to analyze rate changes for selected reactions. Subsequently, much less attention has been directed towards chemical features of the rate processes studied, which have included a range of reactants that is much more diverse than the simple solid-state reactions with which early thermokinetic studies were principally concerned. Moreover, the theory applied to these various reactants does not recognize the possible complexities of behaviour that may include mechanisms involving melting and/or concurrent/consecutive reactions, etc. The situation that has arisen following, and attributable to, the eclipse of solid-state decomposition studies by thermal analysis, is presented here and the consequences critically discussed in a historical context. It is concluded that methods currently used for kinetic and mechanistic investigations of all types of thermal reactions indiscriminately considered by the same, but inadequate theory, are unsatisfactory. Urgent and fundamental reappraisal of the theoretical foundations of thermokinetic chemical studies is now necessary and overdue.

While there are important, but hitherto unrecognized, delusions in thermokinetic methods and theories, an alternative theoretical explanation that accounts for many physical and chemical features of crystolysis reactions has been proposed. However, this novel but general model for the thermal behaviour and properties of solids has similarly remained ignored by the thermoanalytical community. The objective of this article is to emphasize the now pressing necessity for an open debate between these unreconciled opinions of different groups of researchers. The ethos of science is that disagreement between rival theories can be resolved by experiment and/or discussion, which may also strengthen the foundations of the subject in the process. As pointed out below, during recent years there has been no movement towards attempting to resolve some fundamental differences of opinion in a field that lacks an adequate theory. This should be unacceptable to all concerned. Here some criticisms are made of specific features of the alternative reaction models available with the stated intention of provoking a debate that might lead to identification of the significant differences between the currently irreconciled views. This could, of course, attract the displeasure of both sides, who will probably criticise me severely. Because I intend to retire completely from this field soon, it does not matter to me if I am considered to be ‘wrong’, if it contributes to us all eventually agreeing to get the science ‘right’.

Keywords: *activation energy, Arrhenius equation and solid-state kinetics, solid-state reaction kinetics, thermal analysis, thermal decompositions of solids, thermal reactions*

Introduction

It has been a feature of many recent studies concerned with thermal decompositions of initially solid reactants that the most significant contribution towards the advancement of knowledge resulting from the work appears to be the measured magnitude(s) of one (or more) activation energy (E_a). The presentation of numerous articles in the current thermoanalytical literature strongly implies that the most important scientific outcome of the investigation is the values of E_a reported for selected reactants. Current practice implicitly regards determination of activation energies as an intrinsically worthwhile research objective, invariably yielding results adjudged

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as meriting publication. However, articles of this type do not often provide an adequate introduction that explains the scientific objectives of the research program, in particular identifying the theoretical importance of the E_a values obtained. Moreover, it is customary practice to analyse kinetically the measured rate data for thermal chemical changes of reactants that are solid at ambient temperature using those rate equations that are specifically applicable to the decompositions of solids [1]. The possibility that the reactant melts, before or during the reaction studied, is not usually investigated experimentally or even mentioned: an important mechanistic assumption that is rarely explicitly justified. Brown has stated [2], in a slightly different context, that 'Too much emphasis has been put on determining (and interpreting) the activation energy in isolation'.

Against this established methodology, and mindful of shortcomings in the theory currently available, the following question (the article title) is raised here for critical discussion. 'What theoretical and/or chemical significance is to be attached to the magnitude of an activation energy (E_a) determined for a solid-state thermal decomposition?' In considering possible answers, the appraisal presented below reviews comparatively the current situation in the field of thermokinetic analysis and discusses prospects for advancement in an area of chemistry that has been regarded as stagnant [3]. It is hoped that recognition of various inherent, but hitherto unresolved, problems within the subject might stimulate overdue theory development. Detailed re-examination of assumptions, to identify inherent limitations in the accepted reaction models, can be recommended as an essential first step towards strengthening the scientific framework available for chemical interpretations of rate measurements for thermal reactions. Inadequacies in the theoretical foundations of models applied for the kinetic analyses of rate measurements obtained for the thermal reactions of solids have all too often been ignored in many recent articles. Consequently, reported magnitudes of E_a appear as the dominant outcome, the greatest achievement, in numerous (completed) research programs, which elucidate neither the mechanisms nor the reactivity controls of the reactions studied.

Measurements of individual E_a values, in isolation and without appraisal of the significance of their magnitudes, has little obvious merit [2]. In contrast, identification of patterns and trends, within and between, the numerous E_a values that have been published for diverse crystolysis reactions [1] is potentially much more likely to contribute towards elucidating the reactivity controls and mechanisms of reactions in solids, individually and generally. However, the literature includes remarkably few such systematic comparisons [4]. Science seeks to order all the information available, through general theoretical models, and trends identified can be used to predict behaviour in hitherto untested systems. Comprehensive and critical appraisal of the quantitative data already available, including E_a values, is overdue in a field where theory and the recognition of scientific order [4] have often been routinely disregarded. Few attempts appear to have been directed towards identifying relationships that may exist between measured E_a values and to correlate these with chemical properties of the reactants concerned. It is reasonable to ask, therefore: what purpose is served by continuing to extend the list of E_a values measured for the thermal reactions of diverse novel reactants, when so few attempts [4] have been made to correlate the many magnitudes that are already available? Moreover, it is already well known that, for some of the most extensively investigated reactants (e.g., $CaCO_3$ decomposition) [5], different kinetic studies have given widely, even wildly, different values for both Arrhenius parameters. Perhaps a more realistic and critical discussion of the theoretical significance of the term 'activation energy', as applied to crystolysis reactions [1], is now overdue [5–9]. This important objective is advocated and discussed here in the hope of stimulating refurbishment of a subject that currently appears to lack order that is based on scientific principles [5].

The present review starts with a brief historical account of the concepts that contributed to the introduction, development and subsequent wide acceptance, of the theory associated with the Arrhenius equation:

$$k=A\exp(-E_a/RT) \tag{1}$$

where k – rate constant, A – pre-exponential factor, E_a – activation energy, R – gas constant and T/K – reaction temperature. This article does not attempt to review comprehensively this extensive topic, which is of central theoretical importance throughout reaction kinetics and was originally developed to account for the rate characteristics of simple homogeneous reactions. The more modest (but nevertheless challenging) objective now addressed is to identify the particular relevance of these general theories, in their later specific applications, to consideration of the kinetic characteristics of thermal reactions of solids [1]: this is rarely examined critically.

The assumptions inherent in using models applicable to homogeneous rate processes to interpret chemistry and mechanisms of solid-state reactions are critically examined. This is approached by tracing some of the consequences that result from the extensive use of this theory for the analysis of thermal kinetic data, which became accepted practice during the early development of thermoanalytical techniques. Introduction of these novel experimental methods expanded rapidly during the 1970s, facilitating the efficient and rapid investigation of kinetics and mechanisms of thermal reactions generally. The present paper is mainly concerned with some consequences of subsequent developments in the field [5]. The strengths and weaknesses of the older theories of reaction kinetics are critically discussed because these models continue to be used in many of the more recent thermokinetic studies that relentlessly expand to include an ever widening range of reactants. References are made to the present status and possible future theoretical developments in solid-state thermal chemistry. The critical appraisals given here concern the validity of interpretative methods that are currently available for the formulation of reaction mechanisms and for the identification of the factors that control the reactivity of the chemical changes observed to occur on heating diverse, and initially solid, reactants.

Aspects of the history of the Arrhenius equation

A history of the applications of the Arrhenius equation (Eq. (1)) to chemical kinetics, has been given by Laidler [10–12]. The present account is limited to those aspects of this general theory that underlie and relate to its specific applications to solid-state decompositions and to the interpretation of thermokinetic measurements. This reconsideration of its value to solid-state chemistry is considered timely because the origins, assumptions and specific applications of Eq. (1) seem to have become forgotten in many reports and discussions of kinetic results for crystolysis reactions.

Early kinetic studies identified the empirical relationship between rate constants, k and temperature as having the form $k=A\exp(-B/T)$. In 1887, Van't Hoff suggested modification into the now familiar form of Eq. (1), the change being based on the perceived parallel with the variation of the equilibrium constant (K) with temperature. K is determined by the ratio of the rates of forward and back reactions, ($K=k_1/k_{-1}$):

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T}=\frac{\Delta H}{RT^2} \quad \text{or} \quad \left\{\frac{\mathrm{d}\ln K}{\mathrm{d}(T^{-1})}=\frac{\Delta H}{R}\right\}$$

where ΔH is the reaction enthalpy and the alternative (bracketed) equation is a differential form of Eq. (1). At about the same time (1886–1888), Arrhenius visited both Boltzmann and Van't Hoff [13]. Soon afterwards (1889), he reported a kinetic study of the acid catalyzed inversion of cane sugar, identifying the exponential increase in reaction rate with temperature (12% $°\mathrm{C}^{-1}$). This result was explained through the assumption of equilibrium between inactive and active molecules. Greater variation of reaction rate with temperature occurred when greater energy was required to activate the reactant species. This introduced the concept of activation energy to represent the barrier to chemical change, a model that is retained in current theories of reaction kinetics [13]. The provision of a theoretical significance for E_a, an essential and central feature in the scientific model, remains the valuable feature of Eq. (1) [11]. Other relationships between k and T have been proposed and, for these, the relative excellencies of fit can be similar, or sometimes even better, than Eq. (1). However, Laidler points out that such functions are theoretically sterile, and, therefore, have found fewer applications and less favour [11]. The name Arrhenius remains associated with the equation (Eq. (1)) for which he provided the theoretical foundation and which has endured for more than a century. This is a fitting tribute to the chemist who has been described as 'the founder of physical chemistry' [14].

While the essential concept that energetic activation precedes reaction has endured [11], the early representation has been substantially refined during the subsequent century. From the Boltzmann distribution, the term $\exp(-E_a/RT)$ expresses the fraction of intermolecular collisions that occur with a kinetic energy in excess of E_a. Such collisions may result in chemical change and, from rate measurements across a suitable temperature interval and the use of Eq. (1), the value of E_a can be determined. Magnitudes of E_a have been of value in elucidating reaction mechanisms [11].

Reactions of gases

Collision theory

From kinetic studies of the reactions ($H_2+I_2\leftrightarrow 2HI$), Lewis (1918) showed that the rate predicted, from the calculated frequency of collisional encounters and the determined E_a, was close to twice the value measured [15]. This was regarded as satisfactory agreement. However, for other reactions the agreement was less satisfactory and, in general, it is accepted now that collision frequency does not measure the number of encounters that are the precursors to chemical change. Reactions between complicated molecules may become possible only after impacts between particular constituent atoms or bonds and may be subject to further stereochemical constraints. This introduces the steric factor [16] into the pre-exponential term, wherein the rate of product formation is only a small fraction of the rate predicted from the collision frequency between reactants [15]. However, in some other reactions the rate is greater than expected, e.g.: $K+Br_2\rightarrow KBr+Br$, here because there is a facile initial electron transfer step, and the consequent electrostatic contribution increases the encounter probability [16]. The limited range of applicability of simple collision theory, together with the absence of any consideration of the magnitude of E, has resulted in its inevitable replacement.

Activated complex theory of reaction rates

This reaction model differs from the collision theory by identifying the controlling step in reaction with breakdown of an activated complex. The theory is given in detail in most textbooks of physical chemistry (e.g., [16]). The equilibrium constant that expresses the concentration of the activated complex, the precursor to possible product formation, is determined from the standard molar partition functions for the species participating in the equilibria, and this includes due allowance for the stereochemical constraints. Also, in principle, the energy requirements for formation of the activated complex (E_a) can be calculated. In practice, however, this can be difficult for all but reactions involving the simplest of molecules, though qualitative considerations of energy diagrams for the possible activated complexes can be used to identify the configuration offering the minimum energy barrier to reaction. Highspeed spectroscopic techniques are progressing towards characterization of short lifetime species that are similar to activated complexes [16]. Developments from the original Arrhenius theoretical concept, identifying molecular activation as determining reaction rates, continue to provide insights into the kinetic controls of reactions between gaseous species.

Reactions in liquids

The application of kinetic theory to reactions in liquids is complicated by two interdependent effects. (*i*) In the liquid, relative movements of molecules in the dense, closely packed condensed phase, are much more restricted than in a gas: ease of diffusion is reduced. (*ii*) Solute molecules, or ions, may bond with the solvent, perhaps weakly. Individually, these properties are difficult to characterize quantitatively in forms that are suitable for incorporation into equations capable of expressing their contributions towards influencing reaction rates. The close proximity of all molecules and ions in a liquid phase ensures that there are repeated collisions between neighbours (referred to as the 'cage effect'), before thermal motions result in separation with the redisposition of former neighbouring species into different proximity groupings. The solvent structure in the immediate environment of a solute species (ion or molecule) may be different from the bonding dispositions within regions of pure solvent, due to specific solvent–solute interactions of various strengths. Both effects may influence the effective collision frequency between reactant species and also the magnitude of E_a, particularly when molecules of solvent are involved, because solute–solvent bonds also may undergo modification in the reaction. Two limiting conditions of rate control can be distinguished for reactions in liquids. Diffusion control applies when the rate of product formation depends on the rate at which reactant species move through the liquid phase towards encounter: for these, E_a values are relatively small. Where E_a values are large, the activation process controls the reaction rate through energy obtained from neighbouring solvent.

In some simple reactions, for which the solvent can be regarded as 'inert', similarities with collision theory have been found [17]. For other reactions, involving ions, a form of the activated complex theory can be used to express the relative influences of electrostatic interactions on reaction rates [16]. However, for many reactions in solutions, the partition functions are not known due to uncertainties in the translation, vibration and rotation motions of the participating species [17]. The contributions from the various different interactions that influence behaviour in the condensed phase complicate the development a general theory of reaction kinetics involving dissolved reactants, though, for some of the simplest systems, the models widely used in homogeneous reactions may be applicable.

Homogeneous reaction kinetics theory

The above brief and selective account of the development of the kinetic theory that is applicable to homogeneous rate processes, is intended to emphasize that progress in advancing quantitative understanding of the factors that determine reaction rates has been slow and is, as yet, incomplete. (This theory is presented in much greater detail in the many excellent monographs and general textbooks in print.) Although the essential concept, that reaction requires energetic activation, has endured, there remain significant limitations in current theory both for the prediction of E_a values generally and, for reactions in solution, explaining the rates, including accounting for the magnitudes of both A and E_a. Nevertheless, the reaction models now available provide a valuable framework for discussion of reactivity controls and for the formulation of mechanisms of a diverse range of homogeneous reactions.

Reactions of solids

Thermal decompositions of solids (crystolysis reactions) are characterized by immobilized reactant constituents and the chemical steps that determine rate often occur within an advancing interface, a reactant/contact zone of unknown structure [1]. This (probably) simplest group of solid-state reactions has been selected for detailed consideration here because the controls apparently differ from the systems for which the theory applied was originally developed. Moreover, very many crystolysis reactions have been studied, much data is available, and, if the factors that determine chemical reactivity can be characterized, the conclusions may have general applicability to other reactions involving crystals. More specifically, Arrhenius theory is often used (apparently uncritically) in thermoanalytical studies, for kinetic analyses and mechanistic interpretations of measured rate data. Aspects of the validity of the assumptions inherent in these extended applications are critically examined here to assess the reliability of currently accepted thermokinetic methods and practices.

Activation energy

It appears to be widely believed, but rarely precisely confirmed, that sets of rate constant/temperature values determined for crystolysis reactions fit the Arrhenius equation. This has often been accepted as sufficient, but implicit, justification for the application of the theory of homogeneous reaction kinetics to the interpretation of observations obtained from studies of thermal reactions of selected solids. In particular, E_a values are frequently reported, though the significance of their magnitudes is not clear because, as pointed out by Garn [18–22], the distribution of energy in solids is not represented by the Boltzmann equation. The redistribution of vibrational energy within a crystalline phase differs from the mechanism of collisions between freely moving molecules, as envisaged in homogeneous reaction rate (Arrhenius) theory. However, Brown and Galwey [23, 24] have shown that the distribution of energy, both in those electrons and in those phonons that occupy the highest levels, can be approximately represented by an exponential dependence on temperature. This provides a theoretical foundation for the representation of rates of activated reactions in solids by a relationship having the same form as the Arrhenius equation. The physical significance of the slopes of such plots is, however, expected to differ from interpretations based on the model derived for reactions in gases [20].

Pre-exponential factor

Kinetic analyses of homogeneous reactions make due allowance for the progressive changes of reactant concentrations with time and the earliest representation of A was identified with the frequency of collisions between reactant molecules of identical reactivity. In contrast, reactivities of species within the solid material that undergoes chemical change in heterogeneous reactions may vary with position and time. Moreover, the term ‘concentration’ has a different significance in describing solid-state reactants. Consequently, kinetic analyses are invariably based on the dimensionless ‘fractional reaction’, α, which does not represent the numbers of species participating. Some values of A for crystolysis reactions are close to the ‘Polanyi–Wigner magnitude’ [1], i.e., about 10^{12} s^{-1} [25], identifying the reduced pre-exponential term with a vibration frequency, perhaps the bond ruptured in a ‘rate limiting step’. However, the spread of A values is too large ($10^8 < A/s^{-1} < 10^{14}$) to identify a ‘normal’ or ‘preferred’ value [25].

Arrhenius parameters

In portraying homogeneous reactions, it is assumed that the equivalent molecules that participate in the rate limiting step are identical, possessing equal reactivity and probability of reaction. Thus, the reactant concentrations and the frequencies of encounters between species of established compositions and structures are known, enabling the precursor (activated) complex to product formation to be represented fairly reliably. This is the secure foundation upon which the collision theory, and its subsequent refinements, is based. No such adequate model exists for most crystolysis reactions [1, 5]. The nature of the chemical steps by which solid reactants are transformed into products have not been established for the reactions of greatest interest; proposed mechanisms are often inferred through assumed parallels with homogeneous kinetics. Moreover, neither roles nor the structure of the interface, the specialized zone within which reactions preferentially occur [1], are known in detail or with certainty. Reaction may involve multiple product–reactant interactions, or other more complicated processes (e.g., [26]). In the absence of evidence from which the rate determining step at a reactant and/or product surface can be recognized, we cannot assume (as is possible for homogeneous reactions) that a single, simple activated step controls overall rate. Furthermore, we do not know the identities, and therefore the concentrations and the reactivities, of the species that participate in this/these reactions or whether the theory imported from homogeneous kinetics is valid for application to some, or to all, heterogeneous reactions.

Other reactions

Decompositions of solids with melting

The set of characteristic rate equations, widely applied in the kinetic analysis of crystolysis reactions [1, 27], were originally derived for various patterns of microscopically observed systematic changes of reaction interface dispositions with progress of the chemical change. No comparable rate expressions are available for thermal reactions proceeding with partial melting because a larger number of independent parameters are required to define the system completely. Concurrent reactions occurring in solid and in liquid phases may proceed at different rates [28]. Amounts and compositions of the contributing reactants present and the reaction rates in the different phases during the progress of reaction can be experimentally very difficult to measure individually. Consequently, apparent Arrhenius parameters calculated for combined contributory reactions may be composite quantities. In the absence of detailed kinetic information for every reaction that contributes to a complex process, magnitudes of A and of E_a for the overall rate of change cannot be identified with individual rate controlling steps.

These practical problems do not, however, justify the widespread practice, in thermokinetic studies, of completely ignoring the possibility that melting may occur during thermal decompositions of reactants that were originally solids when cold. Moreover, the practice of assuming that the 'best fit description' of a set of kinetic data to a characteristic solid-state rate equation confirms that the reaction proceeded in the solid-state is to be deplored [5–7]. The shapes of isothermal α–time graphs for reactions with and without melting may be closely or generally similar. Currently it is not possible to confirm the participation of melting by rate measurements alone.

Three representative situations, involving liquid participation in a thermal reaction, may be mentioned, though the kinetic properties of these have not been adequately characterized. (*i*) Comprehensive melting before reaction takes place in the melt, to which homogeneous kinetic models are presumably applicable. This is reaction in a solventless liquid phase: the reactant concentration may not change (if product is precipitated) but its volume must progressively diminish. (*ii*) A thin layer of liquid is formed within an active, advancing interface: kinetic behaviour is expected to resemble that characteristic of crystolysis reactions [1] (if the relative thickness ratio of liquid layer to crystal size is sufficiently small). (*iii*) Progressive melting during reactions within both liquid and solid phases: kinetic behaviour is complex, and also may be difficult to distinguish from reactions of type (*i*) or (*ii*). Examples of reactions that first appeared to proceed in the solid-state but for which later investigations provided evidence of the participation of a melt include the thermal decompositions of copper(II) malonate [29], ammonium dichromate [30], ammonium perchlorate [31] and *d*-lithium potassium tartrate [32]. As these, and other, studies have demonstrated, the detection of melting may be difficult but this does not excuse its exclusion from consideration as an essential feature to be taken into account in the formulation of the reaction mechanism. Kinetic analyses alone may not reveal fusion and complementary experiments, including microscopic observations and/or enthalpy measurements, are required to establish the participation of a fluid [29–32].

Heterogeneous catalytic reactions

Heterogeneous catalytic reactions proceed through the interactions of species in or at a surface, one or more participant being chemisorbed on the active solid. As with reactions at interfaces, the controlling steps in such chemical changes may not proceed to completion through a simple, single step; the overall process can be the resultant of several consecutive interactions. The experimental difficulties in characterizing the contributing factors that determine the dominant rate controls in heterogeneous processes (adsorbed reactant concentrations, mobilities and reactivities) introduces uncertainties into the provision of mechanisms and explanations for the magnitudes of A and E_a measured for the overall reaction.

Difficulties in accounting for the significance of Arrhenius parameters, determined for heterogeneous rate processes, is particularly apparent when considering sets of related reactions that exhibit a kinetic compensation effect (KCE) [33]. Within each such set, the pairs of (A, E_a) values determined for the individual reactions often show large variations, though all of the rate processes have been studied within comparable temperature intervals. It has been shown [33, 34] that this behaviour pattern can be explained by different variations with temperature of the frequency of occurrence of the reaction situation (resulting from changes of concentrations of adsorbed precursors, surface reactant reactivities, active catalyst area, etc.) for the different reactions of the set. (This feature of kinetic analysis of heterogeneous rate processes, that variations in apparent E_a values that ignore a dependence of A on tempeature can be rather large, was identified and discussed in 1977 and has again recently been pointed out by Criado *et al.* [35].) Such patterns of behaviour can arise when the overall rate of reaction is the outcome of more than a single controlling process. Unlike the simple, single encounter that controls the rate of many homogeneous processes, the observed Arrhenius parameters for many heterogeneous catalytic reactions cannot be identified with the frequency of occurrence of the reaction situation (A) and the height of a particular energy barrier (E_a) to chemical reaction. The effective rate constants vary with temperature, differently for each reaction in the KCE set. There may be similar uncertainty about the possible complexity of chemical processes between surface and surface-bonded species for all reactions involving solids so that the significances of measured Arrhenius parameters may be different from those for reactions in gas or solution.

Theory of reaction kinetics in the interpretation of thermoanalytical data

Thermal decompositions of solids

Before the 1960s, solid-state reactions, which occurred on heating pure crystalline compounds, were regarded as a slightly esoteric aspect of general chemistry, but to which the same general theories of kinetics and thermodynamics were expected to be applicable. For many solids, the significant but distinctive feature was that chemical changes occurred preferentially within a characteristic reactant/product contact zone, accepted as possessing locally heightened reactivity. Product was formed during the progressive advance of such interfaces into unchanged reactant [1]. This behaviour differed from homogeneous reactions and introduced the concept of reaction geometry into kinetic analysis. Systematic, and microscopically observable, changes in interface area and disposition occurred within the solid reactant-product assemblage as the reactant was increasingly transformed into product. Novel kinetic equations, based on observed spatial patterns of interface advance, were developed to account for changes of rate with time during isothermal reactions. Identification of the ‘best fit’ rate equation from these three-dimensional geometric models could (sometimes) be confirmed by microscopic observations of partially decomposed reactant. Other experimental methods that, similarly, were applicable to reactions of solids only, included X-ray crystallography, which can detect topotaxy. Studies of crystolysis reactions often included an extensive variety of complementary techniques to characterize the chemical controls and mechanisms, e.g. [36].

For rate processes taking place within an advancing contact interface, it was (usually implicitly) assumed that the theory of rate control could be expressed (at least approximately) by the Arrhenius model, as applied to homogeneous reactions. Thus, the rate limiting step was regarded as being determined by the height of an energy barrier (E_a) to be surmounted to achieve reactant breakdown through an activated transition state. Numerous articles describing decompositions of diverse solids routinely reported (and indeed continue to report) results obtained from kinetic measurements interpreted on this assumption. The most important conclusions almost invariably include the Arrhenius activation energy, E_a, the (geometric) rate equation, $g(\alpha)=kt$ and (perhaps) the pre-exponential term, A (sometimes referred to as the ‘kinetic triad’). A massive literature of such studies has now accumulated [1].

The similarities of thermal behaviour characterized for that group of reactions that were regarded as occurring in crystals resulted in the perception that these formed a distinctive group and the subject became recognized almost as a separate discipline, particularly between the 1930s and the 1960s. Interest tended to be directed towards a relatively limited range of reactants, some of which were the subject of several or many studies [1]: representative examples are mentioned below. Rate data were well described by the distinctive equations applicable to isothermal crystolysis reactions [1] and temperature dependencies of rate were discussed through the Arrhenius activation model and its later developments, including the transition state theory. This is unsatisfactory for the reasons given above: values of A and of E_a are not necessarily to be identified with a simple, single rate determining step and the Boltzmann energy distribution does not apply in solids.

The representative examples, listed below, illustrate the distinctive group of reactions that were recognized and treated as (the distinct discipline of) solid-state decompositions during the middle decades of the twentieth century. It is interesting to reconsider now (admittedly with hindsight) how some of the early mechanisms proposed for these reactions have subsequently been modified. The present literature comparisons emphasize the inherent (but not always adequately appreciated) difficulties that arise when making meaningful experimental investigations of solid-state, often complicated, rate processes. It is stressed that it is necessity to use all available kinetic and complementary experimental evidence [36] to elucidate reaction chemistry. The importance of analytical evidence in characterizing the chemical change occurring and the identity of the reactant has been pointed out by Koga and Tanaka [37]. Koga has showed that physical pre-treatment influenced the reactivity of bayerite [38].

Early kinetic studies, supported by microscopic observations, appeared to confirm [1] that dehydrations or decompositions of the following reactants proceed in the solid phase (crystolysis reactions [1]) and many have been accepted as being completed through a single, simple rate process:

- crystalline hydrates: $CuSO_4\cdot 5H_2O$, $CuSO_4\cdot 3H_2O$, $CaSO_4\cdot 2H_2O$, $KAl(SO_4)_2\cdot 12H_2O$, $KCr(SO_4)_2\cdot 12H_2O$, $NiC_2O_4\cdot 2H_2O$, $CaC_2O_4\cdot H_2O$, $Li_2SO_4\cdot H_2O$, etc.
- alkali permanganates: $KMnO_4$ and others: Li, Na, Rb, Cs; also Ba, etc.
- metal azides: NaN_3, KN_3, $Pb(N_3)_2$, $Ba(N_3)_2$, $Ca(N_3)_2$, etc.
- metal carbonates: $CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, $ZnCO_3$, $PbCO_3$, $AgCO_3$, etc.
- ammonium chromate: $(NH_4)_2Cr_2O_7$
- ammonium perchlorate: NH_4ClO_4
- metal oxalates: NiC_2O_4, FeC_2O_4, ZnC_2O_4, CaC_2O_4, PbC_2O_4, $Ag_2C_2O_4$, etc.
- metal carboxylates: $CuC_3H_2O_4$, $Cu_3C_{12}O_{12}$, etc.
- metal perchlorates, chlorates, etc.: $KClO_4$, $NaClO_4$, $NaClO_3$, etc.

Examples of repeated studies of some of these decompositions that have proposed alternative mechanisms, in which the reaction does not take place in a single, simple step, include the following. The dehydration of $CaC_2O_4 \cdot H_2O$ involves two concurrent reactions, proceeding at slightly different rates [39]. Adsorbed intranuclear water was identified as an essential participant in nucleus growth during some alum dehydrations [26, 40]. Subsequent work has shown that the decomposition of $KMnO_4$ (which shows a 'classic' sigmoid shaped α–time graph) proceeds with formation of the intermediate $K_3(MnO_4)_2$ [41]. The kinetics of $CaCO_3$ decomposition, notably the Arrhenius parameters, vary significantly with changes in reaction conditions [5]. Evidence has been given that the decompositions of copper(II) malonate [29], $K_2Cr_2O_7$ [30] and NH_4ClO_4 [31] involve liquid intermediates. The decompositions of several copper(II) carboxylates proceed with stepwise cation reduction ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$) [42]. Decompositions of some alkali azides and various halates also probably involve melting. Additional references are given in [1]. Subsequent work has shown that many of the reactions considered to be representative of simple solid-state decompositions are more complicated than had been thought originally.

Expansion and development of thermal analysis

During the 1960s, considerable advances in instrumentation increased the efficiency of experimental methods for rate measurements of thermal reactions [5]. The development of detectors capable of the sensitive determination of enthalpy changes [initially differential thermal analysis (DTA) and later differential scanning calorimetry (DSC)] provided new approaches to kinetic studies. Quantitative measurements of these and other physical properties [43], notably reactant mass (thermogravimetry (TG)), lead eventually to the wide (commercial) availability of reliable equipment, capable of precise, frequent and accurate detection and measurement of the (mainly physical) changes that occur on heating diverse materials. Initially, these observations were regarded as having potential value in two complementary respects: to extend knowledge of the kinetics and mechanisms of the particular chemical process being studied and also to confirm the reliability of the thermoanalytical techniques then under development. Thus, from their origins, those experimental methods that were used for thermokinetic investigations, through (often physical) measurements of either enthalpy changes (DTA or DSC) or mass losses (TG), were closely associated with crystolysis reactions [1]. The demand for these efficient experimental facilities soon was sufficient to attract the interest of manufacturers, after which commercial equipment for thermoanalytical studies became increasingly obtainable, a market that continues to thrive.

These advances in our ability to measure physical, sometimes chemical [5, 43], changes during reactant heating coincided with the remarkable expansion, both in capabilities and in availability, of computer technology. Thermal analysis and increasing versatility of electronic instrumentation developed together in a form of mutual symbiosis that contributed to the advancement of both subjects. It became possible to interface the new and increasingly powerful computers with laboratory equipment to control thermoanalytical experiments, to record the data measured and to analyze kinetically the observations stored. During the last three decades, there has been a steady increase in the sophistication of laboratory automation and in the ability to program the (partial) interpretation of stored information. This trend of advances appears to be capable of being continued into the foreseeable future though, for the present purposes, it is not necessary to trace these developments in detail. The significant aspect here is that reliable thermoanalytical equipment can now be purchased, which is capable of performing largely automated experiments, for diverse thermal reactions across a wide range of experimental conditions (temperature, pressure, atmospheres, times, etc.). Large, even very large, numbers of accurate data measurements for the physical changes identified as being of interest (mass, enthalpy, etc.), together with sample temperatures, can be collected during pre-programmed non-isothermal experiments, or alternatively during either rapid or extended slow isothermal rate processes. Subsequently, the collected data can be effortlessly analyzed to present the computer programmed results of computations in forms (printed tables, graphs, screen displays, etc.) suitable for whatever purpose is required. Results displayed in this way may give a superficial impression of greater reliability and authority than can be supported by a critical consideration of all the underlying assumptions, including the inherent limitations of the experimental measurements and of the computational methods. The problem of the validity of conclusions often remains inadequately addressed in published reports.

From a critical appraisal of the literature, I conclude that former interests in thermal decompositions of solids [1, 27] have now effectively been replaced by, and the topic accomodated within, thermoanalytical science [5]. Moreover, it can be argued that the virtual coalescence of these distinct and different alternative approaches to the investigation of solid-state reaction kinetics, have not achieved maximum benefits for either subject. The theory of crystolysis reactions contains (amongst other limitations) the unjustified assumptions mentioned above, which remain unaddressed in most thermokinetic reports. Thermochemical studies frequently focus on computational aspects of kinetic analysis and/or studies of individual reactants without reference to the wider chemical contexts of the selected decompositions. There is a preoccupation with measurements of E_a values but less interest in the significance or relationships with chemically similar reactants. Such kinetic investigations often use a minimum quantity of experimental data and the observations contribute little towards chemical understanding of the reactions studied. An introspective ethos appears to have become estabished within the thermoanalytical community, often apparently dedicated to obtaining the maximum number of kinetic parameters (A, E_a and rate equation) from a minimum (or, sometimes, an insufficient) number of experiments. Because thermal analysis appears now to be dominated by this objective, the (considerable) problems of extending understanding of the chemistry of solid-state reactions, formerly studied by a wider range of techniques [36], have become ignored. Nevertheless the kinetic models applicable to solid-state reactions remain in uncritical use. The generalizations made below consider the consequences of this change of interest and are intended to identify and appraise the value of the widely used methods and theoretical concepts that have dominated recent thermokinetic publications [5–8]. These approaches and attitudes also appear frequently in papers submitted for publication. Exceptions to the trends described below undoubtedly exist. Nevertheless, I believe that the pattern given in this appraisal represents fair comment on a majority of articles that constitute the body of knowledge to be found in recent research reports on thermal reactions [5].

Kinetic analysis is based on a minimum number of experimental measurements

During recent decades, increasingly sophisticated laboratory equipment, usually commercially manufactured, has massively increased the ease of data collection and analysis. However, these remarkably enhanced efficiencies apparently do not satisfy everyone. In the scramble to obtain the maximum yield of data from the smallest number of experiments, one dominant thrust of research effort has been towards characterizing the kinetic triad (A, E_a and $g(\alpha)=kt$ [1]) through the analysis of rate data measured for a single non-isothermal experiment. It has been shown that this is not acceptable and that such results are not sustained by theory [44, 45], though the practice continues. Such analytical methods claim to be able to deduce more kinetic information than is contained in the data available. Much research effort has been directed towards these objectives. Throughout its history, thermokinetics has been preoccupied with the mathematics of data analysis, often based on inadequate or unsatisfactory theoretical principles, insufficient experimental evidence and without regard to the chemistry of the reactions taking place [5–8]. Theories accepted during the earlier (i.e., before the 1960s) studies of solid-state decompositions are uncritically applied in interpretations of thermokinetic data, without regard to, or attempts to address, their limitations. It appears that preoccupations with calculation methodology have so dominated thermokinetics research that too little attention has been directed to developing or to understanding the chemistry of these reactions.

Preoccupation with E_a values

There exists a preoccupation with the determination of E_a magnitudes for thermal reactions [2], though the chemical and/or mechanistic significance of the values obtained are not usually considered or discussed. Also, it appears that, in the computational approaches used, the original definition (indeed the theoretical significance [11]) of E_a, or even that this term is associated with a single bond redistribution step, has become forgotten [1–25]. Other aspects of the controls of solid-state reactivity and mechanisms of these reactions are rarely reported in detail. Consequently, many of the research programmes described in the literature have not contributed to the theory of crystolysis reactions and, because this has been ignored, the topic has failed to advance. The rise of thermokinetic analysis appears to have caused, or coincided with, a decline of interest in chemical investigations of solid decompositions through the classical approaches formerly used (i.e., before about 1970). I believe that kinetic investigations by thermoanalytical methods is a subject that now lacks both an adequate theoretical foundation and a scientific framework: consequently, it must be regarded as approaching a state of chaos and/or a crisis.

Theory of solid-state reaction kinetics in thermal analysis

In the above critical survey it was emphasized that the extensive use of solid-state reactions in the original work lead to the currently preferred use of these rate equations for the conventional and routine kinetic interpretation of thermoanalytical data. This approach is suitable for kinetic analysis of reactions that have already been shown to proceed in the solid-state. Nevertheless, in many of the early studies concerned with crystolysis reactions, inferred interface models were often confirmed by direct microscopic observations, because some geometric interpretations for solid-state reactions are ambiguous [27].

The possibility that previously uninvestigated decompositions may proceed by mechanisms other than those included in solid-state reaction rate theory, is an unrecognized and unacceptable limitation in thermokinetic studies that must be addressed [2] (and should never have been tolerated). When heated, a novel reactant may undergo melting and/or complex/concurrent reactions, these possibilities must be considered in any comprehensive interpretation of measured rate data. For complex reactions that undergo partial melting, a complete kinetic description of behaviour may require extensive experimental data, if concurrent reactions that proceed in the solid and in the melt proceed at different rates [28]. Moreover, some characteristic patterns of kinetic behaviour approximately fit the isothermal yield–time relations characteristic of crystolysis reactions but are capable of representing other types of rate processes equally well, including, for example, reactions involving melting. Alternatively, (and also possibly additionally, if there is the participation of melting), a particular solid-state reaction may be complex, involving more than a single rate process, reactions proceeding concurrently and/or consecutively. Such mechanisms are not easily characterized through conventional thermokinetic investigations [29–32, 39, 41] and many possible models may, therefore, be effectively, though not necessarily intentionally, excluded from consideration by use of the methods that are currently applied in the kinetic analysis of thermal data.

Complementing rate studies with microscopic observations may provide evidence of melting, but only where this is obvious and extensive: for some systems detailed microscopic examinations may be required [29]. The recent trend towards using thermal analytical methods to undertake kinetic studies of decompositions of substances that have never been previously investigated must result in great uncertainty for any mechanistic conclusions that are based on rate measurements alone. The implicit, and effective, exclusion of all but the simplest of solid-state reaction models from consideration is a massive restriction in the interpretation of kinetic data because all reaction models involving melting and/or complex reactions are thereby excluded. Nevertheless, articles continue to be published in which kinetic results, sometimes extending to mechanistic interpretation, are reported on the basis of a single, or a small minimum number of, experiments. Such studies should be regarded as preliminary work only. More trustworthy conclusions require extended and confirmatory investigations [36]. The present, inherently restricting, methods of kinetic analysis of thermal rate data are not capable of distinguishing all the types of rate characteristics that may reasonably merit consideration.

The application of the Arrhenius model to crystolysis reactions is justified mainly through parallels with homogeneous rate processes. The Boltzmann equation, expressing the concept of reaction through activation, does not represent the energy distribution within a solid [18–24]. These fundamental problems in developing a theory of reaction kinetics for solids have yet to be solved, an omission that has never been adequately addressed in the thermal analysis literature. Some aspects of the mechanistic complexity of reactions proceeding in condensed phases have been discussed by Šimon [46]. In many recent reports, earlier theoretical views on the significances of A and of E_a are implicitly taken as remaining valid but the foundations for these assumptions are not discussed. Theory in the thermal analysis literature is almost exclusively concerned with the mathematics of data interpretation, including the calculations of A and of E_a, while the unsatisfactory features of the possible physical meanings of these terms remain unconsidered.

Approximate methods in kinetic analysis

Early applications of thermal analysis in kinetic studies included the development of non-isothermal methods and discussions of the relative merits of isothermal and dynamic kinetic methods continue [47], together with appraisals of the reliability of data obtained [48]. However, exact analysis of rate data by this approach may not always be possible. This is because the three variables measured (α, T, t) are linked by three equations (the rate equation, the (often linear) temperature increase with time and the Arrhenius equation) and these are not, in general, capable of giving analytical solutions. Consequently, before high-speed computers became available, a variety of approximate methods of data analysis were proposed and widely applied [1, 27, 43]. During the late 1950s and the 1960s, these were published and were initially used to enable the calculations required in rate data interpretations to be completed (by hand) within a reasonable time. Also, it was (then) widely accepted that all three components of the ‘kinetic triad’ (the rate equation: $g(\alpha)=kt$, A and E_a) could be determined from a single non-isothermal kinetic experiment, though this has since been shown to be impossible [44, 45]. A surprising feature of the more recent literature is that these early approximate methods of kinetic analysis should have continued in general use for so long. As Flynn has pointed out, in reviewing selected aspects of this general methodology [49], ‘…in this age of vast computational capabilities, there is no reason not to use precise values for the temperature integral when calculating kinetic parameters’. The persistent, continuing uses of now obsolete and, indeed inaccurate, methods of data analysis is unacceptable, introducing doubt into the validity and precision of reported quantitative results obtained by only approximate methods. Urgent reconsideration of computation programs is essential and, indeed, now well overdue, as has recently been discussed in detail [5–8].

Data reliability

Methods of measuring reaction rates based on enthalpy changes, DSC and DTA, frequently assume that the integrated enthalpy change is directly proportional to the extent of reaction. The fractional reaction, α, at time, *t*, is, therefore, determined as a simple ratio: (enthalpy change to *t*/the overall enthalpy change on completion of the reaction)=α. Few studies have demonstrated that there is a linear relationship between the amount of chemical change and the amount of heat evolved: a direct proportionality that is not always easily confirmed. This ratio does not usually apply when reactant breakdown is complex, involving overlapping concurrent and/or consecutive rate processes, possibly also including the formation of intermediates. Non-reaction enthalpy contributions can also arise from a variety of other processes, including, for example, the late completion of water removal from an initial dehydration step, melting perhaps with later solidification, surface area changes including sintering, reaction with impurities in a gas atmosphere, etc. These effects may be taken into account through estimated changes in the response baseline but the magnitudes of any errors introduced are not always known. (Comparable assumptions are usually inherent in other detection methods. A significant feature of TG is that mass independent processes, e.g., crystallographic transformation, melting and/or solidification, make no contributions to the response.) In addition, there are errors inherent in the measurement process. Moreover, the different types of error may be random or show systematic variations with one or more variable, α, *t* or *T*: such trends may exert a significant influence on any kinetic conclusions reached.

Self-cooling/heating

The enthalpy of an endothermic (exothermic) reaction occurring may be sufficient to cool (heat) the reactant solid, relative to that of the measured temperature of the reactant container. The magnitude of this discrepancy is expected to vary with temperature, time and position within the reactant mass and thus introduce error in the value of E_a determined. Many early studies included a correction for this effect. Garner [50] advocated single crystals for dehydration studies because '…corrections for self-cooling are made more manageable than with numbers of small crystals'. This source of uncertainty in E_a values reported in recent thermoanalytical studies is, however, almost totally ignored. Nevertheless, its importance has recently been restated by L'vov, who discussed [51–56] the significant, temperature-dependent, contributions to kinetic behaviour (values of E_a) by the self-cooling that may develop during endothermic, reversible reactions.

Unsatisfactory reporting of kinetic results

Reports of thermokinetic investigations usually give values of some (or all) of the kinetic triad, perhaps together with some limited [5] stoichiometric information. Geometric conclusions, inferred from the 'best fit' rate equation, are not usually confirmed, e.g., by direct microscopic observations. Moreover, the precisions of the quantitative magnitudes reported are often in considerable doubt. A statistical measurement (usually a single value), expressing the relative excellence of data fit to various alternative (solid-state) rate equations, may be of limited significance where (usually) the range of α across which the comparative tests have been made is not specified. In addition, whether the deviations from prefect fit are random scatter or are systematic variations within particular α intervals is not always mentioned: such trends can be important in identifying an adequate description of kinetic behaviour. Tests of reproducibility between nominally identical experiments are rarely mentioned, many reports appear to be based on results obtained from a single data set (experiment) only. It is surprising, therefore, that E_a values may be given to quite unrealistic numbers of 'significant' figures, often five or six. Such implied (spurious) accuracy is clearly unreasonable, values of E_a for crystolysis reactions can rarely be measured with an accuracy of better than ±1% or ± 1 kJ mol^{-1}, and often rather less.

Application of thermal analysis methods to all reactants of interest

The original extensive use of solid-state reactions for the development of thermokinetic analytical methods focussed attention on rate processes for which there was already evidence available to show that decomposition was not accompanied by melting. More recent applications have extended thermal methods to investigate novel, hitherto unstudied, reactions but using comparative kinetic interpretative methods that are capable of distinguishing only between rate behaviours that are characteristic of crystolysis reactions. Restricting kinetic models to this set is totally unacceptable and a much wider range of possible types of rate equations must be available for consideration [2]. Many reactions, originally accepted as single, simple, solid-state process have, on subsequent detailed mechanistic examination, been shown to undergo more complicated chemical changes [1, 5]. $CaC_2O_4 \cdot H_2O$ dehydration involves two concurrent rate processes [39]. The decomposition of $KMnO_4$

proceeds through two steps [41]. The thermal decompositions of $(NH_4)_2Cr_2O_7$ [30] and of NH_4ClO_4 [31] proceed with molten intermediates and several distinct reactions contribute. Copper(II) malonate [29] decomposition involves fusion and (as with other Cu(II) carboxylates) proceeds through stepwise cation reduction: $Cu^{2+}\rightarrow Cu^{+}\rightarrow Cu^{0}$ [42]. The pursuit of apparent efficiency has disregarded, even obscured, the reasonable consideration that chemical reactions can be, and often are, complicated.

Lack of additional, complementary and/or confirmatory experimental observations

It is a feature of many thermokinetic studies that conclusions based on the interpretation of kinetic data only are not supported by complementary observations, capable of confirming any mechanisms proposed. This contrasts sharply with many of the earlier studies of solid-state decompositions, where rate observations were interpreted in the context of various, diverse other types of relevant experimental information [36]. The minimalist approach, widely accepted, revered and applied in thermokinetic analyses, restricts the interpretational possibilities. For example, microscopic examinations of interface (nucleus) generation and spatial development, during representative reactions, were used for the original formulation of the rate equations that are now accepted as characteristic of crystolysis reactions [1, 27]. Consequently, it might further be argued that the use of thermal analysis to characterize reactions proceeding by nucleation and growth mechanisms is less reliable than directly observing, by microscopy, the existence of nuclei in partially reacted salt. Other complementary, and/or confirmatory, observations applied in mechanistic investigations solid-state reactions included X-ray diffraction to identify topotaxy and surface area measurements to characterize textural changes accompanying reaction. In [36], Boldyrev has elegantly demonstrated the value of using detailed and extensive complementary information to elucidate the controls of a solid-state reaction, the decomposition of silver oxalate.

Conclusions from thermokinetic analyses are not classified or correlated in a chemical context

The early ('pre-1970s') studies of solid-state decompositions tended to be concerned with extending understanding of reaction controls, including attempts to recognize behaviour trends that could be identified with chemical properties of the reactants studied. In contrast, thermal analysis reports have been more often concerned with a single, or a few comparable reactants that are usually individually discussed, without reference to the properties of related processes or correlated within any wider chemical context. Indeed, it is probably fair to generalize further and suggest that thermal analytical studies rarely seek to integrate results into the broader perspectives of chemistry. There also seems to be an inexplicable reluctance by thermokinetic researchers to review their subject either comprehensively or through more limited comparisons of their results with the similarities and/or the differences reported from previous studies for the same reactant. Consequently, the literature appears as a collection of separate, individual papers, linked by common experimental methods and the set of equations used in kinetic analysis, rather than as contributions to the coherent organic and scientific growth of a branch of chemistry.

Comment

Dominant features, in the extensive literature concerned with the invention and the development of thermokinetic methods for experimental investigations of reaction rates and mechanisms, are the reported efforts to improve: (*i*) the accuracy and reliability of experimental techniques and apparatus, and (*ii*) the ability of mathematical/analytical methods to interpret kinetic data easily and rapidly from a minimum number of experiments. Both of these are laudable objectives and each has considerably advanced the capabilities and values of the technique. The general availability of powerful automated equipment has, however, apparently resulted in the unfortunate practice of basing investigations almost exclusively on thermal rate measurements, which (apparently) yield kinetic data so easily. It has now become conventional to omit completely those complementary and confirmatory observations, by other techniques (microscopy, X-ray crystallography, etc.) which are capable of increasing the reliability of kinetic data interpretation. Consequently, results obtained are often insufficient to characterize adequately reaction kinetics or to formulate substantive reaction mechanisms because scant regard has been directed to the comprehensive elucidation of the physics and chemistry of each individual step that contributes to the overall thermal processes being studied. These wider investigations formed an integral feature of earlier work on solid-state thermal decompositions, which were directed towards identifying the factors that control both reactant reactivity and the mechanisms of thermal reactions. The theory maintained from the 1960s remains unsatisfactory in important respects, in particular concerning the establishment of detailed interface mechanisms and controls and in providing a quantitative model to explain the fit of rate data to the Arrhenius equation [18–24]. Nevertheless, despite these limitations, and remembering ('Thermal decomposition of solids') the complex behaviour of some of those salts that had been formerly regarded as simple crystolysis reactions, theory from the thermal decompositions of solids literature is usually and uncritically still accepted as being applicable to all thermokinetic studies. Moreover, some central features of this theory were derived from homogeneous kinetics and aspects of the transfer to and application in solid-state chemistry have remained largely unsubstantiated. This absence, in thermokinetic studies, of adequate reconsideration of theory, together with regular reappraisal of inherent assumptions, is unacceptable and unscientific, representing important gaps in current practice.

Recent contributions to theory

The above survey, believed to be representative of the greater proportion of the literature concerned with thermokinetic studies, intentionally has not yet mentioned three recent proposals that have been developed to address specific limitations in the theory used for the investigation and interpretation of rates of crystolysis reactions. Each of these three ideas is briefly outlined here (more detailed treatments are given in the articles cited) to continue, from 'Aspects of the history of the Arrhenius equation' and 'Theory of reaction kinetics in the interpretation of thermoanalytical data', the historical and general consideration of the applications of the Arrhenius equation to thermal decompositions. Again, particular interest is centred on the magnitude of E_a.

Concept of variable activation energy

In 2000, Vyazovkin [57] expressed the view that 'for the kinetic analysis of solid-state reactions' there could be introduced the 'acceptance of the concept of a variable activation energy'. My generally negative ('rather pessimistic' [2]) view of the value of this proposal has already been critically presented [5, 8], with emphasis on the conflict that arises with the accepted significance of activation energy [11]. It is also noted that this proposal [57] is specifically applied to solid-state reactions, implicitly regarding such rate processes as (presumably) distinct from other (i.e., homogeneous) chemical reactions. It may (again) be mentioned that no definition is given for the term 'variable E_a'. Moreover, any set of 'variable E_a' values, obtained through the use of alternative rate equations in data analysis, appears not as a continuous variable but as a series of particular magnitudes, each of which is associated with an individual kinetic model [7]. In the period since my previous adverse comments on this proposal [8], I have found no reason to change my view that this concept does not contribute towards any explanation of the measured magnitudes of E_a and does not detectably or usefully advance the theory of crystolysis reactions.

L'vov physical model for solid-state decomposition

According to the L'vov theoretical model [52, 54], the primary step in a solid-state decomposition is the congruent dissociative evaporation of the reactant to give primary products, which may be different from those present under equilibrium conditions. It is assumed that complete equilibration is reached between vapourized molecules and the condensed material on every collision. This involves the approximate equipartition of condensation energy of the less-volatile products between reactant and product phases, energy that is directly consumed by the reactant for the decomposition (contributing to the reaction enthalpy change). In contrast with the (chemical) model represented by the Arrhenius treatment, this alternative (physical) approach regards surface evaporation as the precursor step to reactant breakdown. This original concept predates (1882) the model proposed by Arrhenius. The reaction rate can be determined through the classic work by Hertz, as later (1913) expressed [52, 54] in the form of the Hertz–Langmuir equation:

$$J=(N_A P_{eq})/(2\pi MRT)^{1/2} \tag{2}$$

where J is the number of vapour molecules incident on the surface, N_A is the Avogadro number, P_{eq} is the equilibrium pressure of molecules and M is the molar mass. Using this physical model, with the above assumptions, the L'vov theory [52] accounts for many of the essential features of solid-state thermal decompositions. These include the characteristic nucleation and growth behaviour, the autocatalytic properties of interfaces, the low temperature stability of some explosives, the role of self-cooling and the kinetic compensation effect. Moreover, the theory enables both Arrhenius parameters, A and E_a, to be calculated so that the absolute rates of solid-state decompositions can be estimated. E_a represents the specific enthalpy of the decomposition step that yields the primary products [52].

The theory is presented in detail in [52], together with citations of L'vov's many earlier, relevant publications. An important feature of this proposal is the recognition that, hitherto, the Arrhenius representation has not provided an adequate explanation for E_a or of the distinctive kinetics of solid-state reactions. The new alternative approach, based on a long-accepted physical principle, proposes a theoretical foundation that the subject requires but has lacked hitherto. Significantly, the review demonstrates [52] that the new reaction model has successfully interpreted and correlated the rates of dissociative evaporation, or sublimation, for more than one hundred (relatively simple) compounds from several different chemical classes.

While the quantity referred to as 'activation energy', E_a, in the above model [52] shares some common features with the identically labelled term in the Arrhenius equation, there are also essential differences in the Hertz–Langmuir parameter, as stated by L'vov. (In [58]: '…the value of the E_a parameter is actually the molar enthalpy of the real reaction...'. From Eq. (19) of [52] '...the E_a parameter corresponds to the specific enthalpy, i.e., the enthalpy of decomposition…'.) Consequently, in this treatment, the energy diagram for reacting entities, during their progress along the reaction co-ordinate, shows only the enthalpy difference between reactants and primary products (the latter may undergo further, secondary reactions). This contrasts with the energy maximum that is characteristic of the transition state envisaged in the activated complex representation. Thus, according to the L'vov model [52], during the decomposition of a solid, the energy barrier associated with product formation, through bond reorganization steps at the reacting surface, apparently offers a negligible increment to the volatilization enthalpy (as for the evaporation of a liquid). This is a fundamental difference, which distinguishes it from the accepted homogeneous reaction model, in which activation energy must be 'invested' in bond modifications ('loosening') before 'later repayment' through the formation, and strengthening, of the linkages present in the reaction products.

The use of identical term-labels, most notably including E_a, to specify significantly different kinetic parameters has been particularly prevalent, and conventionally accepted, throughout the thermal analysis literature (e.g. [5, 8, 57]). It is, therefore, reasonable to conclude that the use of alternative, and in some articles incomplete, term-definitions to refer to distinct, sometimes even undefined, quantities has contributed to the lack of cohesion that pervades kinetic conclusions obtained from thermal analysis studies [5]. In the 'Arrhenius context', the term 'activation energy' specifically distinguishes [by the Boltzmann fraction, $\exp(-E_a/RT)$] those energized 'molecules' that are capable of product formation, through the transition complex, from all others within the overall group of freely moving and chemically identical reactants. The controls in the Hertz–Langmuir treatment applied by L'vov [52] to solids are significantly different and E_a might, therefore, be represented more appropriately by a different symbol (E_H is one possibility, and is used below). More importantly, a label of greater descriptive accuracy might be preferred, e.g., enthalphic (stimulation, excitation, etc.) energy. Emphasis of this significant difference should serve to assert the fundamental theoretical distinctions between the L'vov [52] and the classical models [1]. Moreover, it is debatable whether a process involving removal (volatilization) of entities from a crystal surface, requiring rupture of structural bonds, can be correctly labelled as a 'Physical approach', Fig. 4 of [52].

Little is known (from direct experimental observations) about structures of the interfaces that participate in crystolysis reactions [1], at the ionic and bonding level, and, importantly, about the particular features that are responsible for promoting chemical changes within the active reactant/product contact zone. The concept of the autocatalytic interface underlies the most widely accepted model for solid-state reactions, though the reasons for this locally enhanced reactivity tend to be expressed in imprecise terms such as local strain, enhanced mobilities, modified bonding, catalysis, etc. [1]. The L'vov model emphasizes the thermodynamic quantities of the material that is the precursor to reaction, while the mechanistic representation of interface structures and geometric development are considered in less detail. Use of the term 'free-surface decomposition' for the evaporation model [58] expresses a distinction from the more classical view that chemical reactions are facilitated at interfaces. It seems to me that, if agreement about common features and properties of the interface could be achieved between the researchers favouring these alternative models, this would contribute substantially towards the resolution of the outstanding differences perceived between these two apparently conflicting and/or inconsistent descriptions. Agreement on theory applicable to this central, but now disputed, aspect of solid-state reactions might contribute towards the provision of a new foundation that could stimulate coherent growth of a subject that currently lacks an agreed theoretical framework of scientific concepts. A compromise approach is tentatively proposed in the following paragraph.

The L'vov model [52] requires that there is no 'excess' (Arrhenius-type) energy barrier to oppose the evaporation step of the volatile (primary) products of reaction and/or the incorporation of non-volatile material into the juxtaposed residual phase (nucleus growth). One possible view of this representation of solid-state reactions is that the active interface accommodates a maintained dynamic equilibrium (through bond redistributions) in which both reactants and (primary) products participate. At reaction temperature, the chemical change becomes possible and takes place because volatile products separate through escape, perhaps after their formation through secondary reactions, and there is concurrent assimilation of the non-volatile products into the juxtaposed residual phase. An alternative, qualitative but more mechanistic (and traditional [1]), portrayal of this thermodynamic (equilibrium) model is as follows. In the approach to reaction temperature, thermal energy promotes the locally dynamic and reversible rearrangement of bond dispositions within the reactant/product contiguous zone. Such modifications of the dispositions of primary chemical linkages include the formation of an equilibrium proportion of products at the interface. These dynamic bond rearrangements within the phase discontinuity become displaced during reaction by the escape of, and/or secondary reactions between, the volatile primary products (as in the L'vov model) together with incorporation of residual material into the nucleus with which it is already in contact, contributing to growth. The facile assimilation of non-volatile products into the juxtaposed residual phase accounts for the absence of the condensation term from the E_H parameter. The dynamic disposition of bonds, between reactant and (interface-incorporated) incipient product, accounts for the reactivity enhancement, and also the forms and functions of possible structural components, within the classical reactant/product interface. This proposed working model for the interface alternatively emphasizes the physical, equilibrium, thermodynamic features [52] of the L'vov treatment while also accommodating the classical approach, which is more concerned with the chemical, kinetic and mechanistic [1] aspects of behaviour. L'vov notes that questions remain unanswered about the physical significance of the τ parameter [58]. All these features of reactivity, composition and structure must be consistent and reconciled in any interface theory capable of adequately representing solid-state decompositions. Advance of the active, dynamic interface zone described, within which chemical changes occur, determines the isothermal pattern of kinetic behaviour, giving the geometric characteristics of crystolysis reactions that have long been of interest to solid-state researchers [1].

Third-law method of investigation of decomposition kinetics

From the thermodynamic relationships, L'vov has shown [58, 59] that the Hertz–Langmuir function E_a (or E_H) can be calculated by the third-law method, from:

$$E = T(\Delta_r S_T^0 - R \ln P_{eq})$$

entropy changes can be obtained from tabulated data and the rate, P_{eq}, can measured from J (Eq. (2)) at a single temperature. If the reaction temperature is low, and the rate is sufficiently slow, the effect of self-cooling on the reaction rates and on the kinetic parameters determined is small. L'vov has strongly advocated [58, 59] this method for measurements of E_a (E_H). Advantages claimed include a considerable reduction in time of experimentation (perhaps ×0.1) and a significant increase in precision (in general ×10), compared with second-law and Arrhenius plot methods.

As with the proposed Hertz–Langmuir (physical) model for activation energies (E_H, 'L'vov physical model for solid-state decomposition'), the recommended [59] use of the third-law kinetic methodology for determination of this parameter has (also) been comprehensively ignored by the thermoanalytical community. However, having stressed the value of objective and constructive criticism in contributing towards subject advancement above, I must now express some of my own reservations about this method.

- The point is made in [58, 59] that, compared with the traditional methods, this approach to E_a measurement is capable of saving both time and effort. However, at present, this advantage must be expected to have limited appeal because so very few people now use the relatively laborious Arrhenius plot method. Moreover, rapid experimentation is unlikely to be attractive to the majority of those workers active in the field, who are already convinced that the great (apparent) success of thermokinetic methods is the ability of automated computer techniques to collect and process data efficiently and with a minimum of effort. The effective dismissal, by most researchers, of what might superficially be regarded as an alternative rapid method for determining E_H has had the unfortunate consequence of by-passing the point that is central to the debate on the applicability of the new theory to these reactions [52]. The significant feature is that the L'vov model provides a theoretical meaning for E_H, whereas the more widely used minimalistic thermokinetic methods either assume validity of the homogeneous reaction kinetic interpretation for E_a or provide no meaning for this parameter (as mentioned above and in [5–9]). The possibility that self-cooling may influence rate behaviour, minimized in third-law studies, remains unconsidered in a majority of thermokinetic investigations.
- The pattern of reaction geometry, isothermal kinetic control through advance of an active interface, appears to be disregarded in the experimental procedure described [58, 59], thereby excluding from consideration this highly characteristic feature of solid-state reactions. The use of reactant in a powdered form and the representation of the surfaces participating through empirical ratios appears to restrict kinetic analysis to the determination of Arrhenius parameters only, with omission of the geometric characteristics that have long been of interest. An adequate reconciliation of the classical

and L'vov models would (in my opinion) include consideration and examination of the shapes of isothermal α–time curves, with quantitative explanations for the progressive changes of interface spatial dispositions as reaction advances, as, for example, in nucleation and growth reactions. This limits the value of the new theory as currently presented.

- Kinetic analyses based on a single measurement are incapable of revealing complexity of behaviour. The single value for NH_4ClO_4 in Table 2 of [59], from Jacobs and my work [60], excludes all possibility of detecting the low temperature reaction [31]. Any reaction exhibiting complex kinetics, involving concurrent and/or consecutive overlapping rate processes, or in which melting before breakdown was not detected, might not be adequately characterized. The chemical steps involved in the breakdown of salts more complicated than those mentioned in [59], might not be correctly or completely elucidated when only very limited observations are made.
- A comprehensive demonstration of the applicability of the L'vov physical model to a particular reaction requires experimental confirmation of the identities of the primary products, to establish that these are in accordance with thermodynamic expectation. The necessary analytical measurements may, however, be difficult to obtain where rapid secondary reactions at the interface participate in the breakdown of complex reactants. Information about the primary processes may then be used to characterize the intermediates and the subsequent chemical changes that yield the final products. Both steps should be identified to provide a complete description of the overall reaction mechanism.
- The experimental evidence upon which L'vov recommends the use of the third-law method is summarized in Tables 2 and 3 of [59], in the form the T_{in}/E_a ratios: [initiation sublimation temperature (T_{in})/sublimation enthalpy (E_a)] collected for 100 different, but relatively simple, compounds. The overall mean recorded is $T_{sub}\ /\ \Delta H_T^0=3.63\pm0.22$ K mol kJ^{-1}. There are, however, significant variations of the individual values, which range from 2.96 to 4.70: 15 were below 3.2 and 17 above 4.0 (i.e., 32% were more than ±12.5% from the average) and 7 were above 4.3. These are significant deviations: one in three values differ from the mean by more than 10%. Only a single $T_{sub}\ /\ \Delta H_T^0$ value for each substance is recorded and criteria for selection of the particular values included are not completely explained. Data were obtained under different and varied experimental conditions: reactants were investigated alternatively in the forms of either a submonolayer, a powder, a crystal, a pellet or a liquid and were volatilized in vacuum, in air, in nitrogen, in oxygen or in argon. The compounds mentioned ranged from the highly volatile ($NH_3{\cdot}NI_3$, T_{in}=253 K) to the refractory (TaC, T_{in}=2973 K), covering a very wide interval of sublimation temperatures. This range of very different substances can be expected to reveal general trends, though I find it difficult to appraise the overall reliability of the mean relationship, found from comparisons for data collected under such diverse experimental conditions. I would also have been interested to know the precision of agreement between results obtained by different workers studying the same compound: information about individual reproducibility is not provided. Before I could regard the experimental method as having general applicability, I would welcome further observational support, including T_{in} and E_a values and T_{in}/E_a ratios from dedicated measurements, together with E_a values measured by alternative techniques, for more diverse substances, including crystalline complex compounds.
- The majority of applications of the L'vov model have concerned endothermic, reversible reactions, particularly the dissociations of calcite and other carbonates. If the theory is to have general applicability, it is important to establish the kinetic characteristics of representative irreversible rate processes under the conditions given in [58, 59], and others, and the influences of self-heating for exothermic reactions.

Comment

It has been a feature of the recent extensive literature concerned with thermal analysis that Professor L'vov's two proposals, the physical model for decomposition of solids ('L'vov physical model for solid-state decomposition' [52]) and the third-law method for determination of the E_a (or E_H) parameter ('Third-law method of investigation of decomposition kinetics' [58, 59]), have been almost totally ignored. No obvious explanation for this absence of critical comment by the thermokinetic community is apparent. It is unlikely that the theory has not been noticed and understood (many articles have appeared in widely available Journals and the scientific principles are already well known). It is also difficult to believe that knowledgeable researchers can agree that the theories presently applied to formulate mechanisms of thermal reaction of solids are incapable of improvement. A more cynical view is that there might be an unscientific reluctance to question the assumptions and norms of the subject, as now accepted, so that its unchallenged status can be maintained, despite its inadequate foundations. Most surprising is that there has been no reasoned criticism of the L'vov theory and no detailed comparison with current practices. It appears that the attitude is that 'if we ignore it, possibly it will go away'. This could be a self-fulfilling aspiration, but is it in the best and long-term interests of thermal analysis?

My personal view is that the present reluctance to appraise critically the relative merits of the classical [1] and the L'vov theories [52] is unacceptable and unsustainable. Attempts must be made to resolve this impasse. This paper is offered to initiate the debate that must take place sooner or later. As an adherent to the classical tradition (with reservations [4–8]), I have attempted here to identify points of significant difference between accepted theory and the newer proposals. It is hoped that a discussion of controversial or inconsistent features might ignite exchanges capable of resolving the essential differences between theories that currently appear to lack any hope of reconciliation. For reasons presented above, I have reached two considered general opinions. First, given the essential shortcomings of the Arrhenius/chemical theory of crystolysis reactions, the (so-called) physical model [52] offers our best hope for an acceptable replacement, a way forward. In contrast, and second, I believe that the proposed third-law method of kinetic analysis [58, 59] encourages an experimental approach that yields insufficient information to enable the chemistries of solid-state reactions to be adequately characterized. These criticisms are intended to be entirely constructive: identification of resolvable points of disagreement and the recognition of common methods and procedures offers the only path towards the future meaningful development of thermal chemistry.

Appraisal

Objective of this critical survey

The selective, even idiosyncratic, historical survey given above, summarizing the slow progress that has characterized the development of theory associated with the Arrhenius reaction model [10], is intended to outline the significant advances that have been achieved so far. Realistically, there remains much more to be done to provide a general, quantitative kinetic model applicable to all homogeneous reactions. Even less progress has been made in elucidating the factors that control the rates of heterogeneous reactions. Although transition state theory has been applied to crystolysis reactions, as the Polanyi–Wigner theory [1, 25, 27], important limitations remain in the theoretical foundations underpinning this aproach. Subsequently, when thermal analysis became the method by which thermal decompositions of solids are almost invariably studied, the primary focus of research was redirected away from chemical theory and towards increasing the efficiency and exploitation of automated methods of data collection and interpretation [5]. During this time, weaknesses in the underlying science of solids were disregarded, possibly even forgotten, but certainly not addressed. The inevitable consequence has been that the chemistry of these rate processes now lacks a coherent theoretical foundation. This critical chemist believes that these inadequacies are not adequately appreciated, and are certainly not sufficiently discussed, by many, perhaps most, researchers active in this field.

In this situation, it is reasonable to expect that the appearance of a completely novel theory would immediately excite the interest of forward-looking scientists, motivated by the welcome prospect of advancing the fundamental concepts of their discipline. (Science proceeds by identifying principles through which knowledge can be systematized: the models and criteria used for this ordering require continual reappraisal, with modification or replacement when found wanting.) Two types of response to any authorative challenge to the existing scientific principles of the subject (thermal analysis) might be anticipated. First, a reappraisal of the established framework of ideas, to determine whether accepted models are comprehensively satisfactory and/or whether there are identifiable gaps. Second, a dispassionate appraisal of the new proposals, to appraise their potential for improving understanding of the phenomena of interest. Such activity would be expected to include critical comparisons between theories old and new, reexaminations of the validity of all accepted assumptions, tests of the applicability of models to 'difficult' systems and assessments of the relative capabilities of the rival theories to predict behaviour in hitherto untested systems. Publications reporting work specifically directed towards resolving perceived differences between rival theories should serve to excite discriminating debate, vital for the healthy and organic development of any scientific subject. Whether or not a newer idea ultimately triumphs over an older, established theory, the critical reassessment of all relevant aspects of the topic must benefit the subject as a whole, in which the dominant concept emerges successful, strengthened by critical appraisal. The alternative possible response from the active research community, to boycott (ignore) a novel proposal, should be unthinkable to professional scientists, dedicated to the extension of systematized knowledge.

The present paper is concerned with the specific problems that currently exist in the field of thermokinetic analysis, see also [3–9]. In this situation, it might have been expected that a new theory, founded on established physical principles, would be universally welcomed, particularly a model of such general applicability and potential value [52], as that formulated by Professor L'vov. However, the response, 'Let us ignore it, and perhaps it will go away', appears to express the attitude of the thermal analysis community. In 2001, L'vov stated [52]: '…the physical approach has been completely ignored by all workers in the field of traditional thermal analysis for the interpretation of crystolysis kinetics, …". In 2004, the situation had not changed, referring to the comparison of reaction enthalpy with the Arrhenius E_a parameter, he could say: 'However, any impact of this approach on traditional scheme of interpretation of the decomposition mechanisms is practically absent' [58]. At the very least, I would have expected that research leaders in this field would have welcomed the opportunity to organize and to witness a presentation of these ideas at one of the International Conferences, arranged (presumably) for the discussion and (hopefully) the resolution of controversial topics. This courtesy, the opportunity for face-to-face debate to remove differences, does not seem to have been extended to the author of the only truly novel proposal in thermal analysis/crystolysis chemistry for decades. I find this situation both inexplicable and sad.

It appears that no adequate forum exists to encourage any debate between what now must be recognized as two opposing 'research groups', in this (unevenly) divided subject. One 'group' is composed of the extensive 'Community of Thermal Analysts', who seem to be disinclined to admit even the possibility that their subject might contain imperfections and apparently prefer silence to dialogue, with the implicit maintenance of their current ideas. Professor L'vov and his St. Petersburg colleagues, in the other (numerically smaller) 'group', continue to promote and develop their alternative theory, so far with little obvious penetration. In this unresolved conflict situation, surely universally unsatisfactory, I suggest constructive debate as the only possible way forward. In this, I accept the possibility (probability?) that arbitrators can, and often do, attract the wrath of both sides. Peacemakers (particularly when self-appointed) do not always realize their ambition to resolve conflict: usually peace and concord are not easily achieved. Nevertheless, believing that scientific enquiry is barren if fundamental principles are not upheld, I have, in previous sections offered my personal reservations about both of the concepts formulated by L'vov. Taken with my adverse comments above on 'conventional' thermal analysis, I have to cnclude that discussions, constructive dialogue and theory modification, by both 'groups' are essential to resolve the present impasse. The current paucity of meaningful exchanges of views is sterile, representing stagnation [3]. The maintenance of alternative scientific theories, believed to apply to the same phenomena, is unacceptable and should be unsustainable. If the situation described here does not initiate argument capable of resolving the differences identified, then the hope of making future progress towards developing understanding of the chemistry of thermal reactions must continue to be remarkably bleak.

Comment on the content of the thermoanalytical literature

A slightly exaggerated appraisal of the extensive literature reporting kinetic and mechanistic studies, using the methods of thermal analysis, is as follows. Thermoanalytical equipment has massively increased the efficiency of laboratory experiments, very large numbers of accurate rate data measurements can now be collected by computer-automated apparatus that also performs the kinetic interpretations. Interest in theory has (almost exclusively) become restricted to increasing the efficiency of the laboratory equipment and of the mathematical analysis of data. Interpretation of kinetic observations relies heavily on models developed from earlier studies of solid-state decompositions, a discipline that has been effectively superseded, even eclipsed, by thermokinetic investigations. Former considerations of chemical principles in the analyses and discussions of results and the use of supplementary experiments to confirm and extend the available observational evidence, on which conclusions can be based, have featured little in the new discipline [5]. The imperfections of theory, the inadequate characterization of the significance of rate measurements and the discounting of the inherent complexity of many chemical changes (amongst other reasons) means that results from many thermokinetic studies are empirical. These limitations are not always explicitly recognized in research publications. It appears that the theory of thermal reactions has effectively become dissociated from its chemical foundations and is now in a state of unacceptable disorder. Many recent studies do not contribute to the organic growth of a coherent and recognizable body of scientific knowledge and appear as independent, separate reports.

Thermokinetic investigations can yield empirical results remarkably quickly (with minimum effort) which, when these are presented in the conventionally accepted pattern, continue to expand an already very large literature. Fundamental shortcomings inherent in the theory normally applied in these reports, described above, often remain unconsidered. Consequently, many such papers do not contribute to the systematic growth of an ordered science. Referees, encouraged by Editors, could discourage continuation of this well established, but unacceptable, situation by (not unreasonably) demanding more care in the design of research programs, more criticism in the interpretation of observations and discussions which include wider comparisons and correlation with related rate processes. International Conferences could also encourage Plenary Lecturers to address those theoretical aspects of this chemical subject that, hitherto, have not been given the prominence and critical attention that they deserve. Recognition of limitations inherent in concepts available and models used for data interpretation is only a first step in providing an adequate theoretical framework for the subject. Theory regeneration might reasonably be identified as the 'rate limiting step' in scientific advance. Once the existence of problems and limitations in existing models have been perceived, and are seen as 'ripe for debate', the way will be opened for progress. Information already available may then be systematized and developed through scientific models capable of ordering data available. Some progress in this direction has already been made. We can all retain optimism about future advances in our scientifc discipline. However, progress and achievement is only possible if all of us always maintain our highest scientific principles and critical integrity, working with open and receptive minds.

Footnote

Several comments made above draw attention to the possible role of a participating liquid, before or during, the thermal reaction(s) of initially solid reactants [28–32]. This fundamental feature of a chemical change must be incorporated into both kinetic interpretation of rate data and the formulation of a reaction mechanism. However, the melting of a pure solid, fusion without a chemical change of the constituents, can be regarded as a type of crystal breakdown, which resembles, in (at least) some respects, thermal decompositions. There is modificaiton of intercomponent but not intracomponent bonding. Similarities and differences between melting (physical change) and thermal reactions (chemical change) have been discussed recently [61] in the context of several papers discussing the melting of simple crystalline solids [62–65].

Possible responses to the title question

More than a single answer may be given to the question posed in the article title: 'What theoretical and/or chemical significance is to be attached to the magnitude of an activation energy (E_a) determined for a solid-state thermal decomposition?' From parallels with homogeneous reactions, E_a is sometimes identified with a bond ruptured in a postulated rate limiting step. In the thermal analysis literature, E_a often appears as a 'result' but its significance is often not discussed (or defined) and its empirical value may vary with calculation method. In the L'vov theory 'the E_a parameter corresponds to the reaction enthalpy' [52]. Thus, in the absence of an agreed term definition (and theory), the chemical significance of the activation energy varies with context. This unsatisfactory ambiguity can be removed only by reconciling the diverse inconsistencies in the theories used to calculate E_a values. The objective of this paper is to emphasize the importance of achieving an agreed consistent terminology, methodology and realistic theoretical framework.

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