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What is meant by the term ‘variable activation energy’ when applied in the kinetic analyses of solid state decompositions (crystolysis reactions)?

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Abstract

A recent review [1], ‘Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective’ recommends ‘acceptance of the concept of variable activation energy’. Such a modification to the accepted meaning of so important a fundamental kinetic parameter requires critical scrutiny of the consequences that this change might make to the theory of the subject, some aspects of which are discussed here. Section 1 distinguishes five possible alternative definitions and/or explanations for the variability of activation energy, E; the meaning of this term is not adequately addressed in [1]. Section 2 discusses the experimental evidence offered in [1] to justify the proposal that E values should be regarded as variable. It is concluded, for stated reasons, that the supporting information provided is insufficient and unsatisfactory. Some of the selected systems appear inappropriate because there is evidence that the initially solid reactant would have melted before the reaction of interest. For others the kinetic behaviour pattern has already been adequately explained by contributions from secondary or complex controls. The introduction of the concept E (variable) seems to be unnecessary to account for the patterns of rate characteristics presented. Section 3 discusses the aims and objectives of kinetic interpretations of thermoanalytical observations generally and the measurements of E values in particular. It is concluded that the long-term development of the chemical understanding of reactions proceeding in condensed phases is most satisfactorily approached by individually identifying and quantitatively determining each contribution from every factor that influences or controls the rate of any reaction of interest. Although, considerable theoretical problems currently beset this subject, attractive and optimistic prospects for future advances are however identified. This does not include the use of E (variable) because this parameter is regarded as being predominantly empirical in character with the consequence that this concept tends not to extend either the theory or the scientific foundations of behaviour observed. It appears that the new parameter is unlikely to contribute to the direct and reliable measurement of reactivities and of absolute reaction rates or in the formulation of reaction mechanisms. It is concluded here, therefore, that the proposed introduction of this term, E (variable), is a retrograde step, unlikely to advance science through the development of theory, and its use is not recommended for reasons that are explained. Appendix extends and develops, into a wider perspective, these kinetic and mechanistic themes by identifying some interim conclusions about the methods generally used to interpret rate data obtained from thermoanalytical measurements.

Keywords: Variable activation energy; Crystolysis reaction; Thermoanalytical measurements

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1. ‘Variable activation energy’: alternative definitions and meanings

Vyazovkin has recently published a thought-provoking review [1] concerned with those selected theoretical aspects of chemical kinetics that form an historical background to the methods currently available for the interpretation of rate measurements for thermal decompositions of solids. In particular, the currently accepted usages of essential terms, including (amongst others) rate constant (k) and activation energy (E), are discussed in the perspective of previous and wider significances. In this context, uncertainties and inconsistencies inherent in some recent applications of the relevant theory to kinetic analyses of reactions involving initially crystalline reactants are discussed. Emphasis is (rightly) directed towards recognizing the general paucity of our detailed knowledge of the rate determining controls and mechanisms of the chemical changes that participate in the thermal conversion of a solid reactant into products. Vyazovkin also points out that many such reactions are more complicated than the single-step processes that are so often assumed to occur. At the end of his account of aspects of currently employed practices [1], he proposes that ‘for the kinetic analysis of solid state reactions’, there should be ‘the acceptance of the concept of a variable activation energy’. This is suggested as a ‘reasonable compromise’ at the present state of subject development.

The view that activation energy should be accepted as a variable parameter [1] represents an important, indeed fundamental, reappraisal of this essential theoretical concept, generally regarded as being of the greatest significance throughout chemical kinetics [2]. Accordingly, before this radical change of meaning of such an important term could and should be accepted, the revised concept, model or definition, must be subjected to the most rigorous and critical scrutiny, to which the present article is intended to contribute. I approach this evaluation following a recent, wide examination of the relevant literature [3], from which I have concluded that the meaning of the term activation energy, specifically as used in solid state chemistry and including thermal decompositions, has become less precise in recent years. Furthermore, the concept associated with E appears to vary somewhat between different published reports. I believe that a reappraisal of the theoretical significance to be attached to the calculated magnitudes of E for solid state kinetic analyses is now timely (even overdue). It seems to me that a very suitable starting point for initiating such a reconsideration is an examination of the consequences of ‘the acceptance of the concept of the variable activation energy’ (from the last sentence in [1]). Some wider implications of the term activation energy, together with related aspects of kinetic analyses and the formulation of mechanisms for crystolysis reactions [3], are also discussed here, in a survey that is intended to be generally relevant to recent thermal analysis kinetics (TAK) literature.

The activation energy is an important parameter in the interpretation of rate data throughout chemical kinetics, because it possesses theoretical value in relating, through the Arrhenius equation, the temperature coefficient of reaction rate to the height of the energy barrier opposing reaction [2]. In contrast, other rate/temperature relationships have been described [2] as ‘theoretically sterile’. Variable values of the calculated magnitudes of E have been recognized [1] for some thermal reactions of initially solid reactants because the measured temperature coefficient of the overall reaction rate exhibits change as reaction advances. There are several alternative explanations for such different variable activation energy types (VAET); some possibilities are listed later, which do not appear to have been distinguished and separately considered in [1]. (There may, of course, be others and more than a single effect may exert appreciable and variable influences on reaction rate and on its temperature coefficient during any particular reaction of interest.)

Meanings of essential terms as used in the present review: At present, the mechanisms and controls of chemical changes that occur during the reactions of solids are effectively experimental (and theoretically) inaccessible. There is (unfortunately) no general representative concept or model for these processes, analogous to the dominant, preferred path in a homogeneous reaction for which rate is controlled by the slowest rate limiting step. The interfaces, within which it is believed that many crystolysis reactions occur [3], may be complex structures wherein a particular sequence of interlinked bond redistributions provide the most effective pathway through which the reactant is transformed into products. These have not been characterized for most reactions of interest. However, by analogy with the 'rate limiting step' model, reactions in solids may proceed through a preferred and dominant route of chemical change. This approach, without knowledge of specific details, accounts for the enhanced reaction rate within the active interface. It appears to me that the measurement of kinetic properties of this process, through Arrhenius parameters, offers one possible approach to characterization of the rate limiting process (the slowest step in the most rapid path available for product formation). The absolute rate of this process must be measured in the (confirmed) absence of additional controlling factors, such as the influence of volatile product present (which may undergo recombination or modify equilibria within the reaction zone) and the effects of self-heating or self-cooling. Comparisons between absolute reaction rates and Arrhenius parameters for the (forward only) interface process for groups of related reactions might then possibly provide suitable evidence from which properties of the factors controlling reaction rates may be inferred (evidence of this type is required to infer the rate limiting step for homogeneous chemical changes). Discussions of Arrhenius parameters below refer to a single reaction, perhaps involving a rate limiting step and uninfluenced by secondary effects or processes: for any particular reaction this may or may not be experimentally measurable. Reaction chemistry refers to the steps involved in the making and breaking of bonds during any transformation of a reactant into products, together with all essential accompanying or participating physical processes, including formation of transient intermediates, recrystallization, melting, sublimation, etc.

1.1. The temperature coefficient of reaction rate varies (VAET1)

Perhaps the most obvious literal, even pedantic, meaning of the term 'variable activation energy' is that the absolute value of E, usually regarded as the energy barrier to bond redistribution in the rate limiting step [2], undergoes systematic changes during the progress of a particular reaction. Although, it is accepted that such a reactivity pattern might occur, as discussed later, I am aware of no example of a solid state reaction for which this has been conclusively demonstrated. This meaning does not, however, appear to be implied in [1] and would require extensive, detailed and precise comparative rate measurements to provide an acceptable confirmation.

A variation of E as reaction progresses implies a systematic change of reactivity that appears to be impossible for a homogeneous reaction where all freely moving reactant molecules are regarded as identical. Each collision-type encounter, potentially leading to reaction, is isolated in space so that such precursor steps to chemical change are regarded as being unaffected by product formation. The magnitude of E for a specific (single) reaction must, therefore, remain constant throughout that particular chemical step or process. In contrast, the reacting entities in a solid are not isolated during chemical changes proceeding in the rigid structure but interact with neighbours to which each is bonded. There is the possibility that during reaction, the particles of reactant may undergo progressive modification of their reactivity (including E), by factors may include crystal defect formation, particle disintegration, development of intracrystalline strain, etc. Furthermore, the initial reactivities of the individual particles that constitute the original reactant may be appreciably different due to variations of particle sizes, boundary faces of different indexes exposed, crystal imperfections and damage, etc. Thus, the average reactivity of the assemblage of reactant particles may not remain constant as reaction progresses. Because the material that is inherently most reactive will be chemically changed most rapidly, the reactivity of the reactant remaining might be expected to diminish progressively (and the value of E change).

1.1.1. Change of inherent reactivity and of E with progress of reaction

The influence of crystal imperfections in determining reactivity has been discussed by Brown and Brown [4]. Every preparation and each sample, of any particular reactant, 'will have a unique set and distribution of imperfections of various kinds, so that, in practice, no two samples of solid can ever be identical, although they may be similar'. It is concluded from the well-known variations of kinetic characteristics with particle sizes and with (some) impurities that 'deviations from an ideal structure may have greater influence on some solids than the crystal structure itself . . . '. This emphasizes the difficulties of identifying and distinguishing the contributions from different reactant characteristics in determining the overall reactivity for solids.

The suggestion that the reactivity of each crystal is unique [4] identifies the necessity to undertake directed quantitative investigations to measure the magnitudes of the variations that occur between individual single particles for a representative range of specific solid reactants. Whether or not such effects are sufficiently large to cause appreciable changes in the apparent values of E during the course of a single reaction can only be established by comparative experiments of sufficient sensitivity and capable of distinguishing the various specific contributions to reactivity in individual crystals.

1.2. Complex reactions (VAET2)

If two (or more) chemical controls determine the rate of product formation, the temperature coefficient of reaction rate (and thus E) will vary with the extent of reaction (fractional reaction, α) and/or temperature (T), if the relative contributions from the alternative processes (of different E values) change with these (α, T) or other variables. Various possibilities exist, including the following: (i) In nucleation and growth processes [3], the composite reaction requires an effective nucleation step before interface advance becomes possible. A complete kinetic description of behaviour requires characterization of both (or all) contributory processes (in general exhibiting different E values) so that their relative significances change with α. (ii) The kinetic characteristics of some reactions have been shown to vary with temperature (e.g. dehydrations [5–8]). Rate data obtained across the temperature at which a change occurs is likely to give an apparently variable activation energy. (iii) In principle, the decomposition of a solid could occur by two (or more) concurrent, alternative pathways so that a change in these relative contributions with α, T or any other parameters would be expected to result in variations of E. I am aware of no confirmed example of this pattern of concurrent reactions in solid state decompositions, but the possibility exists. (iv) Significant overlap of consecutive reactions may also result in an apparent variability of E.

These kinetic characteristics (VAET2) are found because the parameter used to measure the overall reaction rate (e.g. reactant consumed, product yield, etc.) contains contributions from two or more distinct chemical rate processes that are kinetically distinct and proceed concurrently or with substantial overlap. Similar behaviour is possible, of course, in homogeneous processes. However, it appears to be frequently assumed, though not usually explicitly stated, that solid state reactions proceed as a single chemical change (an interface reaction) and that overall, reactions can usually be adequately expressed by a single Arrhenius equation (i.e. constant (average) E). This representation should not, however, be accepted as being generally applicable because, for many of these reactions, there is evidence that the apparent, overall magnitude of E varies with α. This rate characteristic has been discussed and shown to be detected by isoconversional methods of kinetic analysis in [1]. There is a strong case for including specific tests of the variability of E with α routinely in the computer based programmes used for analysis of TAK data, particularly for heated solids.

1.2.1. Interface reactions

Since the initial formulation of the geometry-based rate equations, now regarded as a most characteristic kinetic feature of thermal rate processes involving initially crystalline reactants [3], it has been known that there may be rate control by more than a single parameter. In nucleation and growth processes, the energy barrier (and E) for the initiation of reaction, nucleation, is sometimes relatively large. Once established, the subsequent interface advance, during nucleus growth, proceeds relatively more easily and the magnitude of E may be relatively lower than for nucleation. Because these processes are interdependent, and the relative contribution from nucleation may diminish as α increases, the activation energy for the overall nucleation and growth process is composite and varies with α. Recently, however, it has become customary to ignore any such changes and report only the average (overall, composite, apparent) E value, implicitly (but sometimes incorrectly) assumed to be constant throughout reaction. Some problems in this approach are discussed in [1].

For this type of behaviour (VAET2), involving concurrent and/or overlapping reactions, it may be assumed that the E value for each individual contributing chemical controlling step is a constant quantity, its magnitude being characteristic of that particular rate process. The detection of variations of E for a (single) specific rate process (VAET1), and distinguishing the magnitude of such variations from the contributions given by concurrent or consecutive reactions, would be experimentally most challenging. This has not, as far as I am aware, yet been achieved or perhaps even attempted. However, in kinetic analysis of data for complex chemical changes with two or more contributory reactions, the overall temperature coefficient of reaction rate is a composite quantity and E may therefore vary with α, T and/or, indeed other parameters.

1.3. Procedural variables (VAET3)

The measured rates of many crystolysis reactions [3] are highly sensitive to local experimental conditions, through interactions with the environment of the zone within which the chemical change is proceeding. These are the influences of the so-called ‘procedural variables’ [9]. For many, perhaps most reversible and/or endothermic solid state decompositions, kinetic characteristics are sensitive to control by the factors that determine the transfer ease of mass and of heat, respectively. These reactions constitute a high proportion of the chemical changes that have attracted the greatest interest in crystolysis studies [3]. However, despite important and perceptive research, identifying reasons for variability, even sensitivity of kinetic behaviour to reaction conditions, these considerations have been widely and systematically ignored. In general, little interest has been shown in adopting, for kinetic and mechanistic investigations, experimental conditions in which the influences of mass and heat transfer are minimized or eliminated. For example [10–12] reports precise studies designed to measure the rates of the ‘forward’ reactions (only) in reversible dissociations, and [13–15] for assessments of the significance of self-cooling in influencing the kinetics of endothermic reactions, mainly dehydrations. In the absence of direct determinations of the contributions by the volatile product at the active reaction interface (for reversible reactions) and of the effective interface temperature (for reactions that are not thermoneutral) or a demonstration that these effects are absent, such rate data must be regarded as empirical.

The procedural variables [9], the physical characteristics of the reactant sample including particle sizes, their dispositions and total mass, the pressure of product, the reactant heating rate, etc. exert greater or lesser control on the ease of volatile product escape together with the movement of heat within and between particles as reaction proceeds. During reversible and/or endothermic reactions, locally inhomogeneous and time dependent variations of the distributions of product pressures and temperature may be developed within the mass of reactant. Both factors exert control on reaction rates and in consequence, their influences must be expected to lead to variable, and therefore unreliable kinetic measurements. The changes of kinetic characteristics resulting from modifications of experimental conditions is easily demonstrated by comparative experiments using reactant particles of different sizes, determining the effect of altering prevailing gas pressure or other adjustment of the procedural variables [9]. Measurements of the quantitative dependencies of rates on controlled changes of these parameters is however less easily achieved and such investigations, qualitative or quantitative, are rarely reported (an important exception to this generalization is found in the work by L’vov who has discussed quantitatively the isobaric and equimolar modes of decomposition: Section 3.2.1 and references therein). It is obvious that kinetic characteristics that are conditions-sensitive cannot be used as a suitable experimental justification for formulation of a chemical reaction mechanism or the identification of the factors that control the rate without quantitative determination of the individual influences of all controlling parameters. There have been many demonstrations that kinetic parameters calculated from such data vary widely with conditions prevailing within the reaction zone. For example, Arrhenius parameters reported for the dissociation of calcium carbonate extend over an unrealistic and unreasonable range of values, a rate process showing compensation behaviour [16].

The distinction between VAET3 and 2 effects (Section 1.2) is that the influence on reaction rate arises through secondary controls that are a direct consequence of the reaction of interest (volatile product present, heat flow) rather than from the inherent complexity of the overall chemical changes being studied. Moreover, the contributions from these incompletely or more usually, uncharacterized controls may vary with α, T or other factors. These varying secondary controls provide a realistic explanation, for some reactions, of temperature coefficients of reaction rates that have been shown to be variable, as discussed in Section 2, for examples from [1].

1.4. *Melting of a solid reactant (VAET4)*

The literature of thermal analysis tolerates a particular widespread omission in the description of reactions and interpretation of kinetic data: little attention is directed towards establishing positively the phase/state in which the reactions occur. Kinetic analysis is conventionally and frequently directed exclusively, or mainly, towards identifying the 'best fit' for the measured rate data to one or other of the conventionally accepted set of rate expressions that are characteristic of reactions of solids [3]. These equations have been derived through consideration of interface advance, a geometry-based parameter, some models also incorporate diffusion control, and additionally, first, second and sometimes the third order processes may be included. This approach was originally developed for kinetic analysis of crystolysis reactions for which conclusions were often supported by confirmatory microscopic observations [3]. From these, observed progressive changes in texture in solid reactant particles were shown to be consistent with the interface advance conclusions based on kinetic fit. Many recent studies by thermal analysis methods have been concerned with the same reactants, where there may be some supporting evidence for the assumption that reaction occurs in the solid state. However, additional investigations by the same methods have now been extended to include other reactants where it has not been confirmed that an initial solid has undergone no phase change before onset of reaction. Despite this omission, kinetic results from thermogravimetry (TG) (where melting is not detected), differential scanning calorimetry (DSC) and/or differential thermal analysis (DTA), are conventionally tested for fit to the same set of rate equations that are characteristic, predominantly, of crystolysis reactions [3]. Without explicit discussion, this approach seems to imply strongly that the reaction has occurred in solid particles. An important, perhaps the most important, feature in any mechanistic description of reaction, the phase in which the chemical change has taken place, therefore, often remains unaddressed. It is reasonable to suppose that in a proportion of reactants, there will be melting before reaction; fusion is probably the most frequent consequence of heating a solid. This shortcoming in the interpretation of thermal rate data often places emphasis on the mathematics of data fitting to solid state kinetic models by automated data computational programs but ignores the chemical and physical realities of the reactions occurring.

The relevance here of the possibility that a decomposition reaction may be accompanied by melting complete, partial, local and/or temporary, is that changes in the amounts of active melt or in the composition of the molten phase with α, T or other parameter, are capable of causing variations in the temperature coefficient of reaction rate, and thus of E (VAET4). This type of behaviour is discussed in Section 2, with reference to some examples from [1]. There is strong evidence that some reactions, formerly regarded as proceeding exclusively in the solid state, involve the participation of a local melt and may include the involvement of transitory unstable intermediates. From detailed kinetic and mechanistic investigations of the following decompositions, it has been concluded that reactant breakdown is not completed in a single step, melting occurs and the compounds identified as participating intermediates are shown in {brackets}: copper(II) malonate [17] {copper(I), acetate}, ammonium dichromate [18] {chromium(VI) oxide} and ammonium perchlorate [19–21] {nitryl perchlorate}.

1.5. *Change of E with rate equation (VAET5)*

The concept of activation energy as originally formulated in homogeneous reaction kinetics and accepted throughout other branches of chemistry, identified E with the (rate determining) energy barrier that had to be surmounted during the transformation of reactant to product [2]. The magnitude of E for a specific (single) reaction must, therefore, be constant and is characteristic of that particular chemical step or process. Thus, alternative methods of calculation using the same data must be expected to give the same E value, though this expectation appears not to have been satisfactorily sustained in recent TAK studies. Reports in the literature of values of E, calculated from identical data, but which vary with the rate equation used in the calculations, or other mathematical procedure (examples are given in the next paragraph), is a further results pattern that can be described as 'variable activation energy' (VAET5).

Considerable ranges of calculated magnitudes of Arrhenius parameters, obtained by different kineticists, experienced in this field and using the same sets of (α, t, T) data, were reported in an ICTAC comparative kinetic study [22]. A similar range and spread of values of A and E were reported in an earlier comparable study [23], which differed in that each of the several participating research groups made experimental rate measurements for the same reactions (dehydration and decompositions of calcium oxalate monohydrate). A common feature of the conclusions obtained in both extensive comparative sets of reported results [22,23] is that a range of varied kinetic models (rate equation, $g(\alpha) = kt$ function) were used by the various individual groups of participants and the calculated Arrhenius parameters reported from identical or comparable measurements were different. The view that the apparent magnitudes of A and of E vary with the kinetic model used in the calculation programs has been widely accepted: examples demonstrating this result include the thermal reactions of HMX (Table 2 [1]), ammonium dinitramide (Table 2 [24]), europium complexes (Tables 4 and 5 [25]), Schiff's bases (Tables 7–10 [26]) and many further comparable patterns of variation can be found in the literature. Reasons for this have not yet been satisfactorily determined but one (possibly contributory) cause is that the different definitions of the rate constant (k) have been used in the different kinetic models (discussed at p. 121 of [3]). Unless k is defined in units (time^{-1}), the use of rate equations involving different exponents (n) changes the computed magnitudes of $\ln A$ and of E by a factor $\times n$. This may account for some of the systematic trends found in the earlier examples. It is also possible that other, but hitherto unidentified, features of the mathematical calculation procedures used in manual methods, spread sheets or incorporated into the automated computer programs widely used in kinetic analysis contain errors that are responsible for this mutability. A common feature of the Arrhenius parameters arising from these sets of 'alternative pairs' of $\ln A$ and E magnitudes for each reaction mentioned earlier [22–26] is compensation behaviour [27]: this pattern has been discussed in a recent re-analysis [28] of the results in [22]. (A compensation effect is isokinetic behaviour and is characteristic of reactions that proceed at the same rate, k values are identical at the isokinetic temperature [16,27]. This condition is obviously met when the same data are used in multiple kinetic analyses).

If E and A are regarded as characteristic features of a particular rate process (the model accepted implicitly throughout homogeneous kinetics), then it follows that, if alternative calculation methods are used to analyze kinetically the same set of data, the expectation must be that the same values (perhaps ± a small error) will always be given. Large variations, obvious in the examples cited earlier [22–26] and many others, should be regarded as unacceptable (but tends not to be in many TAK reports). This is not a trivial problem for the subject but may arise through the widespread use of calculation methods and/or computer programs that contain one or more errors or inconsistencies that could be simple (e.g. resulting from different definitions of k or other parameter) or could be more complicated. The present situation is comparable with the unwelcome activities of an unrecognized computer virus within commonly trusted programs that will have to be identified and eliminated before reliable values of E again become routinely available. At present, the frequent reporting of results that are mutually inconsistent with respect to the concepts and tenets established and accepted throughout other branches of chemistry theory inexplicably seems to have become modified in thermal analysis where it has become accepted that calculated apparent values of E can vary with the kinetic model, $g(\alpha) = kt$, identified here as (VAET5).

1.6. Types of variable activation energy: comment

Vyazovkin has pointed out [1] that some reactions of solids are more complicated than single rate process. A measured temperature coefficient of reaction rate (used to calculate E) may vary with α and this arises through the 'tangled interplay' [1] of (possibly several) contributory single and species-dependent rate processes. The factors involved appear to be regarded as extending beyond the fundamental rate determining characteristics of solid state reactions [3], i.e. contributions arising from the nucleation and the growth steps. It appears that parallel reactions, and/or the other controls mentioned earlier, may contribute to this 'tangled interplay', and I believe that these must be disentangled and the components individually characterized (preferably quantitatively) if a reaction mechanism and its controls are to be elucidated in detail.

The paper advocating 'the acceptance of the concept of variable activation energy' [1], does not define this revised term, explain the advantages of the new concept, or indicate how this modification to theory will contribute towards the advance of the subject. It seems to me that examination and consideration of possible chemical explanations for the constituent components contributing to such variability offers potentially more useful insights into the chemistry (absolute reactivities and mechanisms) of the reactions showing such behaviour. This appears to be a more profitable approach than simple 'acceptance' and for this reason the five VAET of thermal behaviour of solid reactants as distinguished (there may be others) are summarized as follows:

VAET1: the magnitude of E is inherently variable,
VAET2: the process is complex, changing contributions from reactions of different E,
VAET3: the reaction rate is influenced by mass and/or heat flow etc.,
VAET4: the reactant melts, an alternative type of complex reaction, and/or
VAET5: the variations, or multiple values of E arise as computational artefacts.

The reaction systems cited in [1] as examples of reactions (apparently) in solids for which variable activation energies have been identified are discussed later in the context of the given VAET classification. The objective of these comparisons is to argue that it is likely to be chemically more profitable and inherently more interesting to understand and to characterize the reasons for the so-called variability of E values [1] than to simply passively accept such a significant modification to the definition of this fundamental and central concept in the theory of chemical kinetics [2].

2. Reappraisal of the kinetic data discussed in [1] as evidence of 'variable activation energies' for representative reactions in solids

The experimental information offered in [1], to support the proposal that magnitudes of E should be regarded as variable, is insufficient and unsuitable. The reaction conditions for these kinetic measurements are not described in [1] and there was no information about whether or not the measured rates were reproducible or were sensitive to procedural variables [9]. This is an approach that appears to becoming increasingly widely applied in the TAK literature. Little information is given about the reactant and reaction conditions, while the observational data so obtained are interpreted (kinetically analyzed) through the use of ever more sophisticated mathematical methods. This increasingly acceptable trend or fashion is characterized by the tendency to undertake fewer experiments overall and rate data interpretations frequently make no reference to support from any confirmatory observations using techniques other than rate measurements. Kinetic analysis of the measurements discussed in [1] used model-free isoconversional methods. The conclusions reported are not examined or discussed in the context of the extensive literatures available concerning at least some of the reactants investigated. Selected relevant aspects of these omissions are addressed later in consideration of additional features concerning the significance of the constancy (or otherwise) of E for the reactions mentioned in [1]. Although no acceptable criteria for the classification of decompositions of initially solid reactants have been generally adopted in the literature (as discussed in [8]), it is convenient to group the systems mentioned in [1] according to relevant descriptive characteristics in the headings later.

2.1. Reversible and endothermic reactions

The literature concerned with kinetics and mechanisms of crystolysis reactions contains numerous investigations of chemical changes that are endothermic and/or reversible [3,8]. Many of these decompositions include the feature that the kinetic characteristics [9–16] are almost invariably influenced, to a greater or lesser extent, by the rates of movement of heat and/or mass within the sample (VAET3). For many reactions, E for the controlling (primary) chemical step may be assumed to be constant [12]. However, influences from additional (secondary) rate influencing factors, arising through heat and mass transfer, may or may not remain constant during reaction and control, to some extent, the absolute overall rate of product formation, together with the kinetic model (rate equation). Consequently, the (composite) temperature coefficient may or may not vary with α, T, etc. Indeed, three decades ago, Draper could say [29] of calcite dissociation: 'we found that we could design the shape of the decomposition curve by systematically violating the conditions of the equation with respect to heat flow'. Attempts to remove the contributions to the measured reaction rate from such 'violations', by suitable design of experimental conditions, have been remarkably rare. The few studies in the literature, [10–12,30], that have reported attempts to measure rates of 'forward' only reactions, through elimination of any contributions from mass and/or heat movements, have attracted remarkably little attention, confirmation or interest. In my view, it is of considerable importance, for the development of the theory of crystolysis reactions to advance experimental methods capable of removing, or of separately determining quantitatively, all factors that influence the apparent magnitude of E. This should be accorded higher priority than attempts to interpret the significance of this parameter (E) through the use of sophisticated, often complicated, mathematical expressions applied to analyze overall data for rate processes that are already known to be complex. The following account reappraises the kinetic information presented in support the proposal of interest and concern here, the variable activation energy: figure and page numbers mentioned later refer to [1].

2.1.1. Calcium carbonate decomposition

In Fig. 1 [1], it is shown, for $CaCO_3$ ($\rightarrow$ $CaO+CO_2$) dissociation at six temperatures between 515 and 550 °C, that (p. 48) the 'experimental (rate) data do not closely follow any of the (solid state rate expression) model plots' (my added clarifications in parenthesis). However, a fit to a particular solid state kinetic model cannot necessarily be expected here because the reaction is subject to controls in addition to a simple carbonate dissociation step at an active interface [12]. At the pressures mentioned (0.5 mbar, Fig. 1), the overall dissociation rate is appreciably (and in general, variably) influenced by the availability of the volatile product that participates in the reverse process and possibly also in the interface reaction. Darroudi and Searcy [30] have shown that, when the CO_2 pressure is greater than 1% of the equilibrium value, rates are sensitive to the pressure of this product. At the mean temperature of the studies of interest here (about 805 K), it is estimated from the data in [30] that the equilibrium CO_2 dissociation pressure of calcite (0.4 mbar) is approximately equal to that of the vacuum during the experiments reported in Fig. 1. This pressure is two orders of magnitude greater than that below which all contributions from the reverse process have been shown to be absent [30]. It seems reasonable, therefore, to conclude that the reactions in [1] are composite and the reverse process made significant contributions to rate control, and these probably varied with both α and T. The CO_2 product present may modify equilibria at the interface [12] and the ease and frequency of the carbonate breakdown step (VAET3). This accounts for deviations from ideal solid state decomposition, controlled by a single interface dissociation step, so that the fit of data to a geometric rate expression cannot necessarily be expected [1].

The range of E values reported for this reaction (Fig. 5 of [1]) under similar pressure (but different rising temperature) conditions, approximately 170 $kJ\,mol^{-1}$ at the start of reaction (α just above zero) decreasing towards 100 $kJ\,mol^{-1}$ on completion ($\alpha \rightarrow 1.0$), are reasonably explained by an increasing influence exerted by the CO_2 present and a changing contribution from the reverse process as dissociation advances. These values of E are well below those found for reaction in a vacuum capable of removing all influence from the reverse (readsorption) process [12,30]. Reaction activation enthalpy was reported as $209 \pm 12\,kJ\,mol^{-1}$ [30]. The rate limiting process was identified as condensed phase diffusion of CO_2 or a surface step prior to its desorption. This is close to the value reported earlier, 205 $kJ\,mol^{-1}$, obtained from measurements made between 10^{-5} and 10^{-6} Torr [12]. The enthalpy of the equilibrium dissociation reaction was 173.5 $kJ\,mol^{-1}$, close to the initial (low α) value given in Fig. 5 of [1] and many other reported values [16]; for discussion see [12]. Much more significant here is the demonstration that, under high vacuum conditions, rates remained constant during interface penetration through samples up to about 1 mm thickness [12]. This evidence was regarded as being consistent with no change in temperature coefficient of rate as reaction progressed, showing that under these conditions, there was apparently a single controlling process and that there was no indication that E varied with α. The behaviour reported for calcite in [1] may, therefore, now be identified as VAET3.

2.1.2. Calcium oxalate monohydrate dehydration

This reaction has been most extensively investigated. For example, the dehydration was the first step in the sequence of three rate processes subjected to comparative analysis in a 'kinetic evaluation of a complex solid state reaction from 13 European laboratories' [23]. The Abstracts for this two-part report stated that 'the results allow an optimistic assessment for the application of kinetic procedures to solid state reactions with well-known chemical course investigated by TG (Part 1) (or) ... DSC (Part 2)' (reasons for this optimism and precisely what was achieved in this comparative study are not clear to me). The computed Arrhenius parameters contributing to these comparisons for dehydrations in air and inert atmospheres show a considerable range of magnitudes, exhibiting compensation behaviour. Again dehydration is probably an endothermic, reversible rate process that is sensitive to water vapour availability within the reaction zone. However, it had earlier been shown [31] that the loss of the one water molecule from $CaC_2O_4{\cdot}H_2O$ involves two parallel, concurrent rate processes, each resulting in the evolution of $0.5H_2O$, and that these distinct and overlapping dehydrations proceed at different rates. This report [31] ends with the statement 'further work will be required to derive proper kinetics for the dehydration of calcium oxalate monohydrate'. Because the dehydration of $CaC_2O_4{\cdot}H_2O$ is composed of overlapping, concurrent but varying contributions from two distinct and different rate processes, this is sufficient to explain the occurrence of variations of the temperature coefficient of reaction rate, and E, with α shown in [1] (other factors might also be involved). More precise kinetic investigations are still required to establish fully the rate characteristics of this complex dehydration, for which a variation of E with α is reasonable (Fig. 6). The variability of E identified from the results in [1] might, therefore, contain contributions from both VAET2 and 3.

2.2. Extensive or comprehensive melting

Kinetic analyses of rate data for decompositions that occur on heating initially solid reactants sometimes disregard or do not explicitly mention the possibility that the reactant melts within or below the temperature range of a decomposition of interest, see VAET4 earlier. If it can be accepted that the phase (crystal, liquid or even gas) within which the breakdown step occurs is an indispensable feature of any mechanistic description of the reaction, it follows that a failure to detect melting is the omission of an essential characteristic required to describe that rate process completely. Melting, particularly when partial, local and/or temporary, can be difficult to detect; microscopic examinations have provided evidence of the participation of a melt in decompositions [17–21] that had previously been regarded as proceeding in the solid state. Some thermoanalytical methods used for rate measurements do not detect fusion, e.g. TG, and where there is progressive melting, as during the evolution of a molten intermediate [17], no characteristic sharp (fusion) response in DTA or DSC measurements will be observed.

Some reactions proceeding in a melt may, in principle, proceed through two or more pathways or by diverse and complex mechanisms [17–21], that may result in variations of E with α. Also, at least a proportion of thermoanalytical response measurements are unsuitable for use as a method for detecting the presence or absence of fusion. However, I do not understand the reasons for including the following reactions in [1] 'kinetic concepts of thermally stimulated reactions in solids'.

2.2.1. Ammonium nitrate decomposition and volatilization

Inspection of the α-reduced time curve for NH_4NO_3 decomposition (Fig. 1 in [1]) shows this to be close to zero-order (constant rate) for reactions between 156 and 168 °C. This kinetic behaviour is apparently in reasonable agreement with results reported by Koga and Tanaka [32] who note that the mass loss follows 'melting at around 165 °C' and 'seems to include evaporation [their ref.] and/or decomposition ... ', in an article [32] having a title that refers to 'molten NH_4NO_3'. In the absence of knowledge of reaction conditions, information about the exact fusion temperature and the relative roles of decomposition and sublimation in [1], it is not clear what processes are being studied. However, it does appear to be unsafe to use observations that probably involve melting (VAET4) to discuss the principles of solid state chemistry.

Another report on the thermal properties of ammonium nitrate by Vyazovkin and Wight [33] was directed to 'Estimating realistic confidence intervals for the activation energy determined from thermoanalytical measurements'. Again, it seems that no consideration was given to the chemistry of the reactions contributing or to the roles of the two distinct 'gassification' processes (sublimation and decomposition) which are expected to exhibit different temperature dependencies. It is stated that the reactant particle sizes (perhaps implying a solid state reaction?) were $<300\,\mu m$ but the role of melting known to occur at around 438 K [32], is not mentioned. The phase from which the gassification proceeds in this study is impossible to ascertain because the reaction temperature intervals are not mentioned and fusion is not detected by the TG method used. Fig. 1 [33] records the mass loss curves for different heating rates but I regard the absence of any quantitative assessment of reproducibility of the original rate data to be an important omission from this paper, which is explicitly concerned with the precision of measurements. The kinetic analysis of these data [33] proceeds through comparative tests of fit to twelve alternative kinetic models (usually regarded as characteristic of crystolysis reactions [3]) using the Coats-Redfern model in which the temperature integral 'can be replaced with various useful approximations'. (It would have been interesting to know reasons why this particular expression was selected for the kinetic analysis from the many that are available [3] but no explanation of this choice is given here). The approximate form of the calculations used in these kinetic analyses is justified by several citations, including [34] from which the final conclusion (last sentence) in this paper by Flynn is apparently disregarded: 'Indeed, in this age of vast computational capabilities, there is no valid reason not to use precise values for the temperature integral when calculating kinetic parameters'. Another apparently significant omission from this kinetic analysis is that the dozen equations comparatively tested do not include the zero-order expression, identified by Koga and Tanaka [32] as being applicable to this reaction. These authors ascribe rate control to mass loss from the melt surface: rate is determined by one-dimensional phase boundary advance. The omission of this kinetic model from [33] is all the more surprising because this, of course, is the same (simplest of all) rate expression that is applied in the so-called 'advanced isoconversional method', recommended [33] as eliminating uncertainty in kinetic analyses. However, the final conclusion from this analysis is 'the resulting averaged relative errors in the activation energy were found to be 26, 21 and 17% for three, four and five heating rate estimates, respectively'. It seems to me that this is a remarkably large tolerance, and consequently should not be accepted as a successful outcome of a kinetic analysis. Perhaps the mathematical procedures employed merit a critical reappraisal for their relevance. Some of the contents of this paper appear in [35] and the analysis is compared in detail with earlier observations reported for the same reaction by Koga and Tanaka [32]. The agreement is satisfactory but again the relevance of melting and of the two contributory rate processes, in the generally similar pattern of variation of E with α, are not discussed. This subsequent work [33,35] is mentioned here to emphasize that this reactant is not a suitable system for analyzing kinetic characteristics of solids (VAET4), though this appears to be implied by the inclusion of this reactant in [1].

There appears to be an inconsistency in the kinetic analyses presented in [33]. On one hand it is shown that E is more or less constant (around $90\,kJ\,mol^{-1} \pm 20\%$) throughout the whole reaction (Fig. 4 [33]). On the other hand, using the same data, magnitudes of E calculated for twelve different reaction models (rate equations) vary between 11.5 and $156.7\,kJ\,mol^{-1}$ (Table 1 [33]). One possible explanation for the differences in calculated temperature coefficients is that the alternative definitions of the rate constant (k), or other scaling factor have been used in the mathematical operations. For example, k is correctly defined with units of $(time)^{-1}$, and other values (n) cause the apparent values of E to be scaled by a factor of n ([3], p. 121). In the absence of details of the program used in this work [33], the precise reason for the alternative E values cannot be identified from this article, such results appear to be unsuitable for use in the formulation of reaction mechanisms.

2.2.2. *Ammonium dinitramide decomposition*

Reference is made in [1] (p. 56) to variations of E with α for thermal decompositions of some ionic salts, including ammonium dinitramide where, after an initial small rise to about $175\,kJ\,mol^{-1}$, E progressively decreases with α to about $125\,kJ\,mol^{-1}$ or below, towards completion of reaction [24]. Aspects of the decomposition mechanism are discussed. However, the relevance of these kinetic studies between about 400 and 500 K, for a reactant that melts at around 365 K [24], to discussions of the variations of E with α for solid state chemistry are not made clear [1]. This appears to be an instance of VAET4.

2.3. Partial or local melting and sublimation (ammonium perchlorate decomposition and volatilization)

The decomposition of ammonium perchlorate is one of the most intensively and comprehensively studied condensed phase thermal decompositions. A selected set of references from the extensive literature is given in [36], this reactant is briefly referred to in [1] (p. 56). This article also reports isothermal and non-isothermal TGA rate measurements for ‘high temperature’ [3] decomposition of the cubic form of the salt (stable above 513 K) but this shows mechanistic similarities with the ‘low temperature’ reaction below the phase transformation. Values of E, calculated by advanced isoconversional analyses, showed variations with α (Fig. 4 of [36]) but the results from the two alternative temperature control regimes did not agree particularly closely. The significance of these appreciable differences cannot be appraised because evidence of reproducibility and the sizes of deviations between successive identical experiments are not reported. Moreover, variations in the temperature coefficient of total mass loss rates are to be expected during the progress of the concurrent distinct and different rate processes: decomposition and sublimation. It is reasonable to suppose that the relative contributions from these will change with experimental conditions and α, influenced by amount of reactant, its texture (surface area), particle disposition, etc. (VAET2 and 3).

The kinetic data measured are interpreted in considerable detail in [36]. However, it seems to me that the first step in the proposed kinetic scheme, Fig. 7 [36], contains a surprising, and unjustified, assumption or conclusion. The first step in reactant breakdown is identified as nucleation, after which decomposition and sublimation (vacuum) are portrayed as being initiated as concurrent, separate processes with significantly different magnitudes of E. This scheme accounts adequately for some aspects of the (kinetic) behaviour pattern and the view that activation energies for these different processes are different is not unreasonable. However, two aspects merit more critical examination. First, at relatively low temperatures, this salt may be sublimed at significant rates only in vacuum. Nevertheless, even in the presence of gas, some salt will inevitably be volatilized but remain in the vicinity of the crystal surface while diffusive removal is slow. That it has not been detected during short time intervals does not mean that it is absent, insignificant or irrelevant to the reaction. Second, there seems to be no justification for the conclusion that sublimation can only follow nucleation. Indeed it is inherently more probable that sublimation and nucleation will initially proceed together, superficial ions may alternatively participate in dynamic equilibria with volatilized material above the crystal face or undergo breakdown at or on the crystal surfaces to establish the nuclei that subsequently grow. Kinetic evidence alone is inadequate to resolve this problem because it is unable to provide a detailed mechanistic description of the local and microscopic processes that contribute to the initiation of decomposition, when account is not taken of the material readsorbed following early volatilization. It is not known whether sublimation and nucleation are concurrent, complementary or competitive processes occurring on the initially heated surfaces. No evidence is provided here [36] about, when, during onset of reaction, growth nuclei become established. I believe that more detailed information (e.g. from microscopy etc.) about processes contributing to the earliest stages of reaction is essential to sustain the view that nucleation precedes both decomposition (to which nucleation is a contributor) and sublimation [36].

Two other features of the literature citations in this paper [36] merit comment. First, although 54 references are listed, no mention whatsoever is made of the decomposition mechanism proposed [19–21] for this salt which accounts for the (possibly unique) cessation of reaction before completion with the participation of an active liquid decomposition phase and the intervention of nitryl perchlorate as an intermediate. The ‘low temperature’ and ‘high temperature’ reactions of this salt, separated by the phase transformation at 513 K, exhibit strong chemical similarities, [3,36]. The explanation of decomposition through melt formation (VAET4) is equally capable of explaining variations of E with α. Second, it is difficult to understand why the decomposition of copper(II) malonate [17] is cited in [36] as an example of a reaction for which the value of E for nucleation is lower than that for growth. This article [17] emphasizes that the carboxylate breakdown is complex and proceeds in a melt, the quantity of which increases as the first reaction advances. The sigmoid curve is identified with an initial autocatalytic behaviour pattern through which progressive reaction yields increasing amounts of acetate intermediate present as a melt in which anion breakdown occurs relatively more rapidly. Copper(II) malonate decomposition [17] is not a nucleation and growth reaction in the conventional meaning of these terms [3]: this citation in [36] seems to be most inappropriate.

3. Discussion and conclusions

3.1. Why do we measure activation energies?

This is a crucial question for crystolysis chemists, which is rarely addressed and to which, I believe, there is currently no agreement, no acceptance and no adequate answer. In the recent thermal analysis literature, values of E have been reported for innumerable and diverse reactions. Indeed, in some articles, the magnitude of an activation energy reported appears to be the principal result, perhaps even the dominant motivation for the investigation. However, compelling reasons for such a preoccupation with the measurement of Arrhenius parameters are not usually provided. Individual magnitudes of A and E (also the form of the kinetic model, $g(\alpha) = kt$) have not been demonstrated to have significance in or to provide parameters suitable for the classification or systematic ordering of the information now available for many and diverse solid state decompositions [3,8]. Consequently, many reports of kinetic studies appear as isolated (sometimes effectively empirical) observations, with limited mechanistic conclusions that do not contribute to the organic development of a coherent and systematic scientific subject. Furthermore, for some reactants, several different magnitudes of E have been reported [16,22–26]. In a minority of papers, some mechanistic conclusions may be advanced to account for rate observations for specific reactions, most usually the kinetic model, but sometimes also extending to the Arrhenius parameters. However, up to now, little progress has been made towards developing these into quantitative theoretical models having general applicability. One view of the consequences of this proliferation of kinetic results, without reliable means of ordering or modeling of these observations, is that the subject is becoming ever more empirical. I believe that a debate is now overdue, which recognizes shortcomings of present methods, appreciates the value of theory development and could stimulate progress throughout TAK.

The absence of an adequate theoretical framework within this subject can be ascribed to the unsatisfactory character of much, perhaps even most of the reported kinetic data. As already discussed, values of E (also A and the kinetic model, rate equation) are frequently sensitive to experimental conditions so that rate data change with alterations in the procedural variables. Reliable identifications of rate controlling or dominant chemical steps can only be based on kinetic data that has been positively demonstrated to relate to the rate of the interface controlling process [10–12]. The measurement of E values defined on this model, and similar to those used elsewhere throughout chemical kinetics is recommended here as a most realistic objective. Correlations, most likely to be of value in general theory development, are identifiable only when results of this type have been obtained for sets of representative and related crystolysis reactions. However, it must be accepted that most of the results of kinetic interpretations currently available in the literature are less reliable and refer to overall reactions that have been controlled by the unresolved tangled interplay of several factors, some of which were described as VAET2–5 earlier. Additional influences of these types are less significant in most kinetic studies of homogeneous processes; this unfamiliarity might be one probable reason for the tendency to disregard such effects during the interpretation of rate data for reactions of solids. The concepts of homogeneous kinetics are frequently imported into discussions of crystolysis reactions but it must be remembered that there may be fundamental differences between these distinct types of chemical changes. However, in the hope that the theory of this subject will develop through sound scientific principles, I suggest that cognizance must be taken of the shortcomings in kinetic analyses of reactions of solids as described. The contributions of all relevant controls must be recognized, separated and individually characterized quantitatively, to enable the significance and role of each to be understood. This approach cannot be reconciled with, indeed is in conflict with the suggestion in [1] that the definition of E should be modified from accepted practice [2] to become (what appears to be) effectively a compound and empirical parameter, in which the contributions from several controls remain undistinguished. The contribution that this practice [1] is expected to make to the wider development of theory is not clear to me. Science is concerned with the systematization of the information available, summarizing observed properties through theories and using the representational models to predict, by induction, results of experiments for hitherto untested systems. The concept of variable E does not (in my view) contribute towards realizing either of these objectives.

Vyazovkin mentions ([1], p. 56) problems in model fitting 'for practical purposes such as predicting the reaction kinetics at an arbitrary temperature'. I believe that reliable kinetic predictions must be based on quantitative characterization of the (constant) value of E associated with the controlling chemical process (as described in [12]) together with due allowance for the individual contributions from all other factors that may influence reaction rate, separately determined and characterized. I disagree strongly with the view ([1], p. 53, the last two sentences of Section 4): 'The concept of variable activation energy is more adequate to the multiple-step nature of solid state reactions. It should be used to describe the temperature dependence of the overall reaction rates'. Incorporating all controlling factors into a single theoretically undefined term is unlikely to be the most efficient approach to quantitative representation of rate characteristics. In the absence of a theoretical model, extrapolated magnitudes of E beyond the range of its empirical determination cannot be expected to be trustworthy. This proposed modification [1] of the term that is arguably the most important concept in chemical kinetics by a parameter that appears not to have been adequately defined (but given the same label) cannot be supported as a profitable direction for increasing understanding of thermal chemistry. Indeed, I would regard this as a retrograde step, loss of theory from a topic that is already profoundly 'challenged' in that direction.

The origins of TAK are found in the development, since the 1970s, of automated techniques for rate data collection (TG, DSC, DTA, etc.) and their subsequent interpretation by computer methods. This approach has dominated the experimental investigation of thermal reactions in condensed phases. The apparent efficiency, power and convenience of using computer programs to control almost all the experiments has been (rightly) welcomed. One consequence, however, has been the progressively increasing role of ever more sophisticated mathematical methods of data analysis based on smaller numbers of individual experiments. The measurements (α, t, T) obtainable have undoubtedly increased in frequency and precision but, in many reports, the conclusions from kinetic interpretations have become less clear, with multiple values of Arrhenius parameters being reported for the same rate process, [1,16,22–26,28,36]. Such results continue to be described through the chemical terms from earlier studies of crystolysis reactions, but the definitions now seem to have become more flexible and are not supported by an adequate theoretical framework. At the same time, the use of complementary observational methods, to obtain information by techniques other than rate measurements, appears to be less frequently employed. Support from microscopic inspections of textural changes occurring during reactions in crystals can provide valuable confirmation of geometric interpretations of rate data [3]. Indeed such direct methods can be both more reliable and less laborious than kinetic studies, an approach that seems to have become forgotten in the preoccupation with the perceived advantages of automated instrumental techniques. Now few papers concern themselves with the chemistry of the reactions studied, which is not easily and sometimes not reliably deduced from rate measurements alone. Thus, little progress is being made in characterizing the bond redistribution steps and their controls in thermal chemical reactions, the participation of intermediates or even the occurrence of melting.

There is a choice for the future. We can continue to 'collect reactants' for which the kinetic model for thermal breakdown, and the corresponding Arrhenius parameters, have been measured under (more or less) defined reaction conditions, perhaps remembering that such results are often empirical. The other alternative is to design experimental methods demonstrably capable of directly measuring interface reactions rates, uninfluenced by or corrected for self-cooling, and with the contribution from the 'back' reaction removed [10–13,15,30]. The subject must be expected to benefit from investigations yielding confirmed reproducible kinetic data, that are not dependent on reaction conditions. The influence of secondary rate controls (VAET3) may then be identified and separately characterized by measuring the consequences of systematic variations of the procedural variables. Further useful information about the reaction chemistry involved may be obtained by complementing kinetic investigations with supporting studies, including crystallography (X-ray diffraction, etc.), microscopy, and all other observations [37] capable contributing to the elucidation of the complicated combination of steps whereby a solid reactant is converted into products.

An important objective for future research advocated here is the necessity to establish reasons for any 'variable activation energies' found, rather than passively accepting their existence. A useful start would be the characterization of the individual roles of the various controls (VAET1–5, Section 1) for each reaction of interest. The range and magnitude of each effect could then be established quantitatively, as appears, for example in the influence of CO_2 on calcite decomposition [30]. Systematic examinations of all such trends for reversible and endothermic rate processes characterizing the conditions and magnitudes of control by mass and heat transfer would enable rate determining factors to be recognized and incorporated into kinetic representations of thermal reactions for different conditions. The rate (also E and A) of the chemical interface step might then be determined, enabling comparative investigations involving a range of different reactants to systematize behaviour towards theory development, including possible identification of the controlling chemical steps. Some progress in this direction has already been achieved [8–15] and I believe that thermal analysts will progress the subject more effectively by pursuing chemical objectives than focussing attention on mathematical interpretation of data collected under incompletely or ill-defined experimental conditions. However, there are alternative optimistic signs that new concepts will provide a theoretical foundation for elucidating the controls and mechanisms of thermal reactions proceeding in condensed phases. These are now discussed.

3.2. Future prospects for kinetic analysis of thermoanalytical data

Hitherto, the theory applied in interpretation of thermal analytical kinetic data has largely (exclusively?) been derived directly from that originally developed to explain thermal decompositions of solids, itself arising by modifications of the concepts that previously and successfully accounted for rates of homogeneous reactions. The shortcomings of these concepts, in thermoanalytical applications to systems other than those for which they were originally intended have resulted in a progressive contraction of the theoretical foundations of the subject during a period of its expansion to the ever diversifying range of reactants now studied. This has resulted in a remarkable absence of order and overall coherence within the aggregate contents of published reports [8]. Frequently, only limited mechanistic conclusions are proposed in many of the papers that constitute the large number of individual and largely unrelated articles that constitute much of the recent literature on thermal reactions in condensed phases. However, two recent trends that offer real optimism for profitable future progress can be recognized.

3.2.1. L'vov theory

For those crystolysis reactions for which the necessary thermodynamic information is available, a new, quantitative theoretical approach based on an initial reactant volatilization step has been proposed [38]. This has already, in the many papers by L'vov [38], been shown to be capable of providing new insights into the chemical processes involved. It has also introduced order into sets of hitherto unrelated reports, an unusual but most welcome feature, in a literature that has hitherto been characterized by an absence of perceived chemical relationships. Subsequent work by L'vov [15] has focussed attention on the significance of self-cooling at the reaction interface in influencing reaction rates and the apparent magnitudes of Arrhenius parameters. These initiatives merit further examination and development as the most promising prospect for the unification and the introduction of coherence that this subject so conspicuously lacks. These theories have been concisely summarized in the context of the necessary literature sources [15,38] and will not be repeated here. However, a strong recommendation is given for their most serious consideration as an alternative, and preferably more systematic approach to the subject than any theoretical model currently available including the suggested concept of the variable E. Indeed, in L'vov's theoretical model, a constant activation energy is a central feature and this must be identifiably related to the chemistry of the reaction under consideration; the experimental conditions capable of influencing the measured (equimolar or isobaric) rates must be known [38].

3.2.2. *Reactant melting and the formation of transient reaction intermediates*

Thermal reactions of solids are complex, as shown by the several distinct and different controlling characteristics distinguished and discussed earlier. Consequently, the elucidation of mechanisms and establishment of controls for crystolysis reactions is less straightforward than seems to be appreciated in a majority of the recent literature. The belief that a small number of automated experiments even if subjected to highly sophisticated mathematical analysis can be used to elucidate comprehensively reaction chemistry must be accepted as overoptimistic and must be expected to be ultimately unsuccessful. This approach alone is unlikely to yield insights into all the factors controlling chemical reactivities, properties and mechanisms of thermal reactions of solids. Several recent studies have shown that decompositions of some solids, initially crystalline, proceed through the intervention of a molten phase and/or involve the participation of reactive and transitory intermediates [17–21]. Unless specifically sought, such complex behaviour may pass unnoticed, so that approximately sigmoid shaped curves (usually regarded as indicative of nucleation and growth processes but alternatively can arise during progressive melting [17–21]) will be accepted as evidence of crystolysis reactions. The relationship of these complex mechanisms to L'vov's theory of solid state decompositions ([38], Section 3.2.1) may be difficult to determine but at this early stage might, as an interim measure, be regarded as a problem for the future.

3.3. *A comment on 'variable activation energies'*

This appraisal of aspects of kinetic analysis is intentionally presented in robust terms because the shortcomings of the subject are serious, even fundamental. There is no adequate theoretical framework introducing cohesion into the topic so that contributions tend to be individual and are sometimes empirical. Remarkably few general reviews are available to discuss the theory, the techniques and the observations for thermal analysis. Accordingly, to initiate a productive debate about the present status of an important and extensive topic, these criticisms are presented in forthright terms. I have been aware of many important problems within that part of the thermal analysis that is concerned with kinetics for some time and now, what I perceive to be a particularly inappropriate further proposed change in theory [1], has prompted this critique (an author's activation to nucleation). I hope that the views expressed here will ultimately be accepted as being correct. However, I regard it as more important that the theoretical foundations of the subject should now be critically and meaningfully reappraised, the definitions of the terms used may be reconsidered, calculation procedures reassessed and attempts should be made to find a theoretical basis for re-establishing the comprehensive and coherent growth of a systematic subject firmly based on scientific foundations.

This critical comment on the proposal [1] (that it is reasonable to accept the concept of 'variable activation energies') presents the alternative case, emphasizing the importance of extending and strengthening the limited subject theory that is currently available to explain the kinetics of crystolysis reactions. The case presented in [1] does not define exactly what, from the several possible explanations (VAET1–5, earlier), is meant by a variable E, on what theory, model or concept it is based and how it can contribute to advancing the kinetic analyses of such rate processes. My impression from [1] is that E (variable) is to be regarded as a composite and, therefore, empirical parameter which, in the absence of a precise definition, apparently becomes theoretically sterile [2]. I identify this approach as containing serious shortcomings, demanding wide and general discussion in the literature. Moreover, the supporting evidence provided in [1] appears to relate to chemical changes that we already know to be complex and for which the participation of subsidiary controls is already well-known. A more productive approach than redefining E would, in my opinion, be for us to examine quantitatively each contributory influence on reactivity and to characterize the interface reaction controls together with the individual factors that appreciably change its effective rate.

The paper most directly discussed here [1] recommends a view of E, for reactions of solids, that differs from that accepted throughout chemistry [2]. Later, Vyazovkin [35] has argued that 'the pre-exponential factor is strongly correlated with the activation energy via the compensation effect [ref.], which makes the pre-exponential factor a dependent and, therefore, inferior parameter'. Taken with the conclusion, from the extensive statistical analysis of kinetic data for thermal reactions of ammonium nitrate [33], that methods for identification of the kinetic model from thermal analytical data are unreliable and *E* values may have errors of the order of ±20%, it might be concluded that there is little to be gained by any further investigations of the kinetics of these reactions. I cannot accept such a pessimistic view. I suggest that variations in activation energy, VAET1–5, see also [1], must be recognized by the thermoanalytical community as evidence of one or possibly several massive inconsistencies, even crises in the theory and methodology of this subject. I do not agree with Vyazovkin that recognition of *E* variable represents any advance (or reasonable compromise [1]) in the subject. I believe, in contrast, that a fundamental reappraisal of the methods currently in use is urgent and that this will lead to a more optimistic future which will ultimately prevail. With reappraisal of the significance of experimental measurements of rates and of the theory applicable, something of the former confidence in the subject can be restored by discarding the unproductive consequences that arise, at least in part, through the excessive use of mathematical methods for the elucidation of essentially chemical problems. This approach cannot and should not continue to be sustained in its present form. A more 'physico-chemical' approach is likely to tell us more about chemical reactions and the physical changes that frequently accompany them.

It seems to me to be essential to regard activation energy values that are 'variable', or give 'multivalue magnitudes' from calculations based on the same data or for the same reaction to be regarded as inherently unreliable. This is evidence of computational inconsistencies or errors. I suggest that one criterion for recognizing the reliability of the kinetic interpretation of rate data should be that the alternative analytical calculation methods lead to a constant value of *E*.

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Appendix A. Aspects of kinetic and mechanistic analysis of rate data obtained by thermoanalytical methods

This review contrasts two alternative methodologies in TAK research concerning the significance of the term activation energy, a concept of central importance throughout chemical kinetics. The case that I advocate strongly is that the theoretical value of this model developed through fundamental studies is likely to be of greater ultimate value in extending scientific order than the alternative variable *E* [1] which appears (to me) to be empirical. Because the kinetics of many thermal reactions are determined by multiple controls, the interpretation of temperature coefficients of reaction rates require careful appraisal, if all the possible factors controlling the chemical changes are to be individually identified and their roles understood. Recognition of the complexity of such reactions, together with factors determining absolute reactivities and reaction mechanisms, is preferred to any alternative empirical approach, unfounded in theory.

Some of the uncertainties in TAK analysis, particularly those relating to the determination of *E*, have been mentioned as VAET1–5, Section 1. To these, the following Sections A2–5, may be added. These are necessarily related to the topics already discussed but are alternatively emphasized here for consideration in the wider context, as important general aspects of TAK investigations that are not always or adequately recognized. It is intended that these features of kinetic analysis will be discussed at greater length, with examples, in a forthcoming review. The diverse problems, difficulties and inconsistencies specifically mentioned now relate to the use of the term 'activation energy' in the current literature on thermal analysis. The significance and reliability of the Arrhenius parameters, and all other deductions derived from TAK rate measurements embody the significance and reliability of the original observations and also the methods used for their interpretation.

A.1. Fundamental and empirical research

A.1.1. Fundamental studies

Fundamental studies measure rates together with all other relevant characteristics of reactions and seek to represent observed behaviour patterns by theoretical concepts and chemical models. These, through application of scientific principles, are expected to achieve two objectives: systematization of the information available through theoretical representation and provide a basis for useful predictions of behaviour and properties beyond the ranges for which observations are available. Because the theoretical principles used for interpretation of TAK data have been derived from concepts found successful in describing reactions of other types, and there have been few recent achievements in this (TAK) field, the available theory has now become limited in application and restricted in value. Despite many reported thermoanalytical kinetic studies of numerous reactions, few patterns of systematic order have yet been discerned [3,8]. The present review is principally intended to draw attention to the desirability and the potential value of identifying scientific foundations suitable for the ordering of results from TAK studies of thermal reactions proceeding in condensed phases. Shortcomings perceived in the literature and consideration of how these may be rectified through theory development, are discussed in the following paragraphs. The emphasis is on restoring the chemical approach to the interpretation of TAK observations, which was an essential and integral feature of the early work on solid state decompositions [3], crystolysis reactions.

A.1.2. Empirical studies

Empirical studies are directed towards comparing behaviour, determining relative or absolute reactant stabilities or reactivities from measurement of temperatures and/or rates at which reactions proceed. Results can be useful, particularly for commercial purposes. Theoretical reasons for behaviour patterns recognized are not sought but data may be capable of useful extrapolation using formulae for which no reaction models need to be provided. The ‘variable activation energy’ [1] is regarded as such a term, appearing in the thermal analysis literature from studies using essentially an empirical approach.

A.2. Stoichiometry

A value of E refers to only a single rate limiting process with which it must be identified through comprehensive characterization of the reaction stoichiometry. This can be interpreted widely to include the precise chemical change of interest, identifying reactant, products and (if solid) their structures together with the phase within which the reaction occurs. Complementary observations may be required to support and to confirm the physical measurements on which TAK methods are based. Many thermal studies are interpreted from limited stoichiometric evidence and this may introduce uncertainty into conclusions; earlier limitations have invalidated some published conclusions [31,39,40].

A.3. Precision, error and reproducibility

Experimental measurements include errors that are both systematic and random. These can be detected, and sometimes minimized, by the use of complementary, alternative determination techniques and tests of reproducibility between successive, nominally identical, experiments. Many published TAK study reports simply do not discuss data precision or the accuracy of calculated kinetic parameters (A, E, etc.) that are nonetheless, often reported to an unrealistic number of significant figures. The possible influence of error on the correlation coefficient, frequently used as the single criterion for recognition of a ‘kinetic fit’, is not usually discussed. Furthermore, the magnitude of this single parameter (correlation coefficient) is insufficient evidence to express adequately the results of the kinetic analysis of a large set of (α, t, T) values, when comparatively tested for precision of data fit to each of various rate equations included, particularly when the significance of experimental error remains unconsidered.

Just as important as characterizing the reaction that has taken place, is the necessity to define all terms used in discussion to enable unambiguous communication of results and ideas. This has been central to consideration of the significance of E throughout this paper, but other terms (and their units) require similar precision of treatment, e.g. A, k, etc. and consistency must be maintained in the formulae used for kinetic calculations.

A.4. Literature

The relatively few critical, comparative surveys of the TAK literature has probably contributed to the absence of theory development and lack of chemical correlations of conclusions. It seems to me that more useful contributions towards subject advancement are likely to result from careful consideration of published results for one well-researched reactant, or a small group of related rate processes, than TAK investigations of yet more additional novel and unfamiliar reactants. A further unconstructive feature of many articles is that the introductory sections frequently omit adequate comment on related systems and fail to provide compelling reasons for interest in the work being introduced.

In recognition of the limitations of TAK theory as usually applied, it is essential that an adequate scientific basis for systematizing results should be provided, which contains the capacity for extension. The earlier, general Polanyi-Wigner model [3] must now be regarded as having little value in this respect and the present discussion emphasizes limitations associated with the significance of the 'activation energy'. The L'vov theory [38], therefore, should be welcomed to fill the obvious 'theoretical vacuum' and has already demonstrated its value in reconciling different and apparently inconsistent results. The successes, so far, have shown the ability of this approach to introduce order into sets of published results and this is potentially capable of extension to other systems.

A.5. Concluding comment

The review surveys diverse problems, difficulties and inconsistencies that are identified as characterizing the current TAK literature and which are ascribed to significant shortcomings in accepted practices and to the decreasing effectiveness of the theory of this subject. My interest in the field has been particularly concerned with investigations of solid state decompositions, crystolysis [3] reactions, including the interpretation of kinetic measurements, the formulation of reaction mechanisms and the identification of rate controls. It is my intention now, at what appears to me to be a time of crisis in this subject, to contribute positively and optimistically to the discussion required to restore acceptable scientific foundations, suitable for its regeneration and its subsequent growth. I believe that a change of direction is essential to replace the increasingly empirical character of the current research ethos. Although, one motivation for writing this review was the paper [1], I regard the problems and difficulties existing within this subject as being much more profound and general than has hitherto been recognized. Chemical reactions of solids are more complicated than appears to be accepted in most published reports. I suggest that a culture change is necessary in planning future TAK studies. The increasing reliance on automated computer mathematical methods of rate data must be modified to include supplementary and confirmatory complementary measurements that apply chemical techniques to characterize the chemical features of chemical changes. A detailed and general analysis of the thermal analysis literature, relating to the various types of thermal decompositions is currently in preparation, to explain in greater detail reasons for the above (interim) generalizations. Recognition and acceptance of the shortcomings of the methodology of TAK is an essential first step, that must be achieved, before there can be a renaissance of this subject, based on its development from more secure foundations and through advances of relevant theory. A more physiochemical approach to interpretation of data, recalling and developing the earlier methodology applied in studies of crystolysis reactions, must proceed in the context of directing attention towards the chemical properties of reactions for which reactivity controls and mechanisms cannot be elucidated by mathematical analytical procedures alone. As a personal opinion: a fundamental reappraisal of the methods, aims and objectives of TAK research is now overdue.

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