Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 413 (2004) 139–183

thermochimica acta

www.elsevier.com/locate/tca

Is the science of thermal analysis kinetics based on solid foundations? A literature appraisal

Andrew K. Galwey

18, Viewfort Park, Dunmurry, Belfast NI BT17 9JY, UK

Received 31 May 2002; received in revised form 17 October 2003; accepted 20 October 2003

Abstract

A critical appraisal is made of the recent literature concerned with the kinetics and the mechanisms of thermal reactions, particularly research using the methods of thermal analysis (TA). It is concluded that many features of the theories and the practices in customary use are inadequate and/or unsatisfactory. The reaction models that are currently employed lack the necessary coherence required to introduce systematic and scientific order into the extensive information available. There are few reliable, general concepts and chemical principles which are capable of coordinating and classifying the experimental observations and which can contribute to the organic growth of an ordered discipline. Many, though not all, recent published TA studies appear as individual articles that remain largely unrelated to comparable investigations or to the general theoretical principles that are applicable throughout chemistry.

This unacceptable situation is identified as having arisen during the emergence and establishment of thermoanalytical science as a distinct discipline, which effectively replaced the former interest in the thermal decompositions of solids, while also retaining concepts from this precursor topic. Overall this transformation was uncoordinated and perhaps has remained largely unrecognized. A consequence was that only some selected aspects of the heterogeneous and homogeneous kinetic theory and reaction models were incorporated into the developing (burgeoning) thermoanalytical subject area. However, during the initial rapid expansion of TA experimental methods, about three decades ago, shortcomings in the theories of thermal decomposition of solids were already becoming apparent, inhibiting advances. Consequently, some earlier optimistic hopes for progress in advancing solid state thermal chemistry were not fully realized. During the redirection of interest from thermal reactions of solids towards thermal methods, TA development proceeded without the appearance of new chemical principles or novel reaction models for general application. Progress in instrumentation predominantly focussed attention towards developing and applying automated calculation methods. This was essential to permit the analyses of larger number of accurate measurements that could be obtained, retained and processed by the more powerful computers that were becoming available to control experiments and to present processed results. The collection and collation of data was achieved more easily and efficiently than ever before, for ever larger number of data measurements, of ever greater precision, for an ever widening range of reactants and reaction conditions. The concurrent and continual extension of mathematical and computational techniques, for the analysis of thermal kinetic data, became, and remains, a principal preoccupation of TA research. Its early relationship with studies of thermal decompositions of solids has meant that thermal kinetic studies continue to apply, largely unchanged, aspects of the theory originally developed for application in thermal studies of solid state reactions.

The adaptability and convenience of thermoanalytical methods for kinetic measurements has resulted in their application to a diversifying range of reactants, including thermal processes which sometimes proceed with melting and/or complex behaviours involving varied types of chemical changes. For these, the conventionally accepted range of kinetic models (predominantly solid state rate equations) may not be applicable, though the consideration of alternative possibilities is frequently ignored. The identification of *chemical* controls of reactivity and characterization of *chemical* reaction mechanisms are evidently now of much less importance in studies by TA methods than was usual formerly, when (originally) such interest was specifically concerned with the decompositions of solids. In recent work much less attention is directed towards designing experiments suitable for complementing kinetic interpretations and to contribute towards the formulation of chemical reaction mechanisms. Relevant additional observations include microscopy, spectroscopy, X-ray crystallography, etc., intended to provide information of value in the elucidation of the sequence of *chemical* steps participating in any reaction being studied.

This tendency to minimize the application of chemical concepts in the analysis of TA rate data is self-perpetuating (autocatalytic) and results in a lack of coherence (or absence of scientific order) within the large accumulation of individual articles that constitutes the recent TA literature concerned with reaction kinetics. Because there are no widely applicable theoretical concepts that unify the subject, the possible generality of important results in particular reports tends to be disregarded. Reasons for this unsatisfactory situation are identified, from the

---

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

0040-6031/$ – see front matter
doi:10.1016/j.tca.2003.10.013

present survey, as including the following: shortcomings in establishing reaction stoichiometry, uncertainty in the significance of kinetic data (rate measurements are often accepted uncritically and may, therefore, be empirical, varying with experimental conditions, and unsuitable for fundamental interpretation of reaction chemistry, including reactivity controls or mechanisms), and ambiguities in the definitions of essential terms, including *mechanism, rate constant, activation energy*. These, and other problems evident in TA studies, are discussed, together with the tendency to consider kinetic behaviour exclusively through rate equations applicable to solid state reactions. This convention results in the effective exclusion from all consideration of the possible participation of melting, the intervention of intermediates, concurrent or consecutive rate processes, secondary rate controls and other alternative, but nevertheless possible, reaction mechanisms.

It is concluded that an important part of the thermoanalytical literature, concerned with kinetic and mechanistic TA studies, is in urgent need of a general and radical reappraisal. The introduction of systematic order into the contents of the continually expanding set of publications is now urgent, so that the significance of each new set of observations reported can be appreciated in its widest possible context. Science represents systematic knowledge, including the expectation that inductive prediction will generalize theory, through expansion of established trends: neither of these reasonable aspirations (order and prediction) are discernable in much of the recent TA literature.

Following the decline of interest in solid state chemistry, together with the tendency within current TA reports to focus primarily (sometimes only) on kinetic characteristics of the reactions studied, it is appropriate to examine critically the options now available. These include the following. For each individual rate process studied, reaction stoichiometry must be established and the possible effects of secondary controls determined. Removal of the conventional constraints (probably unintentional and unappreciated) on kinetic analysis of TA data by extending interpretations to include all possible reaction models and influences on rate behaviour. It is also necessary to provide support for conclusions by complementary experimental observations whenever possible. Theoretical models that are applicable to solid state thermal decompositions are discussed, together with allowance for the possible participation by alternative reaction mechanisms (i.e., melting, etc.). The overall, and optimistic, conclusion from this survey is that thermoanalytical kinetic studies is a subject of considerable interest and promise. However, its potential can only be realized through fundamental reassessment of the methods and theories that continue to be used in a topic that appears to have stagnated and in which the chemical foundations have become eroded, or even forgotten.

Keywords: Compensation effect; Crystolysis reactions; Kinetic analysis; Mechanisms of reactions; Reaction rates; Solid state kinetics; Thermal analysis

---

1. Introduction

A critical appraisal of the present status and credibility of the theoretical foundations of those aspects of thermal analysis (TA) that are concerned with kinetic measurements and their interpretation, has lead me to a distinctly disappointing result. I conclude that current procedures and methods, used in rate and mechanistic studies of thermal reactions by TA methods, must be regarded as offering little optimism for the favourable future development of this subject area, if recent practices are maintained.

This situation has arisen following the initial undoubted successes achieved during the early establishment of TA. The technique enables the efficient measurement of changes of (usually) physical parameters during reactant heating and the methods developed are correctly recognized as representing spectacular advances in instrument evolution. Equipment improvements have increased both the accuracy and the rapidity of measurements made by a versatile range of alternative detectors. Automation of these experimental methods, through the timely advances in computer technology, enable mathematical and statistical analysis of the large number of data measurements obtainable to be presented to the researcher in the form of results that have been, at least partially, interpreted. This is a generally attractive approach, and has been widely exploited, to give the now extensive literature reporting changes of various types that occur during the heating of many and diverse reactants. Commercially available instruments permit the rapid and efficient completion of thermal experiments, obtaining quantitative data that are suitable for many purposes: measurements of reaction enthalpies, specific heats, reaction temperatures, determinations of stoichiometry, melting points, uses in quality control, etc., and includes rate measurements. This review is particularly concerned with this last-mentioned, and widely applied, use of TA in studies directed towards investigating reaction kinetics and formulating mechanisms of thermal reactions. This is a large, important and active research topic. It is concluded here, however, that a high proportion of the results reported and the limited theories available for use in interpretations of TA rate measurements are much less satisfactory than might appear from a superficial reading of the many recently published research reports. The case presented in this critical survey is that the theory applied in TA kinetic studies has failed to advance with the subject, it lacks adequate chemical and physical foundations and it has now effectively ceased to evolve.

When TA techniques were in their developmental phase, about three decades ago, an approximately symbiotic relationship became established between the emerging TA discipline, and that branch of chemistry concerned with decompositions of solids. The latter interest benefited from improved methods of measuring reaction rates and researchers advancing TA methods adopted those aspects of the available theory that were applicable to thermal reactions, particularly those involving crystals. One recent interest in continuing the development of TA methods has been towards the expansion of the range of reactants investigated. Another has been towards increasing the applications of mathematical and statistical kinetic analysis programs and procedures to maximize the information, concerning rate characteristics, which can be extracted from a minimum number of experiments. A central shortcoming in these developments, now becoming progressively more evident, is that consideration of the chemical properties and controls of these reactions, an integral feature of the precursor studies concerned with decompositions of solids, has been effectively abandoned. This is an important change of methodology because TA responses are often based on physical measurements and such observational data require an interpretation step to yield information of chemical significance. Consequently, an increasing range of TA studies are inadequate because the research does not consider whether the rate processes investigated are influenced by crystallographic/structural properties, melting, involve the participation of transitory intermediates, are subject to secondary controls on rate, or proceed by any of the wider range of mechanisms that are familiar to chemists. Understanding reaction chemistry, including reactivity controls and all relevant participating influences, is often much too complicated to be elucidated from rate measurements alone.

Notwithstanding these reservations, the overall conclusion resulting from this wide and critical survey of the TA kinetics literature is intended to be strongly positive and optimistic. I believe that if the limitations inherent in current TA research methods can be recognized, accepted and replaced by new theoretical principles, capable of resolving the complexities of thermal reactions, then foundations for profitable future advances can be established. I am pessimistic about the present situation but believe that a more chemically based approach to the investigation of chemical phenomena is capable of initiating a renaissance in TA science. The ever-expanding and largely unreviewed literature of generally individual and unrelated thermochemical reports urgently requires comprehensive and critical reappraisal to introduce adequate theoretical foundations. This might be expected to provide systematic order and scientific coherence. (Just as a mound of bricks requires an architectural plan, together with skilled craftsmen and connective material, to transform the random aggregate into an ordered, useful structure, such as a house, a bridge, etc.).

These far-reaching and fundamental criticisms of some aspects of TA research are made seriously. This critical survey is intended to initiate, to provoke and to encourage a general debate about shortcomings in the scientific credentials of particular theories applied in rate data analyses by TA methods. Important limitations in current practices, identified and discussed below, have restricted the effective achievements of research undertaken to obtain chemical and mechanistic insights from thermal rate studies. The prevailing attitude seems to have discouraged open-ended interest in imaginative curiosity-driven research programs, conceived to give the widest possible understanding of all characteristics of thermal (chemical) reactions. One probable reason for stagnation now evident in TA kinetics research is that there are few relevant critical reviews. The present relatively tolerant communication conventions have become acceptable because automated laboratory methods yield readily publishable observations.

Future progress towards increasing the overall value of rate studies by TA methods requires the establishment of satisfactory theoretical and scientific foundations. The introduction of novel and unfamiliar concepts, however potentially important, must be expected to be accompanied by disruption, that may be both considerable and uncomfortable. Advances in science sometimes proceed through discontinuous steps, quantum-like leaps forward. In TA kinetic studies, any such fundamental progress should perhaps be keenly and urgently anticipated as offering possibilities for resolving the problems that result from the present almost complete absence of systematic order and limitations inherent in the theory available. To stimulate and advocate this essential transformation, I present here a critical and comprehensive appraisal of the existing situation, identify significant inadequacies in the older theories that remain in use and suggest some prospects for rectifying unsatisfactory aspects of the present situation.

1.1. *Aspects of TA*

The literature concerned with TA is extensive [1–4], reporting on various aspects of the diverse changes that occur on heating numerous different reactants, including many that remain solid throughout. These are conveniently and specifically referred to as *crystolysis* reactions [1,5,6]. (This term derives [6] from *cryst*al pyr*olysis*, describing crystalline material undergoing a thermochemical reaction and avoids the prefix *sol*, from *solid*, which might appear to imply solution phenomena.) The preferred objectives of many, perhaps most, kinetic TA research programs, judging from the contents of published reports, include identification of the *kinetic model* for the reaction (an *isothermal* expression of the form: $g(\alpha) = kt$, where α is the fractional reaction, k the rate constant and t the time), the rate equation which most satisfactorily expresses, ‘fits’, the kinetic characteristics of the process under investigation. Identification of a kinetic fit is almost invariably complemented by determination of the temperature coefficient of reaction rate constants (k), conventionally reported as Arrhenius parameters: the reaction frequency factor (pre-exponential term), A, and the activation energy, E. The significance of these terms is often discussed through the theoretical concepts from the theory of homogeneous kinetics. E is sometimes regarded as providing a measurement of the energy barrier to a controlling (rate limiting) bond rupture or bond redistribution step. Frequently, such observations provide evidence used in the formulation of reaction mechanisms and/or the identification of reactivity controls. In addition to their possible theoretical significance, the Arrhenius parameters, together with the kinetic model, the *kinetic triad*, A, E and $g(\alpha) = kt$, provide a convenient and conventionally accepted quantitative summary of rate characteristics obtained from a TA kinetic study.

Although, in recent literature, the range of reactants selected for kinetic and mechanistic investigation by TA methods continues to widen, the evidence presented in support of stoichiometric descriptions of these reactions is sometimes meagre. The observational data provided often appears to be less than the minimum required to characterize adequately the chemical change(s) that occur. Moreover, the properties and controls of solid state reactions are often more difficult to determine than appears to be generally discussed in many TA reports. This review is primarily concerned with articles of this type, which constitute a significant proportion (most, but by no means all) of the recent TA kinetic literature. Three important chemical characteristics of condensed phase reactions, and which should be included in the planning of any fundamental TA research program, are as follows. These, and possibly others, must be addressed if the chemical significance of kinetic measurements are to be elucidated and realistic reaction mechanisms and rate controls are to be formulated. First, many studies fail to establish, or even to mention, the phase within which the reaction of interest takes place: this is important where there is any possibility of melting, total or partial, temporary and/or local. Second, reaction may involve the intervention of intermediates, perhaps reactive and transitory. Any comprehensive description of behaviour, including mechanism, requires their identification and the role of each to be characterized. Third, during endothermic and/or reversible solid state dissociations, kinetic properties are often (perhaps usually) sensitive to self-cooling and/or the ‘back’ reaction which can occur when the volatile product remains available within the reaction zone. Discussions often ignore all possible influences of these secondary reaction controls, even though their importances have been conclusively demonstrated for many representative reactions of solids. Similarly, for exothermic processes the kinetic consequences of self-heating are rarely mentioned though, in many of these, reversibility is usually regarded as unlikely.

Another pervasive uncertainty in the TA literature concerns the precise meanings of certain terms used in descriptions and discussions of kinetic data. Their significances appear to have become modified from their original usage and consequently are different from those conventionally accepted throughout other branches of chemistry. Examples, explained in greater detail below, include the usage of the terms *mechanism* and *activation energy*. There is also the importance of the consistent use of units. Accepted definitions are essential to achieve the transparent transmission of information between researchers and to present all results and conclusions in forms that are suitable for comparisons and discussions in the widest chemical context.

1.2. Content of this review: fundamental investigations

The primary objective of the present critical review of the TA literature is to appraise generally the present status of the subject and to identify possible shortcomings that can be modified to improve prospects of future progress. Broadly described, thermoanalytical science is the experimental study of chemical reactions and/or physical changes under controlled thermal and other conditions [4]. Each laboratory program must include a sufficient number and range of observations to elucidate quantitatively all aspects of the processes that contribute to the reactions studied. It is usually not possible to forecast the amount, and difficulty, of the work required to complete the objectives planned in a thermoanalytical study. However, the investment of time, equipment required and effort rises massively with increase in complexity of the changes participating and where the reaction chemistry and controls are to be determined in detail. There is, however, a substantial proportion of this literature in which a relatively small number of TA experiments have been used to obtain (apparent) kinetic parameters for complicated reactions. In these papers the reliability of observations reported, together with the chemical deductions drawn therefrom, are not always obvious. Overall, the scientific standards and theoretical values of TA reports are highly variable in quality.

When research is undertaken only to measure the stability of a particular compound (mixture, etc.) or the rate of a specified reaction, within a limited range of predetermined conditions, a small number of dedicated experiments may be sufficient to obtain all the data required. Empirical studies of this type do not require theoretical explanations for the behaviour observed. Such results can, nevertheless, be of considerable importance for specific purposes. Empirical observations are often valuable in the design of manufacturing processes, for developing efficient preparation procedures, in measuring stability and for numerous other identified reasons. Fundamental studies, in contrast, are undertaken with the intention of determining the chemistry of selected reactions. The present review is almost exclusively concerned with fundamental research directed towards investigating and characterizing, in the greatest practicable detail, reaction chemistry. Such studies are intended to elucidate the factors that control reactivity, every significant step that contributes to the transformation of reactants into products (the reaction mechanism) and all relevant aspects (steps, rates, controls, etc.) of the physics and chemistry of the changes participating. As in other branches of chemistry, the information required to formulate each reaction mechanism is obtained through kinetic and other measurements, to which TA experiments may, and frequently do, contribute valuable data. Interpretations of rate measurements are often, but not invariably, supported by other observations to confirm or complement conclusions.

In this survey, emphasis is directed towards those aspects of TA practices that require examination and improvement. Attention is focussed on particular unsatisfactory features in such work that should be recognized by those active in the field as unnecessary and untenable. The publications available have been surveyed by the author, in a personal appraisal of the perceived problems, limitations and difficulties, some of which, if generally understood, could be rectified. My overall assessment is intended to present an optimistic view of the future for TA and there is much to be admired and commended in recent publications. However, and inevitably, a critical survey must focus principally on the less satisfactory features of the published material which, therefore, dominate this text.

The TA literature can be described as exceedingly diverse. Most of the generalizations made here are not intended to be universally applicable but should be taken to refer to practices or views that are widely expressed. Similarly, the citations giving illustrative examples have been selected to be representative of several, often many, articles of similar content. The overall objective here has been to identify, with reasons, the limitations of TA techniques and conventions that appear to be responsible for reducing the achievements of the subject. Recognizing the variability and diversity of reports, the difficulties of defining the subject area, the variety of talents, skills and aspirations of thermal analysts, we seek here to establish any 'middle ground' of generally acceptable TA conventions and practices. From the comparisons made, the less reliable practices may, in future, be recognized and eliminated to enable more the promising aspects of the subject to be profitably pursued.

TA is surveyed here within this, admittedly ill-defined, reference frame. Some skeletal themes, which give form to the presentation, are briefly summarized as follows. These are generalizations, intended to express the principal conclusions of this critical and comparative literature review, discussed and justified in the sections that follow:

1. The theory applied in the analysis of TA rate data is inadequate and often incomplete. In the absence of a suitable theoretical framework, contributions tend to be considered individually so that systematic order is not developed and the wider chemical aspects of behaviour are not recognized and explored. The scientific expectation, that useful predictions for hitherto untested behaviour can be deduced through scientific induction from data already available, is now extremely rarely found in TA research.
2. Thermal changes, including chemical reactions, are often more complex than is recognized so that kinetic data, and their interpretations, may be incorrect. In measuring rates of thermal changes, the following factors may influence kinetic characteristics: reaction reversibility, melting, reactant self-cooling/heating, multiplicity of rate processes (concurrent and/or consecutive), etc. Secondary controls all too often remain unconsidered in the analyses of kinetic data.
3. In addition to the above uncertainties, mathematical procedures used to calculate kinetic parameters may be insensitive, perhaps incapable of discriminating between alternative rate expressions, and/or may be incorrectly applied.
4. Some chemical terms have progressively become 'locally' modified in the TA literature, which limits their value, reduces the precision of their use in communication and diminishes their ability to relate to other branches of science. Terms of particular significance here include *activation energy* and *mechanism*.
5. The history of TA, including the incorporation of some theoretical models originating from studies of thermal decompositions of solids, is discussed. This approach is of value in understanding why some of the present difficulties have arisen.
6. Theoretical models widely, often uncritically, used in kinetic analyses of TA rate data are based mainly on (solid state) geometric models and are applicable to single rate processes. TA studies do not always confirm that each reaction studied conforms to both conditions. Theory applied when discussing the significance of Arrhenius parameters is usually derived from homogeneous (gas, solute) kinetic concepts.

Within this article the term TKA (ThermoKineticAnalysis) describes any research in which physical measurements (usually) are made to determine the course and/or extent of the changes occurring in a reactant sample held within a constant or a programmed temperature environment. Coverage in this survey is specifically concerned with fundamental TKA studies that are primarily directed towards chemical objectives, usually including one, or more, of the following aspects of behaviour: (Interpretations are sometimes, though not invariably, supported by other relevant measurements.)

(i) elucidation of reaction mechanisms (in the usual *chemical* meaning of this term),
(ii) identification of the parameters that determine absolute and relative levels of reactant reactivity and that control reaction rates,
(iii) relate observations for any particular reactant to the chemical behaviour established for other comparable substances,
(iv) develop and expand the theoretical framework for TKA studies, of the most general possible applicability, that will maintain links with other branches of chemistry, and
(v) present information available from TKA studies for groups of different reactants systematically so that inductive predictions can be made for hitherto untested systems.

These objectives are generally approached through experimental investigations which attempt to characterize, for suitable reactants: what chemical reactions have occurred (*stoichiometry*), how rapidly (*kinetics*) and obtain any other information capable of elucidating all relevant aspects of the changes identified (textures from *microscopy*, structures and topotaxy from *crystallography*, bonding from *spectra*, etc. [6]).

The research surveyed here is focussed towards the published reports of those fundamental TKA investigations that address objectives ((i)–(v)). This literature includes articles concerned with the chemical dynamics of thermal reactions involving participation of condensed phase materials, particularly those that were originally solid. The content is less concerned with empirical studies. In addition, the present review does not discuss those alternative, outstandingly successful, and important applications of TA for measurements of reaction enthalpies and other thermodynamic quantities. TKA here specifically refers to kinetic and mechanistic studies, which represents only a single aspect of the wider subject of TA and is mainly concerned with inorganic reactants. However, aspects of the theoretical principles discussed are probably equally applicable to other reactant types: organic substances, pharmaceuticals, polymers, etc.

An essential objective of any scientific subject is to develop a systematic classification of the information available, through the use of theoretical concepts and models, and also generalize results to identify wider principles, by induction. The scientific theories so developed are expected to include the ability to predict properties and/or behaviour patterns that are applicable beyond the range of the observations originally used in their formulation. The recent TKA literature contains little evidence of the systematic classification of the information that is already available, or that scientific order is currently developing. With some exceptions, there are relatively few recent proposals directed towards developing the necessary theory. The prediction of hitherto untested behaviour patterns is now infrequently attempted, and comparative surveys of related sets of reactions are rare. An intended implication of the title of this article is that the scientific foundations of the subject are now inadequate and require critical reexamination and refurbishment.

1.3. Topics discussed and outline index

The range, and interrelationships, of all phenomena encompassed within the TKA subject area are considerable, complicating the presentation of any comprehensive survey. To simplify the text, while giving ease of reference, the content is divided into the following section (‘Chapter’) headings; each is intended to be largely self-sufficient, but these are, nevertheless, linked to provide coherent overall coverage. This inevitably introduces some repetition, to emphasize points of general applicability:

1. *Introduction*. Above.
2. *Origins and development of TA kinetics*. The relationship between thermal rate studies by TA methods and previous studies of crystolysis reactions is reviewed, including the continued use of theory deriving from this antecedent subject. A definition of TA is included.
3. *Reaction stoichiometry and reaction mechanism*. Kinetic interpretations must be based on precise information about the single chemical reaction studied, including stoichiometry and identifications (including structures) of reactant, products and intermediates (if any).
4. *Kinetics of reversible and/or endothermic dissociations of solids*. Discussion of the roles and significance of secondary controls (resulting from reaction reversibility and/or reactant self-cooling/self-heating), on rates of chemical change. Procedural variables.
5. *Kinetic analysis: interpretation of rate measurements*. Aspects of the kinetic analysis of thermal rate data and mechanistic interpretation of each individual rate process being studied. Determination of α, reproducibility of kinetics, isothermal and non-isothermal rate studies including the use of approximate equations, computer methods of kinetic analysis, literature inconsistencies in reports of rate observations, the compensation effect (CE), melting, other phase changes and complex reaction mechanisms (transient, unstable intermediates), complementary measurements in interpretation of TKA data.
6. *TA literature*. New contributions to the subject should be related to information already published and all the available material critically surveyed. There are shortcomings in citation coverages in article introductions and few general reviews.
7. *Theory developments*. The potential values of theoretical explanations for crystolysis reactions are discussed, together with the necessity to include consideration of (or, at least, the possibility of) melting and other complex mechanisms in kinetic analyses.
8. *Future prospects*. The prospects for advancing our understanding of thermal reactions through TA methods are discussed. Aspects of this review that are regarded as most significant are summarized.

2. Origins and development of TA kinetics

The subject history presented here is concerned with modern methods and practices of TA reaction kinetics (TKA) as originating in and developing from that specialized branch of chemistry concerned with thermal decompositions of solids [1–3], now conveniently described as *crystolysis reactions* [1,5,6]. My view is that in recent years (the last three decades) TKA has exerted a dominant control in investigations of crystolysis reactions [1–6]. The progress of TA instrumentation, including automation of experiments, permits the kinetics of thermal reactions of crystals to be studied more rapidly, easily and accurately than previously. Product yield (fractional reaction, α), time (t) and temperature (T) values can be measured with ever increasing efficiency, for almost any thermal process that occurs on heating reactants, at least one of which is initially in a condensed phase: solid or liquid (glass, mixture, etc.). Subsequent advances have enabled the computer controlling the TKA experiments also to perform kinetic analyses of the data collected. However, it appears that, at the same time, comprehensive investigation and characterization of the *chemistries* of thermal reactions of all types has become less important than the central preoccupation with enhancing the ease and speed of kinetic analyses of data. Often interest is directed mainly, sometimes exclusively, to mathematical developments. A consequence has been that this research effort has not benefited from guidance through the essential accompanying advances in theoretical principles. Moreover, this has resulted in the generation of a subject area, or discipline, that is becoming largely composed of unrelated fragments, without systematic order. The topic remains without the adequate theoretical foundations that are essential for the organic growth of a coherent scientific subject area. TKA studies continue to proliferate, extending the already extensive literature [6] with numerous reports appearing in dedicated, specialist journals, including this one. (Different emphases can perhaps be sensed in the subject titles. Chemical and/or scientific objectives are seen to be of interest in studies of *Decompositions of Solids*, *Crystolysis Reactions*. Methods and techniques might be expected to result from investigations of *TA*.)

A high proportion of recent TKA research represents a relatively restricted approach that has effectively replaced the wider range of experimental techniques that were previously (and profitably) used to investigate solid state thermal chemistry, including decompositions. The former (instrumentation and computer applications) is currently enjoying considerable favour, whereas the latter (chemistry) is now very much less in fashion. Because the early TA research was extensively concerned with crystolysis reactions, these (then) appropriate solid state models initially became accepted, and subsequently retained, as essential methods for all TKA data interpretation. The initial development of apparatus and subsequent reliability confirmations of the TA experimental methods (thermogravimetry (TG), differential TA (DTA), and later, differential scanning calorimetry (DSC), etc. [4]) included comparisons with rate data for selected well-known solid state thermal decompositions. This introductory research frequently involved the interpretation of rate measurements through comparative testing of the fit of data sets to kinetic models, rate equations, based on geometric principles applicable to crystolysis reactions, see [1, Table 3.3]. This group of rate equations, with others occasionally included, has become the preferred, often exclusive, range of possibilities considered in TKA data kinetic analyses.

The increasingly divergent objectives and attitudes that have progressively arisen between TKA and crystolysis studies now requires that there should be critical reexaminations of their interrelationships to eliminate some of the unacceptable inconsistencies that have become apparent. This should, of course, cause no fundamental conflict within alternative approaches to studies of the same reactions but removal of some of the incompatibilities in theory that have developed is now overdue. For a range of crystolysis reactions, the TKA theory used may be entirely appropriate. However, there is also the probability that these same models may be inapplicable, even misleading, when applied to other thermal processes, perhaps for reactions involving intermediates, melting, etc. In the absence of complementary observations, the occurrence of a complex reaction mechanism or secondary controls may not be detected.

The currently used and widely accepted TKA approach to rate data interpretation is ultimately limiting for reasons summarized below. Detailed explanations, supported by examples, are given in the sections following:

1. A majority of TKA studies appear to assume (implicitly) that measured kinetic data inevitably provide an accurate determination of the rate of the chemically controlling step for the reaction under investigation. In mechanistic studies intended to elucidate the chemical controls of reaction, however, this implicit assumption requires experimental confirmation. For many chemical changes, there is evidence that the rates measured are significantly influenced, even determined, by alternative factors or secondary controls which derive from reaction reversibility, reactant self-heating/cooling, melting, concurrent/consecutive reactions, etc. To obtain chemical conclusions, observed kinetic data must be demonstrably related to a single reaction of interest. If experimental conditions influence behaviour, then the results are empirical, unless quantitative allowance can be made for the contributions from all secondary effects.
2. Comparative tests of the relative excellence of fit of rate data within only a limited set of kinetic models is restricting and may not include consideration of every reasonable possibility. The earliest TA research was concerned with reactions known to proceed in the solid state, thus tests for applicability to these kinetic models only were appropriate. Now a wider range of kinetic models is required where reactions include possible influences from reactant melting, reversibility, etc. TKA studies have extended beyond the range of (often simple) reactions for which the theory was originally intended and to which it will not be invariably applicable now.
3. The theory applied in analysis of TKA (α–t) data was originally based on geometric models, applicable to heterogeneous (interface [1–3]) reactions. This contrasts with theory used in the interpretation of Arrhenius parameters which derives from proposals for homogeneous reaction rate models, originally applied to gas or solution reactions. This theoretical conundrum has yet to be adequately resolved.
4. A predominant, sometimes exclusive, focus of TKA attention has been on the mathematical interpretation of rate data. This trend has been accompanied by a notable diminution in the use of multiple and complementary experimental techniques that were a feature of earlier crystolysis studies. (I have never understood why a kinetic study is necessary to determine that a solid state reaction proceeds through interface advance when, in favourable systems, the same conclusion might be more readily, and reliably, obtained by some simple microscopic observations.)

Overall, the present unsatisfactory relationship between the (sometimes introspective) fields of TKA and crystolysis chemistry might be expressed as follows. Some 30 years ago, thermal studies of solid state decompositions encountered considerable difficulties in theory development that limited subject advance. At about the same time, the foundations of TA were established, pioneering exploratory instrumental developments that often selected simple solid state decompositions to establish and to confirm the new methods. Such advances offered solid state kineticists attractive new possibilities for rapid and efficient collection of rate data. These were enthusiastically adopted. Initial successes in TA were exploited by the continued development of equipment, through combinations of methods, giving ever greater accuracy, wider and more precise temperature controls, etc. The concurrent advances in computer technology were similarly adopted and found to be particularly suitable for the automation of data collection and later for the kinetic interpretation of the recorded rate data. Subsequent effort and progress has continued the evolution of TKA methods towards increasing the versatility and accuracy of the apparatus, together with extensions of data processing facilities for kinetic analyses. This pervasive preoccupation with kinetic studies (easily completed by automatic machines) has, however, meant that other aspects of chemistry of all reactions subjected to TKA studies have become neglected. This has undoubtedly resulted in a restriction of the extent and value of the conclusions. Indeed, the TKA literature contains remarkably few proposals directed towards advancing theory (other than the mathematical aspects of kinetic data interpretation). In summary, the preoccupation with TKA methods has contributed relatively little to the advancement of the theory of reaction kinetics or to the systematic chemistry of the elements. Moreover, without recognizable correlations, the possibility of making predictions of behaviour patterns beyond the range of available observations is eliminated: progress by inductive reasoning is an essential feature of successful science. Perhaps the rather obvious omission of chemical principles and methods in TKA reports is the central feature that requires correction. The case for a reversal of this trend, emphasizing the necessity develop chemical theory, capable of introducing systematic order between reactions of different substances, is made below.

A factor that has undoubtedly contributed to the absence of recognizable order amongst the numerous Arrhenius parameters reported in the literature is that methods used for their calculation may not be based on secure theoretical foundations, a problem discussed further below. Significantly, it has not yet been found possible to provide criteria for the systematic classification of the accumulated TKA reported results through the chemical compositions and/or constituent groupings of reactants or through trends in the kinetic triads. The inherent uncertainties in results from kinetic analyses have been convincingly demonstrated in two recent comparative studies [7–9] (for selected crystolysis reactions) which show significant and disturbing inconsistencies. Different groups of workers reported wide variations of calculated Arrhenius parameters, together with other results, derived from observations for the same reactions [7], and, in the other study [8,9], from the same sets of measurements.

Nevertheless, many recent TKA reports represent valuable contributions towards the advance of chemical knowledge, including interpretations of observations within the limitations of theory available. The problem is that the wider literature contains a high proportion of articles in which the theoretical concepts applied appear to be based on insecure foundations that now require critical scrutiny. Many publications cannot, even by the most generous assessment, be regarded as contributing to the systematic growth of a coherent discipline or to advancing chemical knowledge. Agreed theories and definitions of terms are indispensable currency of scientific communication and the present review is intended to recognize and to develop promising ideas into firm foundations for subject development. The emphasis is towards a critical appraisal of general principles and overall trends rather than with detailed aspects. Perhaps this can stimulate a wide-ranging debate between concerned researchers about the validity of fundamental tenets which hopefully will lead towards an overdue and necessary reappraisal ("Back to Basics") that will be REAL: problem Realization → Examination → Appreciation → Lasting solutions.

2.1. TA: a definition

"TA measures changes, during a controlled temperature program, of the properties of a substance or other reaction mixture". (Whether the method can be regarded as *analytical* is mentioned in [4].) This descriptive definition (there are others [10]) summarizes essential features of TA, and here is regarded as including constant temperature (isothermal) measurements. (In contrast, crystolysis reactions [5,6] are concerned with the investigation and characterization of all aspects of the physical and chemical changes that occur in the solid state on heating solid reactants, including controls of absolute reactivity, reaction stoichiometry together with mechanisms, crystallographic modifications and allied phenomena.)

An essential feature, not always explicitly emphasized, is that most TA methods measure the changes in one, or more, suitable *physical* properties. These have been listed by Brown [4] and include: mass (TG, DTG), temperature (DTA), enthalpy (DSC), dimensions, together with various physical properties determined through mechanical (TMA), optical, magnetic, electrical, acoustic, emanation and other observations. Evolved gas analysis (EGA) may be based on chemical measurements, depending on the method of detection used. Consequently, an essential subsequent interpretation step is usually required to relate these *physical* TA measurements to each *chemical* change that is of interest. Conclusions based on TA measurements are often reported, without comment, in the form of stoichiometric equations.

Observations of the changes of a physical properties that are made may not, however, be sufficient to characterize completely, or even adequately, the chemical reactions that have occurred. Consequently, the representation of an overall reaction by a balanced equation frequently requires more than the single measurement, usually a mass loss, that is sometimes given as sole evidence for a stoichiometric conclusion. The unambiguous characterization and complete confirmation of chemical changes, including crystal structures, may require much more detailed analytical and crystallographic (X-ray diffraction) measurements than are usually obtainable from the usual TA methods. Each report should usefully contain a complete description of all the observations made. Confirmatory analytical evidence identifying every substance formed is particularly valuable when the parameter monitored includes contributions from the loss of one, or of several, volatile reaction products, perhaps arising through different and concurrent or overlapping processes.

Enthalpy changes can contain composite contributions, for example, where there are two (or more) concurrent chemical reactions and/or a phase change, such as progressive melting and/or reactant sublimation. Furthermore, some types of change in the reactant are not detected by particular TA methods: for example, TG does not record enthalpy changes due to a reaction, to melting or to other crystallographic transformations. To overcome method-specific limitations, complementary TA techniques may be used, TG and/or DTG is often accompanied by DSC and perhaps EGA (which may use chemical and/or physical detection methods). Another limitation is that TA techniques, in contrast with microscopic observations, do not give *direct* evidence of the changing (geometric) dispositions, with α, of active, advancing interfacial reaction zones within the reactant particles. Reaction geometry is often inferred indirectly through the interpretation of rate data by heterogeneous, interface advance, kinetic models [1–3].

3. Reaction stoichiometry and reaction mechanism

Rate investigations have conventionally tended to focus on the mechanistic interpretation of kinetic data: here it is emphasized that the full identification of each chemical change that occurs is equally important. Mechanistic interpretation of kinetic data is of value only when the reaction concerned has been fully characterized. The complete stoichiometric description of any chemical reaction of interest requires determinations of the structures and the compositions of all participants, including reactants and products. Rate data may then be related to a single, characterized chemical change. For the mechanistic interpretation of kinetic observations, this may require the recognition of any essential, but transitory and reactive, participating intermediates. The phase in which the reaction takes place must also be established, including whether or not any reactant, initially solid, undergoes melting, and if this is temporary, partial and/or local. The reversibility of reactions may also be important in data interpretation. The present discussion of stoichiometry considers the widest applicability of this term to include all those features that may be relevant in the elucidation and discussion of reaction mechanisms.

Kinetic data are most successfully interpreted when related to a single, simple reaction: the discussion below is principally concerned with such processes. For more complex reactions, it is necessary to obtain sufficient information to recognize and to characterize the individual contributions from each distinct rate process when concurrent and/or consecutive overlapping reactions participate in the overall change. Unless methods suitable for complex processes are applied, the contributions from each participating rate process must be separated for kinetic analyses of every individual reaction. Interpretations of measured data, known to contain contributions from two or more rate processes, by a single reaction rate model, are unlikely to yield meaningful conclusions. Rate data do not 'average': each rate process is individual.

Many TKA studies appear to presume that reactions proceed in the solid state because the original reactant was initially crystalline or because the rate data fits an expression from that set of rate expressions which are characteristic of crystolysis reactions [1]. This practice may obscure consideration of any alternative mechanistic possibilities. However, for a variety of systems (where reactions are complex, due to melting, involvement of reaction intermediates, and others), the most frequently mentioned [1] kinetic models, $g(\alpha) = kt$, used in solid state kinetic analyses are not invariably, or necessarily, applicable. Allowance for all possible instances of atypical or exceptional behaviour must be made when interpreting data obtained by any experimental method for a novel reactant. Many (though by no means all) TKA studies do not include adequate evidence that each one of the chemical changes taking place has been individually characterized, even though every reaction may be reported in the form of a balanced stoichiometric equation.

3.1. Reaction mechanisms

The term *Reaction Mechanism*, as used in many TKA reports, specifically refers only to the characterization of the kinetic model, that rate equation, $g(\alpha) = kt$, identified as providing the (relatively) most satisfactory representation of the yield–time data for a particular reaction. Consequently, this use of the term 'mechanism' might be regarded as approximately synonymous with 'reaction order' from homogeneous kinetics. This is a much more restrictive usage than the practice accepted throughout other branches of chemistry, where *mechanism* describes the complete sequence of all simple molecular steps through which the reactants are converted into products. (This broader meaning can be regarded as loosely comparable with molecularity, but, for solids, might require extension to include some associated interactions, crystallography, etc.) A subtle, even insidious, consequence of this use of the term *mechanism* in TKA studies is that identification of the kinetic model giving the best fit to a data set can become regarded as the only significant mechanistic conclusion to be expected from a kinetic analysis. Nevertheless, the other features revealed by a more comprehensive interpretation are equally important and require elucidation of the detailed processes that participate in crystolysis reactions (e.g., within interfaces, melting, intermediates, etc.). Such complete interpretations must be preferred but require additional observations, including stoichiometry, crystallography, observational microscopy, etc., to complement rate studies. Investigations of these mechanistic aspects of crystolysis reactions are exceptionally difficult. Little real progress towards understanding the chemistry of these solid state reactions, including interface processes and controls, either in general or for specific reactions, has yet been achieved. However, I suggest that this terminological restriction (inconsistent with the original and more widely accepted meaning of mechanism) cannot be used as a justification for ignoring all consideration of the chemistry involved in the transformations of solid reactants into products.

3.2. Determination of reaction stoichiometry

A comprehensive survey of the methods used, including problems that arise, in the determinations of reaction stoichiometries in TKA studies, including reactions of solids, would be a valuable addition to the literature. The present discussion is restricted to selected difficulties and identified shortcomings, to draw attention to the extent of the problems that can appear and to indicate their relevance here. Many of the earliest TKA studies were concerned with solid state reactions for which the stoichiometries were regarded as already well-established, e.g., for the dehydrations of hydrates (such as alums and other metal sulphates, etc.), the decompositions of $CaCO_3$, NiC_2O_4, etc. On heating in vacuum, these reactants did not melt, or at least not obviously and comprehensively, and the sigmoid-shaped fractional reaction α–t curves were interpreted through nucleation and growth reaction models [1], often with positive support from microscopic observations.

Advanced TA methods have been applied in investigations of a wide range of thermal reactions. However, kinetic analysis theory has not been appropriately extended or modified and such TA results are not usually complemented and confirmed by suitable additional observations. Shortcomings evident in recent TKA research reports include at least two factors (the resultant from their combined consequences are probably greater than the sum of the parts). First, the use of a small sample mass retained within an enclosed environment renders the reactant effectively invisible. In the absence of supporting microscopic examinations (formerly extensively used [3]), the valuable inferences made from direct observations, including changes of the sample texture that occur during reaction, are no longer available. Second, the widespread use of, and often exclusive reliance upon, automated, intraapparatus calculation programs present the already largely ‘interpreted’ kinetic results to the researcher in (what may appear to be) a final printed form. This can reasonably be accepted as a ‘completed’ analysis, particularly when results include an ‘excellent’ correlation coefficient, r, apparently representing a good fit of data to a kinetic model. In the absence of the stepwise (manual) analysis of α–t data, the complexity of behaviour may not be suspected or detected. Such observation limitations may not be taken into account when elucidating the reaction stoichiometries, including the following types of measurements.

3.2.1. Crystal structures

Reactant structure determinations are important in crystal chemistry because solids can be polymorphic, form double salts, mixed crystals and/or solid solutions, participate in topotactic reactions [1,2], etc. Different crystal polymorphs may exhibit different reactivities and transformations involve enthalpy changes. TKA techniques, including structure determinations by diffraction methods for samples heated in controlled environments, have been developed and are referred to in [1,2]. A precise discussion of the role of crystallographic transformations involved in some selected reactions has been given by Petit and Coquerel [11]. Crystallographic evidence can also be used to characterize and to confirm the identities of the residual products.

3.2.2. Single measurement observations

TKA measurements of (physical, Section 2.1) changes of a single parameter during a chemical reaction may be insufficient to characterize fully reaction stoichiometry, as exemplified below. In many reports, the reaction is identified from a measured mass loss, which may be described as representing (alternatively) ‘satisfactory’, ‘good’, even ‘excellent’ agreement with an anticipated chemical change. There do not, however, appear to be accepted criteria by which such ‘satisfactory/etc.’ correlations with expectation are generally agreed and alternative possible stoichiometries can sometimes be perceived. Often such data analyses may be complicated, or the reliability of conclusions reduced, by the occurrence of precursor reactions (surface drying or initial losses of impurities) and/or by overlap, to a greater or lesser extent, with previous and/or successive steps, where the reaction is one in a sequence of consecutive rate processes. Sometimes mass losses, reported to apparently, or to claimed, great accuracy, are inferred from a point of inflection on a TG curve, but criteria for the measurement are not provided. Evidence confirming that behaviour is reproducible is not usually given. Different stoichiometric conclusions, by different workers, were reached from mass loss measurements for the stepwise dehydration of $NiSO_4 \cdot 6H_2O$: the results supported by characterization of the phases present, by diffraction methods, were preferred [12]. El-Houte et al. [13] described a dynamic apparatus that is capable of separating, for identification, the individual steps in sequential dehydrations. The rate of temperature rise is relatively reduced during product evolution, because this improves distinguishability of the contributory reactions.

The exclusive use of mass loss to characterize stoichiometry can be unsatisfactory because of possible interpretational ambiguity and where the response measured may include contributions from more than a single rate process and/or sublimation. For example, the mass loss on HCl evolution corresponds closely with the loss of $2H_2O$: the difference is a $[(36.46 - 36.03)/36] = 1.19\%$ error, which, if used to distinguish alternative possible reactions, demands great precision of mass determinations. Other TA methods may be more specific in response and the use of more than a single measurement, through complementary observations, is always to be recommended.

3.2.3. Reactant characterization

Many TKA investigations have studied decompositions that take place following a precursor reaction, which may involve changes of crystal structure, accompanied by alterations of surface area, particle size, imperfection, also defect content and distribution, etc. Decompositions of various carboxylates, including oxalates, etc., are usually the breakdown of the anhydrous salt, formed after a precursor dehydration step. Moreover, some dehydrations are accompanied by hydrolysis [1]. Ideal and complete characterization of the reactant should include confirmation of chemical composition and crystal structure, together with determination of impurities, particle sizes, etc. This is relevant only after completion of all precursor steps, such as dehydration, phase transformation and any other accompanying changes. Some TKA studies, investigating the chemistries of steps in a sequence of consecutive reactions involved in the overall breakdown of complex compounds, taking place in successively higher temperature ranges, fail to characterize adequately the structures and compositions of the reactants for all the steps after the first. Thus, while the kinetic data may be reliable, the reaction stoichiometry may not have been satisfactorily established. Reaction products should also be fully determined, with due consideration of the possibility that molten materials may solidify with crystallization on cooling and before removal from the apparatus for examination. Such rigorous and ideal confirmations of the stoichiometry of reactions investigated by TKA methods are described relatively infrequently. Many reactants are characterized, most simply, only from the label on a manufacturer's bottle, and products are inferred only from a mass loss, sometimes estimated from an inflection on a TG curve.

3.2.4. Concurrent rate processes

Separation, through quantitative determinations of the individual contributions from two or more concurrent rate processes contributing in TKA measurements, can be difficult and may be subject to error. Aspects of the analysis of data that include contributions from parallel reactions and variations in E values have been discussed by Burnham and Braun [14] and Vyazovkin [15]. These theories can have some value in providing insights into inherently complex reactions and concurrent chemical changes proceeding in intractable reactants. However, the alternative approach sometimes reported, where composite data, already known to include contributions from two, or more, distinct rate processes, are regarded as a single reaction for the purposes of kinetic analysis, is totally unacceptable in fundamental work. Conclusions based on such composite data cannot be accepted as characteristic of any (or of either) component process and the kinetic model and Arrhenius parameters cannot be identified with any single stoichiometric reaction. The only possible use of such 'averaging' is to provide an empirical representation of the overall behaviour, which may have no theoretical value.

Some crystolysis reactions, formerly regarded as single, stoichiometric decompositions, have subsequently been shown to be complex, in which two, or more, overlapping rate processes contribute to the overall change. Examples include the decomposition of $KMnO_4$, which is now accepted as involving the intervention of $K_3(MnO_4)_2$ [16], and the dehydration of $CaC_2O_4{\cdot}H_2O$, in which water is lost from two different sites at appreciably different rates [17]. The decomposition of $KMnO_4$ was, for a long time, regarded as a representative, simple solid state reaction [1,16] and the dehydration of $CaC_2C_4{\cdot}H_2O$ has been used as a model reactant in comparative studies [7]. Nevertheless, new kinetic analyses and data interpretations are required, based on these demonstrations that neither reaction is simple, necessitating reformulation of each reaction mechanism.

The decompositions of many salts of halogen oxyacids [18] have been described as proceeding through the sequential elimination of oxygen from the anion as reaction progresses. Partial reactions yield mixtures that contain two or more anions, the proportions changing as reaction advances. There may also be melting. The full kinetic characterization of these complex concurrent reactions would require extensive analytical measurements to determine the amounts present of every participating species and their variations with α, t and T. In another set of complex reactions, the decomposition products of some trivalent (Group IIIA) oxalates between 573 and 693 K have been found to vary with both T and pressures of the gases present [19]. Reactant breakdown proceeds through various oxycarbonates, sometimes accompanied by cation reduction, perhaps involving the CO product. Gases evolved contain both CO and CO_2, the former undergoing some disproportionation with carbon deposition ($2CO \rightarrow CO_2 + C$). It is difficult to characterize fully the stoichiometry, which may vary with reaction conditions, α, t, T, etc. The collection of sufficient data for comprehensive stoichiometric and kinetic analyses would require the most careful design of experiments to obtain sufficient information, capable of being reliably related to identified individual, simple reactions in these complex, often stepwise, degradation processes. Such investigations are much more difficult and complicated than may appear at first sight.

Further difficulties in elucidating the chemistry, including stoichiometry, of some complex, condensed phase, decompositions are illustrated by the thermal breakdown of $(NH_4)_2Cr_2O_7$. This was originally (implicitly) identified as a solid state reaction [20] in which analytical observations identified the participation of nitrate and nitrite. A later study [21] expressed the various steps of the overall reaction as balanced stoichiometric equations. Subsequent work, however, has shown that this reaction proceeds with melting [22]. The behaviour was regarded as complex, reactant dissociation being followed by local melting (of CrO_3), in which oxidation of ammonia (ammonium ions?) accompanied chromium reduction. The several interrelated reactions (homogeneous, in the melt) could not be distinguished within the overall kinetic characteristics. Their elucidation would require individual investigations of suitable synthetic mixtures to provide a complete description of reaction chemistry, including stoichiometry. This was not undertaken, but the complexity of the participating reactions was demonstrated [22]. Similarly complex mechanisms, again involving transient intermediates and probably proceeding in specialized local, liquefied reaction zones, have been shown to occur during the decompositions of NH_4ClO_4 [23] and of copper(II) malonate [24]. The breakdowns of several copper(II) carboxylates proceed in two consecutive steps through cation reduction, $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$ [25]. Overall, these reactions cannot be represented by a single stoichiometric equation or a single kinetic model, but each process is the outcome of two or more interlinked decompositions. Thus, the temperature coefficients of reaction rates, and the apparent values of E, are the composite resultants.

3.3. Melting, before or during reaction

While melting might not strictly be regarded as a feature of stoichiometry, it is usefully mentioned here because it is an important property of reacting participants and an essential consideration in the formulation of reaction mechanisms. Kinetic and mechanistic reports of TKA studies involving initially crystalline materials have, however, frequently omitted all mention of any possibility of reactant liquefaction, liquid intermediates and/or the formation of a reactant/product molten eutectic. This is unreasonable because melting is probably the most frequently observed consequence of heating a solid. Moreover, it is believed [26] that many reactions proceed relatively more rapidly in the liquid phase. After fusion, the intracrystalline stabilizing forces are relaxed and the stereochemical constraints, capable of opposing the adoption of the most effective precursor molecular disposition for chemical change (activated complex formation), may be significantly diminished.

One (now inapplicable) reason for discounting all consideration of melt participation in TKA studies, is that many of the early reactants were specifically selected from a relatively restricted range of compounds, already known to undergo crystolysis reactions [1–4]. However, the general practice of disregarding the possibility of fusion cannot be sustained, now that studies have been extended to include a much wider range of substances beyond those (almost 'model' solid) reactants, that formerly attracted the greatest interest. Moreover, some reactants, previously accepted as decomposing in the solid state, have subsequently been shown to undergo melting during breakdown [1,22–24]. Nevertheless, literature reports of analyses of rate observations are frequently based on the comparatively 'best fit' of data to a kinetic model selected exclusively from the set of solid state geometric models. When discussions, presenting such conclusions, make no mention of the possibility that melting could have occurred, it follows that the kinetic interpretation reported carries the strong implication that the reaction has occurred in the solid state. This is clearly an unsatisfactory practice: perhaps the most important mechanistic feature of any chemical change, whether the reaction proceeds in a solid or a liquid, remains unaddressed, while the kinetic interpretation presents a strong, but unstated, implication that a crystolysis reaction has occurred. The accepted convention, that there is no requirement discuss the possibility of fusion, before or during a reaction, is, on the view expressed above, a major restriction on the adequate interpretation of TKA data. This can be a self-fulfilling prophecy; a phenomenon conventionally and conveniently ignored is not, or is less, likely to be detected.

The possible participation and role of melting merits much more careful consideration than is usually provided in TKA investigations; many reports simply ignore the possibility. This is particularly important because melting is not detected by that most extensively used TKA measurement technique, TG. Liquefaction is, however, significant for the following reasons. First, at least some chemical changes proceed more rapidly in a melt than in a crystal [26]. Second, while comprehensive reactant melting is relatively readily detected (by microscopy, a sharp DSC endotherm, etc.), the identification of transitory fusion, which may be temporary, partial and/or local, is much less easily characterized, even when specifically sought [24]. An enthalpy of fusion response, during progressive melting, can be obscured by that of an overlapping reaction. A liquid phase present at reaction temperature may solidify on cooling. Detection of melting from characteristic surface textures, such as bubble and froth-like structures, through microscopic observations may require fracture of crystals to expose internal features when melting is intracrystalline. Fracture is necessary because the integrity of individual reactant crystallites is sometimes maintained throughout reaction due to particle preservation, resulting from early development of a superficial coherent but unreactive boundary zone [24]. Examples of reactions involving melting, which mention the experimental problems and difficulties in recognizing fusion, include the decompositions of $(NH_4)_2Cr_2O_7$ [22], NH_4ClO_4 [23] and copper(II) malonate [24], discussed above. A further type of mechanism, only cited here to illustrate the complexity of the behaviour possible, is reaction within a liquid solute provided by condensation of a low boiling point product [27].

3.4. Reaction intermediates, transitory and unstable

3.4.1. Crystolysis reactions

Solid state reactions that proceed stepwise through a sequence of rate processes are well-known, for example, dehydrations of crystalline hydrates frequently proceed with the intervention of one, or more, lower hydrates [28]. Such intervening (often stable) phases will not be referred to (here) as reaction intermediates but, in kinetic investigations, each must be regarded as the product of one reaction and as the reactant for the next, in a stepwise sequence of consecutive rate processes. A reaction intermediate, as generally accepted in chemical kinetics, is an essential participating species, often present at low concentrations, usually unstable, reactive and having transitory existence, frequently existing only during the progress of reaction. Whether or not a transitory, unstable intermediate can be properly regarded as a stoichiometric feature of the reaction depends on which aspects of the steps that contribute to the overall change are being considered. However, such unstable participants are relevant in the formulation of reaction mechanisms and in determining the controls of reactivity: intermediates, therefore, merit mention here. As with recognition of the importance of melting, the participation of intermediates has conventionally been virtually ignored in studies of crystolysis reactions and subsequently, possibly consequently, in TKA. Again, what is not sought is less likely to be found, so that the roles of intermediates appear to have remained unsuspected and unconsidered during many interpretations of kinetic results [16,17,22–25].

Considerable difficulties attend the characterization of the steps through which a solid reactant is transformed into solid products, because such changes are often believed to occur, largely or exclusively, within a specialized, localized active interface [1–3]. The detection of very small amounts of unstable species within an advancing reaction zone, which may be of molecular thickness, is experimentally particularly difficult. The physical or mechanical separation, the isolation or penetration of the reactant/product contact zone in the laboratory, for a partly reacted crystal, might be expected to result, most usually, in the destruction of those unstable structures or components sought. Non-invasive methods, such as spectral examination, have been suggested [29] but accepted practices do not include, or have methods generally suitable for, the identification of any species present in, or precise structures of, the reactive and inaccessible zones wherein reactions take place in solids. Detailed interface chemistry at the molecular level and methods for determining reaction controls have not been established for most solid state reactions of interest [1]. Some progress towards characterizing the structural changes that occur across a reaction interface has, however, been reported by Boldyrev et al. [30].

3.4.2. Reaction intermediates in melts

The detection of intermediates in melts (in contrast with the interfaces characteristic of crystolysis reactions) may be more readily achieved. The active participants may themselves be present as liquids at reaction temperature or perhaps be capable of forming a eutectic with the reactant, to which it must be chemically related. However, because partial fusion is so rarely detected in this field, only a few examples of reaction intermediates have been described, including for the examples mentioned above (with melted intermediates): the decompositions of ammonium dichromate (CrO_3 [22]), ammonium perchlorate (NO_2ClO_4 [23]) and copper(II) malonate (acetate, copper(1) [24,25]). More details concerning these mechanisms are given in the references cited. Intranuclear *liquid* bromine was identified as a solvent for the low temperature, interface reaction of potassium bromide with chlorine gas (possibly proceeding through $K[BrCl_2]$ [27]).

3.5. Complementary measurements

During the early crystolysis studies, before the advent of TA, kinetic data was implicitly accepted as being only one of several complementary sources of experimental evidence required to characterize chemical behaviour in intracrystalline reactions [1–3]. Recognition of a ‘best fit’ kinetic model was discussed and interpreted in the context of support from microscopic observations. Geometric conclusions were often based on quantitative information of two independent but complementary types. The extent (α-range) of kinetic fit could be reported and the kinetics of the contributory (solid state) controlling steps (e.g., nucleation and growth) were sometimes individually measured. If a diffusion process was indicated as rate controlling, attempts were made to identify the migrating entity. In more recent work the (printed) output of kinetic results based on TKA automatic methods of data analysis often appears to be acceptable as all the evidence necessary to establish the reaction mechanism, if the value of a correlation coefficient is regarded as being sufficiently close to unity. Chemical and mechanistic aspects of behaviour, such as the identification of the diffusing species participating in reactions identified as subject to diffusion control, are frequently ignored. It is now suggested that characterization of such migrants should be a requirement for the full stoichiometric description of the reaction.

It is emphatically not the purpose of this review to denigrate the achievements of the many researchers who have positively advanced thermal chemistry by TKA methods. It is my intention to point out that the undoubted and valuable achievements of TKA techniques should not be accepted as a complete replacement for all the alternative and complementary experimental methods that formerly were used in crystolysis studies [6]. Overall, this subject could be much more effective if the advances in all the types of experimental apparatus were now to be fully exploited and directed in a coordinated attempt to understand the chemistry of solids.

In a high proportion of TA studies, little effort is made to exploit the benefits of the other methods available for this research, though the older literature provides ample evidence of the value of such complementary observations [1–3,6]. These include all relevant observations obtained from microscopic, crystallographic, analytical, spectroscopic and all other suitable measurements [6]. One explanation for the current contraction in use of this broader range of techniques is an apparently implicit belief that TKA methods are capable of answering all relevant questions about any selected reaction. However, a moment of reflection by anyone active in the field must surely reveal the unsatisfying incompleteness of this answer. More specifically, characterization of the stoichiometry of an unfamiliar reaction requires observations that are of at least equivalent status and reliability as those used to determine the kinetic data. Stoichiometry must never be regarded (as sometimes appears) as a 'useful by-product', of TA observations that have been obtained primarily for use in rate studies.

3.6. Secondary reactions between primary products

The reaction stoichiometry should (ideally) establish the composition of the primary products, which can provide evidence of the particular bond rupture steps that control the reaction. (This feature of solid state reactions has been discussed by L'vov for studies of the kinetics of crystolysis reactions [31,32].) To identify primary products, it may be necessary to withdraw product gases rapidly from the reaction zone, at low pressure, to minimize possible interactions between reactive primary products in the gas phase and/or on catalytically active surfaces [33]. The reaction products identified from stoichiometric measurements are not necessarily those released by the (interface or other) reactant breakdown step. Secondary reactions, yielding the stable product mixture that is ultimately detected, are then regarded as further contributory processes in the overall reaction mechanism. If the secondary reactions between the primary gaseous products of an irreversible decomposition are sufficiently rapid, their occurrence does not necessarily influence the observed overall kinetic characteristics. Under such conditions, yields of (secondary) products remain quantitatively directly proportional to those of their precursors. However, if the product compositions change during reaction, perhaps by temperature or pressure dependent equilibria, the rate data measured may not remain linearly related to the extent of reaction, α. Rate variations arising from changes in CO/CO_2 ratio and/or CO disproportionation ($\rightarrow CO_2 + C$) introduce uncertainties into kinetic studies, e.g., for decompositions of Group IIIA oxalates [19].

Rapid secondary reactions have been shown to participate in many decompositions, e.g., metal formates. The decomposition of nickel formate in vacuum yields a high proportion of CO but, if gases are not rapidly withdrawn from the reaction zone, the CO/CO_2 ratio is that expected from the water gas shift reaction [33] (this reaction may be promoted catalytically by the nickel metal residual product). The decomposition of copper(II) formate similarly involves secondary reactions [34], there is evidence of the intervention of the unstable volatile intermediate, copper(I) formate. Decompositions of some azides have been shown to yield a proportion of atomic nitrogen [32], though the detection and measurement of this product is experimentally difficult.

4. Kinetics of reversible and/or endothermic dissociations of solids

4.1. Influence of reaction conditions on kinetic characteristics

Many reversible and/or endothermic reactions have been of particular interest in TKA studies [3]; these include the release of water of crystallization from hydrates [28] and the dissociations of carbonates. Kinetic characteristics are generally sensitive to changes in the procedural variables (sample size, particle size, heating rate and pressure of gas product present [35]) which introduce contributions to kinetic control from the rates of mass (volatile product) and of heat transfer/diffusion processes. Two alternative approaches may (in principle) be used to measure the (maximum) reaction rate, characteristic of control (only) by an interface process, which may enable the chemical rate determining step to be identified [36]. First, reaction conditions, suitable for such kinetic measurements, may be established by dedicated experiments [36–39], so that product availability (i.e., gas pressure) is maintained below that identified as influencing reaction rate. Similarly, rates must be sufficiently slow to avoid effects from reactant self-cooling. Second, it may be possible to make compensatory quantitative allowances for secondary controls. In practice, uncertainties concerning the factors that determine reaction rates have not been adequately resolved for most of these reactions. Moreover, in numerous published studies the role of secondary controls remains unaddressed.

Apparent kinetic characteristics should be interpreted with quantitative allowances for each individual secondary control that is capable of exerting an effective influence on reaction rates, though there have been remarkably few such studies. When multiple kinetic controls are significant, the overall rate data measured should be regarded as empirical, possibly referring only to the specific, not often precisely defined, conditions that prevailed during those particular experiments. Such reaction rates may be the resultant from different contributions for locally variable conditions distributed within a kinetically inhomogeneous reactant mass. Furthermore, the intrasample kinetic characteristics can be expected to vary as reaction proceeds, due to local changes in distributions of product gas pressure and of temperature with position and with time. These are due to self-cooling [35,40–43] and the ease of diffusive escape of volatile products [36–39] along the intraparticular pores and/or interparticle channels of various dimensions. Thus, in many TKA experiments, conditions within the sample are often inhomogeneous, varying both in time and within space, and remain incompletely identified leading to empirical kinetic characteristics.

Self-cooling. Draper [40] could say in 1970, referring to calcite dissociation, "we found we could design the shape of the decomposition curve by systematically violating the conditions of the (rate) equation with respect to heat flow". The relatively low rate of heat flow resulted in self-cooing which, therefore, exerted a significant kinetic control in this endothermic, reversible reaction. Similarly, the importance of self-cooling during dehydrations was effectively demonstrated by Bertrand et al. [41]. However, as pointed out by L'vov [42], who has also contributed to quantitative assessments of the relatively large significance of the effect [43], this work "did not receive as much recognition".

Reversibility. The overall kinetic characteristics of many solid state dissociations are sensitive to the quantity of volatilized product available at the active reaction zone. Darroudi and Searcy [37] showed that the rate of product CO_2 evolution from calcite is relatively insensitive to carbon dioxide pressure only when this is less than 1% of its equilibrium value. One method of determining if a particular, untested reaction is condition-sensitive is to determine whether, or not, the kinetic behaviour varies with changes in procedural variables (product pressure, particle sizes, packing in the reaction vessel, etc. [35]). However, such tests are rarely reported or even mentioned.

Measurement of the absolute rate of the 'forward', dissociation, step in reversible reactions, under conditions that confirm the absence of, or minimize, contributions from the 'back' reaction, have been shown [36–39] to require dedicated, high vacuum equipment for such experiments. Exceptionally careful studies, addressing the difficulties of obtaining reliable rate measurements and comparing kinetic results with previous literature reports, have been made for the decomposition of $CaCO_3$ [36,37] and the dehydration of $NiC_2O_4{\cdot}2H_2O$ [38]. These TG studies were designed carefully and applied stringently: the relevant results are summarized below. Because the considerable difficulties inherent in such fundamental experimental measurements of reaction rates were confronted, the controlling (maximum) rates of product evolution were determined. These important results appear to have received very much less interest than they deserve, with few, if any, attempts at replication or extension by similar investigations for other comparable systems.

4.2. Dehydration of nickel oxalate dihydrate

Flanagan et al. [38] showed that the dehydration of $NiC_2O_4{\cdot}2H_2O$ was severely inhibited by the presence of small water vapour pressures: it was estimated that at 383 K the rate was reduced 0.04× by 5 Pa H_2O. Dehydration rates were measured by TG in an efficient vacuum system, capable of 10^{-4} Pa and always maintained at low pressures. Minimum practicable sample masses (3–0.2 mg) were used and data extrapolated to zero mass to eliminate the influence of the water reuptake reaction. From dehydration rates measured between 333 and 397 K, E was $130 \pm 3\,\mathrm{kJ\,mol^{-1}}$. This is significantly larger than several other values reported and it is shown that dehydration rates reported in previous investigations were underestimated by factors of at least 100×. A similarly precise study is reported for the dehydration of copper(II) formate tetrahydrate [39]. However, the extensive literature on dehydrations of crystalline solids [28] contains few measurements of the influences of low water vapour pressures on dehydration rates.

4.3. Thermal decomposition of calcium carbonate

The CE is discussed under Kinetic analysis in Section 5.5. However, because essential features of this kinetic behaviour pattern are relevant to discussions of calcite dissociation [44–47], some background information is given here. Sets of rate measurements for $CaCO_3$ dissociation ($\rightarrow CaO + CO_2$) have been obtained under a range of experimental conditions, and are, therefore, subject to different secondary controlling influences from rates of heat and product CO_2 movements. These result in marked variations in calculated (apparent) magnitudes of $\ln A$ and E which exhibit a pronounced CE, representing approximate *isokinetic behaviour*: values of k, tend towards a common value at the *isokinetic temperature* [46]. Such a set of kinetic data normally encompass comparable ranges of reaction rates that were measured within similar temperature intervals. This approximation to isokinetic behaviour arises because the absolute reactivity of the calcite is almost constant and within such data sets a CE appears [44–47]. Such diverse magnitudes of A and E cannot identify a rate controlling step in salt breakdown, unless experimental conditions have been suitably [36,37] designed to eliminate the effects from secondary controls.

It is generally agreed, within the large and relevant literature [1], including many TKA contributions, that calcite (a reactant extensively used both in early and in more recent, crystolysis studies) dissociates to CaO and CO_2 (only) by a (reversible and endothermic) interface reaction [1]. Kinetic characteristics are highly condition-sensitive, though surprisingly few of the numerous studies have attempted to measure quantitatively and separately the individual influences of these secondary controls, and/or of conditions, on reaction rates. Overall, a CE has been found [44,45,47] across an exceptionally (and theoretically unacceptably) wide range of reported Arrhenius parameter magnitudes.

Beruto and Searcy [36] discuss the controls of calcite decomposition, through a kinetic study of reaction at the single face of a large crystal heated in a vacuum maintained below 10^{-2} Pa. Isothermal reactions, between 934 and 1013 K, proceeded at constant rate, E was $205\,\mathrm{kJ\,mol^{-1}}$. During inward advance of the interface, the rate was not decreased by the progressively increasing thickness of the solid product layer. Heat transfer was regarded as a negligible source of error, though this was later discussed by L'vov [43]. This magnitude of E is larger than many reported values, some of which are comparable with the equilibrium dissociation enthalpy (173.5 kJ mol^{-1} [36]). Many values of E, obtained under less rigorously controlled conditions, are close to the dissociation enthalpy. This is ascribed [36] to overall rate control by the diffusive loss of product CO_2 along the pressure gradient developed between the approximately equilibrium dissociation pressure established within the outer pores of the sample and the gas beyond. When this diffusive removal of product is rate controlling, for reactions in the presence of gas(es), the measured rate cannot be identified with an interface step. Darroudi and Searcy [37] later showed that calcite dissociation rates were essentially independent of CO_2 pressure below about 1% of the equilibrium dissociation pressure but, above this value, rates became relatively sensitive to product pressure. Other investigations and discussions of the kinetics and mechanisms of calcite dissociation have been given by Barret [48] and Reading et al. [49]. A problem in the complete characterization of this reaction was identification of the initial solid product. Although the intervention of a metastable modification of calcium oxide was proposed [36], later work [50] suggested that this nascent product might be very small CaO needles (about 10 nm): this remains unresolved.

4.4. Dehydration of lithium sulphate monohydrate

L'vov [51] has made a comparative survey of literature reports for $Li_2SO_4{\cdot}H_2O$ dehydration kinetics, considering the influence of water vapour on reaction rate. From the diverse published data available, he concluded "Despite the significant differences between the methods and conditions of these studies, the product partial pressures and activation energies turn out to be in good agreement with theoretical calculations".

4.5. Controlled rate thermal analysis (CRTA)

CRTA was originally developed to reduce, perhaps even to eliminate within the reaction zone, contributions from variations of those factors capable of influencing reaction rate, when using TKA techniques [52,53]. During CRTA experiments, the rate process of interest is often controlled to proceed at a constant, predetermined rate that is maintained automatically by feed-back controls, based on product pressure (or other appropriate parameter) measurement, that operate by variations of the sample temperature. Consequently, the influences of volatile product pressure on the reversible process and endothermicity from self-cooling may be eliminated or substantially diminished, to remain effectively constant throughout the progress of reaction.

If the constant (and potentially reaction rate influencing) product pressure in the environment of a reversible reaction is maintained below the value at which the reverse process appreciably influences kinetics, then this provides a reliable method for measuring the rate of the interface process. Reaction rates at a representative temperature can be compared at progressively lower pressures to determine the value at which the amount of product present ceases to influence the rate of the dissociation reaction [54,55]. The same approach may, in principle, be used to detect onset of the influences of inhomogeneities within the reactant mass. No experimental method is known that is capable of eliminating all possibility of any reverse reaction. However, through the use of low pressure CRTA, small sample sizes and low reaction rates, the results may be critically compared to determine the contribution (if any) from experimental conditions on reaction rates. Thus, CRTA offers a valuable technique for determining rates of 'forward' reactions only. It may further provide evidence that the contribution of the reverse reaction is small and the conditions established within the reaction zone are maintained more nearly constant than during other kinetic methods. Applications of the CRTA method have been used in kinetic studies of the dissociations of calcite [49,55] and of dolomite [56].

4.6. Comment

From the studies of $NiC_2O_4{\cdot}2H_2O$ dehydration [38] and $CaCO_3$ dissociation [36,37], it is reasonable to conclude that certainly some, perhaps many, possibly all, endothermic, reversible reactions exhibit comparable sensitivity of dissociation kinetics to the presence of small pressures of the volatile product. It cannot be assumed, however, without more experimental evidence, that kinetic data determined under only a single set of conditions can be of fundamental significance or yield measurements from which a rate determining step can be inferred. Where there is a possibility that reaction rates are condition-dependent, this can be readily investigated by observing whether or not kinetic behaviour changes with variations of the procedural variables [35]. Results obtained can be expected to yield important insights into reaction chemistry and/or secondary controls (roles of heat and/or volatile product movements, diffusion, etc.) and thus mechanisms.

Comparative kinetic studies, under complementary alternative and varied conditions, preferably including some low pressure measurements, representing appreciable changes in the procedural variables, can usually be undertaken for any reaction in which there is any possibility that reversibility or self-heating/cooling may influence reaction rate. Interpretation of observations may then proceed with reference to all factors found to change kinetic characteristics and rates are identified as being (totally, or at least partly) controlled by secondary parameters. For example, the flow of inert gas through a reaction vessel may be insufficient to remove completely the participation of intrapore equilibration by a gaseous product which then influences the apparent overall rate [36]. Ravindran et al. [57] have shown that the isothermal kinetics of $CuSO_4{\cdot}H_2O$ dehydration at about 500 K were consistent with a diffusion control model whereas non-isothermal reactions were identified as a nucleation and growth process. These variations of apparent behaviour demonstrate sensitivity of kinetics to reaction conditions.

The most reliable method for determination of the rate of the 'forward' reaction in a reversible dissociation must be through dedicated, specifically designed experiments [36–39]. Similarly, careful high vacuum kinetic studies may be required to assess the value, and to determine the reliability, of methods advocated [55] for the correction of kinetic data for a reversible reaction, in the presence of the volatile product (e.g., [58], to remove the influence of CO_2 present from rate control in calcite decomposition). (It seems to me that there are considerable uncertainties in devising a method for the rate determination of an interface process that occurs *behind* a zone in which there is gas–solid equilibration of the type described in [58]. Features of the rate of initial product release, at an active interface, are likely to be modified by the presence of any significant amount of gaseous product within the zone before its detection. The rate measured will then be dominated by the equilibrium displacement process. I suggest that the absolute rate of product formation at the reaction site requires its *direct* measurement, in the demonstrated absence of all concurrent or consecutive rate processes. Confirmation of the validity of any correction method ultimately depends on a knowledge of the rate of the uninhibited 'forward' reaction which, presumably, must be reliably measured experimentally: apparently this is only possible by high vacuum experiments.)

It could be useful to assume, at least initially, and until demonstrated otherwise for each individual substance, that published kinetic results for any reversible, endothermic dissociation are empirical rather than fundamental. The confirmation that such rate measurements are reliable, and refer to the chemically controlling step, must precede all attempts to interpret kinetic data through formulation of detailed reaction mechanisms, to recognize the rate limiting step, or to identify the parameters that determine the absolute reactivity. Many kinetic results in the literature refer to reactions proceeding in locally changing, and incompletely characterized, conditions within an inhomogeneous reactant, though apparently this possibility remains widely unrecognized. Further work is required to establish how widespread are the effects mentioned above [35–47] and how (fundamentally) reliable are many of the published kinetic reports for thermal reactions.

5. Kinetic analysis: interpretation of rate measurements

5.1. Empirical and fundamental kinetic studies: the Arrhenius equation

Throughout chemistry, measurements of reaction kinetics are undertaken for two principal reasons, though sometimes rate observations can be useful in both contexts. *Empirical studies* are used to determine rates of chemical change for a specific purpose, under conditions relevant to an identified objective, such as to obtain data to use (for examples) in the design of a manufacturing process, to investigate a preparative method, to determine compound stability, including its slow degradation during storage ('shelf-life' of foodstuffs, drugs, explosives, etc.). If reaction conditions are incompletely characterized, sensitive to changes of procedural variables or are inhomogeneous within the reaction zone (etc.), the results are unsuitable for fundamental chemical purposes including theory development, unless proper allowances can be and are made for all secondary controls. There may also be further restrictions in the applications of empirical observations, perhaps due to research limitations from restricted budgets, classified programs and/or commercial confidentiality. *Fundamental studies*, with which the present article is almost exclusively concerned, are intended to contribute to scientific theory, through the ordered extension and development of chemistry generally. Work is directed towards formulating systematic theoretical explanations for chemical reactions, towards classifications of behaviour patterns amongst related reactions and towards providing foundations so that predictions can made, by scientific induction, for the properties of untested systems. In pursuit of these scientific objectives, kinetic studies are frequently directed to the formulation of reaction mechanisms and to the identification of those parameters which control reactivities. In fundamental research, rate data, and interpretational models derived therefrom, are of greatest value when applied to stoichiometrically characterized single reactions and where the measured data can be demonstrated to refer directly to a dominant and identified controlling process (after removal or quantitative allowance for secondary influences on rate, Section 4). (Dictionary definitions of science refer to ordered, systematic knowledge and to the identification of generality by induction from particular instances. The TKA literature exhibits little evidence of systematic order of content or coherence of contributions which are the precursors to generalizations leading to theoretical concepts and models.)

The present review discusses problems, mainly from recent TKA literature, which are inherent in the mechanistic interpretation of measured rate data, including reactions of solids. There are well-known similarities between some kinetic characteristics of crystolysis reactions and those for homogeneous reactions. These resemblances include the adequate fit of data to rate equations based on reaction order (concentration terms) and to the Arrhenius equation, which provides a widely, almost universally, acceptable representation of the variation of rate constants, k, with T [59]. However, while the application of the Arrhenius equation to solid state chemistry is generally accepted, its interpretive extensions, through use of the transition state theory models to represent crystolysis reactions, requires considerably greater justification and support than has yet been provided [29]. This shortcoming arises from the lack of detailed information concerning the nature of any rate determining steps that control reactions in solids, which are probably dissimilar from the gas collisional encounters and activated transition complex formation steps that are envisaged in the theory of homogeneous reactions [59]. Different, but related and equally pertinent, inherent uncertainties exist in the interpretation of kinetic data, for complex reactions of all types. Dedicated and specifically designed experimental measurements may be required to characterize each and every factor that contributes to the control, or to perceptibly influence the rate of formation of each product.

5.2. Aspects of kinetic analysis of rate data obtained by TKA measurements

Probably the most significant mechanistic concept in the theoretical development of solid state reaction kinetics was the (early) recognition [3,60] that chemical changes often occur preferentially at, or within, that thin, advancing zone that is the active interface. For many crystolysis reactions, the characteristic variations of rate, as the chemical change proceeds, are represented by kinetic equations based on geometric models [1–3]. The reaction rate is regarded as directly proportional to the area of reactant/product contact. Kinetic geometric interpretations, for many favourable reactions, have been supported by microscopic observations (see, however, [28, Section 6.1]). The difficult, and hitherto unresolved, problem now is how to characterize the nature and controlling parameters of the chemical steps occurring within these interfacial zones of locally enhanced reactivity.

A primary objective of the present review is to advocate a general reexamination of all possible mechanistic explanations of TKA data, which should now be profitably extended beyond kinetic analyses based exclusively on solid state models. Rate data interpretation also requires consideration of those chemical processes that are accompanied by melting, which may be complete or partial, local and temporary. Furthermore, the overall change may be achieved through more than a single step, and perhaps include the intervention of unstable, transitory intermediates. Increasing the accuracy of data interpretation by mathematical methods, the precision of fit to a kinetic model (a present preoccupation in some recent publications), is capable of achieving only slight improvements in the analysis and interpretation of kinetic measurements. Moreover, kinetic analyses alone may be of limited ultimate value if the 'correct' reaction model has not been included in the set of models comparatively considered. More difficult are identifications of all participating steps in complex reactions. Problems arise in the recognition, and characterization, of all rate controls that influence such chemical changes, whether these occur within an active, advancing interface or in a melt containing several active components, perhaps including transitory intermediates.

A most immediate, general problem in the recent TKA literature is the appearance of uncertainties in the determinations, the calculations, the interpretations and the significances of the magnitudes of Arrhenius parameters:

- *Determinations*. Reaction rates measured represent a chemically controlling step only in the absence of secondary influences (Section 4).
- *Calculations*. Changes in the apparent magnitude of E with the kinetic model used in the calculation are evidence of inconsistencies between current practices and the original concept of activation energy [59]. This problem appears to have resulted from modifications to the meanings, or implicit definitions (including units), of the kinetic terms A, E and k [61,62].
- *Interpretation and significance*. Without information about the structures and bonding interactions controlling the transformation of reactant into product, for crystolysis reactions, the value of E cannot be associated with any particular chemical step [63]. A comparable uncertainty in the significance of E may arise in homogeneous reactions (and also after reactant melting) where complex behaviour involves the participation of multiple (concurrent and/or consecutive) reactions and unidentified intermediates are involved. For many reactions of the types studied by TKA methods, much more information than is currently available, or is readily obtained, may be required to establish the chemical significance of the temperature coefficient of an overall reaction rate.

5.3. Kinetic analysis of rate data for crystolysis reactions

Kinetic analysis is most frequently undertaken to obtain a mathematical representation of rate (α, t, T) data, usually through the isothermal model, $g(\alpha) = kt$ [1], and from the temperature dependence of k the Arrhenius parameters, A and E, are calculated. The (α, t, T) measurements may be isothermal, from several constant temperature experiments, or from non-isothermal experiments using a range of different constant rates of temperature rise or during various programs of controlled temperature variations (e.g., constant $\mathrm{d}T/\mathrm{d}t$, or constant $\mathrm{d}\alpha/\mathrm{d}t$ (CRTA), etc). This use of TKA temperature programming methods has made outstanding contributions in the investigations of thermal reactions. However, it is now accepted that, to obtain meaningful kinetic conclusions, data must be based on several heating rates [64,65]: the former expectation that only a single non-isothermal experiment was necessary is now generally regarded as having been over-optimistic. (Nevertheless, articles reporting kinetic results using data measured for a single reaction continue to appear.) Most usually analyses of (α, t, T) data sets are completed using computer programs to identify the 'best fit' of observations to distinguish [66] the kinetic model most satisfactorily describing the reaction. Such identifications are often based on limited criteria, most frequently comparisons of the relative magnitudes of the correlation coefficients, r, for each of the kinetic models considered: the value approaching unity most closely is accepted as the preferred result.

Aspects of one general approach to TKA data interpretation are summarized in Scheme 1. The present discussions are intended to review both isothermal and programmed temperature measurements, for which the theory has been given in [1–4]. Prior to the development of TA, predominantly isothermal data had been largely recorded and kinetically analysed by relatively laborious, slow manual methods. Results were interpreted through solid state reaction models [1–4], often with support from microscopic, textural observations [3]. Subsequently, the massively increased computer capabilities and capacities have enabled progressively larger numbers of measurements of greater accuracy for a wider range of reactants to be collected, stored and rates analysed to determine kinetic characteristics.

The practices now most widely accepted and applied appear, however, to have had (at least) two unintentional consequences, which have been insufficiently recognized. Together these have, nonetheless, contributed to the inhibition of theory development and probably limited the value of some research. First, the uncritical acceptance of conclusions based on kinetic analyses by computer programs operating within the apparatus, solely directed towards identifying the ‘best fit’ within only a limited range of possibilities and based on inadequate comparative criteria (e.g., the magnitude of r only), is restricting. This, taken with the vagueness in the meanings attached to the terms A, E and other parameters [61,62], introduces uncertainties into the reliability, the value and the chemical significance of many reported conclusions. Second, increasing dependence on the facile and efficient methods available to undertake the (apparently [61,62]) sophisticated mathematical analyses has resulted in the preferred, even exclusive, use of rate studies to elucidate reaction mechanisms. This appears to have discouraged the former interest in seeking supporting evidence that might be obtained from alternative (non-kinetic) complementary and confirmatory experiments. The diminished input from visual, usually microscopic, inspections means that less is known about the textural changes, including interface advances or melting, that occur on heating the ever widening range of reactants now being studied by TA methods. This leaves uncritically examined and unchallenged many of the conclusions that have been based mainly, or totally, on kinetic observations, which now appear as almost the sole experimental evidence obtained in many TKA investigations. The motivation for this review is to confront some of the unpalatable consequences of this uneven experimental development, which has expanded mathematical methods of kinetic interpretation at the expense of theory and of all alternative techniques. My hope is that recognition of the shortcomings of these present practices will rejuvenate interest in extending the experimental base for a subject that currently seems to lack cohesion and should benefit from enhancement of observational input (Section 5.12).

5.4. *Determination of α values for use in kinetic analysis*

The following criteria must be satisfied if TKA data sets (α, t, T) are to elucidate reaction mechanisms successfully. The ideal objective is to characterize all the chemical steps and controls involved in the conversion of reactants into products. This includes identification of the chemical factors that determine absolute reactivity, the parameters that govern the dominant bond redistribution steps and regulate the mechanism. As presented, the criteria listed below might appear obvious: possibly most of these comments will, in principle, be acceptable to most readers, although some of the details will, perhaps, remain debatable. However, examination of the literature shows that, in practice, these basic and indispensable necessities for meaningful kinetic studies have not been fulfilled, or even addressed, in many investigations. Obviously, if the original data are unreliable, and/or are incorrectly analysed, the conclusions derived therefrom must be regarded as correspondingly untrustworthy. For completeness, all the factors identified as containing possible problems are mentioned here, though some are discussed in greater detail elsewhere in this review:

1. *Reaction stoichiometry*. Kinetic measurements exhibit their greatest value for the elucidation of reaction mechanisms and chemical controls when these refer to a single, simple rate process of completely established stoichiometry. Additional information, extending the usual term meaning, may contribute to providing a comprehensive description of kinetic data, including identifications of intermediates, diffusing species, specific crystal (topotactic) relationships, melting, etc.
2. *Definition of fractional reaction, α (the fraction of the reactant present that has undergone the identified chemical change in time t, at temperature T)*. The magnitude of α [1–4] is frequently calculated, assuming direct proportionality, from the measured changes of the (often) physical parameter measured during the TKA experiments. This assumed direct proportionality is usually acceptable for many simple reactions, e.g., the mass loss resulting from CO_2 evolution during simple decompositions such as $CaCO_3$ or $MgCO_3$, the release of water in some dehydrations (without hydrolysis), etc. However, appearances can, on occasion, be deceptive and some evidently simple reactions have been subsequently shown to be complex, e.g. [16,17]. Generally, a direct proportionality is not necessarily acceptable for more complicated reactions, where two or more products are given, perhaps having different TA detection sensitivities. For example, in a study of the decomposition of NH_4ClO_4, it was explicitly demonstrated [69] that the evolution of permanent gases (N_2 and O_2) quantitatively measured the extent of reaction, α, though these products constituted only a proportion of the total gases evolved. Where primary products undergo rapid and quantitative chemical changes, the secondary products may be used to measure α. However,

SCHEME. Kinetic Analysis: Interpretation of TKA Data for Crystolysis Reactions
(A Single Rate Process of Already Established Stoichiometry)

KINETIC DATA Isothermal (α, t) for several values of T
or Several programmed T for constant (dT/dt) or ($d\alpha/dt$)
↓ *or* Other temperature programs (several varied experiments)

↓		(α,t) CURVE SHAPE	INTERPRETATION
RATE EQUATION	Reaction geometry	*SIGMOID* (An, Bn, Pn)•	*Nucleation,* *Interface Advance* *(Nucleation + Growth)*
		DECELERATORY (Rn)•	*Interface Advance* *(Contracting Geometry)*
		STRONGLY DECELERATORY (Dn)•	*Diffusion control* *(+Interface Advance)*
	Reaction order	*DECELERATORY* (Fn)•	*(i) Homogeneous* *(ii) Various*: see [1-4]
	Other	*VARIOUS*	*(i) Melting (total, local)* *(ii) Overlapping Processes* *(iii) Homogeneous, Complex* *(iv) Intermediate Formed*
REACTION RATE and/or 'BEST FIT' KINETIC MODEL ↓	Either or both VARY WITH REACTION CONDITIONS and PROCEDURAL VARIABLES		*Complex Reaction Contols: Possible Contributions from Reversibility and/or Heat Transport*
TEMPERATURE COEFFICIENT OF REACTION RATE	*ACTIVATION ENERGY FREQUENCY FACTOR*		*Relate to Chemical or Controlling Step (Theory from Homogeneous Kinetics)*

• Kinetic model, equation designatory letters listed in [1], n is usually 1, 2, 3 or 4.

Scheme 1. Kinetic analysis: interpretation of TKA data for crystolysis reactions (a single rate process of already established stoichiometry). Notes on scheme: (1) Mechanistic interpretation of rate data usually involves two steps in analyses of the (α, t, T) measurements: the *kinetic model* and the *chemistry* of the changes occurring. The (usual) first step is *identification of the rate equation*, which is the isothermal yield–time mathematical relationship, together with the *Arrhenius parameters*. Many TKA studies do not proceed beyond this stage. It may be possible, however, to deduce information of mechanistic significance from the kinetic model, which usually distinguishes chemical changes taking place (i) at an advancing interface (following nucleation, which may be rare and difficult or rapid and facile), (ii) with diffusion control, (iii) in a homogeneous phase, with some melting and (iv) more complex behaviour, including concurrent or consecutive rate processes where there may be overlap, a changing contribution from melting (local, temporary or progressive), participation by intermediates and/or all other possible mechanistic routes to product formation. The second step, *characterizing the participating chemical changes*, is much more difficult and involves consideration of evidence of all the types that may be capable of revealing the intermediates and structures that could contribute to the chemical changes proceeding at the interface, or within any other identified reaction zone. For example, crystallographic evidence can reveal the occurrence of topotactic reactions [1], chemical comparisons can be used to identify possible heterogeneous catalytic-type processes at the surface of an active product and chemical analyses may be required to characterize species contributing to (homogeneous) reactions in a melt. (2) If the kinetic model is identified solely from the 'best fit' of data, through comparisons based on a selected, but restricted, list of candidate equations, there is always the possibility that a 'better fit' might be available from a further equation, one that had not been included in the set for comparative analyses. This method will not recognize the possibility of changes of the rate controlling factors, and thus in the kinetic model, as reaction progresses (e.g., completion of nucleation during a reaction [67]) or different mechanisms in different temperature ranges (some examples for dehydrations are given in [28, Section 6.3]), etc. Complex reaction mechanisms, including intermediate formation, transient melting, etc., may not be recognized unless additional observations, suitable for their specific detection, are used. There is also the problem of discriminating between two alternative equations which provide apparently equally 'excellent fits' (see [68]). This is particularly evident when comparing correlation coefficients (r) as the only distinguishing criterion; more detailed information may be required to enable the distinction to be made and to confirm any conclusion. In some published reports, e.g. [68], alternative kinetic models were found to be almost equally applicable to the same rate data, identifying, for the reaction, different controlling processes, representing different classes of mechanisms, in this example: interface advance and diffusion control.

this is only reliable if the composition of these products remains constant throughout the reaction and does not change with product pressure (as may occur in some equilibria), α, t or T (particularly in non-isothermal studies). Where there are concurrent or consecutive overlapping rate processes, care must be taken to identify parameters that provide a reliable measure of the extent of each particular chemical change which is of interest. Complex reactions include, e.g., the decompositions of some oxalates [19], dehydrations that result in some hydrolysis, and other types of complex behaviour. Moreover, few of the many TKA studies based on enthalpy changes (DTA, DSC) provide confirmation that the amount of heat evolved/absorbed is directly proportional to the extent of the chemical change that is intended to be measured (α). It is always necessary to consider the possibility that, during such reactions, there may be perceptible contributions to the measured enthalpy from melting, recrystallization or sintering. It has been shown [70] that experimental conditions and sample emissivity can influence DSC data. Where there is any doubt, and before undertaking the kinetic analysis, the precise relationship between the measured TA response parameter and the extent of the target reaction must be established to enable values of α to be correctly defined and measured. Nevertheless, these sources of uncertainty, together with any consequent unreliability of α, are rarely discussed in kinetic studies.

3. *Reproducibility*. Representative, identically repeated, observations to determine the accuracy with which TKA data can be replicated between successive similar experiments should be an indispensable feature of every kinetic study. However, most of the recent TKA studies omit all reference to such a tests, indeed the results in many such presentations appear to be based on a single experiment (because there is no mention of any duplicated observations). Reproducibility tests are essential to enable the accuracy of calculated magnitudes of A and E to be stated. Nevertheless, in some published articles that omit references to any demonstration of reproducibility or discussions of accuracy, Arrhenius parameters are reported to an unrealistic apparent precision (5 or more significant figures) without mention of error ranges. Investigations of the possible kinetic consequences of systematic variations of reaction conditions or of procedural variables are rarely mentioned. These are particularly important to confirm the reliability of rate measurements for reversible and endothermic reactions (Section 4 and points 4 and 5 below).
4. *Single rate process only*. Kinetic characteristics ($g(\alpha) = kt$, the kinetic model and the values of A and E) may be significant to chemical theory only when these describe an identified, individual reaction, a single rate process. Unless system-specific analytical methods, capable of distinguishing individual contributions from two or more processes, are used, rate analysis cannot be successful in measuring the yields from each participating reaction in composite measurements containing contributions from two or more substantially overlapping reactions. Product yields from consecutive or concurrent, parallel reactions and also from any initial, rapid product evolution (perhaps a limited surface or precursor processes [71]), should be separated and data analysed individually, which can be difficult, e.g. [16,17,25], or alternatively treated by methods suitable for complex reactions [72]. Kinetic data do not 'average', each reaction is individual, as are its specific rate parameters, A, E, etc.
5. *The 'back reaction' does not contribute in reversible rate processes*. If kinetic measurements are intended to identify a controlling chemical step, it is essential that

---

Complementary or confirmatory measurements may be valuable, even indispensable, for the interpretation of TKA rate data. (3) The TKA literature contains numerous examples of kinetic analyses which report an 'excellent fit' of data (even to two or more alternative kinetic models) demonstrated by r values that approach unity very closely, i.e., 'better than' 0.999. Other articles describe mathematical aspects of the test procedures used to compare data with theoretical expectation. However, despite the considerable efforts directed towards data fitting, much less interest has been concerned with the chemical foundations and assumptions in the models of interest. The comments below draw attention to possible limitations, or inherent weaknesses in some assumptions that underpin the theory of solid state reaction kinetics, most of which is uncritically accepted and applied throughout TKA studies. The following aspects merit discussion: (i) The relationships between reaction geometry and those kinetic models that are most frequently used for analysis of TKA data sometimes involve approximations [3]. Moreover, some kinetic models are represented by more than a single pattern of interface generation and development [1,2] so that rate analysis does not necessarily give a unique geometric result [2, pp. 84–86]. (ii) Rate equations do not invariably correlate directly with geometric evidence obtained for the same reaction by microscopic observations. Inconsistencies found for some dehydrations are described in [28, Section 6.1]. This has not been explained and raises problems about the relationship between kinetic models and the chemical/geometric processes which they are used to represent. (iii) Another aspect of data fitting is the necessity to confirm that the parameter used to measure reaction rate is directly related (through α) to the chemical change under investigation. Under (ii) above, for example, one possibility is that water loss may precede initiation of the kinetic dehydration measurements [28]. In many other systems of interest, uncritically accepted assumptions are made about the relationship between the measured TA response (heat absorbed, weight loss, etc.) and the particular chemical change that it is assumed to represent. (iv) A principal result from many TKA studies is that the reaction of interest is characterized, through rate measurements, as an interface process (nucleation and growth, contracting envelope, etc.). It should, however, be remembered that the formulae used in these analyses were themselves originally developed from geometric observations of partly reacted crystals. Consequently, it appears that a simpler, even a more direct and reliable, approach to characterization of reaction geometry would be to examine partly reacted material microscopically and, if nuclei can be observed, then this conclusion is at least as trustworthy as the indirect inferential method. Throughout most of chemistry it is impossible to 'see' reactions, or their textural consequences, so the obvious advantages of direct visible (microscopic) evidence should be exploited to its maximum advantage, but, inexplicably, this approach is often omitted from studies of solid state chemistry.

data refer to the (maximum rate) ‘forward’ process only. Contributions from any reverse step must be removed (Section 4) otherwise rate data may be empirical.

6. *Self-cooling/heating does not contribute*. Deviation of reactant temperature within the zone of chemical change, due to the reaction enthalpy (Section 4), will similarly yield empirical rate data for which the kinetic results are characteristic of only the specific conditions that apply. The significance of this effect can be determined through rate variations resulting from procedural variable changes [35,43].
7. *Transitory intermediate participation and/or melting*. When TKA methods are used to study a hitherto unfamiliar solid reactant, the design of experiments should include positive investigation of the possibility that the overall change may be complex. A reaction is not necessarily completed by a single step but (at least some) may proceed in concurrent and/or consecutive overlapping processes, with or without the participation of melting and/or the intervention of unstable, transitory (but essential) intermediates. Traditionally, complicated reaction models have not been considered in solid state kinetics, but are possible routes for some decompositions [16].
8. *Reactant container participation*. Although rarely mentioned, there is sometimes the possibility that a sample container may participate in thermal reactions and thus contribute to the measured TKA responses. This may arise either by direct interactions with the reactant or product, or by catalysing secondary chemical changes. Reactive products, e.g. alkaline oxides, may react at high temperature with the glass or silica walls of a container. A transition metal reactant vessel may become corroded by products. An active noble metal container may be capable of promoting alternative chemical changes in the reactant and/or promote (catalyse) the reaction being studied [73].

5.4.1. Comment

The above discussion emphasizes that measured rate characteristics may be determined by the conditions existing within the sample reaction zone. To elucidate behaviour fully, it is necessary to consider the possible participation of intrasample changes, including chemical, structural and textural modifications that accompany or follow reaction. These are an indispensable features of any full mechanistic description of a crystolysis reaction and their detection often requires observations complementing the kinetic studies. It is, however, the contributions from extrasample conditions that must be addressed in order to obtain rate data that are not modified by secondary controls. For some reactions the interface step may be inaccessible to direct experimental measurement, and for others minor contributions may influence apparent behaviour. It has been shown already [36–39], however, that careful design of reaction conditions can reduce the contributions from some secondary controls. These results must be accepted as providing a preferred approach to crystolysis kinetics and must replace the practice of accepting (implicitly) that any and all rate measurements are capable of yielding kinetic conclusions that have identifiable chemical significance.

The CRTA method (Section 4.5) has been successfully applied to the precise investigation of reaction rates in solids [52–56]. Advantages include the use of low pressure which, for some systems, can be below that required to eliminate the reverse process [37]. The method is capable of making comparative rate measurements to determine quantitatively any dependence of rate on product gas pressure. Slow reaction rates can be used to minimize any contribution from self-cooling. The ‘temperature jump’ technique [56] enables changes of E with α to be investigated under conditions that can be shown to contain no, or very little, dependence of rate on secondary controls.

5.5. Kinetic analysis: theoretical background

5.5.1. Definition of rate constant and magnitudes of Arrhenius parameters

The use of fractional reaction, α, in kinetic models [1] replaces the concentration terms widely employed in homogeneous kinetics to express the amount of unchanged reactant remaining or of product yields. However, α cannot be regarded as a truly ‘reduced’ (dimensionless) kinetic term because the particle sizes of solid reactants usually influence the absolute reaction rate. A dimension term, the crystal edge length, is [1] included in some geometric expressions (e.g., the contracting envelope equations) but this term is less frequently remembered for other interface advance processes. Volumes of participating phases are included in the formal derivation of solid state kinetic models in [74] and aspects of crystal dimensions in kinetic comparisons are discussed in [75, pp. 171–172]. (Reactant particle sizes exert a control on rate characteristics, and are mentioned for completeness only; this aspect of kinetics is not examined further here.)

Homogeneous rate constants always include the unit reciprocal time, whereas kinetic expressions of the set applicable to solid state rate process allow the possibilities that:

$$g(\alpha) = k^n t^n \quad \text{(for which the units of } k \text{ are (time)}^{-1})$$

or

$$g(\alpha) = Kt^n \quad \text{(for which the units of } K \text{ are (time)}^{-n})$$

These alternative definitions may appear to be only a relatively minor discrepancy but the modification results [1] in considerable changes of the calculated *apparent* magnitudes of both $\ln A$ and E, by the factor $n\times$. Fatemi et al. [76] show, for the Avrami–Erofeev equations, $-\ln(1-\alpha) = Kt^n$ and $-\ln(1-\alpha) = k^n t^n$ that $A_K = A^n$ and $E_K = nE$. The calculation of Arrhenius parameters directly from α–t data [77], using a ‘model-free’ method, may help to avoid some of these problems. Consistency of kinetic analysis methods would be improved, and a source of confusion removed, if it was conventionally accepted that k values are always expressed with units $(\mathrm{time})^{-1}$.

5.5.2. Arrhenius parameters

The calculation of (apparent) magnitudes of A and E is obviously regarded as an important objective in recent TKA research because publications reporting values determined for these terms constitute a considerable proportion of this literature. There are, however, unsatisfactory and intractable features, common to a wide range of these articles, in the methods for determining [62] and for interpreting the significances [61] of both Arrhenius parameters. A discussion of the theoretical foundations for E, including the applicability of the Arrhenius equation to reactions of solids, has already been given [29] (though this analysis represents less progress towards understanding the significance of A). These explanations originated through model development for homogeneous rate processes and the theory was later applied to heterogeneous reactions, for which the foundations are less secure. In a reaction proceeding through the constant advance rate of an unchanging interface, the magnitudes of E and A are expected to remain constant, characteristic of the specific reaction involved. The same rate determining controls [59] are identified with the same magnitude of E. In TKA, in contrast, it has become acceptable that E values may vary widely with the kinetic model used in the data analysis, e.g. [7–9,61,62,78,79]: this problem is discussed further below.

5.5.3. Approximate formulae in kinetic analysis

Important advances in kinetic analyses, particularly for non-isothermal measurements, were made from about the mid-1950s onwards by the introduction of simplifications to the calculations of kinetic parameters using approximate formulae. Simplifications were necessary because it is not possible, in general, to integrate the three functions, which contain the three variables, α, t and T:

$$g(\alpha) = kt \quad \text{or} \quad f(\alpha) = k^{-1}(\mathrm{d}\alpha/\mathrm{d}t) \quad \text{(kinetic model)}$$

$$k = A \exp\left(\frac{-E}{RT}\right) \quad \text{(Arrhenius equation)}$$

$$T = T_0 + \beta t \quad \text{(at constant heating rate from } T_0\text{; other programs are used)}$$

The several, alternative and widely used, calculation routines are based on differential or on integral expressions that incorporate these three essential components. Most have since been associated with the names of their original proposers [1,2,4]. In particular, these enable the E values to be calculated, but some also give A and the kinetic model. Several of the earliest formulae rapidly became well-established and continue to be widely used. To simplify mathematical treatment of the intractable exponential term (before the general availability of computers), an approximation, the ‘temperature integral’, $p(E/RT)$, was introduced, for which a variety of functions have been proposed [1]. In a recent article, entitled “The ‘Temperature Integral’—Its use and abuse”, Flynn [80] provided a quantitative survey of the applications and inherent shortcomings of this approach to kinetic analysis and points to the unreliability of many published results based on these methods. It is worth quoting the final sentence of his article: “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”. This sentiment is completely in accordance with the views expressed throughout this article. Indeed, it is now suggested that this recommendation should be extended beyond its specific application to the temperature integral to include all aspects of kinetic analyses, where other approximations are equally capable of adversely influencing the reliability of calculations to unknown extents. Again quoting Flynn [80]: “... as scientists, we should strive to calculate kinetic parameters as precisely as we are able to”.

Throughout the substantial literature devoted to non-isothermal kinetic analyses, authors usually provide neither justification nor explanation of the reasons for their preferred choice of the (one or more [81]) expression(s) that they have used for their data analysis. These are (often apparently arbitrarily) selected from the many approximate forms conventionally accepted [1,2,4]. Each of these can always be quoted, and regarded as suitable and reasonable, because every one of the established favourites boasts a long citation list. This is not, however, satisfactory because there are few [82,83] authoritative comparative and critical reviews of the strengths and weaknesses of the various alternative approximate mathematical procedures enshrined in those various classical expressions that have now served generations of thermal analysts. Criteria identifying which equation is most suitable (justified by stated reasons) for the analysis of particular types of rate process are rarely discussed [82,83]. Moreover, it is surprising that the recent advances of computer capabilities have not lead to more precise methods of kinetic analyses [80] than the present continued and uncritical use of those simplified calculation methods that were developed, decades ago, for use at a time of much less computation capacity and application of fewer sophisticated mathematical techniques. This relative absence of critical comparative surveys, contrasting the discriminatory capacities of the various non-isothermal methods of kinetic analysis, differs from the situation in isothermal kinetics where the distinguishing capabilities of the alternative isothermal kinetic models have been described [66]. Knowledge of the comparative shapes of these rate equations can be used to facilitate identification of the best fit to the α-ranges considered. This approach [66] to enhancing distinguishability in kinetic analysis has been discussed, but comparisons of the relative capabilities of the approximate non-isothermal equations used are rare. Nevertheless, the literature contains numerous examples of apparently outstanding precisions of kinetic fit, for example, values of r up to 0.99999 are given in [68], see also [62].

5.5.4. Comment

TKA would benefit considerably from further critical and comparative appraisals of the accuracy and reliability of the analytical methods applied to thermal reactions, and the conclusions deduced therefrom, particularly under non-isothermal conditions [82,83]. An important consideration for the future is whether the conventionally accepted set of approximate equations, still widely used for the kinetic analyses of non-isothermal data [1,2,4], should maintain their preeminence indefinitely. When first introduced, these methods were unquestionably the best available and, during the precomputer era, enabled kinetic interpretations to be completed within a reasonable time and with the (then) best achievable accuracy. Nevertheless, there has long been evidence (Section 5.9) that results from kinetic calculations using alternative but generally accepted methods (e.g. [7–9,61,62,81]) do not agree particularly well, for reasons that do not seem to have been investigated with any rigor. Furthermore, the merits of developing advanced, more sophisticated, replacement (computer) mathematical procedures do not appear to have been seriously considered. This might be regarded as the expedient maintenance, by default, of a theory that has stagnated [84]. Taking the lead advocated by Flynn [80], the shortcomings of older, approximate methods can, and should, be upgraded now through the generally available computing facilities that can calculate results "which are as precise as we wish to make them". There is an overdue necessity for a new generation of equations and calculation methods that are capable of accurately analysing non-isothermal (and, perhaps also, isothermal) kinetic measurements. This should be an opportunity for mathematicians and computer programmers, stimulated by a demand (at present unaccountably latent), to provide upgraded methods for interpreting the increasingly precise data that can now be collected by automated, accurate equipment. Statistical analysis of kinetic results obtained from imprecise calculations, by approximated, restricted and now outmoded analytical methods [80] should no longer be tolerated.

5.5.5. Interface reaction rate theory

Attempts have been made to provide a theoretical expression for the rates of interface reactions. The most significant early approach was by the Polanyi–Wigner (PW) equation [85], which was based on a molecular evaporation type model [86]. The PW treatment was applied [3] to some crystal dissociations at a time that the transition state reaction rate theory [87] was being successfully used in consideration of homogeneous rate processes and this was regarded as its (logical) extension to reactions of solids. In some early discussions, examples of crystolysis reactions that deviated from the PW predictions were regarded as 'anomalous' or 'abnormal' [3,63]. However, the optimistic hopes with which the PW theory was initially greeted have remained ultimately unrealized for good reasons.

1. *Magnitudes of A and E*. It has not been found possible to correlate calculated magnitudes of E for crystolysis reactions with enthalpies of specific interatomic links, bonds ruptured in an identified rate controlling step [63]. For crystolysis reactions little is known about interface conditions at a molecular level and the transition state theoretical concept of rate control by a single bond rupture step model may (or may not) be applicable. Evidence demonstrably capable of resolving the fundamental problems of interface rate controls is difficult to obtain. While some (estimated) values of A are close to bond vibration frequencies (usually regarded as from 10^{12} to 10^{13} Hz), there is a greater overall spread of values than can be reconciled with the theory [63]. Agreement of the available data with the expectations of the PW theory is generally unsatisfactory and it is now mentioned with ever decreasing frequency.
2. *Reliability of kinetic measurements*. The PW model was first applied mainly to endothermic, reversible rate processes (dehydrations, carbonate dissociations [3]) for which the measured magnitudes of the Arrhenius parameters are sensitively influenced by the procedural variables. Apparent values of A and E vary with reaction conditions, so that it is essential to use kinetic data that has been confirmed as representing only the rate of the 'forward' decomposition (e.g. [36,38]). In considering calcite dissociation through activated complex theory, Shannon [88] apparently takes E as 166 kJ mol^{-1}, which is significantly less than 205 kJ mol^{-1} found by Beruto and Searcy for this reaction in vacuum [36,37,89]. The value of A determined for the dehydration of nickel oxalate dihydrate in a good vacuum "does not agree with that predicted by the PW equation" [38]. Testing the validity of the PW equation must be based on demonstrably reliable Arrhenius parameters. At present, this is not generally possible because relatively few reports include the necessary tests for data reproducibility (Section 4).

5.5.6. Little is known about factors controlling the chemistry of interface crystolysis reactions

From direct observations we know remarkably little about the conditions and structures of the active interfacial zone within which crystolysis reactions proceed and the factors that participate in controlling the bond redistribution processes involved in these chemical changes. Reaction models, such as the transition state theory, that focus attention on a specific bond rupture step, can be usefully applied only when the linkage undergoing modification has been (or might be) positively identified.

Progress in understanding the factors that control interface reactions is severely inhibited by the absence of knowledge of two types. First, the assumption, borrowed from theory developed for homogeneous rate processes, that a single bond rupture step controls the rate of the overall chemical reaction, is not necessarily applicable within the condensed, largely immobilized and interbonded atomic array that appears to constitute the reactant/product chemically active contact. The coordinated interactions of several (largely immobilized) atoms and/or their links may be involved in any chemical change. This contrasts with the brief, energetic bimolecular collision, in a gas or in a solution, identified as leading (directly or subsequently) to activation which may result in reaction. Within active interfacial reaction zones, the closely juxtaposed constituents may undergo countless successive vibrational interactions. Thus the potential reaction event, contact between colliding or energetically interacting molecules in free flight, assumptions on which homogeneous kinetic theory is based, cannot be recognized. The effective molecularity of reaction, within the crowded interacting array, may exceed 2 (unlike the large majority of collisions) because energetic encounters occur between all neighbours located in a condensed phase. Immobilization in a lattice array introduces a massive ‘cage effect’ (repeated collisions believed to occur between neighbouring molecules, retained in immediate proximity in solution) which contrasts with the brief encounters that characterize molecules in free flight. Second, presently we cannot identify with certainty, for most intracrystalline chemical changes, the reaction precursor species and have no model for interactions of between participants for chemical changes that occur within an interface between two, at least semi-ordered, condensed phases.

This situation contrasts fundamentally with the representation of homogeneous reactions by transition state theory. During such rate processes, it is assumed that the molecular structures of the reacting precursors are retained during the (very brief) lifetime of the activated (transition state) species where the feature of interest is reorganization of only one unstable linkage. An essential difference between homogeneous and heterogeneous representations of the absolute reaction rate theory is that for the former we can make plausible assumptions about all bonds in the unstable (very short-lived) intermediate, the activated complex. These links are believed to resemble, even be identical with, those of the precursors. We then focus interest on the individual interatomic bond that changes. At present, for all solid state (interface) reactions, we have no knowledge of how the bond undergoing modification (even if it could be identified) might be influenced by its environment and whichever stereochemical constraints apply within the short range electronic interactions. Perhaps further effects may be felt through longer range influences from the band and defect structures of the crystals involved. Additionally, and again contrasting with homogeneous rate processes, in the absence of detailed knowledge of atomic structures throughout the active interfacial reaction zone, we have no measure of the concentrations of active precursors to chemical change [89]. The area of the reactant/product contact interface is not accessible and susceptible to measurement: there may be a ‘roughness factor’ influencing the number of reaction precursors which cannot easily be estimated. The reactive contact zone may be a single, or several, molecules thick, so that the effective ‘concentration’ term that is incorporated into the frequency factor cannot be directly measured. Also, the energy distribution function within the condensed phase assemblage of precursors to reaction is different from that (Maxwell–Boltzmann [87]) for gas molecules in free flight [90]. A theoretical explanation for the applicability of the Arrhenius equation to solid state rate processes has been given [29]. This appraisal of the present state of our knowledge of interface structures and reaction chemistry leads us to conclude that the PW reaction model cannot be usefully applied to interpret interface mechanisms and, indeed, its use now appears to be declining.

The different approach, recently developed and advocated by L’vov [31], identifies overall rate control as an initial reactant evaporation step, and this offers an alternative and simplifying interpretation of interface chemistry, eliminating some of the problems and uncertainties mentioned above. The applicability of this model and its potential value in describing crystolysis reactions has yet to be tested comprehensively by those seriously interested in advancing the fundamental theory of crystolysis reactions.

5.5.7. *Compensation effect*

CE is the interdependence of apparent magnitudes of Arrhenius parameters, for a set of related rate processes, expressed by (Section 4.3):

$$\ln A = bE + c \tag{1}$$

CEs are found within sets of Arrhenius parameters measured for groups of different but related, reactions (Type 1 CE [9]), also for sets of rate data for the same reaction proceeding under different conditions (Type 2 CE) and for alternative calculations based on a single set of original kinetic data (Type 3 CE). For any such group of reactions, that exhibits a CE, there exists an *isokinetic temperature* ($T_i = (Rb)^{-1}$ and $c = \ln k_i$) at which all the individual data sets that comprise the CE are characterized by identical values of the rate constants, k_i [46]. When a Type 2 CE applies to data for the same reaction under different experimental conditions, e.g., decomposition of calcite [47], these comparable measurements are usually obtained within a relatively restricted temperature interval: the (same) reactant must exhibit a consistent level of reactivity, and this approximates to isokinetic behaviour. The variable effects of self-cooling and/or of reversibility, which are a principal cause of the large changes in temperature dependence of k between the individual sets of measured rates for the same reaction, is the reason for the often large variations in A and E values. The inhomogeneities in mass movements of the volatile product, carbon dioxide, and heat transfer [43] result in relatively large influences by the secondary controls, leading to changes in the variations of k with T for individual reactions. However, the same level of overall reactivity results in a CE through the similar (isokinetic) k_i values for the single reactant. Consequently, calculated apparent and condition-dependent values of $\ln A$ and E must be regarded as empirical.

No explanation has yet been generally agreed for the widespread occurrence of CE relationships, although many have been suggested [46,91]. CEs for reactions of many types, in addition to decompositions of solids, have alternatively been regarded as an artefact arising from calculation methods or simply as an enigmatic, hitherto inexplicable, phenomenon. In the absence of any explanatory model, the CE gives no insights into reaction controls or mechanisms, in contrast with the Arrhenius equation, for which the A and E relationship is based on a theoretical foundation [59].

Similar ranges of reaction rates, measured within almost constant temperature intervals, require (for mathematical reasons [46]) that there must be compensation within the sets of calculated $\ln A$ and E magnitudes. Several reported instances of CEs can be explained through the approximately isokinetic behaviour within such data sets: three examples are as follows. First, the projects [7–9], undertaken to determine the degree of agreement achieved by different workers participating in two comparative kinetic studies, reported extended ranges of magnitudes of apparent Arrhenius parameters, for each reaction set considered. Each showed a (Type 3 [9]) CE which can be ascribed to differences in the calculation methods applied to the indisputably isokinetic character of the original rate data. Second, TKA studies of calcite decomposition, under a variety of experimental conditions but within similar temperature intervals (approximately isokinetic behaviour), showed that the rate of reactant breakdown is sensitive to the procedural variables and the data fit a Type 2 CE [44–47]. Third, many reports, e.g. [62,78,79], have calculated widely different values of A and E from single sets of TKA data sets using different kinetic models, these exhibit a Type 3 CE. These three representative examples, from the very many available, provide indisputable evidence that the present approach to kinetic analysis does not lead to consistent theoretical conclusions (i.e., constant kinetic parameters). Consequently, the appearances of CEs in diverse sets of comparable groups of rate data should now be accepted as providing evidence of shortcomings in the kinetic studies and/or the computational programs, which now require urgent and critical scrutiny. The detection of a CE should no longer be reported as an (apparently or implied) ‘interesting’ kinetic result but recognized as a demonstration of serious inadequacies in the experimental and/or computational methods used for the data collection and interpretation.

The present, currently unresolved, problem in solid state kinetic investigations, including TKA methods and studies, is to obtain reaction rate measurements that are demonstrably characteristic of the controlling chemical reaction. The most reliable methods currently available appear to be through the dedicated experiments, hitherto made for relatively few systems, which used low pressures, slow reaction rates and (sometimes) small reactant masses [36–39]. The CRTA approach further develops these principles by ensuring that flows of heat and product removal are maintained close to a constant (usually very low) value throughout each experiment. The ‘temperature jump’ method [56] allows direct determination changes (if any) of E with α. Nevertheless, whatever experimental method is used, it is essential to interpret data through computation programs avoiding inconsistencies that incorrectly cause variations of apparent magnitudes of E with units of k and/or kinetic model [61,62].

Previous studies, see [61], report patterns of variation of E with α but these appear to be based on empirical data for which experimental conditions were not described and the absence of influences from secondary controls was not demonstrated. Variations of E during the progress of $CaCO_3$ dissociation have been reported without reference to the previous, careful low pressure kinetic study in which no such trend was discerned [36]. If the specialized active interface is constant, as generally accepted for $n + g$ reactions [1–3], then the temperature coefficient for interface advance is expected to be constant.

5.6. Kinetic analysis: fitting experimental rate data to kinetic models

The literature survey of procedures and practices used in kinetic analysis, undertaken for this review, is regarded as revealing substantial shortcomings in the ‘curve fitting’ computer techniques currently in use. Some conclusions, such as the variable and multivalue magnitudes of Arrhenius parameters obtained [61,62] from the same or similar data through the use of alternative kinetic models (previous paragraph), are regarded here as theoretically unacceptable and demonstrating inconsistencies within both measurement and calculation procedures. Consequently, and because ‘correct’ conclusions are unavailable for most (if not all) real systems of interest, such kinetic results cannot be uncritically accepted as suitable foundations for theory development. In the present discussion, kinetic analysis refers to the calculation programs employed to determine (at least) the ‘best fit’ kinetic model, $g(\alpha) = kt$, and the Arrhenius parameters (Scheme). Calculations of A and E are not readily, or meaningfully, separated and recognition of this reality complicates discussions of current problems. (The present author disagrees with Vyazovkin’s view [92] that the CE “. . . makes the pre-exponential factor a dependent and, therefore, an *inferior* parameter”. My italics.)

5.6.1. Sufficient accurate data must be obtained across the complete reaction

To perform an adequate kinetic analysis, the number and distribution of data points, the α-range encompassed and the accuracies of values measured must be sufficient to demonstrate conclusively the fit of (α, t, T) values to one (only) of the appropriate rate equations. The analysis must also be capable of distinguishing this fit from all other reasonable possibilities [66]. At present, agreed criteria by which the kinetic model is to be recognized are not available, or discussed. The (currently) preferred approach appears to be that the relatively 'best' correlation coefficient (r) provides the sole justification necessary to identify the 'best fit' kinetic model (often together with its Arrhenius parameter values [93]). Such kinetic analyses do not specify any minimum precision required for an acceptable fit. Moreover, the extent of the α-range across which the kinetic model fits is a feature of any reaction, arguably equally as important as identification of the kinetic model. Many recent publications do not include this important information which should always be determined and reported. Methods to obtain these important parameters (with criteria for their determinations) must surely be incorporated into the next generation of computer programs for TKA data interpretation.

5.6.2. *Sample variability*

Brown and Brown [94] have suggested that the absolute reactivities of different samples of the same solid reactant may vary due to the types, numbers and distributions of defects and imperfections in the crystals that constitute each individual reactant sample studied. The absolute reactivity of every individual crystal is, in effect, unique and consequently the kinetic characteristics measured are the resultant average of the somewhat different contributions made by particles possessing a range of slightly different absolute reactivities. Experimental measurements determining the magnitudes of such variations between different individual crystals do not appear to be available.

There is, however, an alternative view of the factors that determine crystal active interface reactivity. This regards the reactant/product contact as a dominant, complex and multiple imperfection, which, maintained during interface advance (nucleus growth), is insensitive to, and little influenced by, the presence of minor defects. Thus, the principal reaction, which occurs within this active zone and is responsible for virtually all the chemical change, remains (effectively) constant in all samples of a particular reactant. This assumption is implicitly accepted throughout much of the literature concerned with kinetic studies of crystolysis reactions [1–3] and represents constant interface reactivity during growth of established nuclei, see [95, Fig. 5]. Growth can occur only after successful nucleation which, in some solids, is a relatively rare event. Theory suggests that different numbers and distributions of the growth nuclei generated in different crystals may exert a large, even incommensurate, influence over the kinetic characteristics of the overall reaction. This latter view is supported by observations on the decomposition of irradiated silver malonate [5,96]. Previous exposure of this reactant to high energy radiation, γ-rays, significantly modified the kinetics of subsequent salt breakdown, ascribed to the introduction of crystal defects or of reactive radicals, identified as sites of potential nucleation. The observed increase in reactivity with predecomposition radiation dose is explained by an increase in number of active nuclei. It was concluded that the very small amount of reaction associated with nucleation (or even prenucleation phenomena) can have a profound, even disproportionate, effect on the shape of the subsequent α–t curve. The significant conclusion was [96] "the chemistry of the main reaction is unaltered by the pre-irradiation (because this pretreatment caused no perceptible change in reaction stoichiometry, kinetic characteristics or activation energy)".

The roles of specific defects in determining absolute solid state reactivity have not been established quantitatively for particular reactions but might be investigated through comparative tests of kinetic reproducibility for single crystal reactants. Significant differences in dehydration rates of different large single crystals of d-$LiKC_4H_4O_6{\cdot}H_2O$ were ascribed [75] to variations in the small (non-statistical) number of nuclei, often less than 20, that were irregularly disposed at reactant surfaces. Overall kinetic characteristics are strongly influenced by the nucleation step, which represents a minute proportion of the total reaction. The subsequent interface advance is, however, responsible for the overwhelming proportion of the chemical change. Quantitative determinations of the specific roles of imperfections would require particularly precise rate measurements. Moreover, great care would be required to distinguish these rate controls from those for other effects, such as particle sizes, shapes and, in some systems, the procedural variables.

5.6.3. *Equations used in kinetic analyses*

The commonly used 'closed' approach to kinetic analysis is the self-imposition of probably inappropriate constraints on the range of equations to be compared, usually restricted to about 20 kinetic models (e.g. [78,79]). Thus, interesting and possibly relevant alternative models may be excluded from consideration. Consequences may include the following: (i) Whereas one particular kinetic model may be identified as providing a good, even excellent, fit to the data, it could be that a reaction pattern other than that assumed in the derivation of the equation is applicable. Several of the kinetic expressions in general use represent more than a single geometric shape of interface development [2], alternatives that may be distinguished only by complementary observations, e.g., microscopy. (ii) There may be a change of kinetic characteristics with α, such as completion of nucleation [67], or, in non-isothermal experiments, with temperature (see [28, Section 4.3.5]). (iii) Rate behaviour, that would be most accurately expressed by unconsidered kinetic models are unlikely to be correctly recognized, or sought, unless correlations throughout the test set are unacceptably poor. This might be regarded as an initial failure of the kinetic analysis, which can be repaired only by extending the search to include additional models. Recent work has shown that two reactions, long regarded as simple solid state decompositions, are composed of at least two contributory rate processes (and other comparable examples probably remain yet to be discovered): the decomposition of $KMnO_4$ [16] and the dehydration of $CaC_2O_4{\cdot}H_2O$ [17]. Reconsideration of these kinetic analyses, in the context of these new observations for the already extensively studied reactions, is essential. (iv) Alternative types of kinetic behaviour, usually unconsidered in TKA comparative analyses, are complex mechanisms, including the participation of transitory, unstable intermediates, particularly when the decomposition is accompanied by melting which may be only partial, temporary and/or local. Kinetic criteria for the recognition of melting are not available.

5.7. Melting

Aspects of melting have already been mentioned in the context of establishing reaction stoichiometry, taken to include the phase in which chemical changes occur (Section 3.3). Fusion is, however, also important when considering reactivity, kinetic data interpretation and mechanism formulation because there is evidence that at least some rate processes proceed more rapidly in a melt than as a solid [26]. Moreover, probably the most commonly observed consequence of heating a solid is melting. Thermal reactions involving liquids may show superficial resemblances to solid state kinetic characteristics, including (often) asymmetric sigmoid-shaped α–t curves, e.g. [22–24,97]. These decomposition mechanisms may be different, involving homogeneous reactions and the possibility of liquid intermediates, rather than at an intercrystalline interface. It follows that the practice of comparative fitting of TKA data exclusively to crystolysis reaction models represents an unnecessarily restrictive approach to rate data interpretation. Any ‘fit’ detected may not be a suitable description of behaviour because the possibility of a complex reaction [97] is implicitly excluded, a constraint that limits the potential value of such work.

Unlike crystolysis reactions, dedicated and characteristic kinetic models capable of recognizing the participation of melting, partial, local and temporary, in thermal rate processes have hitherto found relatively few applications. Rate equations specifically applicable to reactions proceeding in melt/solid systems are discussed by Brown and Glass [97]. It is frequently assumed implicitly, when discussing the thermal breakdowns of initially crystalline reactants, that these substances remain solid throughout (although this is not always mentioned or demonstrated; supporting evidence is not often provided). Determinations of the amounts of liquid present and its variations with α, t and T during thermal reactions, a most difficult objective, are usually not attempted. The similarly difficult experimental measurements of the rates of formation of the individual products, concurrently evolved from reactions proceeding two phases, solid and liquid, are not usually attempted, particularly where, as is quite likely, the proportions and the absolute amounts of the two phases vary with α, t and/or T. Complex rate processes require the introduction of additional terms into the rate equations. These are not easily characterized, independently and quantitatively, so that the statistical comparisons for such kinetic analyses become insensitive and unreliable. It is likely that alternative kinetic models of this type may be effectively indistinguishable, e.g., through r values, from the fits of data to equations characteristic of homogeneous and/or of heterogeneous rate processes. The kinetic characteristics of thermal decompositions in solid/melt mixtures are, at present, a limited topic and measurements other than rate are required to detect the occurrence of fusion and to determine its chemical significance quantitatively.

In principle, the kinetic analyses of reactions that involve fusion could proceed by comparisons of the fit of yield–time data to a set of specific kinetic models, $g(\alpha) = kt$, formulated through relevant melt and/or geometric considerations, analogous to those applied [1–4] to crystolysis reactions. Initially, this approach might usefully envisage three situations: (i) Reaction occurs predominantly, or exclusively, within a ‘thin’ molten phase situated between a solid reactant and a (recrystallized) product. If the thickness of such a fluid layer is small compared with crystal and nucleus dimensions, the kinetic characteristics may be indistinguishable from those for other interface advance models [1]. However, this is an active liquid interface and the chemical (homogeneous) mechanism will be different from those applicable to crystolysis reactions. (ii) If prereaction melting is complete, or extensive, the behaviour can be regarded as a homogeneous rate process occurring in a (solvent-free) liquid reactant. The total volume/amount of the melt progressively diminishes as α increases. (iii) The systems most difficult to characterize through kinetic observations must be those in which the melting is partial, varies with α, t and/or T and the important reactions occur both in the liquid and in the solid phases [97]. Unless the amounts of liquid present at various times and the rates of the parallel, possibly interrelated reactions in both solid and liquid phases can be measured, the rate expressions become intractable and the kinetic data available may be insufficient to characterize adequately all the controls [22–24]. Recognition that a particular reaction is complex, and the confirmation that essential chemical changes occur in a liquid, must be regarded as a more realistic description of behaviour than a ‘fit’ to a single (solid state and, therefore, inappropriate) kinetic model.

5.8. Reproducibility in kinetic analysis

The necessity to confirm that kinetic observations are accurately reproducible is obviously not a high priority in many recent reports of TKA investigations. Nevertheless, the literature contains important investigations that conclusively demonstrate the existence of significant variations of behaviour between successive nominally similar experiments, some are cited below. Chemical conclusions can only be of value when derived from reliable methods of kinetic analysis and based on measurements that are fully representative of the reaction of interest. The importance of reproducibility has been emphasized in point 3 of Section 5.4.

From studies of the solid state thermal reactions of $[Co(NH_3)_5{\cdot}H_2O]X_3$ (where X is Cl^-, Br^- or NO_3^-), LeMay and Babich [98] drew attention to the poor reproducibility of some reported activation parameters. Comparative investigations were, therefore, essential to determine quantitatively the kinetic influences of the procedural variables: particle size, sample size and compaction, atmosphere and heating rate. Apparent activation parameters varied significantly (exhibiting a CE) showing that the kinetic effects from changed reaction conditions effectively concealed the relatively smaller influences from chemical factors and crystal structures in controlling reaction rates (see also [28]). It was further concluded from some cited reports that mechanistic deductions, based on comparisons of the magnitudes of activation parameters, were unwarranted. Later work by House and others, on dehydrations of $(NH_4)_2C_2O_4\cdot H_2O$ [99] and of $K_4[Ni(NO_2)_6]\cdot 0.75H_2O$ [100], for different reaction conditions, showed that the kinetic models giving ‘best fit’ and ‘second best fit’ from many of the multiply replicated rate experiments, were provided by quite different kinetic models. Sets of kinetic data were alternatively represented by nucleation and growth and by deceleratory equations, indicating inconsistent and contrasting interpretations, identifying rate control by quite different chemical processes. The necessity to demonstrate reproducibility in rate measurements, to obtain kinetic observations of the highest quality that can be used to formulate meaningful reaction mechanisms, was mentioned. These studies [98–100] complement other fundamental work emphasizing the importance of precisely defining reaction conditions to eliminate the kinetic contributions from procedural variables, through reversibility and heat transfer, see also [35–45,47].

5.8.1. *Correlation coefficients*

The use of a correlation coefficient, r, or a coefficient of determination, r^2 (each a single number) as the sole measure of excellence (or otherwise) of the fit of a rate data set to a kinetic model must be regarded as an insufficient criterion on which to base conclusions from comparative kinetic analyses. Limitations include:

1. One (usually) missing parameter from reports of kinetic ‘fit’ is the overall α-range across which the identified equation is regarded as acceptable. Deviations of data from the selected theoretical relationship may result from experimental error, or be systematic, for which characterization of the trends, α-ranges and magnitudes of divergences may have significance in the interpretation of rate measurements [66].
2. Distinguishability of ‘best fit’ of data between rate equations, from the conventionally accepted set, is not straightforward [66]. In such comparisons, different segments of the α–t curve provide the most sensitive ranges within which discrimination between alternative possible fits can be discerned: the periods of onset and/or completion of reactions are often the most revealing and effective. This is particularly relevant for kinetic analyses of each rate process in a sequence of stepwise distinct reactions where errors may arise when defining the point representing completion of one step and the initiation of the subsequent process (stoichiometry).
3. A further problem, apparent in some literature reports, is that identification of a value of r that approaches unity closely tends to be accepted as representing all the necessary and sufficient evidence required to recognize an acceptable kinetic description of reaction rate. In certain circumstances this is undoubtedly true. However, the demonstration that more than a single kinetic analysis triad (i.e., kinetic model, A and E) provide fits, characterized by values of r that are close to unity, is clearly unacceptable. See [101], where several values of r, that are significantly greater than 0.999 but less than 1.0, are listed for fits of the same rate data sets. Moreover, these alternative deceleratory kinetic models represent different interface advance reactions, with and without diffusion control. Many articles report similar evidence of ‘excellent fit’ to two or more alternative kinetic models (though r values are generally further from unity, e.g. [78,79,101,102]). It should be remembered, however, that the existence of two or more values of r which are very close to the ideal (1.0) demonstrates a fundamental inadequacy of the analytical method because the statistics have failed to identify which *single* kinetic model ‘best’ represents the rate process. One equation should emerge from the analysis to describe the reaction, which can be represented by only a single kinetic model. For this, the r value applicable is expected to be significantly larger than all others found. The reporting of multiple ‘fits’ cannot be welcomed as the successful outcome of a kinetic analysis, as seems to be often implied.
4. In many kinetic reports, the listed (apparent) values of A and E vary considerably with the particular kinetic model applied [78,79,101,102]. Consequently, the preferred interpretation of the data may be based on small differences of r or even alternative “statistically equivalent descriptions of the process” [92]. This is clearly unacceptable and other criteria must be sought to obtain a method for the reliable characterization of the kinetic parameters.

The above considerations demonstrate unambiguously that a value of r, or any other single statistical parameter, is an inadequate criterion for confirmation of the kinetic model for a particular reaction. Presumably, this altogether unsatisfactory practice has arisen through the tendency to extend mathematical analytical methods in preference to all other experimental techniques. However, this approach has now obviously exceeded what is reasonable and, as a result, considerable uncertainties have been introduced into kinetic conclusions based only on (superficially sophisticated) calculation routines. The methods used in the earlier kinetic analyses for solid state reactions are to be preferred. Agreement with kinetic models throughout the reaction was sought and interpretations were supported, where possible, by suitable confirmatory (i.e., non-kinetic) observations, including microscopic determination of reaction geometry.

It is suggested that TKA would benefit from a comprehensive reappraisal of the conventions used in reporting kinetic results, with a view to establish the type of information that is required to express fully all conclusions. For any reaction, this might include the following: reaction stoichiometry, kinetic model (including criteria for its recognition, r, the α-range(s) of applicability and reproducibility of data), Arrhenius parameters (together with their standard deviations and temperature interval of applicability), the influence of procedural variables on kinetic characteristics and other relevant and complementary data.

5.9. *Appraisal of some kinetic reports in the TKA literature*

The recently published reports of TKA studies considered below are intended to emphasize unacceptable general problems that are not currently being addressed, undoubtedly leading to stagnation [84] in this subject. It is not intended that these citations are a complete list of articles in which such problems appear: the selected examples are representative of a much wider range of comparable reports [61,62]. The problems identified are discussed below under three headings that are complementary, interrelated and together identify comprehensive shortcomings that are now endemic (though widely unrecognized) throughout a significant part of current TKA literature.

5.9.1. *Variation of A and E with kinetic model* ($g(\alpha) = kt$)

Consideration of this unacceptable feature of reported kinetic conclusions [61,62,102] must start from the view that, throughout chemical theory, E is regarded [59,87] as the minimum energy required by the reactants to achieve the activation required for their transformation into products. This quantity is, therefore, an invariable property of the particular bond redistribution step considered and the magnitude of E should not vary with either experimental technique or the mathematical method used for its calculation. A kinetic model, while frequently used to obtain Arrhenius parameters (through k), is not an essential feature and model-free [77], also reduced-time [2], methods, for the determination of E are available. The importance of E in homogeneous reaction kinetics is well-established [59,87] because its magnitude can be valuable in formulating reaction mechanisms, where the energy barrier to transition state formation is an important parameter. Shortcomings and uncertainties in the theory diminish the reliability of deductions based on values of E for solid state reactions [29].

Recent kinetic analyses have reported, even emphasized, apparent variations of E with α [92]. Such relationships have been found and specific instances have been explained by mechanistic models, including the completion of nucleation, change of mechanism, etc. However, influences of heat and product diffusion rates throughout the reactant mass can exert controls over the kinetic behaviour observed (Section 4). Studies, e.g. [92], presenting quantitative determinations of the so-called ‘variable activation energies’ report trends of E with α as empirical observations and do not explore the chemical reasons for such trends. Significantly, the applicable reaction conditions were not adequately described so that the rate data can be presumed to incorporate the effects of reaction reversibility and/or endothermicity on the rates measured. No attempt to remove these secondary controls is mentioned. Consequent variations of E with changes of conditions within the sample and, thus with α, are not unexpected. Apparent values of E reported for calcite dissociation [92] were stated to decrease from about 170–110 kJ mol^{-1} as reaction proceeds under unspecified and probably varying conditions. No such trend was evident, however, for the same reaction studied under carefully defined vacuum conditions unless some product was present [36,37].

There is no reason to regard E values calculated from TKA data to be fundamentally different from the concept of activation energy used in other branches of chemistry [61,62]. However, it has become an accepted practice in some recent TKA literature to report, for the same reaction and without comment [80], several significantly different magnitudes of E obtained by alternative analyses of a single data set by different kinetic models [78,79]. It appears, therefore, that the concepts represented by A and E, specifically as used in TKA studies, have been changed substantially from their original meanings. This transformation has been neither recognized nor adequately discussed. No definition of these new (or modified, variable and multivalue) Arrhenius parameters seems to have been provided [92]. It appears that Arrhenius parameters have acquired two distinct and alternative significances, applicable in different parts of chemistry.

This is a most unsatisfactory situation because scientific communication depends on the use of a precise and unambiguous descriptive terminology. The following alternative possibilities must, therefore, be considered: (i) Either the wider theory is specifically inapplicable to the types of reactions studied by TKA methods (which is obviously impossible, indeed unreasonable). (ii) Or (more acceptably) an aspect of the definitions of the terms and/or the computational methods used in the automated and routinely applied mathematical programs now systematically modifies those features of the kinetic analysis calculations which determine the apparent (sometimes multivalue) magnitudes of A and E. I have no hesitation in regarding the latter alternative, (ii), as infinitely preferable:

1. *Variable E*. This concept has been advocated by Vyazovkin who, in the last sentence of [92], states: “In the meantime, the acceptance of variable activation energy seems a reasonable compromise ... ”. The meaning of this new presentation of E is not explored, the inconsistencies with the accepted view of ‘activation energy’ are not discussed and the possible advantages of this new concept are not explained. Nevertheless, this approach is extensively supported, or perhaps only accepted: some representative examples from the literature are given below. In this convention, the guiding principle seems

to be that the apparent values of E (etc.) vary with the approximate formulae used in their calculation. I do not understand why these computed values should be termed ‘activation energy’, when this usage is so different from the accepted meaning of this parameter. The variable, or multivalue, E is correlated with no activation step [59,87] and provides a measure for no identifiable energy [61].

2. *Unacceptable mathematical methods of data interpretation*. In place of the present unquestioning acceptance of the view that the results of conventional calculations are invariably meaningful, a reasonable alternative is to examine critically their chemical significances. If, from theory, E is a constant, characteristic of a particular chemical step, then calculations that yield alternative magnitudes merit critical scrutiny. The most obvious reason is that the mathematical programs for kinetic analyses, now uncritically accepted, are unsuitable or simply incorrect [62]. The few comparative surveys of the many alternative, but approximate, methods for computation of kinetic parameters [1–4], already mentioned, appears to have induced a reluctance in researchers to seek reasons for the inconsistencies that now so obviously pervade this subject. The present survey is intended to open a discussion of this problem, which must be confronted to resolve the present scientific inadequacies.

It is always essential that kinetic data, used to calculate chemically meaningful magnitudes of E (etc.), are not significantly influenced by procedural variables. Multivalues of E, from different kinetic models, apparently result from computational inconsistencies [61,62], whereas systematic variations of E with α, t and/or T may due to the changing contributions from secondary controls (Section 4).

The citations mentioned below list some of the many instances of apparent variations of Arrhenius parameters with kinetic model and/or calculation method. Such conclusions often result from kinetic analyses that are based only on recognition of ‘best fit’ from ‘best r’. The unacceptable situation now existing in TKA analysis is illustrated by results from two recent comparative data interpretation projects. In [7] participants measured rates of the three breakdown steps for $CaC_2O_4{\cdot}H_2O$ and data were analysed by standardized mathematical interpretation procedures (although some data obtained were “cancelled” because these “did not fulfil the high demands of quality”). In [8] identical sets of kinetic data supplied were (alternatively) interpreted by the participants [9]. Both groups of involved volunteers who were highly experienced kineticists, (presumably) motivated by a common interest in establishing the consistency and reliability of methods used to interpret TKA data. However, for each data set in both projects [7,8], the reported magnitudes of $\ln A$ and E showed unreasonably large variations (Type 3 CE). Despite some expressed optimism [7] (but without explained reasons), these two reports constitute irrefutable evidence that magnitudes of Arrhenius parameters calculated by the most widely used methods are inconsistent and, without additional support, such results cannot be regarded as having theoretical significance.

The unexplained variability of these results, obtained from what should be a consistent kinetic analysis procedure, introduces doubt into the significance of Arrhenius parameters throughout the TKA literature. Until reasons are identified, this uncertainty must be regarded as potentially having a much wider applicability. Reported A and E values from these methods cannot have theoretical significance (i.e., be associated with a bond rupture step [59,87], etc.) or be used to classify chemical features within sets of related reactions. The Arrhenius parameter values reported in [7,8] extended beyond the ranges that might reasonably be attributed to the chemical changes considered, effectively making these parameters theoretically meaningless. It follows that all comparable values reported throughout the literature must be regarded as being subject to similar uncertainties, a generalization that has very serious and widespread implications. These conclusions provide a challenge for all of us to explain these inconsistencies and to urge those active in this field to establish acceptable theoretical foundations, that are essential for future progress.

The calculated results tabulated in [78,79] demonstrate that variations of the models used in theoretical kinetic analyses result in systematic and considerable differences in the apparent magnitudes of Arrhenius parameters calculated from each single set of rate data [62]. (Apparently only a single set of data measurements was obtained for each reaction. This is unsatisfactory because it has been shown [64,65] that a single set of non-isothermal rate sets fitting one kinetic model can also fit most of the other kinetic models used to represent solid state reactions.) In these two articles [78,79], each of the six sets of kinetic observations were analysed for fit to 19 alternative kinetic models, of both ‘Integral’ and ‘Differential’ forms. For each of these reactions, wide ranges of apparent E magnitudes (38 in all) were calculated, including some values that were negative (presumably implying that the reaction rate *decreased* with temperature rise). Values of r were used as the sole criterion for identification of the ‘best’ kinetic fit for each of the several reactions considered. Agreement of rate data with many of the particular kinetic expressions tested was poor. Results for each reaction exhibited a CE, as expected for ‘isokinetic’ (i.e., same data) measurements; two very slightly different CE lines were given by the sets of ‘Integral’ and ‘Differential’ values.

The use of virtually identical methods, yielding similar result patterns from kinetic analyses of TKA data, are also found in many other publications. Predominantly, these were obtained by non-isothermal measurements. Representative examples are cited below and most of these exhibit the following features. Values of E and $\ln A$ (not invariably recorded), calculated from the same data set, vary considerably (usually at least 4×, and often much larger ranges) with changes of the kinetic model, $g(\alpha) = kt$. (Not all reports included results from both integral and differential forms of the kinetic model.) Ranges of α across which 'best fit' kinetic models were applicable were rarely reported. Relative magnitudes of Arrhenius parameters calculated for diffusion control models (D1–D4 [1]) were almost invariably the largest. Values from the Avrami–Erofeev (A1–A4) and power law (Pn) equations [1] were generally smaller and decreased systematically (and significantly) with the exponent, n. Most plots of n against E were linear and intersected the n-axis ($E = 0$) at around $n = 0.1$. Arrhenius parameter sets, for a single, or for groups of chemically related reactions, frequently exhibited a CE and sometimes a single CE line was applicable to more than one reactant.

Examples of these unsatisfactory features of recent kinetic studies, now requiring reanalysis and critical reappraisal, were found in the following representative reports:

- *Decompositions of 10 areneruthenium complexes* [68]. Values of r were predominantly greater than 0.999 for fit to alternative, kinetically distinct, rate equations.
- *Decomposition of manganese methylamine tetrachloride* [81]. Data analysis by several non-isothermal kinetic equations yielded Arrhenius parameters that exhibited a CE.
- *Decompositions of palladium complexes* [101]. A single CE was found for data from five closely similar reactants.
- *Dehydrations of sodium lanthanide sulphate monohydrates* [102]. Values of E vary with kinetic model and the 'best fit' was identified from the relative r value closest to unity.
- *Decompositions of similar palladium complexes* [103]. E was almost proportional to n.
- *Decomposition of copper ammonium chromate* [104]. Values of r for fit of data to nine different kinetic models were 0.992 or greater and the varied magnitudes of E (81–476 $\mathrm{kJ\,mol^{-1}}$) decreased with increase in n.
- *Decompositions of complex hydrated barium and lead oxalates* [105]. For each of the three reactions considered, CEs were found for $\ln A$ and E from different kinetic models.
- *Decompositions of seven polyurethane-polyacrylates* [106]. Decompositions in two temperature ranges showed wide variations of E with kinetic model (values of A were not reported).
- *Dehydration of* $NiSO_4{\cdot}6H_2O$ [107]. Surprisingly, Arrhenius parameters for the four successive dehydration steps, that occur within different temperature intervals, were close to a single CE plot. Apparent values of E, some of which were unrealistically small, increased with (fractional) n values in the AE equation [1]. (Aspects of the stoichiometry have been discussed [12].) See also the dehydration of $NiCl_2{\cdot}6H_2O$ [108].
- *Decompositions of cyanodithioformate complexes of some transition metals* [109]. Values of A and E obtained by alternative calculations for the same complex do not agree and vary significantly for the six transition metals (Mn to Zn). All data fit a CE for which the isokinetic temperature [46] (552 K) is slightly greater than the response peak maxima, 525–543 K.
- *Decompositions of glyoxime derivatives of Co(II), Ni(II) and Cu(II)* [110]. Although the three successive stages of reaction for each salt proceed in similar temperature intervals, Arrhenius parameters show variations, giving three approximate CEs.

5.9.2. Correlation coefficients

Many of these, and similar reports giving results of multiple kinetic analyses, mention r magnitudes that approach unity, identifying (often) apparently excellent fits of the same data to rate equations from the three general classes [1]: sigmoid (nucleation and growth, A2–A4), deceleratory (contracting interface, R2, R3), strongly deceleratory (diffusion control, D1–D4). This is unexpected and unacceptable because the objective of any kinetic analysis is to distinguish unambiguously [66] between such alternatives. For example, [68] gives many values of r between 0.999 and 1.000, [104] gives nine equations for which r is greater than 0.992, and further papers [78,79,101,102] record fits that vary between excellent, good and others that are less satisfactory. One conclusion is that (at least some) of these kinetic analyses are remarkably non-discriminatory. Moreover, the single value of r is an inadequate criterion for identifying a kinetic description of rate characteristics. Perhaps a more suitable test of 'best kinetic fit' is the constancy and consistency of the calculated magnitudes of E. (The range of α to which the r value refers should always be specified.)

5.9.3. Comment

The representative citations above demonstrate the extent and severity of the problems that must be confronted and resolved to introduce scientific order into the TKA literature. Every article mentioned includes one or more of the significant shortcomings listed below, which represent inadequacies or inconsistencies of the theory used and/or a limitation that restricts the elucidation of reaction chemistry. These trends persist into the most recent literature reviewed at the time of writing (late 2003):

(i) Stoichiometry is often incompletely characterized, the identities of inferred products are not always confirmed and, in reaction sequences, only the first reactant is known.
(ii) Reproducibility of results, stoichiometric and kinetic, is often not confirmed, though results are reported to unrealistic numbers of (apparently) significant figures.
(iii) It is accepted in rate analyses that A and E values can vary with kinetic model.
(iv) Kinetic comparisons are often limited to a selected set of equations (for which the selection criteria are not specified), thereby excluding all other possibilities.
(v) Kinetic fits to quite different reaction models give equally satisfactory values of r, though agreement with integral and differential forms of the rate

equations can be significantly different. These inconsistencies presumably arise from kinetic analyses based on insufficient measurements, a single set of rate data [64,65,111].

(vi) α-Ranges of applicability, adequate fit, for each kinetic model often remain unrecorded and may represent a restricted α-range only.
(vii) Kinetic conclusions are not always supported by confirmatory observations.
(viii) The relationship of results with the known behaviour of comparable reactants frequently remains unconsidered.
(ix) The significance of reported conclusions in advancing theory is not always discussed.

These features, there may be others, represent attitudes that are prevalent throughout the recent TKA literature and may be regarded as evidence that the subject lacks a theoretical foundation and is becoming ever more empirical. Ineffectual practices continue to be unquestioningly accepted so that TKA is becoming even further detached from its roots. The proposed new theoretical approach (Section 7) has attracted relatively little interest. This is surprising in the context of the existing poverty of TKA theory and the absence of any alternative proposal. However, the restricting tradition of a subject that has unreasonably few critical, comprehensive and objective reviews or realistic literature appraisals is maintained.

5.10. Discrimination in kinetic analysis: comparisons through model systems

To investigate discrimination in kinetic analysis [66], comparative tests were made for a model representative isothermal reaction. This approach is readily extended but the single example given here recognizes some problems, and exemplifies shortcomings, of current methods of kinetic analysis. A set of 'Calculated Kinetic Data' (CKD), (α, t) values, were obtained for exact applicability to the (isothermal) sigmoid equation, A2:

$$[-\ln(1-\alpha)]^{0.5} = kt$$

The fit of these (A2) calculated α–t values to other selected kinetic models [1] (for crystolysis reactions) were compared by two methods and results are summarized in Table 1 and Fig. 1. Column three of Table 1 shows the maximum α-ranges across which k values were constant, within the (estimated) limits ± 10%. Column four shows the (less quantitative) subjective assessment of the data fit from the α-range of linearity for a plot of $g(\alpha)$ against t. These comparisons are alternatively displayed in Fig. 1 which gives a differential plot, again for the CKD (α–t data), showing variations of the rate constants, $\Delta[g(\alpha)]/\Delta t$ against α. From both the variations of k with α and the ranges of estimated linearity (Table 1) the ability to discriminate between fits of these data to different kinetic models was most satisfactory (apparently much more effective than r in the papers cited in Section 5.9). Apart from the original equation ('perfect fit'), the α-ranges of fit were limited and most were obviously unacceptable.

Results obtained in some calculated comparisons of fit of the CKD data set to the same alternative kinetic models are given in Table 2, which lists 'best fit' values of k with r^2, coefficients of determination (in brackets). Also included are the consequences of selective deletion of the early acceleratory stage, when α is less than 0.148, and of the final slow reaction phase, for α greater than 0.961. (This is the (slightly arbitrary) deletion of the first three and/or the last six data points. Furthermore, the use of coefficients of determination, r^2, presents an apparently larger relative deviation from the ideal fit of unity.) A critical consideration of these values shows that there are several instances of evidently good fit, based on r^2, but only in those analyses that incorporate the more restricted α-ranges. This contrasts with the graphical

Table 1
Range of α values across which "CKD (for rate equation A2)" fitted other rate equations from the set regarded as applicable to solid state decompositions [1][a]

	Relative rate constant, k (arbitrary units)	α-Range[b] of fit by semi-quantitative comparisons for rate ± 10%	Estimated[c] α-range of linear fit from plot of $g(\alpha)$ against t
Avrami–Erofeev equation			
$n = 1$	–	No acceptable fit	0.09 → 0.55 (poor)
$n = 2$	1.00 (by definition)	0.00 → 1.00	0.00 → 1.00
$n = 3$	0.67	0.45 → 0.83	0.15 → 0.75 (poor)
$n = 4$	0.48	0.53 → 0.85	0.12 → 0.58 (poor)
Prout–Tompkins equation	3.2	0.5 → 0.9	Not tested
Power law equation ($n = 2$, 3 or 4)	–	Unsatisfactory: fit only when $\alpha < 0.2$	Not tested
Zero order equation (linear)	0.79	0.22 → 0.67	0.09 → 0.82
Contracting area equation	–	0.43 → 0.81	0.15 → 0.95
Contracting volume equation	–	0.47 → 0.95	0.24 → 0.98
Jander equation	–	Unsatisfactory	0.30 → 0.62

[a] CKD (title) were a set of α–t values that fitted the Avrami–Erofeev equation, $n = 2$, and were then tested for fit to the other rate equations widely used in kinetic analyses of reactions of solids [1]: α-ranges of fit are as shown.

[b] The ranges of fit (for CKD data) were estimated from a constant k value ± 10% from differential plots to determine fit to alternative test equations, see Fig. 1.

[c] The ranges of apparently acceptable linearity were estimated (approximately) by inspection of $g(\alpha)$, for CKD values, plotted against time.

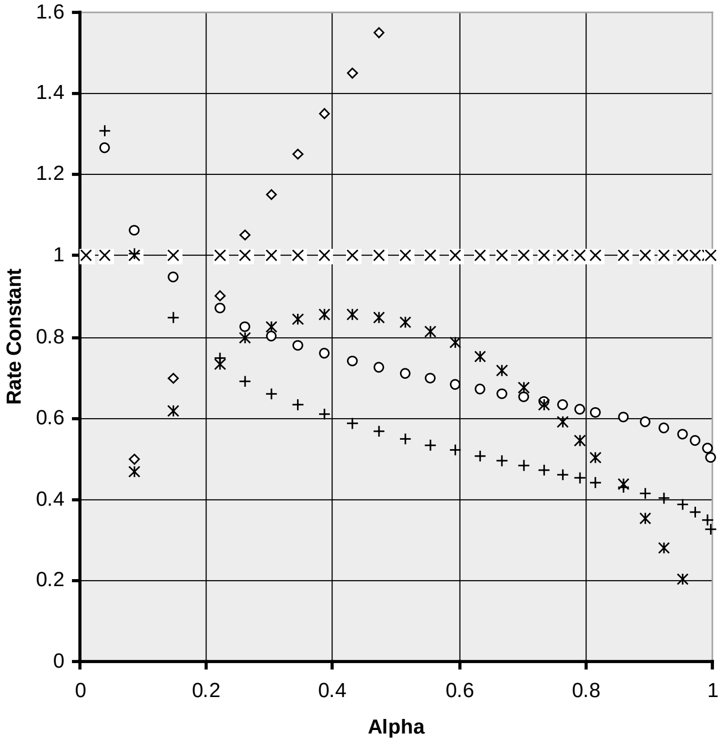

Fig. 1. Plots of rate constants (relative values), slope $\Delta[g(\alpha)]/\Delta t$ against α, to test fit of isothermal yield time data (CKD) calculated for the A2 equation to other forms of the Avrami–Erofeev, $n = 1$ (◇), 2 (×), 3 (○), 4 (+) and zero order (✱) equations. A 'fit' is recognized by a constant k value, a horizontal line, only found for $n = 2$; approximate (generally unsatisfactory) 'fits' for the other equations compared are found over the various α-ranges indicated in Table 1.

comparisons that are identified as the more effective method for kinetic discrimination [66]. Moreover, magnitudes of the apparent k values also change significantly with the α-range. These comparisons (Tables 1 and 2, Fig. 1) demonstrate the considerable uncertainties inherent in kinetic conclusions based on a single statistical parameter, r or r^2 and fit restricted to unspecified (often arbitrary) α-ranges. If kinetic discrimination between alternative rate equations is to be effective, it is essential that comparisons refer to almost the complete reaction and that the α interval for a specified criteria of fit to each kinetic model is reported. The methods of kinetic analysis in many recent publications are inadequate.

5.11. Approximate equations in kinetic analysis

It has been strongly advocated above that the well-known [1,2,4] approximate methods of kinetic analysis of non-isothermal rate data would benefit from detailed reappraisal.

Table 2
Fit of α–t data, calculated from Avrami–Erofeev for $n = 2$, to other solid state kinetic models (26 (CKD) values spread across total α-range)[a]

	k (r^2)			
α-range	0.0100–0.9998	0.148–0.9998	0.0100–0.961	0.148–0.961
First order equation	3.141 (0.9356)	3.390 (0.9590)	2.012 (0.9436)	2.267 (0.9699)
Avrami–Erofeev equation				
$n = 2$	1.000 (0.9997)	1.000 (0.9998)	1.000 (0.9998)	1.000 (0.9999)
$n = 3$	0.628 (0.9833)	0.584 (0.9909)	0.725 (0.9889)	0.664 (0.9961)
$n = 4$	0.473 (0.9616)	0.418 (0.9807)	0.581 (0.9730)	0.501 (0.9907)
Prout–Tompkins equation	4.048 (0.9870)	3.846 (0.9934)	4.122 (0.9612)	3.401 (0.9979)
Zero order equation	0.463 (0.8221)	0.419 (0.7714)	0.642 (0.9776)	0.630 (0.9633)
Contracting area equation	0.420 (0.9487)	0.413 (0.9307)	0.516 (0.9919)	0.545 (0.9975)
Contracting cube equation	0.382 (0.9822)	0.388 (0.9774)	0.419 (0.9843)	0.453 (0.9967)
Jander equation	0.372 (0.9451)	0.401 (0.9740)	0.291 (0.8696)	0.338 (0.9291)

[a] Calculated ('best fit') rate constant values, k and (coefficients of determination, r^2) for fit of data to the other models [1] commonly used in kinetic analyses of TKA observations.

Two recent papers [82,83] have provided important quantitative and comparative surveys. Flynn [80] has reviewed the shortcomings of the ‘Temperature Integral’ in the ‘computer age’. It is now opportune to extend this approach by exploiting the power of the generally available computational capacity to replace what should have been temporary expedients introduced during the developmental stages of TKA. These simplified, but inherently less reliable, computational convenience-methods appear to have become effectively permanent. It is appropriate that this comfortable, but restricting, practice is urgently subjected to cold, critical and comprehensive cerebration.

A general appraisal of the approximate methods of kinetic analysis is not attempted in this already extended review. The above example illustrates some of the problems inherent in non-isothermal TKA methods. This, together with the formulation of revised computational programs essential for progress (including correct use of terms, units, etc.), are interesting and challenging tasks for the immediate future, by those eager to advance thermal chemistry. The seriousness of the prevailing situation is conveniently illustrated by shortcomings of the Coats–Redfern (CR) equation [112] (see also [62]), often used in the analysis of single sets of non-isothermal data. The CR equation is often applied in the form (which is subject to severe interpretational limitations [64,65]):

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

The slope of a suitable plot gives E and A can be found from the intercept. The solid state forms of $g(\alpha) = kt$ [1] include the power laws, Pn with exponent n (see also [113]):

$$\ln\alpha - 2n\ln T = n\ln\left(\frac{AR}{\beta E}\right) - \frac{nE}{RT} \qquad (2)$$

A similar form is given by the AE equation, where the first term in Eq. (2) is replaced by $\ln[-\ln(1-\alpha)]$. Thus, slopes and intercepts yield values of $\ln A$ and E that are scaled by the factor n, evident in some reports [78,79], but this is not a direct proportionality because plots of E against n give exponent values between 0.05 and 0.2, when $E = 0$.

Furthermore, this form of Eq. (2) contains very little capacity to distinguish the fit [66] of data between the curve shapes of the alternative kinetic models, resulting only from variations of the term $[g(\alpha)/T^2]$. The component, $g(\alpha)$, systematically changes with the form of the kinetic model tested [1] but $2n\ln T$ undergoes variations that differ only marginally from a linear relationship across most temperature intervals of interest (where T increases at a constant rate, β). This lack of ability to discriminate between alternative kinetic model curve shapes was confirmed and another shortcoming was revealed by tests of kinetic fit for the model α–t data set (CKD) calculated for the AE equation, $n = 2$. CKD values were analysed according to Eq. (2). The kinetic fit was correctly identified, with acceptable accuracy, when α was greater than 0.01 to almost completion. At low α, however, there was significant divergence from expectation, attributed to dominance of the contribution from the $2n\ln T$ term in this interval. This recognizes a significant weakness in these equations used in approximate analyses of non-isothermal measurements.

The values of the Arrhenius parameters obtained using power law or AE equation forms, $g(\alpha)$ in Eq. (2), depend on the definition of k. Taking the units of k as $(\text{time})^{-1}$ (Section 5.5 and [1], $g(\alpha) = k^n t^n$) the slope given by the CR terms in Eq. (2) is nE (modified slightly by the contribution from $-2n\ln T$). If, however, we alternatively define K (from Section 5.5 and [1]) as $g(\alpha) = Kt^n$, but using the exponent m from [113] where $(-\ln(1-\alpha) = Kt^m)$ we obtain (see Eq. (9) from [113]):

$$\ln[-\ln(1-\alpha)] - 2m\ln T = m\ln\left(\frac{mA^{1/m}R}{E\beta}\right) - \frac{E}{RT}$$

which is shown in [113] to give the ‘correct’ value of E when the rate constant is defined with $k^{1/m}$ in units $(\text{time})^{-1}$. It follows that the variations of E with kinetic model occur when n varies from unity, as in Eq. (2). Thus, plots of first power or first-order functions (containing units $(\text{time})^{-1}$) against T^{-1} approximately represent the temperature coefficient of reaction rate, and E, but the following uncertainties arise in expressions such as Eq. (2):

1. CR plots incorporate contributions from $-2\ln T$ (or $-2n\ln T$) which influence the apparent magnitudes of E and r.
2. Kinetic analyses reports for non-isothermal data do not usually define k or the role of n in Eq. (2) so that the significance of the exponent in calculating E is not known [65].
3. The exponent of time, n, is a dominant control on the characteristic form of the kinetic model [66]. When n is greater than unity the power law or AE equations apply, when n is about unity the contracting interface or first order equations fit and diffusion equations give n values of about 0.5. Thus, the exponent usually, but not invariably, dominates the variation of E with kinetic model. This generalization is indicated by the closely similar pattern of variations of E with $g(\alpha) = kt$ in different studies, which is, therefore, identified as a computational artefact. (Note the values and their identical patterns of variations [62] in the tables from [78,79].)

Vyazovkin discusses [92] the existence of alternative, but ‘statistically equivalent’, representations (kinetic model, A and E) of a data set. One explanation is that Eq. (2) accommodates the differences between the alternative functions $g(\alpha)$ into the nE composite term; together with generally minor contributions from $2n\ln T$. It is also noted that, in discussing the advantages of using ‘master plots’ in kinetic analyses, Gotor et al. [65] tend to favour comparisons through differential (reduced) terms wherein the uncertainties resulting from rate constants and their units do not arise. One conclusion from the above appraisal is that the dominant contributions to the variations in apparent magnitudes of E with kinetic models arise through ignoring the consequences of units in the exponents. The 'best activation energies' are likely to be obtained from plots for which units of k are $(\text{time})^{-1}$ though other sources of uncertainty remain.

5.11.1. Comment

The current computer-automated methods of kinetic analysis may result in inconsistencies, or even serious errors in calculated kinetic parameters, which may be reported unnoticed, if the programs used have not been examined in detail by the researcher and every stage fully understood. Disregard for the significance of the units of time in k is suggested as one pervasive reason for some of the inconsistencies in activation parameters reported in many of the above citations. Recent publications continue to report uncritically results obtained using the CR (and similar) equations, despite their known limitations [64,65,111,113]. (Erroneous conclusions may result from the 'black-box' approach, which can never be recommended in fundamental science. This is the uncritical acceptance of an instrumental output/printout as being invariably correct in all respects, without the necessity for the researcher to understand fully its methodology, the errors and the limitations of each operation taking place within the 'black-box'.)

Another apparently widely unrecognized and unsatisfactory feature in the reporting of computer analysed kinetic data is the custom of uncritically recording excessive numbers of significant figures. Such apparently precise data might appear to be evidence of, or to imply a claim for, unrealistic accuracy. Values of E are sometimes reported to $\pm 10\,\text{J mol}^{-1}$, whereas it is probable that few values, particularly for solid state reactions, are measured reproducibly with accuracy better than about ±1%. A realistic conclusion to be drawn from unduly (apparently) precise kinetic data, without error limits, is that no adequate reproducibility tests or realistic accuracy assessments have been undertaken.

5.11.2. Variations of activation energy with α, progress of reaction

For a number of reactions, systematic variations in E with increase in α have been mentioned [92]. Several explanations are possible, one of which is reaction complexity, where more than a single rate process contributes to the rate of product formation. For example, nucleation is required before growth, and because temperature coefficients of these complementary steps are different, their contributions to the composite overall process vary with α [67]. The changing roles of various factors, including 'chain-branching', differences of reactivity with crystallographic direction, particle size, reaction mechanism [1,114,115], etc., have long been known to solid state kineticists as possible influences on rate characteristics. Thermal effects, self-heating/cooling, reaction reversibility (secondary controls from influences of procedural variables) and phase transformations are also associated with variations in E [35–45]. It appears, however, that this generally available knowledge has not been effectively transferred, accepted or appreciated in the theory as it is sometimes currently applied in the interpretation of TKA observations [61,62]. There is no necessity (or point) in discussing the variability of kinetic parameters, including E, before it has been established with certainty whether or not the reaction rates are determined by the chemical step or are condition-dependent (empirical) being subject to control by procedural variables. Much of the recent work ignores tests of reliability and reproducibility and thus the chemical significance of the data that are being analysed is not known.

5.11.3. Aspects of kinetic analyses

For isothermal rate data, kinetic analysis enables the functional dependence of α on t to be determined and 'fits' to alternative kinetic models distinguished (Fig. 1) [1,66]. (Values of A and E cannot, of course, be determined from experiments at a single temperature.) Similarly, a set of (α, t, T) values from a *single* non-isothermal experiment cannot identify the kinetic model, A and E [64,65]. For an adequate kinetic analysis, more information, e.g., α as a function of t and E [65] or independent verification of the kinetic model (α–t relationship), is required before E can be determined reliably.

5.12. Complementary measurements

Chemical and physical interpretations of kinetic data, including identification of the possible rate controlling factors and formulation of mechanisms require substantiation and support through all available and relevant complementary laboratory measurements. Conclusions based on different types of observations that concur are likely to be more reliable than deductions based on results from a single technique, which notably includes TKA studies. Moreover, some types of complementary investigations, invaluable for the characterization of features that are unique to crystolysis reactions, are simply inapplicable in homogeneous kinetics. These include microscopic and crystallographic characterizations of the textural changes accompanying reaction, which were originally so important in the initial formulation of the advancing interface reaction model. The value of microscopic observations, and other complementary information, for the elucidation of the chemistry of solid state reactions has been discussed in the important and authoritative review by Koga and Tanaka [116]. Boldyrev [117] uses evidence from an exceptionally diverse range of techniques in a detailed and penetrating discussion of the chemistry of the thermal decomposition of silver oxalate. If it is accepted that reactions of solids occur preferentially within specialist crystallographic zones of local activation [1–3], it follows that all appropriate and applicable experimental methods capable of characterizing properties of interface forms and functions must be exploited to elucidate their chemistries. Such information may be of value in establishing rate determining factors and conditions within the solid state specialized regions wherein it appears that idiosyncratic controls and mechanisms operate. Evidence, in addition to kinetic properties, may be essential to obtain insights into the chemical characteristics of interfaces. These interactions are different, less accessible, than those in homogeneous reactions that involve isolated species, following a collisional encounter.

The present practice in TKA studies appears to favour the use, as far as possible, of exclusively mathematical methods for kinetic data interpretation, without support from suitable theoretical models, to yield mechanistic conclusions. However, the view expressed here is that interpretations based on kinetic observations alone are unlikely to provide sufficient insights into the (almost certainly) more complex controls operating in solid state thermal reactions of all types. For the interpretation of kinetic measurements, the incorporation of results from suitable complementary observations, obtained by methods that are not necessarily usefully applied to reactions in gases or solutions, appears to offer the most promising routes to the elucidation of solid state thermal chemistry. It seems unreasonable to exclude or to abandon any route potentially capable of providing insights into chemical controls and reaction pathways. This was appreciated in the early studies of crystolysis reactions, but is less obviously implemented now. Experimental methods that have already been demonstrated to offer valuable information in the elucidation of mechanisms of solid state decompositions and, therefore, potentially of similar value in interpretation of TKA data, include [1,6] microscopy, X-ray crystallography, spectra, etc. In particular, direct observations by microscopy [116], and its more recent advances, still retain underexploited potential value.

Future TKA research should usefully and routinely consider the following possibilities. Thermal reactions may be complex, there may be melting, participation by intermediates (perhaps transitory and reactive), topotactic processes [1,118,119], and all other conceivable behaviour patterns. Devising imaginative experiments, capable of confirming mechanistic proposals, is perhaps the greatest intellectual challenge currently facing researchers in this field. However, the possible rewards are commensurate, in offering the greatest opportunities for increasing our understanding of the thermal chemistry of (initially) solid reactants. The profitable application of investigative techniques of all types, capable of probing and characterizing structures, intermediates, participants and reaction controls within the narrow active zone at the reactant–product contact, is essential to repair this relatively neglected (even widely ignored) feature of those many reactions subjected to TKA investigations.

The recent fashionable trend, the continuing collection of additional, sometimes empirical, thermal kinetic data for yet more and diverse reactants appears (to the author, from extensive perusal of recent publications) to offer little hope for any immediate progress in theory development. The ever-expanding accumulation of E values (etc.) have not yet provided insights capable of extending understanding of, or introducing order into, this subject. There are no obvious reasons why this should suddenly change. The more promising route for advance towards meaningful subject development appears to be to elucidate, in maximum detail, the thermal chemistry of a few selected, relatively simple and well-characterized reactants, e.g. [117]. This is potentially more profitable than to learn a little about each member of ever widening ranges of unrelated and, hitherto unrelateable, reactants, through studies that are often empirical (though this often remains unrecognized).

5.13. *Mechanisms*

When the word *mechanism* is used with restricted meaning, to refer only to the identification of the kinetic model, the chemical significances of the rate data become effectively discarded. Consequently, the literature becomes impoverished by a lack of interest in, or even the discouragement from, attempts to address the more fundamental objective of elucidating the chemical controls. However, if the wider and more conventional concept of mechanism is considered, many features of thermal reactions that are of considerable value may be revealed, as illustrated by the following examples: (i) Evidence has been obtained to show that the decompositions of ammonium chromate [22], ammonium perchlorate [23] and the reaction $KBr + Cl_2$ [27] are not simple interface $n+g$ reactions, as formerly thought. The sigmoid α–t curves, and complementary observations, are more satisfactorily identified as reactions occurring in a liquid phase. (ii) The temperature of $CaSO_3{\cdot}0.5H_2O$ dehydration is unusually high for water loss from a crystalline hydrate, 573–673 K [120]. Moreover, the rate was remarkably similar to that of $Ca(OH)_2$ dehydration [121]. Because both reactions involve the evolution of H_2O from a calcium containing salt, there is the possibility that both rate processes are controlled by the same rate limiting step, perhaps the rupture of a $Ca^{2+}\cdots OH_2$ link, or involving hydroxyl ions [120,121]. (iii) The sensitivity of dehydration kinetics of $NiC_2O_4{\cdot}2H_2O$ to water vapour pressure, $p(H_2O)$, has been demonstrated [38], and contrasts with the relative independence of dehydration rates of alums to $p(H_2O)$. This is consistent with the suggestion [95,122] that alum water loss proceeds with retention of water within the reaction zone. The essential function of these nuclei is identified as an ability to retain a sufficient $p(H_2O)$ to promote recrystallization of the residual product. In support of this model, it was further estimated [123] that the absolute rate of water loss from chrome alum nuclei was comparable, though probably smaller (about 5×), than that from lignite. In lignite water is retained within a carbonaceous matrix and its release requires no rupture of a chemical linkage. Thus, the dehydration rate of alums [95,122] proceeds at only a slightly slower rate, consistent with loss from H_2O retained only loosely within the intranuclear zone. From these examples, it is concluded that open-ended investigations of the chemistry of thermal reactions is of potentially greater interest and scientific value than the present (restrictive) preoccupation with curve fitting and, all too frequently, empirical Arrhenius parameters, that remain unrelated to or by any theory.

6. TA literature

6.1. Comment on literature content

There have been many publications concerned with general [4] and particular [124] aspects of the experimental methods and theory of TKA, together with specialist surveys [125] and discussions of theory with particular reference to crystolysis reactions [1,2]. These citations refer to an extensive, now predominantly older, literature, though [4] was recently revised and there is a new comprehensive review [126].

Any successful scientific subject is (ideally) characterized by a dynamic and coherent series of stimulating reports of continuing advances. Publications include concepts capable of ordering knowledge systematically, resolutions of recognized problems and progress in overall theoretical understanding of all relevant phenomena in the widest possible perspectives. The models developed conceptualize and generalize the information available. Existing order is extended and, by induction, meaningful predictions may be made of properties and behaviour in hitherto untested systems and conditions. However, the TKA literature does not realistically realize these aspirations. Few theories are available to unify the content of a coherent subject, by development through organic growth, and there is no substantial body of organized knowledge suitable for forecasting the results of novel experiments. In contrast, there is substantial evidence of divergences and duplications of effort but little evidence of systematic subject development. Many recent TKA publications address (and achieve) relatively restricted objectives. It is probably true (and is unlikely to be enthusiastically supported by some colleagues), that the thermal chemistry of solids is a more difficult research topic to advance than is evidently appreciated within much of the recent TKA literature.

Perhaps a critical, comprehensive and general appraisal of the status and significance of TKA could now initiate its revitalization through a second transformation or metamorphosis. The first transformation occurred around 30 years ago:

Thermal decomposition of solids
(crystolysis reactions)
→ Thermal analysis kinetics (TKA)
(all thermal reactions: emphasis on kinetics)

It is now appropriate and timely to transform TKA again, by recognizing the diversity of all types of thermal chemical rate processes that are studied, by a second transmutation:

TKA → kinetics considered in a wider context of all
aspects of thermal chemistry

Thus all aspects of condensed phase thermal chemistry should be acknowledged. There is the requirement to recognize that, in general, TKA studies are not necessarily concerned with solids (as sometimes currently implied) but include chemical changes of all types. Reactions involve melting, participation of transitory intermediates, secondary controls, etc. Kinetic interpretations require support and confirmatory observations.

This paper offers the considered opinion that the development of TKA involved a profound, but insufficiently recognized, metamorphism whereby the studies of thermal decompositions of solids were effectively replaced by the predominantly kinetic study of all thermal reactions. The change occurred at a time when the theory of solid state chemical reactivity was encountering difficulties which inhibited its further progress. The mainly experimental and mathematical/analytical features of solid state kinetic analyses that developed through the advent of TA did not, however, address the particular limitations of the then (and still) faltering theory of crystolysis reactions. Such fundamental theoretical limitations are likely to remain until novel reaction models, concepts and explanations for the chemistry of these solid state rate processes are formulated. One such theoretical proposal, providing an alternative and novel explanation for the kinetics of reactions in solids and enabling consistent classification of groups of reported results, has been developed by L'vov [31], Section 7.

6.2. Few review articles

The few comparative surveys published throughout TKA and the crystolysis literatures represents a disproportionately small ratio in comparison with the large number of reports for single, or sets of related reactions. There have been relatively few successes in finding order within the TKA results available, based on any of the more obvious possible classification criteria: reactant chemical compositions or structures, Arrhenius parameters, kinetic models, or, indeed, other potentially distinguishing features of the diverse rate processes investigated. In the absence of adequate theory, uncertainties in the relationships between behaviours of different reactants remain unresolved and are rarely discussed. The chemical significances of kinetic observations also frequently remain unconsidered. There are also doubts concerning the reliability of many published kinetic results. A contributory reason for the reluctance to publish reviews may be the difficulty of comprehensively locating all relevant material, a problem also found for crystolysis reactions (similarly under-reviewed) [1,2]. This absence of theory capable of systematizing the information available may have discouraged reviewers, which should, perhaps, be regarded as a less than satisfactory reason. Effective reviews can be a preferred route towards identifying systematic order, an essential prerequisite for scientific subject advance and for theory development.

6.3. Article introductions

While not necessarily an exclusive feature of the TKA literature, the first sections of many articles in this field do not ‘Introduce’ their subject effectively. This function of research reports represents an essential contribution towards literature development by providing up-dates in the form of specialist reviews for the specific topic being investigated. This is not, however, always effectively implemented and many such introductions must be adjudged to have only limited value. The service to TKA has become particularly important in a subject for which so few general reviews are available. Typical ‘introductory’ reasons for the selection of a particular reactant as worthy of study, include background sources that mention only selective coverage of the relevant literature. Sometimes the emphasis is placed on the previous articles by the author [127] himself. Other papers identify the reactant as being ‘of interest’, apparently only because of its absence from previous work. These reasons are not usually presented in the context of contributions to systematic theory development or explain why it is of value (or should be of interest to the reader) to examine one or more substances from the almost infinite range of diverse, hitherto unstudied, possible reactants. Such research programs can often be regarded as making only the smallest contribution towards subject advances. Relatively few articles avowedly present attempts to resolve problems identified within or between already published material or to extend theory. Indeed most papers refer to relatively few earlier reports that express results and views which differ significantly from any new conclusions being offered. Within many introductory sections, references to earlier work by the authors almost invariably appears (from which I claim no immunity [127]), increasing the impression that TKA articles consist of a set of isolated contributions rather than a coherent and organically developing literature.

(As an example of the esoteric arguments which have been used to ‘Introduce’ TKA reports, some papers recently submitted for publication justify TKA studies of selected reactants because the compounds investigated might have potential as anti-cancer drugs. The relevance and value of extending thermal studies to 1000 K for reactions in a non-aqueous environment for substances containing high proportions of heavy metals (usually toxic) is not explained and does not feature in the discussion. This trend of justification of work beyond the realistic scope of the subject is symptomatic of a general loss of coherent development and the absence of relevant objectives that can be convincingly related to advancing thermal chemistry by theory development.)

6.4. Crystolysis reactions

The term, *crystolysis reaction*, has not yet found general usage but a suggested definition [1,5,6] is: “A decomposition that is identified as proceeding in the solid state”. Its adoption is strongly recommended because there is an urgent necessity for a key-word, index entry, abstract reference, etc., which specifies that the chemical change concerned proceeds without melting. This would enable TKA (and other) studies of crystal reactions to be categorized positively, distinguished by appropriate observations from processes proceeding in a melt or involving fusion: partial, local and/or temporary. The case for adopting this nomenclature appears to be overwhelming for three reasons:

1. A term, specific to solid state reactions would permit more efficient and effective literature searches. Reports of crystolysis reactions tend to be widely dispersed throughout the chemical literature [1,6]. Consequently, comprehensive surveys of indices and abstracts are necessarily laborious because recognition of articles of interest must be based on words of general, or unusually non-specific, meanings such as “solid”, “decomposition”, “thermal reaction”, etc. Moreover, indexes do not always include the necessary and sufficient information in the form of ‘key-words’.
2. There is a reluctance amongst authors reporting thermal reactions of initially solid reactants to state explicitly the phase in which the chemical changes subjected to kinetic analysis take place (see Sections 3.3 and 5.7). Such identification should be an essential feature of any proposed mechanistic description of behaviour and should be clearly identified. Use of the term ‘crystolysis’ would encourage authors to undertake the observations required to establish the condensed reaction phase (solid, liquid or, possibly glass). The absence of phase specification leaves unresolved a most important, indeed fundamental, mechanistic feature of the reaction studied.
3. The recognition of a subject-specific label could contribute to order, throughout TA, by the identification of groups of rate processes within which common chemical characteristics might reasonably be expected.

6.5. Term definitions used in TKA

The (perhaps unintentional) modification of term meanings as used in TKA can be expected to alter profoundly theory developments. The ambiguities, discussed above, that have arisen for usage of the terms *rate constant*, *reaction mechanism*, *Arrhenius parameters* and, most importantly *activation energy*, should be reconsidered to ensure that the precise scientific significances intended are always unambiguously expressed in communication and discussion of TKA information. There is no reason why these terms should have been permitted to become less specific, indeed advantages should result from consistent and correct definitions of these and all terms used for TKA reports.

7. Theory developments

This review presents the case that the scientific theory employed in TKA studies has failed to mature during subject development and is now inadequate. The author believes that, because the older theoretical concepts and models maintained in use have not applied the relevant physical and chemical principles in investigations of thermal reactions, a literature composed largely of individual articles has proliferated rather than progressed. Science is characterized by the development of order within accumulated information: this is not obvious in TKA reports where, so far, unifying principles and/or classification criteria have not been recognized. It is argued above that many recent publications report rate measurements that may be empirical or may solely represent some repackaging of mathematical approaches to data analysis. It is intended here to establish the urgent need for reappraisal of all aspects of this subject, to identify the shortcomings of existing methods and, if possible, to convince colleagues that there is a need to fulfil the expectations of science. This is to identify systematic order so that the trends recognized can catalyse theoretical advances by induction.

One view of this objective is that it requires the destruction of an existing ethos. In general, breakdown is usually achieved more easily than the construction of a replacement. However, the case here, extolling the virtues of change, has been intentionally presented throughout in forms that were intended to indicate the replacement concepts that might be expected to be capable of filling the theoretical vacuum. Indeed, the most promising and optimistic way forward appears to be to reconsider the theory of thermal chemistry in the context of solid state reactivity. The subject of crystolysis reactions was eclipsed during the era of promotion of mathematical methods for kinetic analysis, which now appears to have become spent, without the appearance of the necessary advances in all other aspects of theory. Reversion to the concepts of the pre-TKA era, based on chemistry, both solid state and melt, might contribute towards the widening of horizons and provide a more general and relevant framework for understanding thermal reactions. The following two approaches have already had some success in explaining behaviour and may be potentially capable of profitable extensions. First, the theory proposed by L'vov [31,32] is based on physical and chemical principles and has already quantitatively accounted for the kinetic properties of many simple thermal processes. Second, the assumption (implicit in so many TKA analyses) that reactions studied by TA methods occur in a simple, single step must be critically reexamined by considering a wider range of mechanistic possibilities.

7.1. The L'vov evaporation model for crystolysis reactions

This quantitative model, published 6 years ago [32] was developed to provide a theoretical explanation for the kinetics of crystolysis reactions. Based on the Hertz–Langmuir concepts, the initial step in reactant breakdown is assumed to be the congruent dissociative evaporation of the species with simultaneous condensation of the low-volatility product. The theory is rigorous, self-consistent and quantitative, providing a treatment that is generally applicable in a field where, up to now, both reaction models and order have been conspicuously absent. This concept has already been successfully used to classify several sets of related reactions (see [31,32,42,43] and references therein), through identifications of relationships within groups of sublimations and of decompositions, where the original reports appeared inconsistent or hitherto unrelated. The essential prerequisite for this interpretation of kinetic observations is a knowledge of the necessary thermodynamic quantities for the participants and further similar information is now required to extend the method to additional compounds [128]. In addition, to confirm the method, to obtain insights into the mechanisms of selected reactions and to expand the range of solid reactants considered and similarly classified, it is necessary to develop and to extend the use of quadrupole mass spectrometry. Thus the *primary* volatile reaction products can be identified unambiguously. The theoretical treatment proposed [31] merits careful consideration because it offers more promising prospects for progress in understanding crystolysis reactions than has been proposed for decades. Moreover, no alternative general theory appears to be currently available.

7.2. Melting in condensed phase decompositions

From the literature we can recognize two distinct and different types of mechanisms for the decompositions that occur on heating an initially crystalline reactant. The L'vov theory, and its predecessors (e.g., the P–W model) [31], have been specifically addressed to crystolysis reactions. Alternatively, other solids melt, during which the chemical constituents remain unchanged except for the loss of long-range order. Only at a higher temperature are there valence bond redistributions, homogeneous reactions, in the melt. These may proceed in the presence of a solvent (a reactant constituent, e.g. water, for a hydrate) or by decomposition in a simple melt (reaction in a solvent-free liquid). Both of these (limiting) types of processes have been studied and are well known but difficulties have arisen in distinguishing between them. Even more difficult is the recognition and interpretation of behaviour for thermal reactions that involve features of both. Such decompositions are initiated at, or below, the melting point [97] or when the early breakdown yields some liquid, or molten eutectic and/or fluid intermediate: some reactions may proceed more rapidly in the fused phase [26] (see also [22–24]). This could be represented as an autocatalytic process, involving a 'liquid nucleus': however, this characteristic type of mechanism cannot be a part of the theory of crystolysis reactions. Further, additional mechanisms become possible if there is participation by a volatile unstable and transient intermediate [34].

The greatest problems in characterizing the dominant control(s) of kinetics during (sometimes complex [22–24,97]) thermal reactions occur in processes where liquefaction is incomplete. This may involve a thin superficial layer of mobile material across crystal boundaries, or a small total amount of liquid, perhaps dispersed as separated droplets, from fused intermediate, eutectic, etc. Constituents can be difficult to identify, including any essential, but transitory, intermediates (molten or dissolved) in this fluid, which then represents partially reacted material involving components different from those of the reactant. Detection of intracrystalline melting can require sophisticated and dedicated observational methods [24,27]. Characterizing reactions within such limited, mobile and/or molten reaction zones, during chemical changes within external boundaries of a crystal, requires much more detailed quantitative information about the chemistry of the active zone than is usually available or is easily obtained. This experimentally difficult subject area has hitherto enjoyed limited recognition [97] and correspondingly restricted development. Nevertheless, the possibility that reactions, at present conveniently (but unrealistically) regarded as crystolysis processes, involve melting and complicated mechanisms must be remembered in TKA data interpretation. Melting is perhaps the most common consequence of heating crystalline materials.

7.3. Systematic order in decomposition reactions of crystals

One approach to theory development is to search for systematic order within groups of related reactions, thereby recognizing common controlling principles, which may be capable of wider generalization. The TKA literature contains few such examples of order but some recent articles directed towards elucidating systematic behavioural properties can be cited. Petit and Coquerel [11] have proposed a ‘Unified Model for the Dehydration of Molecular Crystals’. Koga and Tanaka [116] have reviewed the successes, the status and the problems in the physico-geometric approach to studies of the dehydrations and decompositions of inorganic solids. The value of microscopic observations is demonstrated by photomicrographs of unusual good quality. Galwey [28] surveyed the literature on dehydrations of crystalline solids, distinguishing six ‘Water Evolution Types’ on structural criteria. Korobov [129] has discussed aspects of the assumptions made in the formulation of kinetic models applicable to decompositions of solids.

7.4. Model reactants for theory development

Advancement of scientific understanding, including theory development, is most suitably approached through studies of reactions selected to be as simple as is practicable. Such systems must, however, exemplify and be representative of the phenomena to be investigated. This is difficult to achieve for crystolysis reactions because many are unexpectedly complex as illustrated by the following examples:

1. Some crystolysis reactions, long regarded as ‘simple’, have subsequently been shown to consist of more than a single rate process, e.g., decompositions of $KMnO_4$ [16] and of some copper(II) salts [25] and the dehydration of $CaC_2O_4\cdot H_2O$ [17].
2. Rates of endothermic and reversible reactions are often subject to secondary controls, due to rates of movement of heat and/or mass. Although the dehydrations of crystalline hydrates [28] and carbonate dissociations are often used as ‘model’ or representative rate processes, kinetic characteristics vary significantly with reaction conditions (Section 4). See also the distinction between *equimolar* and *isobaric* rate processes, discussed by L’vov [31].
3. Comparative surveys for selected, usually simple, reactions, [7–9,98–100] found considerable deviations in reported kinetic results, attributable to secondary controls.
4. Taplin [130] has emphasized, for heterogeneous reactions, the necessity for making independent measurements of geometric parameters and other physical properties: “we cannot rely on a fit of the kinetic data alone”. He also mentions that ‘obscuring’ the dimensions of k with respect to t can lead to erroneous values of E.
5. Many reactants melt during decomposition and these cannot, therefore, be classified as crystolysis reactions [22–24], etc. There is even the possibility that melting itself can be misidentified as a solid state reaction [131].

It might be concluded that few (even no) truly simple crystolysis reactions exist. Many of the early ‘model’ solid state decompositions have since been shown to be more complicated than had been originally believed.

8. Future prospects

The situation identified in this review demonstrates conclusively that a high proportion of the kinetic studies reported in the recent TA literature is concerned with reactions that are condition-sensitive and experimental method-dependent. The consequences of such sensitivities and dependencies are not, however, always explored. Furthermore, data interpretation frequently ignores the possibility that thermal reactions can (and many do) proceed through complex mechanisms. Thus, the conclusions from such research programs are often isolated, in the sense that the work does not advance development of a systematic subject through coherent growth. The author is convinced that if the subject is to thrive, and to realize its full potential, aspects of the discipline must be constructively addressed: TA must ADAPT:

1. *Acceptance*. It is essential that the unsatisfactory state of much theory, many practices and some term definitions throughout the TKA literature should be widely and fully recognized as being unacceptable. The consequences of shortcomings in currently used concepts, objectives, methods, term definitions, computer programs, etc., must be viewed, by everyone active in the field, as presenting serious and presently unresolved problems. It is hoped that this necessary realization will awaken the enterprise

of researchers interested in enhancing the status of TKA through their critical scrutiny of all aspects of the subject. The acceptance of the existence of a malaise, followed by diagnosis of its form, extent and consequences, must precede any effective curative action.

2. *Diagnosis*. Reasons for the significant inconsistencies in reported TKA results must be established. This must particularly include the identification of all secondary factors that influence rate data and limitations in calculation programs that introduce uncertainties into TKA conclusions. Successful theoretical interpretations can result only from meaningful kinetic analyses of observations.
3. *Application*. It is necessary to recognize that it is more difficult to elucidate reaction mechanisms by thermal methods than appears to have been accepted by many researchers active in this field. The shortcomings highlighted above (and undoubtedly others) must be overcome in experimental design and data interpretation.
4. *Promulgation*. Only by critically analysing and commenting on the relevant literature, to characterize all identifiable inconsistencies, and to review comparatively and critically reported behaviour patterns, can the significance of the information available be appraised and systematically presented through theoretical principles.
5. *Transformation*. Progress in any scientific topic requires objective appraisal of its aims and achievements at intervals. The argument presented here is that the effective replacement of crystolysis chemistry by TA methodology was accompanied by unexamined changes of scientific objectives, some of which have been mentioned. It is now necessary to recognize the significance of these shortcomings before we transform the subject (again) by the introduction of more reliable theoretical foundations and relevant objectives. The development of theoretical models is a priority. It is also important to review the literature to enable TKA to develop as a branch of chemistry and be capable of contributing to growth in this wider coherent discipline. This could transform what currently appears as a largely disorganized collection of independent, often empirical, reports into an ordered science.

8.1. Conclusion

This critical survey, relating the TKA literature to its antecedent subject, the thermal decompositions of solids (crystolysis reactions), has been intentionally presented in a robust manner. Thereby, it is hoped to provoke a debate in this field of potentially great importance but which appears to have stagnated [84] in the absence of overall critical appraisal and of adequate theory. Ample evidence has been presented here to show that there are now important, but apparently not widely accepted, deficiencies in guiding principles for future subject developments, an absence of effective communication together with a lack of recognized and agreed objectives. While these criticisms are not intended to apply to each and every recent article, the shortcomings identified here are sufficiently general to warrant a wide reappraisal of methods and objectives of the subject. Improvements in communication, particularly by literature reviewing and enhancement of the critical content of article introductions, could bring worthwhile benefits. It is not my intention, however, to advocate any unrealistic return to a 'heyday' of solid state chemistry (non-existent and certainly irretrievable), because no such possibility exists (and never did). Maybe the time is now opportune to move towards properly classifying the chemistry of the thermal reactions by accommodation (back) into the subject generally. A revised vision of TKA would accept and build the best (critically reconsidered) features from both theories and practices of the total extensive literature that is now available.

Despite the adverse conclusions that pervade the content of this article, the author remains thoroughly convinced that the overall outlook forward is predominantly bright, but only provided that the subject can adapt appropriately. If this were not the case, the present survey would not have been undertaken. Accordingly, the review is completed by some comments, possibly overgeneralized, that are intended to encapsulate essential features of the comprehensive analysis presented here. It is suggested that, instead of attempting to maintain inappropriate aspects of theory retained from the precursor discipline, TKA should reinvent itself by recognizing the complexity of the extensive and diverse range of thermal reaction types that are being studied. Reappraisal of TKA foundations should lead to recognition of the limitations of the ideas in current use, and all proposed advances through novel theories (e.g., [31]) merit careful consideration:

1. The most important conclusion is that the theories now used to interpret kinetic observations from TA studies are inadequate. These deficiencies remain unrecognized and unaddressed, in a literature that continues to expand without providing insights into the *chemistry* of the reactions investigated.
2. Interpretation of TKA data requires the application of chemical principles to identify reactivity controls and to formulate mechanisms of chemical reactions. This approach is not, however, always adequately exploited. The present undue, sometimes exclusive, reliance on mathematical analytical methods is not capable of elucidating the chemical characteristics of chemical changes. Moreover, conclusions are expected to be more reliable, when supported by relevant, complementary information in addition to deductions based on kinetic evidence alone.
3. The theory used to analyse non-isothermal rate data, traditionally favouring the mathematical approach, continues to be based on the older non-isothermal approximate equations, without fully exploiting the advantages of high speed computing developments that must be capable of improving accuracy [80,83]. Early, primitive analytical methods still appear to remain preferred throughout TKA.

4. In most studies, the theory applied in TKA data interpretation is effectively restricted to simple reactions so that it possesses little ability to detect and to elucidate complex mechanistic behaviour. Most kinetic interpretations are based on solid state models and do not take proper account of the possible diversity of thermal reactions, including transient intermediates and/or melting. Also, and/or alternatively, during crystolysis reactions there may be secondary controls due to self-heating/cooling and reversibility, where reaction rates are experimental-conditions dependent. In principle, it is possible that a novel thermal reaction might possibly proceed by any type of complex mechanism known, or even others hitherto unimagined. Comparative or relative kinetic analysis, within a limited set of rate equations, completely excludes all unfamiliar possibilities from consideration.
5. Confirmation of reaction stoichiometry has traditionally been accorded low priority in TKA studies. The theory of chemical kinetics is based on the premiss that Arrhenius parameters are associated with a single, fully characterized stoichiometric reaction, whereas in many thermal processes the changes are inadequately established. Reactions are sometimes identified from a single mass change or accepted as an expected, but unconfirmed, chemical process, often reported by a balanced equation.
6. The meanings of several terms widely used in the recent TKA literature have become appreciably modified from their original chemical significances. One important alteration has been the appearance of the concepts *variable* and/or *multiple* activation energy [61,62,92], perhaps involving undefined units for *k*. The computation programs used, together with the Arrhenius parameters obtained, and reported in the literature, now require critical reappraisal. In TKA reports, the term *mechanism* has generally become synonymous with *kinetic model*. This is unsatisfactory and restricting because it encourages the limitation of kinetic data interpretation to the identification of reaction geometry (kinetic model) rather than the more general and detailed elucidation of all aspects of the chemistry of every contributing reaction.
7. Despite the absence of adequate theory, the appearance of an alternative, general explanation for the thermal reactivities of solids [31] has attracted little interest, either acceptance or adverse comment. Already this approach, self-consistent and based on thermodynamic foundations, has demonstrated its ability to classify thermal processes by identifying order within sets of related reactions, where none had previously been perceived. Moreover, this proposal is the only general theory for solid decompositions that is currently available and, therefore, represents one possible response to a main objective of this survey, which is to emphasize the absolute need for development of a theoretical framework to unify this subject.
8. Finally, and generally, this review recommends that the roles of chemical methods and principles must be enhanced in (even reintroduced into) TKA studies if the bond redistribution processes occurring during thermal reactions, their controls and their consequences, are to contribute to the advance of chemistry. At present, most chemical aspects of the thermal reactions studied are unaccountably omitted from the central, important position that scientific discussion should occupy throughout much of the TKA research effort.

The answer, given by the above literature appraisal, to the polemical question posed in the article title, appears to be “No”. The view that emerges, from this comparative review of publications concerned with the kinetics, the reactivities and the mechanisms of reactions studied by thermal methods, is as follows. Current concepts of crystal chemistry, that form the theoretical foundation for TKA kinetic analyses, are incapable of constituting a comprehensive culture for continuing investigations of the variety of thermal changes that occur on heating reactants in condensed phases.

Appendix A. Personal comment

The main reason for preparing this appraisal of the methods and achievements of recent TKA research is that the fundamental and severe problems now identified require increasingly urgent reconsideration. Hitherto nobody else has fulfilled a need that is particularly obvious to me. For several years I have been aware of the necessity which has been the motivation this review, however, throughout this time the subject has continued in the mode of ‘Business as Usual’. Now I have finally decided that someone must act. It is more important to me to attempt to initiate a constructive debate, even one that is highly unlikely to lead to popular acclaim, than to maintain a discreet (and retiring) silence. I hope that I am fairly well-informed across a wide range of the subject, having recently co-authored one of the few general books on solid state decompositions [1] and surveyed dehydration reactions, in an attempt to introduce order [28]. I would describe my primary interest as in attempting to elucidate the mechanisms of thermal reactions, particularly involving reactants that are solid, at least initially. It could fairly be claimed, by anyone interested in discrediting my contribution here, that I am not a thermal analyst. However, I can (equally) fairly claim to be primarily a chemist and to have published contributions about many of those reactions that have long been of interest to TKA researchers. Also, we have a English language saying: “The spectator sometimes sees more of the game than the players”. Perhaps this particular ‘semi-detached’ observer has something of value to offer here and now. I sincerely believe that the potential existing for substantive progress has never been more promising ... but only if we all accept the necessity for change, particularly through recognition of the inadequacies in experimental and mathematical techniques, but most of all in theory development.

References

[1] A.K. Galwey, M.E. Brown, Thermal Decomposition of Inorganic Solids, Elsevier, Amsterdam, 1999.
[2] M.E. Brown, D. Dollimore, A.K. Galwey, Comprehensive Chemical Kinetics, vol. 22, Elsevier, Amsterdam, 1980.
[3] W.E. Garner (Ed.), Chemistry of the Solid State, Butterworths, London, 1955.
[4] M.E. Brown, Introduction to Thermal Analysis, Chapman & Hall, London, 1988 (2nd ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001).
[5] A.K. Galwey, M.A. Mohamed, J. Chem. Soc., Faraday Trans. I 81 (1985) 2503.
[6] N.J. Carr, A.K. Galwey, Thermochim. Acta 79 (1984) 323.
[7] H.L. Anderson, A. Kemmler, G.W.H. Hohne, K. Heldt, R. Strey, Thermochim. Acta 332 (1999) 33, 55.
[8] M.E. Brown, et al., Thermochim. Acta 355 (2000) 125; (see also: Parts B-p. 145, C-p. 155, D-p. 165 and E-p. 171).
[9] M.E. Brown, A.K. Galwey, Thermochim. Acta 387 (2002) 173.
[10] W. Hemminger, S.M. Sarge, in: M.E. Brown (Ed.), Handbook of Thermal Analysis and Calorimetry, Elsevier, Amsterdam, 1998, Chapter 1.
[11] S. Petit, G. Coquerel, Chem. Mater. 8 (1996) 2247.
[12] A.K. Galwey, J. Pharm. Pharmacol. 51 (1999) 879.
[13] S. El-Houte, M. El-Sayed, O.T. Sorensen, Thermochim. Acta 138 (1989) 107.
[14] A.K. Burnham, R.L. Braun, Energy Fuels 13 (1999) 1.
[15] S. Vyazovkin, Thermochim. Acta 355 (2000) 163;
S. Vyazovkin, New J. Chem. 24 (2000) 913.
[16] F.H. Herbstein, M. Kapon, A. Weissmann, J. Therm. Anal. 41 (1991) 303.
[17] A.A. Christy, E. Nodland, A.K. Burnham, O.M. Kvalheim, B. Dahl, Appl. Spectr. 48 (1994) 561.
[18] F. Solymosi, Structure and Stability of Salts of Halogen Oxyacids in the Solid State, Wiley, London, 1977.
[19] A. Glasner, E. Levy, M. Steinberg, J. Inorg. Nucl. Chem. 25 (1963) 1119, 1415;
A. Glasner, E. Levy, M. Steinberg, J. Inorg. Nucl. Chem. 26 (1964) 1143.
[20] J. Simpson, D. Taylor, D.M.W. Anderson, J. Chem. Soc. (1958) 2378.
[21] B. Mahieu, D.J. Apers, P.C. Capron, J. Inorg. Nucl. Chem. 33 (1971) 2857.
[22] A.K. Galwey, L. Poppl, S. Rajam, J. Chem. Soc., Faraday Trans. I 79 (1983) 2143.
[23] A.K. Galwey, M.A. Mohamed, Proc. R. Soc. Lond. A 396 (1986) 425.
[24] N.J. Carr, A.K. Galwey, Proc. R. Soc. Lond. A 404 (1986) 101.
[25] A.K. Galwey, M.A. Mohamed, Thermochim. Acta 239 (1994) 211.
[26] A.K. Galwey, J. Thermal Anal. 41 (1994) 267;
A.K. Galwey, Thermochim. Acta 269–270 (1995) 621;
A.K. Galwey, Pure Appl. Chem. 67 (1995) 1809.
[27] A.K. Galwey, L. Poppl, Phil. Trans. R. Soc. Lond. A 311 (1984) 159.
[28] A.K. Galwey, Thermochim. Acta 355 (2000) 181.
[29] A.K. Galwey, M.E. Brown, Proc. R. Soc. Lond. A 450 (1995) 501;
A.K. Galwey, M.E. Brown, Thermochim. Acta 386 (2002) 91.
[30] V.V. Boldyrev, Y.A. Gaponov, N.Z. Lyakhov, A.A. Politov, B.P. Tolochko, T.P. Shakhtshneider, M.A. Sheromov, Nucl. Inst. Meth. Phys. Res. A 261 (1987) 192.
[31] B.V. L'vov, Thermochim. Acta 373 (2001) 97.
[32] B.V. L'vov, Thermochim. Acta 291 (1997) 179.
[33] J. Fahrenfort, L.L. van Reyen, W.M.H. Sachtler, in: J.H. de Boer (Ed.), The Mechanism of Heterogeneous Catalysis, Elsevier, Amsterdam, 1960, p. 23.
[34] A.K. Galwey, D.M. Jamieson, M.E. Brown, J. Phys. Chem. 78 (1974) 2664.
[35] F.W. Wilburn, J.H. Sharp, D.M. Tinsley, R.M. McIntosh, J. Therm. Anal. 37 (1991) 2003, 2021.
[36] D. Beruto, A.W. Searcy, J. Chem. Soc., Faraday Trans. I 70 (1974) 2145.
[37] T. Darroudi, A.W. Searcy, J. Phys. Chem. 85 (1981) 3971.
[38] T.B. Flanagan, J.W. Simons, P.M. Fichte, Chem. Commun. (1971) 370.
[39] P.M. Fichte, T.B. Flanagan, Trans. Faraday Soc. 67 (1971) 1467.
[40] A.L. Draper, Proceedings of the Robert A. Welch Foundation Conference on Chemical Research, XIV, Solid State Chemistry, Houston, TX, 1970, p. 217.
[41] G. Bertrand, M. Lallemant, G. Watelle-Marion, J. Inorg. Nucl. Chem. 36 (1974) 1303;
G. Bertrand, M. Lallemant, G. Watelle-Marion, J. Inorg. Nucl. Chem. 40 (1978) 819.
[42] B.V. L'vov, Thermochim. Acta 315 (1998) 169.
[43] B.V. L'vov, Thermochim. Acta 386 (2002) 1.
[44] J. Zsako, H.E. Arz, J. Therm. Anal. 6 (1974) 651.
[45] P.K. Gallagher, D.W. Johnson, Thermochim. Acta 14 (1976) 255.
[46] A.K. Galwey, Adv. Catal. 26 (1977) 247.
[47] A.K. Galwey, M.E. Brown, Thermochim. Acta 300 (1997) 107.
[48] P. Barret, C.R. Acad. Sci. C 266 (1968) 856.
[49] M. Reading, D. Dollimore, J. Rouquerol, F. Rouquerol, J. Therm. Anal. 29 (1984) 775.
[50] K. Towe, Nature (London) 274 (1978) 239.
[51] B.V. L'vov, Thermochim. Acta 315 (1998) 145.
[52] F. Rouquerol, J. Rouquerol, in: H.G. Wiedemann (Ed.), Proceedings of the Third ICTA, vol. 1, Birkhauser, Basel-Stuttgart, 1972, p. 373.
[53] J. Rouquerol, Thermochim. Acta 300 (1997) 247.
[54] J.M. Criado, A. Ortega, J. Rouquerol, F. Rouquerol, Thermochim. Acta 240 (1994) 247.
[55] J.M. Criado, M. Gonzalez, J. Malek, A. Ortega, Thermochim. Acta 254 (1995) 121.
[56] A. Ortega, S. Akhouayri, F. Rouquerol, J. Rouquerol, Thermochim. Acta 163 (1990) 25;
A. Ortega, S. Akhouayri, F. Rouquerol, J. Rouquerol, Thermochim. Acta 235 (1994) 197.
[57] P.V. Ravindran, J. Rangarajan, A.K. Sundaram, Thermochim. Acta 147 (1989) 331.
[58] J.M. Criado, M. Gonzallez, J. Malek, A. Ortega, Thermochim. Acta 254 (1995) 121.
[59] K.J. Laidler, J. Chem. Ed. 61 (1984) 494.
[60] A.K. Galwey, G.M. Laverty, Solid State Ionics 38 (1990) 155.
[61] A.K. Galwey, Thermochim. Acta 397 (2003) 249.
[62] A.K. Galwey, Thermochim. Acta 399 (2003) 1;
A.K. Galwey, Thermochim. Acta 407 (2003) 93.
[63] A.K. Galwey, Thermochim. Acta 242 (1994) 259.
[64] J.M. Criado, A. Ortega, J. Therm. Anal. 29 (1984) 1225.
[65] F.J. Gotor, J.M. Criado, J. Malek, N. Koga, J. Phys. Chem. A 104 (2000) 10777.
[66] M.E. Brown, A.K. Galwey, Thermochim. Acta 29 (1979) 129;
M.E. Brown, A.K. Galwey, Thermochim. Acta 269–270 (1995) 1.
[67] A.K. Galwey, P.W.M. Jacobs, Proc. R. Soc. Lond. A 254 (1960) 455.
[68] G. Sanchez, J. Garcia, J. Perez, G. Garcia, G. Lopez, G. Villora, Thermochim. Acta 293 (1997) 153.
[69] L.L. Bircumshaw, B.H. Newman, Proc. R. Soc. Lond. A 227 (1954) 116, 228.
[70] M.G. Wolfinger, J. Rath, G. Krammer, F. Barontini, V. Cozzani, Thermochim. Acta 372 (2001) 11.
[71] D.A. Dominey, H. Morley, D.A. Young, Trans. Faraday Soc. 61 (1965) 1247.
[72] A.K. Burnham, R.L. Braun, T.T. Coburn, E.I. Sandvik, D.J. Curry, B.J. Schmidt, R.A. Noble, Energy Fuels 10 (1996) 49.
[73] R.M. Korsi, J. Valkonen, Thermochim. Acta 401 (2003) 225.

[74] P.W.M. Jacobs, F.C. Tompkins, in: W.E. Garner (Ed.), Chemistry of the Solid State, Butterworths, London, 1955, Chapter 7.
[75] A.K. Galwey, G.M. Laverty, N.A. Baranov, V.B. Okhotnikov, Phil. Trans. R. Soc. Lond. A 347 (1994) 139, 157.
[76] N. Fatemi, R. Whitehead, D. Price, D. Dollimore, Thermochim. Acta 104 (1986) 93.
[77] M.E. Brown, A.K. Galwey, Anal. Chem. 61 (1989) 1136.
[78] P. Mu, R.F. Wang, L. Zhao, Thermochim. Acta 296 (1997) 129.
[79] S.-L. Li, D.-X. Liu, S.-Q. Zhang, H. Wang, Z.-H. Yang, Thermochim. Acta 275 (1996) 215.
[80] J.H. Flynn, Thermochim. Acta 300 (1997) 83.
[81] M.R. Alvarez, M.J. Tello, E.H. Bocanegra, Thermochim. Acta 43 (1981) 115.
[82] M.J. Starink, Thermochim. Acta 404 (2003) 163.
[83] B.A. Howell, Thermochim. Acta 388 (2002) 275.
[84] A.K. Galwey, M.E. Brown, J. Therm. Anal. Calor. 60 (2000) 863.
[85] M. Polanyi, E. Wigner, Z. Phys. Chem. Abt. A 139 (1928) 439.
[86] D.A. Young, Decomposition of Solids, Pergamon Press, Oxford, 1966.
[87] P.W. Atkins, Physical Chemistry, 5th ed., Freeman, New York, 1996, p. 878.
[88] R.D. Shannon, Trans. Faraday Soc. 60 (1964) 1902.
[89] D. Dollimore, M. Reading, in: J.D. Winefordner (Ed.), Treatise on Analytical Chemistry, Part 1, vol. 3, Wiley, New York, 1993.
[90] P.D. Garn, J. Therm. Anal. 13 (1978) 581.
[91] A.K. Galwey, Thermochim. Acta 294 (1997) 205.
[92] S. Vyazovkin, Int. Rev. Phys. Chem. 19 (2000) 45.
[93] S. Vyazovkin, J. Therm. Anal. Calor. 64 (2001) 829.
[94] M.E. Brown, R.E. Brown, Thermochim. Acta 357–358 (2000) 133.
[95] A.K. Galwey, R. Spinicci, G.G.T. Guarini, Proc. R. Soc. Lond. A 378 (1981) 477.
[96] A.K. Galwey, P.J. Herley, M.A. Mohamed, J. Chem. Soc., Faraday Trans. 1 84 (1988) 729.
[97] M.E. Brown, B.P. Glass, Int. J. Pharmaceut. 254 (2003) 255.
[98] H.E. LeMay, M.W. Babich, Thermochim. Acta 48 (1981) 147.
[99] J.E. House, R.P. Ralston, Thermochim. Acta 214 (1993) 255.
[100] J.E. House, J.K. Muehling, C.C. Williams, Thermochim. Acta 222 (1993) 53.
[101] J.H. Rangel, S.F. Oliveira, J.G.P. Espinola, A.G. Sousa, Thermochim. Acta 328 (1999) 187.
[102] O. Kolcu, B. Zumreoglu-Karan, Thermochim. Acta 296 (1997) 135.
[103] J. Perez, G. Sanchez, J. Garcia, J.L. Serrano, G. Lopez, Thermochim. Acta 362 (2000) 59.
[104] R. Rajeev, K.A. Devi, A. Abraham, K. Krishnan, T.E. Krishnan, K.N. Ninan, C.G.R. Nair, Thermochim. Acta 254 (1995) 235.
[105] N. Deb, S.D. Baruah, N.S. Sarma, N.N. Dass, Thermochim. Acta 329 (1999) 129.
[106] T. Pattinaik, P.L. Nayak, S. Lenka, S. Mohanty, K.K. Rao, Thermochim. Acta 240 (1994) 235.
[107] S.G. Sinha, N.D. Deshpande, D.A. Deshpande, Thermochim. Acta 144 (1989) 83.
[108] J.N. Charles, N.D. Deshpande, D.A. Deshpande, Thermochim. Acta 375 (2001) 169.
[109] R. Prasad, A. Kumar, Thermochim. Acta 383 (2002) 59.
[110] H. Arslan, N. Ozpozan, N. Tarkan, Thermochim. Acta 383 (2002) 69.
[111] F.J. Gotor, J.M. Criado, Thermochim. Acta 383 (2002) 53.
[112] A.W. Coats, J.P. Redfern, Nature (London) 201 (1964) 68.
[113] J.M. Criado, J. Morales, Thermochim. Acta 16 (1976) 382.
[114] L.K. Avramov, Thermochim. Acta 10 (1974) 409.
[115] P. O'Brien, U. Patel, J. Chem. Soc., Dalton Trans. (1982) 1407.
[116] N. Koga, H. Tanaka, Thermochim. Acta 388 (2002) 41.
[117] V.V. Boldyrev, Thermochim. Acta 388 (2002) 63.
[118] H.R. Oswald, in: H.G. Wiedemann (Ed.), Thermal Analysis, Birkhauser, Basel, 1981, p. 1.
[119] V.V. Boldyrev, React. Solids 8 (1990) 231.
[120] C. Anderson, A.K. Galwey, Can. J. Chem. 70 (1992) 2468.
[121] A.K. Galwey, G.M. Laverty, Thermochim. Acta 228 (1993) 359.
[122] A.K. Galwey, G.G.T. Guarini, Proc. R. Soc. Lond. A 441 (1993) 313.
[123] M.E. Brady, M.G. Burnett, A.K. Galwey, J. Chem. Soc., Faraday Trans. 86 (1990) 1573.
[124] C.J. Keattch, D. Dollimore, An Introduction to Thermogravimetry, 2nd ed., Heyden and Son, London, 1975.
[125] C. Duval, in: G. Svehla (Ed.), Comprehensive Analytical Chemistry, vol. VII, Elsevier, Amsterdam, 1976, Chapter 1.
[126] P.K. Gallagher (Ed.), Handbook of Thermal Analysis and Calorimetry, vols. 1–4, Elsevier, Amsterdam, 1998–2004.
[127] A.K. Galwey, Thermochim. Acta 300 (1997) 283.
[128] B.V. L'vov, Thermochim. Acta 364 (2000) 99.
[129] A. Korobov, Thermochim. Acta 243 (1994) 79;
A. Korobov, Thermochim. Acta 254 (1995) 1;
A. Korobov, J. Therm. Anal. 39 (1993) 1451;
A. Korobov, J. Therm. Anal. 44 (1995) 187;
A. Korobov, Heterog. Chem. Rev. 3 (1996) 477.
[130] J.H. Taplin, J. Chem. Phys. 68 (1978) 3325.
[131] A.K. Galwey, D.B. Sheen, J.N. Sherwood, Thermochim. Acta 375 (2001) 161.