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Review Paper

MELTING AND THERMAL DECOMPOSITIONS OF SOLIDS
An appraisal of mechanistic interpretations of thermal processes in crystals*

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This analysis of interface phenomena considers the alternative processes that may result from heating a crystal, particularly including thermal decomposition, involving chemical reactions, and melting, involving loss of long-range structural order. Such comparisons are expected to provide insights into the factors that determine and control the different types of thermal changes of solids. The survey also critically reviews some theoretical concepts that are currently used to describe solid-state thermal reactions and which provide relevant background information to models used in a recently proposed theory of melting. Probable reasons for the current lack of progress in characterizing the factors that control chemical changes and mechanisms of thermal reactions in solids are also discussed.

It is concluded that some aspects of the macro properties of reaction interfaces in crystal reactions have been adequately described, including geometric representations of interface advance during nucleation and growth processes. In contrast, relatively very little is known about the detailed (micro) processes occurring within these active, advancing interfacial zones: reactant/product contacts during chemical reactions and crystal/melt contacts during fusion. From the patterns of behaviour distinguished, a correlation scheme, based on relative stabilities of crystal structures and components therein, is proposed, which accounts for the four principal types of thermal changes that occur on heating solids: sublimation, decomposition, crystallographic transformation or melting. Identifications of the reasons for these different consequences of heating are expected to contribute towards increasing our understanding of each of the individual processes mentioned and to advance theory of the thermal chemistry of solids, currently enjoying a prolonged quiescent phase.

Keywords: *crystolysis reactions, decompositions of solids, fusion, interface chemistry, melting, melting point, phase transformations, sublimation*

Introduction

Probably the most familiar consequence of heating a crystal of a pure compound is that it melts, without chemical change, at a precise melting point, T_m: the value is a characteristic property of each particular compound. This is not, however, the only possible change that can result from heating, other solids undergo chemical reactions, sublimation, crystallographic transitions, and, in addition, some substances show combinations of these processes, with or without, melting. While undoubted progress has been made in characterizing the phenomenology of the physical and chemical changes mentioned, theory development has been less satisfactory.

Melting

Several alternative representational models for melting can be found in the literature but none has found general acceptance. In an attempt to remove this apparent impasse, the set/liq model for melting [1–4] has been formulated, based on evidence that there is extensive retention of crystal-like order in some melts at the T_m.

Thermal decompositions of solids

Many solids undergo thermal decomposition on heating, crystolysis reactions [5]; this type of chemical change has been intensively studied. The dedicated theory, developed to explain the characteristic behaviour patterns observed, owes much to the kinetic models applied to homogeneous rate processes, though without providing adequate justification for the exten-

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sion of theory to heterogeneous reactions. The subject area has developed almost as a distinct discipline and a critical review of the current situation, particularly concerning those aspects that may relate to fusion, forms the greater part of this survey. Some progress has been made in characterzing the kinetics of selected representative crystolysis reactions, and aspects of the reaction mechanisms have been elucidated [5].

Sublimation

The role of equilibration in sublimation kinetics has been discussed by L'vov [6–8] for 50 substances that yield gaseous products only. Greatest progress has been made through studies of the simplest substances: elements, oxides and other binary compounds. A similar primary volatilization step, congruent dissociation of the reactant, is identified [9] as the primary step in a physical approach to formulation of a theory for decompositions of solids. The relationship of this newer model to the alternative older representations appearing in the current literature is discussed below.

Crystallographic transitions

Many crystalline solids transform from one lattice structure to another on heating, without chemical reaction of the constituents, e.g., metals [1]. Changes may proceed by a cooperative (martensic [4]) transition or by an interface reaction, comparable with those occurring during crystolysis reactions. Little is known about the kinetics and mechanisms of many of these reactions, mentioned here only for completeness: details are not discussed.

Melting with decomposition

On heating, some reactants undergo complex changes, for example, a thermal decomposition may be accompanied by melting, involving the participation of molten intermediates or products. These processes are intentionally omitted from discussion here because it is considered essential first to characterize the chemistry of the simple, contributory steps before making attempts to elucidate the chemistry of more complicated reactions. A problem in the literature is that reactions proceeding through complex, concurrent and/or overlapping consecutive rate processes are not always identified as involving two (or more) distinct rate processes, some of these are described and incorrectly interpreted as a single, simple reaction [10–13]. Elucidation of the mechanisms of complex reactions, including identification of any intermediate compounds participating, measurements of the kinetic parameters, etc., is often experimentally very difficult.

The distinctive types of thermal changes of solids, mentioned above, tend to be considered in different parts of the scientific literature. Melting, sublimation and crystallographic transformations are usually regarded as physical changes, whereas thermal decompositions are undoubtedly chemical reactions. The present comparative analyses are primarily concerned with melting, sublimation and crystolysis reactions because these are the subjects of current theoretical discussions [1–13]. Until recently there appears to have been little overlap of interest and theory development, for these topics, presumably because comparisons of the consequences of heating solids have, hitherto, lacked an acceptable overall theoretical framework. However, if representational models could be developed, capable of contributing to the understanding of the physical or chemical parameters that control each of the different types of change mentioned, this could be expected to advance generally the theory of all thermal properties of solids. (Also the products of these changes, particularly melts [1–4].) Moreover, comparisons of the perceived strengths and weaknesses of theoretical concepts that are applicable to melting and/or sublimation with those that are applied to thermal decompositions may have mutual benefits in advancing understanding of both of these distinctive, but different, types of thermal changes. This aspiration will be addressed in the final section of this review. Before considering these generalities, however, it is appropriate to provide a brief historical survey of theories of solid-state decompositions [5, 14], mainly addressed to readers less familiar with this (almost) specialist and (certainly) distinctive discipline [10–13]. The account is also intended to introduce the terminology used to describe interface reactions and to discuss the kinetic aspects, including mechanisms, of melting in [4].

Melting is a first-order transformation [15], conventionally regarded as a physical change of state because the individual constituents of the solid/melt (atoms, molecules or ions) undergo no chemical change during the (usually) facile and reversible liquefaction/solidification processes. For the simple ionic salts, primarily considered here, the electrostatic interactions that stabilize each crystal can be regarded as primary valence forces. Consequently, any structural changes that accompany melting [1–3] represent modifications to chemical bonding so that fusion can be regarded as including features of a chemical change. It is suggested here, therefore, that aspects of the theory and principles developed to apply to solid-state decompositions [5, 14] may also be applicable to the discussion of fusion given in [4].

Many solids undergo structural transformations, polymorphism, due to temperature dependent variations of the relative stabilities of their alternative possible crystal forms. Examples, not involving chemical changes of the lattice components, include many metallic elements [1], CsCl [16] and NH_4ClO_4 [17]. Peric *et al.* [18] conclude from the (mainly geological) literature that the aragonite to calcite phase change is a heterogeneous rate process. Such transformations are apparently crystolysis reactions [5], which yield a different, crystalline phase, composed of unchanged constituents. Following nucleation, the changes proceed by crystallographic control, in which a (probably activated) structure modification occurs at an advancing interface. These transformations have not been extensively characterized, their relationships with melting and decompositions of solids are not yet established and are not considered further here. Various other thermal changes of solids are known, including, for example, stepwise fusion through liquid crystals, the devitrification of glasses, etc. However, these processes are also outside the scope of the present discussion, which will be principally concerned with the simplest and best-defined systems available.

Thermal decompositions of solids: theory and kinetic concepts that may also relate to melting

Scope

A comprehensive discussion of all aspects of the thermal chemistry of solids is beyond the scope of this survey, which is intended to be concerned only with those specific aspects of this broad subject [5, 14] that may possibly be related to melting. Attention will be focussed mainly on thermal decompositions occurring below the T_m (i.e., without fusion) in which one (or more) crystal component chemically reacts or it interacts with other constituents. These rate processes yield residual products that may be crystalline, amorphous (and/or liquid) and, in many, gases are also evolved. There is a considerable literature relating to crystolysis reactions [5, 14], in which experimental observations are discussed and interpreted through a dedicated theoretical framework. Greatest progress has been made for investigations of the simplest reactions, in which a single, pure solid reactant decomposes to yield a solid product and a single (or simple mixture of) gaseous product(s) [5, 14]. In addition, many examples of complex reactions are known, involving liquids and/or intermediate compounds, but investigations can be very difficult. For these, characterization of all participants (reactants, intermediates, products) together with experimental measurements of the variations with time of amounts present as solids and their concentrations in the melt, pose considerable (often intractable) problems. The kinetics and mechanisms of these complex reactions will not be discussed here.

The reaction interface

It was found necessary to develop a specific theory of reaction kinetics for the interpretation of rate data for thermal decompositions of solid reactants [5, 14, 19]. The essential concept, underlying much of the classical approach used in mechanistic studies of these rate processes, is that the chemical change occurs preferentially, even exclusively, at a *reaction interface*. This is a phase discontinuity, the solid reactant/solid product contact interface, and it is accepted that at this contact the reactant is transformed into product. Decomposition continues at the periphery of the (often compact) assemblages of product, nuclei, which grow in size as reaction continues. Thus, once initiated, the advance of all active interfaces into unchanged reactant represents the progress of the chemical change and the overall reaction rate is directly proportional to total area of all interfaces contributing. This heterogeneous reaction model differs from homogeneous rate processes in that the probability of reaction is greatest, or enhanced, for those reactant species located at an active interface, which progressively moves into the remaining solid (immobile) reactant. Consequently, the reaction rate is determined not by reactant concentrations, or total numbers of species present, but by the *area* of all active interfaces participating.

Two distinguishable features of interface behaviour, *reaction geometry* and *interface chemistry*, are usually considered separately in the interpretation of kinetic data for crystolysis reactions. These are discussed in the following paragraphs.

Reaction geometry and kinetic model

The rate equations, kinetic models, used for the analyses of crystolysis reactions have been developed from geometric representations of interface advance [5, 14, 19], based on quantitative consideration of two essential and complementary processes. (*i*) Nucleation is the frequency and disposition of the generation of new active interfaces throughout the reactant particles. (*ii*) Growth is the rate and directions of advance of the established interfaces into the unchanged reactant. The forms of possible spatial patterns of these nucleation and growth reactions have been confirmed for representative solid-state decompositions by microscopic examinations either during the progress of the reactions or after their interruption, through cessation of change by cooling. From observations of the dispositions of new nuclei and their changing shapes during subsequent growth, various different types of interface development models, proceeding through interface advance in one, two or three dimensions, have been established. These representations of systematic changes of interface spatial dispositions, as the chemical change progresses, provide the foundation for the geometric approach to the formulation of kinetic models, which can be used to express quantitatively the variations of isothermal reaction rates with time. Various kinetic models formulated from appropriate combinations of nucleation and growth characteristics have become accepted and are now widely used in the kinetic analyses of yield-time data measured for reactions believed to proceed in the solid state [5, 14]. This approach to kinetic analysis contrasts with those relationships in which reaction rates depend on concentrations, reaction orders, familiar from the kinetic theory of homogeneous reactions: in crystal reactions ‘concentration’ has a different meaning.

Early microscopic studies of crystolysis reactions showed that many (perhaps all) reactions of solids are initiated at the outer surfaces of the reactant crystals. Product nuclei are usually regarded as being generated at sites of relatively greatest (local) reactivity and, in different reactions, the numbers/densities of nuclei that are formed vary widely. However, nucleation processes are responsible for only a very small proportion of the overall chemical change, though this control of where reaction starts can exert an important influence on the overall variation of rate with time (the shape of the isothermal product–yield time curve) during the subsequent growth process.

The overwhelming proportion of product formation results from the maintained advance of all active interfaces into unchanged reactant. The observational evidence is that, once an active reactant/product interface has been established (a growth nucleus), the rate of its (isothermal) advance into surrounding unreacted material remains constant thereafter [5, 14, 19]. Patterns of nucleation, taken with rates and dispositions of interface development during the progress of reaction, again measured microscopically, have been used to characterize patterns of kinetic behaviour for diverse and representative reactions. From extensive observations, a range of kinetic expressions, based on generally applicable geometric principles and descriptive of interface reactions in solids, have been formulated. The initial mathematical exploration of this model was given by Jacobs and Tompkins [19] and other accounts are available [5, 14]. During the developmental phase of this approach to solid-state kinetics (before about 1970), conclusions about interface advance based on excellence of fit (or otherwise) to alternative geometry-based equations were often supported by microscopic observations. Satisfactory kinetic analyses of shapes of isothermal yield–time curves for many crystolysis reactions have been reported [5, 14, 19]. Direct observational corroboration is, however, only rarely provided in more recent work. Nevertheless, a set of these kinetic models, a representative range of rate equations derived for appropriate geometric behaviours, is still very widely used in the kinetic analyses of crystolysis reactions.

Where only relatively few nuclei are formed initially, due to a ‘difficult’ nucleation step, the slow early rate of reaction is characteristically acceleratory. However, after reaching a maximum value, this rate later diminishes when the total aggregate area of active advancing interfaces is reduced by coalesence of nuclei to form a reaction envelope which contracts into the crystal centre. These sigmoid-shaped isothermal yield–time curves are characteristic of the ‘nucleation and growth’ reaction model [5]. If, in contrast, nucleation is facile, very many nuclei are formed at the onset of reaction, soon covering all reactant surfaces. Rates of such reactions are deceleratory throughout, as interfaces undergo a continual contraction of area during advance to the crystal centre according to the ‘contracting cube (or sphere) model’. The probable applicability of this model to melting is discussed in [4].

Interface chemistry

The molecular-scale sequences of processes by which a reactant is chemically transformed into products at, or within, an active reaction interface (the reaction mechanism) has not yet been acceptably and generally characterized for most solid-state decompositions of interest. However, it is widely agreed that the variations of reaction rate constant magnitudes with temperature for crystolysis reactions are satisfactorily expressed by the Arrhenius equation: the rate constants are obtained using the geometric model kinetic equations [5, 14, 19]. This trend (and the absence of any obvious alternative) provides the main evidence that justifies the widespread application of the Arrhenius activation model to interface reactions proceeding in crystalline reactants. Thus, it has been widely accepted that these reactions proceed through a dominant activation step, comparable with the rate-determining step in homogeneous reactions. Countless values of activation energies (E) and pre-exponential terms (A) (or activation entropies) for diverse reactions have been reported in the literature [5, 14]. From the perceived parallels with homogeneous reactions, E values are identified with activation of a particular bond in the transition state (the ‘rate limiting step’) and A with the ‘frequency of occurrence of the reaction situation’. While this use of A, E (etc.) is a valuable, concise method of expressing kinetic data succinctly, the usage can also imply closer similarities between the reactivity controls and the mechanisms of homogeneous and of heterogeneous reactions than is currently demonstrable from the experimental evidence available.

The theory of reaction rates was developed through the Polanyi–Wigner model [20–22], which sought to correlate interface advance rates with crystal properties. This approach was later accepted as satisfactorily explaining the rate of dehydration of copper sulfate pentahydrate [23] and extended to a range of other solid-state decompositions [24] by including some concepts from absolute reaction rate theory [25]. However, it has since been shown [26] that reported magnitudes of *A* and of *E* show a wider variation of values than is consistent with this approach. More detailed accounts of this theory have been given [5, 14]. During subsequent changing priorities within this research field, summarized below, interest in explaining Arrhenius parameter magnitudes has declined and this theory has effectively been abandoned.

Attempts to provide theoretical explanations for the kinetics of interface reactions in solids have been based on foundations that have not been adequately confirmed to be applicable to crystolysis reactions. In heterogeneous solid-state reactions, it is accepted that the chemical changes occur preferentially within the contiguous zone of contact between two dissimilar crystals. In contrast, homogeneous reactions of gases involve freely moving molecules. These quite different rate processes are not obviously represented by a single theoretical model and the rates of chemical changes cannot be expressed quantitatively by the same parameters without much greater evidence of similarities than has yet been provided. The sweeping assumptions implicit in this extension to solids of theory, which has been successfully applied to homogeneous reactions, can be criticized for several reasons, including the following.

No information is available about the nature of the ‘rate limiting step’

The immediate precursors to chemical reactions at interfaces are inaccessible to direct investigation and the detailed structures of the reactant-product contacts at ‘atomic’ level are effectively unknown for reactions of interest. The concentrations/numbers of precursor reactant species within an advancing interface are not currently amenable to measurement. We do not know the nature of the interactions between reactants during the rate-controlling bond redistribution step. No quantitative information about the ‘activated complex’ (composition, concentration, stability, etc.) is obtainable from the experimental techniques currently applied. This lack of knowledge contrasts with the evidently much more detailed information available concerning the simple homogeneous rate processes from which the theory of reaction kinetics was originally developed [25, 27]. In these, reactant concentrations and molecular constitutions are known enabling the numbers and structures of the ‘transition complex’, including the critical bond transition(s), to be estimated. The subsequent breakdown of this short-lived activated species is effectively independent of interactions with other molecules present (evidently contrasting, in this respect, with interface reactions). Chemical change is identified with reorganization of a specific bond within the unstable activated complex and it follows that the rate-controlling step can be portrayed and its properties considered in considerable detail. Knowledge of product(s) structure(s) may further contribute to characterization of the properties of the short-lived intermediate. Considerable progress has been made in developing, and successfully applying, transition state theory to reactions in gases and in solvents [25, 27]. In contrast, for interface processes the absence of identification of the detailed course of chemical change (nature of transition complex, reaction controls, etc.) drastically diminishes the reliability of mechanistic interpretations.

Reactions of ‘free’ gaseous molecules and of constituents in crystals differ in that the latter are immobilized and must always be subject to interactions with the surrounding lattice components. Moreover, the reactant environment may not be constant as decomposition proceeds. The force fields surrounding a precursor to reaction must change locally and intermittently due to structural reorganization following reactions of neighbouring species, losses of volatile products and (possibly) residue recrystallization when reaction advances stepwise into unchanged reactant. Little is known about how these factors influence rates of chemical changes at a reactant/product contact. Modelling the behaviour of activated complexes at interfaces is much less reliable than for gas reactions. In particular, the factors responsible for promoting reactions at interfaces in solids have not been established.

Energy distribution in solids

While the Arrhenius equation is (perhaps universally) accepted as applicable to crystolysis reactions, the precision of the data fit for a particular rate processes is rarely measured and the possible use of alternative relationships is rarely considered [27]. Garn [28–32] has pointed out that high thermal conductivities means that energy is rapidly redistributed within crystals, minimizing departures from the mean. The (relatively wider) Maxwell–Boltzmann distribution, applicable to energy in gases, does not apply in solids, which means that care must be exercised in interpreting the significance of the conventionally calculated kinetic parameters, apparent *A* and *E* values. However, it has since been shown [33, 34] that, in solids, the highest energy levels occupied by electrons, and also by phonons, conform to distributions that approximate to the exponential energy term. This provides a theoretical justification for using a relationship in the form of the Arrhenius equation for the kinetic analysis of solid state reactions. It also is consistent with the participation of an activation step in component breakdown at the reaction interface, reaction rates generally increase exponentially with temperature. Care must, however, be exercised in assigning significance to the magnitudes of these apparent Arrhenius parameters and in formulating detailed reaction mechanisms from such observations.

Limitations to applicable theory

Some mechanistic generalizations, widely accepted as being applicable to reactions of freely moving gaseous molecules, may not be valid for the description of interface processes. Within the confines of intercrystalline zones, species (largely) immobilized at the reactant boundary may undergo cooperative interactions, possibly involving more than two participants (termolecular reactions, etc.) in reaction steps that are ‘statistically improbable’ in a gas. Other forms of cooperative mechanistic interactions at a crowded interface, of types not permitted in current kinetic theory, as applied to gases, may enable chemical change.

Another uncertainty in the kinetic analysis of interface reactions is that reactions may be complex and involve cooperative or consecutive steps, in which the numbers/concentrations of the precursors to product formation vary with temperature. This is a difficult quantity to measure experimentally and contrasts with the more reliable information usually available for single step homogeneous reactions where reactant concentration variations with time are known and do not depend on temperature. The variation with temperature of effective reactant concentration at an interface means that the measured temperature coefficient of reaction rate is a composite quantity and the calculated (apparent) E value cannot be used as a measure of the energy barrier to reaction [35, 36]. In the absence of adequate information about the identities and concentrations of the precursors to the activated transition species, the mechanism and controls of the (possibly complex) reaction cannot be established. (Closely similar uncertainties may apply in the identification of reactivity controls and in formulating the mechanisms of many heterogeneous catalytic reactions [35]).

Properties of reaction interfaces have been extensively discussed and, in particular, the natures of the controls that facilitate the occurrence of chemical change preferentially, perhaps exclusively, within the reactant/product contact zone. Some early treatments attributed promotion of chemical change at interfaces to local strain at the structural discontinuity [5, 14], perhaps diminishing the energy barrier (E) to electron transfer or other bond redistribution process. The possibility that a solid product enhances anion breakdown has also been discussed: there are mechanistic similarities between metal catalyzed breakdown of formic acid and decompositions of the metal formates [35]. Evidence has also been presented [37, 38] to indicate that retained intranuclear water promotes some alum dehydrations. Indeed, any effect that increases the reaction frequency factor (A) and/or diminishes the activation barrier (E) may account for the autocatalytic character of an interface reaction.

Recent trends in kinetic and mechanistic investigations of the thermal decompositions of solids

Subject development since the 1970s

The above survey summarizes aspects of the general theoretical background and practices accepted by researchers concerned with the thermal decompositions of solids up to (about) the mid 1970s. Up to that time, many publications reported detailed thermal investigations of reactants that were often selected from a relatively limited range of solids [5, 14, 19]. Many kinetic analyses characterized nucleation and growth processes and identified ‘best fit’ geometric model was confirmed by microscopic observations. Significances of the apparent Arrhenius parameters were discussed according to the theoretical principles outlined above.

Almost all activities and priorities in this field after the mid-1970s have been transformed by the development of thermal analytical methods [39]. This has resulted (apparently) in the virtually complete redirection of interest towards expanding the applications of automated and efficient experimental techniques capable of providing a maximum amount of kinetic data from a minimum number of experiments. The author’s critical reviews of recent publications concerned with thermal analysis and its kinetic applications have already been published [10–13]. Some important conclusions resulting from these surveys are summarized below, to provide a background against which the general thermal properties of solids can be discussed and, more importantly here, enable those aspects which relate to the theory of melting [1–4] to be identified.

It is probably true to say that, throughout the period of preoccupation with thermoanalytical investigations, which is still continuing, little effort has been directed towards advancing theory development for solid-state decompositions. This is surprising because a large majority of the published studies, reporting research using these techniques, are apparently concerned with the thermal behaviour of solid reactants, though the absence of melting is not always confirmed. The use of programmable equipment, that controls the course of thermal experiments, has been complemented by computer methods for data analysis that together enable kinetic measurements to be interpreted rapidly. The widespread preference for these largely automated research methodologies has had two (possibly unintended) consequences that have severely curtailed advances in the understanding of the chemistry of crystolysis reactions [5]. First, few investigators have continued to study solid-state decomposition reactions within the essentially chemical context that was central in much of the pre-1970s work. Second, researchers using the new thermal analytical techniques have developed conventions that have tended to define the subject area as a distinctive discipline with practices and fashions that separate the topic from other branches of chemistry. It is argued here that these conventions have effectively resulted in stagnation [40] and, by routinely accepting minimal experimental input, have yielded publications of doubtful scientific validity. A number of shortcomings in the unreliable (but tolerated) customs prevalent in reports of thermoanalytical studies are mentioned below [10–13]. It is not intended to imply that every such unsatisfactory feature appears in every paper but to point out that such inadequacies are sufficiently common, and because they are accepted uncritically, this blights the development of this discipline. It is suggested that careful reappraisals of nomenclature, of term definitions, of the significance of observations, of data interpretation methods and of relationships of conclusions to the wider scientific context are overdue. It might be concluded overall that the metamorphism of the subject of the chemistry and mechanisms of solid-state decompositions into thermal analysis kinetics has not been altogether as successful as it might have been if results had been subject to greater realistic appraisal, through critical and chemical scrutiny.

Appraisal of some kinetic interpretation methods used in thermal analysis

Thermal analysis refers to that group of experimental methods by which changes within a reactant are monitored with respect to time while sample temperature is maintained constant or is subjected to a regime of programmed change [39]. Properties that are monitored include (one or more) of the following: temperature difference (DTA), heat flow difference (DSC), mass (TG), etc. The methods are versatile, the equipment can measure the changes with great precision and reactions can be carried out in controlled atmospheres. These techniques have been used successfully and profitably in the quantitative characterization of numerous and diverse thermal phenomena, including both physical changes and chemical reactions. The present critical appraisal is specifically concerned with practices that are routinely used in the analyses and interpretations of rate data from thermoanalytical measurements but which appear to be at variance with acceptable scientific practices and/or lack adequate theoretical justification. These points are discussed in greater detail in [10–13], which give background information and literature sources.

Non-isothermal approximate kinetic equations

Analyses of non-isothermal rate data still continue to use the approximate kinetic models that were originally developed (around 1970) to facilitate the manual calculations necessary before high-speed computer facilities became available. Flynn has pointed [41] out, particularly considering the temperature integral, '….in this age of vast computational capabilities, there is no valid reason not to use precise values…….'. Tests for data fit based on simplified equations are not as accurate as they could, now should, be.

The kinetic triad is often (incorrectly) determined using data from only a single non-isothermal experiment

Kinetic results are often summarized by reporting the 'kinetic triad': the magnitudes of A, of E and the kinetic model (the isothermal rate equation, $g(\alpha)=kt$). Despite the clear demonstration [42] that data from a single non-isothermal experiment are insufficient to characterize these three results, papers reporting a 'full' kinetic analysis from one set of measurements continue to appear.

Apparent activation energy values calculated from a single data set vary with kinetic model

In some computational programs, calculated E values are found to vary with each kinetic model, $g(\alpha)=kt$, tested. This conflicts with the chemical significance of the term 'activation energy' [25, 27], which is an inherent property of every individual reaction and must, therefore, be independent of the calculation method used to determine it, despite suggestions that it may be a 'variable' [43].

Kinetic analyses of concurrent reactions

Kinetic theory has been developed for a single rate process in which A and E refer to a specific rate-limiting step [25, 27]. However, many reported kinetic triads are calculated for rate data that include contributions from more than a single reaction (concurrent and/or consecutive), to give kinetic parameters that cannot meaningfully be regarded as having mechanistic significance. Some reports mention the difficulties of separating overlapping kinetic processes and report empirical results from the analyses of the composite data.

Rate characteristics vary with reaction conditions

For many reversible, endothermic reactions the rate characteristics are controlled by diffusion, ease of movement of energy and/or gaseous products within the reactant mass. Furthermore, the role of reactant self-cooling is not always considered in such kinetic studies [44]. The apparent E value obtained for such rate a process can, therefore, be regarded as an empirical quantity, determined by local prevailing conditions, unless the experiment is designed to remove the influences of diffusion on reaction rate [45].

Geometric kinetic models are not confirmed by microscopic observations

Whereas in the early work, it was customary to confirm, by direct observation, the interface advance characteristics identified as providing the 'best fit' to the measured kinetic model, recent thermal studies rarely mention microscopy. (The author believes that the geometry of interface advance for many nucleation and growth reactions can be established more easily and more reliably, as formerly [5, 14, 19], by direct observations of interface dispositions in partially reacted material than by indirect thermoanalytical rate investigations and kinetic model. This view is not widely held.)

Reaction stoichiometry is not always confirmed

Many kinetic investigations use reactants for which neither the identity nor the composition is reported. Moreover, in some studies of thermal decompositions, completed in a single rate processes or by a series of consecutive steps, no analytical information concerning the identities, amounts or compositions of participating reactants, intermediates or products is provided. In some articles, all stoichiometric deductions are based on a small number of mass changes that include little reliable evidence about the specific chemical reactions for which the rate data have been measured. Without knowledge of the particular chemical change involved, kinetic conclusions may have little, or no, value.

Melting

In many reports of thermal decompositions, the kinetic analysis of data includes comparisons between only those rate equations that have been derived from geometric models, apparently without investigating whether or not an initially solid reactant melts before or during reaction [10–13]. This approach to kinetic analysis appears to imply intentionally that the rate process occurs in the solid-state, though without explicitly stating this or reporting any supporting experimental evidence. The unacceptable consequence of this uncertainty is that a most important mechanistic feature of the reaction (i.e., whether it occurs in the solid or in a melt) remains unknown: indeed, such presentations are unacceptable and confusing. Clearly, heterogeneous kinetic models cannot meaningfully be applied to reactions involving melts and, for such systems, any mechanistic conclusions are likely to be misleading.

Other

These, and other unsatisfactory practices, conventionally accepted for use in the kinetic analysis of thermal rate data are discussed, with examples, in [10–13].

Scientific order

Because of the prevalence of the above unreliable practices in published reports of thermoanalytical investigations, the significance of the conclusions based on the interpretation of the rate data must always be considered carefully to decide whether any of the above shortcomings in interpretation methods reduce reliability. So many reports base their conclusions on such a restricted experimental foundation that all must be critically examined to appraise their validity. However, one further feature of the accepted conventions in this discipline merits additional (adverse) comment.

Chemical significance of thermoanalytical kinetic conclusions

There is undoubted enthusiasm for the measurement, and the publication, of kinetic results obtained by thermoanalytical methods. For the thermal decompositions of numerous and diverse reactants, kinetic triads have been reported. However, throughout most of this extensive literature there is little evidence of any interest in considering the chemical significance of the results obtained. Kinetic behaviour is not correlated with structure, composition or, indeed, any physical or chemical property of the reactant. Magnitudes of E are not usually compared with the strength of whichever bond may be ruptured in a possible rate controlling process [27]. Reading the thermokinetic literature leaves the impression that each report is an individual study, unrelated to all others, and the limited results described represent complete achievement of the specific objectives addressed by that particular research program. Wider implications of conclusions tend to be ignored and results obtained for specific reactants are not shown to contribute to the organic development of a coherent subject founded on widely applicable scientific principles. Two (very different) responses to this, evidently general, attitude are possible.

(*i*) Science is ordered knowledge

Throughout chemistry, patterns of behaviour define the characteristic properties of each element and its compounds, through similarities and differences in criteria identified as capable of ordering, through theory, the knowledge available. This is an indispensable objective of the scientific method. A scientific imperative, apparently missing from this field, is the explicit wish to identify correlations of behaviour between related reactions that also extend into 'other' branches of chemistry. Indeed, an obvious omission from many recent publications is any attempt to place the work in its wider/widest chemical context.

The one trend that is regularly reported in the thermoanalytical kinetic literature is the compensation effect [35, 36] (a linear correlation between apparent log$A$ and E values for a set of related rate processes). This relationship (unfortunately) has no recognized theoretical value in advancing understanding of crystolysis reactions. It has been suggested [36] that the trend most usually arises as a consequence of the use of incorrect data interpretation methods and is, therefore, a computational artefact.

(*ii*) The empirical nature of many thermochemical observations

The obligation of the scientist to seek systematic order, in contributions to the advance of his speciality, is made particularly difficult in this subject area by uncertainties in the reliability of much of the kinetic information reported, for the reasons criticized in the preceding 'Scientific order'. Nevertheless, these methods and approaches remain acceptable within the thermochemical literature. A consequence is that an unknown proportion of the reported kinetic results (kinetic model, E, A, etc.) are empirical, applicable only to specific, usually incompletely defined, prevailing experimental conditions and have not been shown to refer to kinetic processes that are subject to chemical rate control. Such information may be unsuitable for the elucidation of reaction mechanisms, for identification of chemical reactivity controls and for the advancement of theory.

Comment

The above critical analysis suggests that the subject may be becoming detached from its scientific context because it has become acceptable to modify the meanings of widely accepted chemical terms (e.g., E [43]) and methods [10–13] for specific use within the discipline. This isolates the topic. It appears that the continuing considerable efforts directed towards developing thermal methods tend to emphasize 'instant kinetics', the ability to determine kinetic triads rapidly, through relatively few, sometimes only a single experiment. Earlier interests in characterizing the chemistry of solid-state thermal decompositions [5, 14, 19] appear to have been eclipsed by efforts to advance both the techniques and the 'efficiency' of thermal analysis methods. The loser in this shift of emphasis is the chemistry of solids.

The relevance of these changing fashions, to the present survey, is that (with an important exception, discussed below) relatively little interest is currently directed towards advancing the theory of interface chemistry, despite the continuing studies of crystolysis reactions. The model used to represent rate processes occurring at an active, advancing reactant/product contact has, with a few exceptions, e.g., [45], implicitly remained as portrayed by the Polanyi–Wigner model [20–24], though this model is no longer widely discussed, or even mentioned. It is probably realistic to summarize the theory of solid-state decompositions, currently (probably and implicitly) accepted by many thermal analysts, as: 'A chemical change occurring at an advancing interface, which conforms to one of a small number of geometric patterns of development (i.e., one of the accepted kinetic models [5]). The parameters controlling interface reactivity and mechanism are not well understood.' The point of interest here is that two remarkably similar sentences (probably) express widely held views of the melting/solidification process: 'A physical change occurring at an advancing (retreating) interface, which is determined by the geometry of the system. The parameters controlling interface advance rates are not well understood.'

Some theoretical models used to represent thermal behaviour of crystals: strengths and weaknesses

The L'vov 'physical model' for crystolysis reactions

The 'important exception', referred to in the previous paragraph, was the proposal by L'vov, dated 1997 [46], that kinetics and mechanisms of the thermal decompositions of eight metallic azides could be quantitatively explained by a mechanism of dissociative evaporation.

This approach has since been developed and expanded to include the thermal decompositions of a range of mainly simple solid reactants in the many publications by L'vov and his coworkers, see reviews [7–9, 47]. The 'physical model' is based on the Hertz–Langmuir theory [9] (which, incidentally, antedates the Arrhenius treatment) and accounts for the exponential dependence of reaction rate on temperature. The primary step is the congruent dissociative evaporation of reactant coupled with approximate equipartition of condensation energy from the low-volatility product between reactant and product phases. The primary products vapourized may differ from those at equilibrium [9].

It has long been a feature of the thermal analysis literature that special interest is always directed to the establishment of the geometric patterns of interface advance and to identification of the rate equation that 'best' describes the kinetic behaviour of each reactant investigated. This interest has consistently remained central to the subject since the earliest studies of solid-state decompositions [5, 14]. We note, however, that the brief treatment of this particular feature of solid-state reactions, given in [9] (p. 104), is only qualitative. It is suggested that researchers, perceiving this limited treatment of an important aspect of their subject, may have been reluctant to accept L'vov's primary objective, characterization of interface reaction controls.

The present article includes a discussion of aspects of the physical model, proposed [9] as a mechanistic representation of the rate processes taking place at the reactant/product interface in crystolysis reactions. Aspects of these changes are compared and contrasted with the structural modifications believed [1–4] to occur at the crystal/melt contact at T_{m}, by Scheme 1 in the following section. However, it is appropriate to precede this collation with a comparative appraisal of the status of the alternative theoretical models available for the interpretation of kinetic data for selected reactions, obtained by thermal methods, that are often concerned with rate processes implicitly assumed, but not confirmed, to be crystolysis reactions. The previous Section has drawn attention to the preoccupation in this field with the collection of kinetic data, without always providing chemical explanations of the behaviour observed or establishing patterns of reactivity. We discuss selected aspects of the application of the physical model [9] to interface chemistry below.

Despite the obvious shortcomings of the theoretical framework widely applied in kinetic interpretations of thermally measured rate data, outlined above [10–13], there has been a considerable reluctance to accept (or even to criticize) the L'vov model. He could state in 2001 [9] that '….the physical model has been completely ignored by all the workers in the field of traditional thermal analysis for the interpretation of crystolysis kinetics….'. In analyzing results reported in the literature, together with his own observations, L'vov's treatment differs from current practices in two important respects [9]. He addresses the potential sources of inaccuracy in selected kinetic measurements (reversibility, reactant self-cooling, etc.) and also the inherent limitations in computational methods used for data analysis, so that his interpretations are based on the most reliable observational data available. These results are then considered in the context of the chemistry of the substances involved, through which the trends identified are shown to introduce systematic order into a field where consistent patterns of behaviour had not been found previously. It is difficult to understand why the opportunities that now exist for progress, through the application, the development and/or even the criticism of L'vov's mechanistic proposals [9], have not been exploited in this field, previously described as having 'stagnated' [40]. Due to the lack of experimental facilities, this (retired) author cannot accept this challenge and the present theoretical analysis can be concerned only with those selected aspects of activation/decomposition processes that may relate to melting.

There is a debatable degree of doubt as to whether the label, 'the physical approach', acceptably describes the application of the Hertz–Langmuir (H–L) theory to decompositions of solids in [9]. The concept conveyed by this term appears to be in conflict with the overall objective of such thermal studies, which is to investigate chemical changes in solids. This apparent terminological ambiguity may have contributed to the delay in general acceptance of the physical model by the thermoanalytical community. The H–L treatment infers surface evaporation rates from the (physical) condensation rates [9]. However, the physical theory also regards the evaporation step as the energy absorbing process that controls decomposition rates because the volatilized species are the immediate precursors to the (further) chemical steps in reactant breakdown. It can be argued that the movement of entities out from the surface (on the physical approach) is chemical activation (requiring the rupture of bonding at the crystal boundary) and controls rate. This representation is analogous, in some respects, with the Arrhenius (activation) model but differs in recognizing that the components (or compositions) of the volatilized material, as portrayed by the alternative theories, are quite distinct. One consequence is that, according to the physical model, E is changed by the presence of an excess of the volatile product (equimolar and isobaric conditions [9, 48]). The consideration of equilibration involving volatilized species and the solids, completed on every collision (Point 3, on p. 99 of [9]), is important in assessing the significance of the redistribution of energy after the reaction. Compositional equilibration above the surface cannot, however, be achieved in less time than a single collision interval and the species participating are varying during the concurrent breakdown of primary products. Thus, both equilibrium and kinetic controls may influence the composition of the volatile phase. This identification of the volatilization or activation step, as determining the overall rate of the decomposition of a solid, is intended to draw attention to the similarities between the ‘rival’ approaches (labelled as ‘Physical’ and ‘Chemical’ [9]). It is hoped that appreciation of these parallels might aid a reconciliation between supporters of these alternative approaches, ‘somewhere on common ground (yet to be identified)’, leading to the establishment of a single, but generally acceptable, theory. L’vov’s valuable contribution [7–9] is that a meaningful physicochemical quantity may be extracted from the temperature coefficient of reaction rate, by redefining the physicochemical significance of the E parameter.

The physical model, as described in [9], requires activation to achieve the ‘dissociative evaporation of the reactant’ (Step 1, p. 99 of [9]), species which undergo bond redistributions to form the volatilized entities. One or more of these condenses at the interface and shares (Step 4, [9]) its excess energy with reactant and product phases. The significant difference from the classical treatment is that the products of congruent evaporation may differ from the final, equilibrium products, because here the activation step does not incorporate any allowance for such subsequent chemical (decomposition) steps (p. 110–111 [9]). Thus, the activation process in the physical and in the chemical models differs in the ‘extent of reaction involved in the primary step’: both exhibit the exponential temperature dependence, consistent with the distribution of energy in the highest occupied levels of the solid [33, 34]. It is suggested that the publication of a schematic energy diagram for the physical model, which provides a direct comparison with the well-known reaction profile for activated complex formation on the Arrhenius model [49], would be helpful. This would emphasise the essential differences between the alternative explanations of reaction rate controls. No such representation could be found in any of the papers describing the physical model. The diagram could be additionally valuable if used to portray and explain the significance of the energy-sharing step in the condensation process (Step 4, p. 99 of [9]). Hitherto, primary products of reaction have rarely been determined for crystolysis reactions, the compositions of final (equilibrium) products have usually been of greater interest (though these have not always been reported). In principle, direct experimental confirmation of the initially evaporated species provides a critical, even crucial, test of the validity of the L’vov model [9].

An aspect of the primary step in the physical model that merits further detailed consideration is the use [9] of listed values for crystal molar enthalpy of formation for both reactant and products. This assumes that there is no appreciable energy variation between material within the crystal bulk and that at the solid reactant surface (from which evaporation occurs) or arising from reactant contact with the product at the interface. Furthermore, the solid product is regarded as having a perfect crystal lattice (Point 6, p. 104 of [9]). This author is not aware that such perfection has been confirmed for most thermal decompositions, indeed many studies report products of dehydrations as amorphous (p. 228 [5] and p. 227 [14]). The possibilities of imperfect reactant or product crystallization and/or of stability differences between bulk and surface lattice components is significant because, in principle, both may influence the magnitude of the energy terms used to calculate E, and perhaps also the τ parameter (Fig. 3 in [7, 8]).

The physical model is equally applicable to sublimation and to decomposition rates and depends on identification of initial products and on the availability of suitably accurate data to calculate the specific enthalpy, $\Delta_r H_T^0 / \nu$ ([9] p. 111), the molar enthalpy of the real reaction (p. 185 of [8]). The latter condition at present effectively restricts quantitative application of the method to those relatively simpler reactants for which the necessary thermodynamic data are available. Consequently, many of the more complex solid-state reactants, which are now attracting interest, remain outside full consideration by this model. Development of these potentially interesting systems remains for others to address (‘Conclusions’ of [47]). Nevertheless, the correlations [7–9] of E values obtained experimentally with those calculated from listed thermodynamic data, given by L’vov are impressive. These conclusions [7, 8, 47] provide a physical meaning for the controlling steps in crystal breakdowns and represent the largest ever contribution towards establishing a theoretical foundation for classifying and for understanding the reactivities and mechanisms of solid-state thermal reactions. However, before a scientific theory can be regarded as having been established, other researchers must test its validity, confirm and/or criticize methods used, identify possible weaknesses, determine its range of applicability, etc. Inexplicably, thermal analysts, who might reasonably be expected to be interested in the only proposed, novel representation of the reactions that they study, have apparently chosen to ignore it. Of particular interest in the present context, however, is the identification of the initial products of a crystolysis reaction, or of a sublimation, as an equilibrium mixture of gases: this conclusion defines the nature of one type of thermal change of a solid that is an alternative to melting.

The L'vov 'third-law approach' to kinetic measurements

L'vov's other major recommendation to solid-state chemists is the use of the 'third-law methodology' [7, 8, 47] to facilitate determination of the molar enthalpy for the reaction, corresponding to measurement of the Arrhenius *E* parameter, for the formulation of decomposition mechanisms (Fig. 4 on p. 192 of [8]). There is an interesting (but not necessarily entirely beneficial) parallel between this approach and current practices in the kinetic analysis of thermoanalytical data [10–13]. Both focus on determining the (differently defined [9]) *E* values as the parameter of greatest significance in elucidating reaction mechanisms, together with the desirability of measuring/calculating *E* magnitudes through a minimum effort/number of experiments. For the relatively simple sublimations and decompositions, with which the physical theory has been principally concerned hitherto, the stoichiometry and equlibrium products are already reliably known for most, or all, reactions of interest and few alternatives require consideration. Nevertheless, quantitative analytical corroboration of the primary products from additional representative reactions would undoubtedly add to the reliability of mechanistic conclusions and provide welcome experimental confirmation of the theory. The desirability of positive identification of the initial products may rise markedly with increase in reactant complexity and with the increased possibility of alternative breakdown routes, which would be most reliably distinguished through the support of direct experimental confirmation. It can also be argued that the determination of *E* from measurements at several different temperatures is more reliable than use of rate determinations at a single temperature. Although *E* values may be obtained quickly, the comprehensive and reliable determination of the overall kinetics and the detailed mechanisms of crystolysis (and other thermal) reactions usually requires much greater investment of time.

Comments

While *E* and *A* can (perhaps) be accepted as the most important kinetic parameters in understanding thermal processes, these are certainly not the only features that must be characterized to provide a complete description of a crystolysis reaction. The following types of experimental measurements, while featuring less in recent work, undoubtedly merit study to provide an adequate mechanistic description of any crystolysis reaction or sublimation process investigated.

- Characterizations of all the secondary reactions are necessary to explain the final products. The complete elucidation of the reaction mechanism requires identification of all the processes participating.
- The phase in which reaction occurs should be established: is there melting [10–13]?
- The factors controlling nucleation/interface generation and its subsequent development (the kinetic model) have long been of interest and the overall kinetic behaviour (a continuing objective in thermal analysis) merit more precise characterization than is provided in many recent reports.
- Prediction of the species participating in dissociative evaporation, occurring during the decompositions of more complex salts, can be expected to be difficult because of the greater number of alternative breakdown sequences that are possible. Presumably direct experimental confirmation of primary products will be required to distinguish between these alternatives.

The list of reactants, confirmed as correlating with the physical model [7–9], is impressive and includes diverse types of solid reactants, though a majority are relatively simple substances. It would be interesting to extend this approach to establish whether the same model applies to other compounds of the same general types, including (references in [5]): (a) the dehydrations of alums and other extensively hydrated salts (of high 'molecular' mass) which evolve water at relatively low temperatures [37, 38], (b) the sublimation, low and high temperature decompositions of ammonium perchlorate [17], (c) the decomposition of copper(II) formate involving participation of volatile copper(I) formate dimer [50], together with other copper(II) salts that decompose through the intervention of copper(I) intermediates, reviewed in [51], (d) the two-step decomposition of $KMnO_4$ [52] and (e) the thermal reactions of nickel squarate dihydrate, where decomposition follows dehydration [53].

Consequences of heating a solid: melting or decompositon?

The above background survey is provided to facilitate discussion of the interface processes that may participate in changes at the crystal/melt interface during fusion [1–4]. Despite the long history of interest in solid reactant/solid product contact zones, progress has been slow and thermoanalytical studies have contributed little towards understanding of interface chemistry or to developing a systematic thermal chemistry of solids. Although professing interest in these same reactions, thermoanalytical researchers have undertaken few, if any, studies to test the tenets of L'vov's model [9]. Consequently, given the unsatisfactory state of the kinetic thermal analysis literature overall [10–13], currently the physical model appears to be the most promising theoretical approach available for the elucidation of reaction interface mechanisms. Moreover, the systematic and consistent explanations of observed behaviour, revealed through its use [7–9], indicate its potential ability to extend scientific order in this field.

Mindful of the absence of theoretical correlations between crystal melting and decompositions hitherto, also remembering the difficulties of formulating mechanisms for interface processes, the most reliable conclusions found in the above comparisons are juxtaposed in the Scheme below. This representation summarizes the different types of change that may result from the heating of a crystalline solid. According to the (apparently simple) pattern of behaviour revealed, chemical reactions involving constituents within the solid are improbable: this is consistent with the expectation that species within a crystal will be stabilized by those forces that impose structural order on its components. This generalization suggests that, in the solid, it is the intercomponent forces that can be relatively more readily modified by heating; the changes (see below) that occur (sublimation, phase transformations or melting) are usually classified as physical, though, for some solids, these may include redistributions of primary valence forces. It would appear from the available evidence that chemical reactions, necessitating rearrangements of intracomponent bonds, occur more readily when the stabilizing forces, giving the crystal rigidity, long-range order and coherence, have been removed, after volatilization. This is probably a realistic representation for many of the solid-state decompositions that have been studied.

Changes that occur on heating a pure crystalline compound

Sublimation or thermal decomposition

A theoretical quantitative description of sublimation and of thermal decomposition of solids has been provided by L'vov [6–9, 46, 47]. Ions, atoms or molecules from the reactant crystal surface are activated to volatilize and the species formed equilibrate before either diffusing away unchanged (sublimation) or undergoing secondary chemical reactions or interactions to yield products (decomposition). Use of the tabulated values for the reactant, and for any products, molar enthalpy of formation assumes no significant distortion at the surfaces of the crystalline reactant.

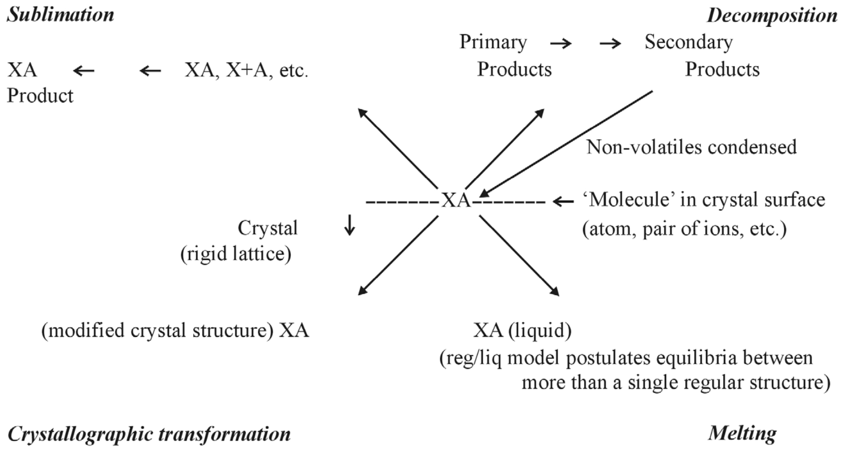
Crystal transformation

If raising the temperature of crystal changes the structure that is thermodynamically stable, a phase transformation may take place to the different, but more stable lattice: reactant constituents undergo rearrangement but without chemical modification. Kinetics and mechanisms of such transformations have not been widely investigated for ionic solids but there is evidence that some (e.g. [18]) proceed by interface advance, as activated rate processes. Other crystals, in a type of change that has been most extensively characterized for metals, may perhaps undergo martensitic transformations [54], where there is a cooperative shearing process that moves rapidly across many lattice units. No activation is required because only small displacements of atoms are involved.

Melting

According to the reg/liq melting model [1–4], fusion occurs through relaxation of the restriction, applicable to crystals, that there can be only a single packing arrangement throughout the solid particle. On melting, the extended regular assemblage of components in the solid is replaced by equilibria between small domains having the alternative stable lattice structures. At temperatures immediately below the T_m, the packing regularity of the crystal surface layers is slightly reduced in the approach to liquefaction and facile transformations at the solid/liquid interface (and within the irregliq contacts in the melt [1–4]) do not require appreciable activation. Melting, therefore, differs from decomposition in that components remain within structures that undergo some local modifications of packing, accompanied by loss of long range order. Initiation of this reorganization ('nucleation') is facilitated by changes throughout the surfaces and proceeds readily because there is no barrier to the relatively minor rearrangements required for these structural modifications. This differs from decomposition by not requiring activated volatilization of individual constituents from a surface of a stable crystal structure. Rates of fusion or crystallization are (diffusion) controlled by the supply, distribution and movements of energy. Melting differs from a phase transformation in that more than a single packing structure contributes to equilibria within the liquid and the dynamic character of flow arises from the inability of irregliq interfaces to withstand stress [1–4].

The behaviour shown identifies a relatively simple pattern of interrelationships between the different



Scheme 1 Showing the alternative type of change, involving rearrangements or reactions of the constituent components, that can occur on heating a crystalline solid. If there is volatilization (↑) and the products are stable→sublimation; are unstable→decomposition. If the lattice transforms (↓) to a single different structure→phase transition; several different structures→melting

types of change that result from heating a solid. Three of the processes are classified as physical changes, the exception is decomposition and even here the first step is identified as volatilization [9] with individual component equilibration. The reg/liq model for melting [1–4] is in satisfactory accord with this scheme.

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