

Structure and order in thermal dehydrations of crystalline solids

Andrew K. Galwey*

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

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Abstract

Criteria capable of classifying solid-state dehydrations are explored with a view to determining whether systematic patterns of order can be identified within this extensive group of reactions. A classification scheme is proposed. Recognition of behavioral similarities, and differences, between different reactants can contribute towards theory development in a field where reactivity controls and factors that determine mechanisms have not yet been established. At present, many fundamental studies of reactions in which water is evolved from crystalline reactants remain unrelated to other, generally similar, rate processes and do not contribute to the development of an ordered subject. It is argued that the establishment of interrelationships between hitherto individual and unrelated chemical changes may be capable of introducing coherence into an important and active research area that is currently composed of mainly separate contributions.

The classification scheme proposed here discusses the role of extended crystallographic structures in controlling the course of the bond rearrangements that occur during the conversion of a solid reactant into solid products. It is suggested that this feature of solid-state processes has been accorded less attention than it deserves in mechanistic proposals that usually focus attention on the movement of individual bonds. This use of extended features of the reactant (lattice) can be regarded as a chemical analogue of the development of band theory used to complement the valence bond model in theoretical explanations of the physical properties of solids. Such consideration of the less localized structural properties of crystalline reactants enables progress to be made towards classifying the many and diverse water elimination reactions identified as 'dehydrations'.

Shortcomings in the theory currently available for application to dehydrations are considered in the context of the problems that arise when interpreting experimental data. Kinetic measurements for these reactions are often sensitive to experimental conditions due to the influences of reversibility and of endothermicity. Problems in the characterization of structures at active reactant/product contacts and in identification of the factors that determine reactivity and rates of the interfaces steps that control water elimination are mentioned in the context of current theory. Aspects of the development of a theoretical framework that increases our understanding of dehydrations are discussed critically. The provision of an acceptable classification scheme is regarded as an essential step to advance theory and understanding of dehydrations and other crystalolysis reactions. © 2000 Elsevier Science B.V. All rights reserved.

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1. Objective

To propose a classification scheme whereby order may be introduced into the extensive literature that is

concerned with dehydrations (and later developed to include other reactions) of crystalline solids. This is intended to contribute towards the reinvigoration of a subject in which the theory appears to have become ossified.

This review has been undertaken because the author believes that the theoretical principles, applied to

* Formerly at: The Queen's University of Belfast.
Tel.: +44-028-9061-1459.

interpret measured data during experimental investigations of solid-state reactions, have failed to advance during recent times. The groups of rate processes surveyed here are primarily kinetic and mechanistic studies of the thermal decompositions of crystalline reactants, and, in particular, dehydrations. There is already available an extensive literature devoted to this subject and further contributions regularly appear, confirming the continuing interest in these reactions. However, in the absence of generally accepted reaction models and theoretical principles capable of unifying the subject, many contributions tend to be individual and do not extend a coherent and systematic body of knowledge. The absence of a classification scheme, capable of systematizing the topic, is seen as a barrier to the development of a theoretical framework for the subject and to the recognition of trends of properties and behaviour. To provide the first steps towards rectifying this omission, regarded as an important gap in the literature, this review distinguishes regularities and differences in reported observations for thermal dehydrations. Dehydrations were selected for this survey because these reactions have probably been studied in the greatest detail, a wide range of reactants have been investigated and the results may be the most reliable for any group of crystallographic reactions. Trends found to be useful here can later be developed and generalized for application to a wider range of reactions involving solids. These aspects of dehydrations are applied, explained and discussed in this review.

A principal conclusion, that emerges from this comparative and critical analysis of the literature, is the proposal that it would be profitable for solid-state chemists to follow the lead of physicists in applying a dual approach towards developing theory applicable to the chemistry of crystals. In physics, the *valence bond theory* is concerned with short-range forces between lattice components, atoms, ions or molecules, while longer range structures and interactions, even extending across large whole crystals, are involved in the *band theory*.

Chemists are almost invariably interested in short-range forces, *valence bonds*, that participate in electron redistributions; the essential feature of a chemical reaction is the changes of bonding linkages between atoms. In the tradition of the subject, rates and mechanisms of rate processes are portrayed through

balanced stoichiometric equations that incorporate the fundamental participating species as ‘molecules’ within, and between, which bonds are reorganized. Refinements to this model have been made in theory development, for example in representing the detailed steps envisaged as participating in the conventional portrayals of reaction kinetics and mechanisms. The transition-state theory was developed largely by consideration of the inter- and intramolecular (‘bond length’) interactions regarded as occurring between isolated species in homogeneous rate processes. This theory has been widely applied in the interpretation of kinetic data for reactions of solids, but there are theoretical shortcomings in this approach which are discussed below. Much less consideration has been given to the significance of extended structures in chemical reactions proceeding in the solid state. Moreover, the participation of non-stoichiometry and crystal defects, and other essentially crystallographic properties of solid reactants, are not always represented in ‘molecular’ type stoichiometric equations. It is probably true to say that chemists favour the *valence bond approach*, except when considering aspects of obviously longer range solid-state phenomena. These include, for example, lattice imperfections, extended structural irregularities, diffusion, etc. and, of course, physical properties, when *band theory* may apply.

Physicists, in contrast, regard these two theoretical approaches as complementary while recognizing their different strengths and weaknesses; these alternatives are seen as involving no inherent conflict or contradictions. It is suggested here that, because the traditional chemical (*valence bond*) approach to interpretation of decompositions of solids is not currently contributing to the advance of the subject, aspects of the alternative (*band theory*) might be more successful. This possibility is critically (and, ultimately, optimistically) explored in this review.

Dehydrations of solids include a range of related rate processes that form a recognizable group of reactions. Some of these are the most intensively studied solid-state decompositions and the conclusions reached have made important contributions towards advancing the subject theory. Classifying behavioural similarities within this group of reactants is expected to provide insights into reactivity controls and mechanistic similarities. Correlations found within these classes may now be systematically

extended to other reactions and even predict properties of as yet unstudied rate processes.

2. Introduction

This review presents a detailed case that argues that there is an urgent necessity to establish criteria whereby the dehydration reactions of crystalline hydrates can be classified. The already extensive, and continually expanding, literature that describes the many features of these rate processes has identified few, if any, general or theoretical principles that can be used to compare, and to contrast, the properties of related reactants or of different reactions. This conspicuous absence of unifying, or of distinguishing, features leads to a lack of coherence and order throughout an important, active research field. Without a central conceptual framework to correlate observations for different reactions, discussions tend to focus on individual systems rather than placing each study in the wider perspective of a developing subject area. Science is the systematization of available knowledge together with the extrapolation of behaviour patterns perceived to enable the results of hitherto unexamined experiments to be predicted with some confidence. The principal reason for the present survey is to suggest that the finding of an acceptable set of criteria for classification of dehydrations would provide a welcome stimulus towards subject development. Not only would this enable the systematic exploration of possible relationships between the different reactants already studied, but inconsistencies between published conclusions could be reconsidered and directions of future research indicated. Moreover, progress in this field could be expected to stimulate the development of theory for other solid-state reactions, following extensive precedents in the past. Dehydrations have contributed considerably to subject advance.

It has long been appreciated that some characteristic features (reactivities, kinetics, etc.) of decompositions of solids cannot be obviously or quantitatively related to identities or properties of the reactants. Compounds containing common, or comparable, chemical constituents often exhibit quite different kinetic behaviours, whereas some apparently dissimilar substances react in similar ways. One approach towards resolving these difficulties is to explore the possibility of classifica-

tions based on factors other than similar constituents that may influence or even control rate processes in solids. One obvious possibility, the foundation of the classification scheme presented here, is the role of extended structures in influencing chemical changes. By grouping together reactions proceeding through similar phase reorganizations, those chemical changes within each group may be examined, thereby enabling only reactions exhibiting common features to be compared and contrasted and the observations within each set of processes to be systematized. The concept of properties of solids being theoretically discussed in the context of extended structures is already well-established with the help of the band theory. This idea is developed in the following text.

The literature analysis presented, and discussed, here is restricted to the dehydrations of crystalline hydrates. This is regarded as only a first, but more realistic and reliable, objective than the consideration of all crystalolysis reactions. Concepts found useful here may later be developed and extended to a wider range of thermal decompositions, and even possibly to other types of reactions of solids. It is hoped that completion of this initial project will demonstrate the value of classification in advancing this subject and, perhaps, encourage, by example, wider correlations extended to other reactions of solids. It is suggested that effort directed towards ordering the information already available is capable of bringing greater overall benefits to the subject than the same investment of time and energy to provide new studies that cannot at present be related to knowledge already available, because of the absence of appropriate theory.

Dehydrations of crystalline solids together represent an important group of heterogeneous reactions. However, these have been the subject of remarkably few general or critical surveys in comparison with the large number of articles published during the long period of active interest in these reactions. The total volume and diversity of the published literature may well have discouraged potential reviewers with the consequence that unifying theoretical concepts have not emerged. Or, perhaps, the reverse is true and it is the absence of unifying theories that has inhibited attempts to systematize these disparate reports.

The present article does not attempt to present a traditional 'current state-of-the-subject' type survey, summarizing the contents, attitudes and ideas

throughout the range of identified articles regarded as relevant within the review title. Such a more conventional presentation has recently been published [1]. A further article, expected to be published soon [2], might be regarded as a ‘literature survey introduction’ to this one.

Format: As an experimental format this review is presented in two parts. Part 1 (Sections 1–6) summarizes all essential features relating to the classification scheme proposed. This is primarily addressed to readers already familiar with the subject or to those having only a superficial interest. Part 2 (Sections 7–12) provides more comprehensive discussions and analyses of the points made, together with extended background information, including additional sources. Cross-references throughout both the parts are given in *Italic Type*.

This unconventional format has been adopted to address the interests of the potential readerships, in recognition of the limited amount of time that most researchers have to ‘read around the subject’. By emphasizing the classification scheme first, those research workers most informed may adjudge the merit of the proposed scheme through their extensive knowledge of the literature. Those with less experience (or greater interest) may find it helpful to use Part 2 to obtain further background and greater insights.¹

2.1. Nomenclature

2.1.1. Crystolysis

An agreed and accepted precise terminology is an essential prerequisite for effective communication. There is, however, no accepted term that defines specifically those thermal decompositions that occur in the crystalline state, though this is a recognizable reaction type. The word *Crystolysis* has been proposed [3,4], because a descriptive keyword for index entry

¹ It may be timely to explore alternative strategies for publication and, in particular, to experiment with varied methods of presentations to aid communication with readers having limited ‘literature time’. The statement of the most important content early in the article might be helpful, in preference to the more usual practice of leading to the point of the work as near to the end as possible. The literature reporting research has experimented relatively little with presentation, though there are indications of impending and widespread changes as the ‘electronic communication age’ rapidly develops.

would considerably aid literature searches. At present, we are forced to depend on particularly non-specific general terms such as ‘decomposition’, ‘solid’, ‘kinetics’, etc. The introduction and accurate use of this descriptive word could also encourage authors to state positively in their article titles that the reaction reported occurs in the solid state: at present this important feature of reactions investigated in this field all-too-often remains unspecified and vague. This increases the difficulties of classifying the thermal behaviour of initially solid reactants.

2.1.2. Reaction mechanism and kinetic model

The present use of the term *mechanism*, as applied to crystolysis reactions, is somewhat variable. Throughout this article, the word *mechanism* is invariably used in the traditional sense to describe the sequence of elementary steps whereby the reactant is converted into products. Included in this definition are all aspects of the interface geometry (often based on the interpretation of yield–time measurements) and the bond redistribution processes occurring at an active reaction interface (often inferred indirectly from magnitudes of Arrhenius parameters) [1,2,5–13], together with any recrystallization and retexturing processes. The *kinetic model* can then be used to describe the more limited mechanistic inferences about reaction geometry that are based on the ‘best fit’ of yield–time data to one from a group of rate equations that have found application to decomposition of solids [1,5,7,11]. The kinetic model, therefore, accounts for rate characteristics through interface advance, involving, perhaps, nucleation and growth and/or diffusion processes. Here, this term is not regarded as including consideration of those aspects (mechanism) of the chemical changes which proceed within the active interfacial zone (including bond rearrangements, recrystallizations, etc.).

Care must be exercised in basing kinetic deductions exclusively on whichever of the rate expressions, characteristic of solid-state decomposition, has been identified as providing the (relatively) most accurate representation of yield–time–temperature measurements for a particular reaction of interest. The set of rate equations applicable to crystolysis reactions, derived through consideration of geometric and/or diffusion controls, include those listed in Table 3.3 of Ref. [1], Tables 5 and 6 of Ref. [5] and Table 2 of

Ref. [8]. Similar lists are often included in original research papers, sometimes with minor variations in content. However, when a kinetic ‘best fit’ is identified from a restricted list of possibilities, there is always the chance that factors other than those considered may provide an even better representation of the data. One such mechanistic factor, that is sometimes ignored in investigations of reactions assumed (often without supporting evidence) to proceed in the solid state, is melting. Some chemical changes proceed more rapidly in a melt, or eutectic, than in the solid state [9]. The experimental detection of limited and local melting during decomposition of an initially crystalline reactant can be unexpectedly difficult [10]. The use of complementary observations, including all suitable techniques (such as microscopy, diffraction measurements, analytical studies, etc.) is necessary to obtain the information required to enable the most reliable interpretation of kinetic data to be achieved. Such support is not always provided in reports that derive from highly automated experimental techniques in which data are recorded and processed by programmes within a controlling computer. (It is invariably necessary to understand completely the assumptions and processing techniques occurring inside any such ‘black-box’ apparatus to avoid uncritical acceptance of printed outputs at face value.) Reports using these methods are becoming more numerous and *can* yield kinetic results that are not of the highest order, sometimes even failing to demonstrate that rate measurements are reproducible. There is also a tendency to report calculated parameters, most notably Arrhenius parameters, to an unrealistic number of decimal places. Such studies also do not often include investigations of the possible variations of rate characteristics with changes in reaction conditions (procedural variables), this information can be of particular significance for many dehydrations. Complementary and confirmatory experiments, relevant in the formulation of proposed mechanistic conclusions are sometimes not described.

It is a widely accepted generalization that no criteria have been recognized whereby either the rate equations [$g(\alpha)=kt$], or the magnitudes of the Arrhenius parameters, namely activation energy, E_a , and frequency (preexponential) factor, A , can be used to classify solid-state reactions and to systematize the subject.

2.1.3. Reactivity

This term is used here to indicate the propensity for the (usually solid) reactant to undergo chemical change and can conveniently be used to indicate, qualitatively, the relative temperatures at which reactions proceed. The higher the reactivity, the lower the temperature at which water is evolved. Most of the kinetic investigations of dehydrations have been concerned with time intervals that are most suitable for laboratory experiments, frequently completed between 10^2 to 10^5 s.

2.2. Dehydration reactions

Dehydrations of crystalline hydrates exhibit the common feature that water is evolved, but include more than one type of chemical change. In one set of reactions, water, present as a ligand coordinated to (usually) a transition-metal cation, is released on heating; this is alternatively regarded as the thermal decomposition of a complex compound. Other dehydrations are accompanied by the structural reorganization of a lattice destabilized by the removal of constituent hydrogen-bonded water. Also, there may be hydroxyl groups that combine to give oxide and water. A wide range of examples of these types of processes occur singly, concurrently, consecutively and in various combinations and sequences. The present paper adopts the accepted convention of considering all water-evolution reactions as a group, but remembers that this group incorporates a range of distinct and different chemical processes.

2.3. Literature reviews of solid-state dehydrations

There have been remarkably few general reviews on dehydrations of solid reactants. One possible reason is the considerable problem of ensuring adequate coverage of the large, diverse and widely dispersed literature. As already pointed out, search of abstracts is made inefficient by the lack of suitable descriptive entry terms. The most important early review, which contributed substantially to all subsequent development of this subject, was that due to Garner [11]. Dehydrations formed the largest contribution in his Chapter entitled *The Kinetics of Endothermic Solid Reactions*. The theoretical importance of the interface model for reactions in crystals was strengthened

through consideration of the relationships between reactant and product phases. This account of these endothermic and reversible rate processes includes discussions of the Polanyi–Wigner theory and the Smith–Topley effect, both of which are considered in the following. Dehydration studies also contributed to the systematic development of geometry-based rate equations, described by Jacobs and Tompkins [7] in the same book [12] (edited by Garner). With the addition of diffusion control, these equations constitute the essential set of rate expressions applied in kinetic analyses of crystal dissolution reactions. Together these articles [7,11] authoritatively summarize much (perhaps most) of the theoretical background that has been, and still is, used in discussions and interpretations of the kinetics and mechanisms of dehydrations.

Subsequent reviews include the following. Young [13] has summarized aspects of the dehydration literature up to about 1965, including comparisons of conclusions for various reactions that have been studied by several authors. Makatun and Shchegrov [14] drew attention to the surprisingly long list of terms (17, or more, are mentioned) that have been used to specify the types and strengths of bonds that retain water in crystalline hydrates. Methods of determining bond strengths are described and it is concluded that many features of dehydration are controlled by the nature of the water in the crystal. Lyakhov and Boldyrev [15] review the factors that influence experimentally measured dehydration kinetics, including self-cooling and the intervention of labile intermediates. Both types of product may influence reaction rates: residual dehydrated solids sometimes impede product escape and volatilized water, at pressure $p(\text{H}_2\text{O})$, may participate in reversible steps. Some surveys of the more recent literature, up-dating the subject, have been given [1,8]. More restricted accounts include [16,17], but there appear to be no other recent comprehensive or critical reviews intended either to systematize or to classify the extensive literature of this subject.

2.4. Theories of dehydrations

Discussions of dehydrations (in common with very many other crystal dissolution reactions) frequently portray the chemical changes as occurring within an active advancing interface. This reaction model, together

with representations through the Polanyi–Wigner equation [1,2,5,11,18,19], and the Smith–Topley pattern of variations of reaction rate with water vapour pressure present, $p(\text{H}_2\text{O})$, [11,20,21] provide the theoretical concepts most widely applied to dehydrations. These are mentioned in this Section only for completeness (see: Sections 10.1 and 10.2, respectively) but their importance is so widely recognized that references to these behaviour patterns will be made throughout the present survey.

The dehydration of a hydrate, for instance copper sulphate pentahydrate, was probably [22] the first solid-state reaction to be identified as a nucleation and growth process. Subsequent work, including many investigations of dehydrations, lead to the recognition of the importance of the *reaction interface* in crystal chemistry. This is the zone, in the immediate vicinity of the contact between reactant and product phases, within which chemical changes occur preferentially. Characterization of the reasons for this local enhancement of reactivity is particularly difficult to investigate because the zone is thin, possibly of molecular dimensions, and between two solids, therefore inaccessible to direct investigation. The prevalent specialized conditions, that promote bond reorganizations, are not understood and there is little information about the structures and properties of interfaces. This gap in knowledge is a central problem in the theory of all rate processes occurring within active advancing reactant–product contacts. This is a difficulty that reappears throughout the present survey.

Various attempts have been made to characterize and to understand the controls of reactivity at interfaces. These are only mentioned in passing here and will be considered at greater length at appropriate places in the text below. Experimental approaches most usually applied include microscopic examinations, X-ray diffraction structural measurements, spectra, etc. Alternatively, the magnitudes of Arrhenius parameters are often taken as a measure of the frequency factor or the height of the energy barrier to reaction, by application of the transition-state theory based on (incompletely established) parallels with homogeneous kinetic theory.

During the earliest years of theory formulation, it appeared to be implicitly assumed that the interface was extremely thin, reaction and product recrystallization being completed within a thickness of (perhaps)

a few unit cells. Development of this model has yielded the geometry-based set of rate equations [1,5,7,8] that are regarded as a characteristic feature of crystallysis reactions. Indeed, this set of kinetic expressions can be regarded as the most important unifying feature of this subject area. The demonstration that measured yield–time data for a particular reaction fits one or another of these equations appears in some reports to imply (not necessarily supported by an explicit statement) that the reaction proceeds in the solid state.

Subsequent work has shown that, at least for some dehydrations, water elimination and structural reorganization (recrystallization) of the residual product (lower hydrate or anhydrous salt) may be distinct and different rate processes. There is also the possibility that these two steps may proceed at separate interfaces. In some crystalline hydrates, including alums [23], it has been shown that water is lost from all crystal boundary faces soon after the imposition of dehydration conditions. This may be followed by the formation of the characteristic ‘orange peel texture’. These superficial losses may, however, be limited in extent to the outermost layers, and bulk dehydration only becomes possible when the difficult (and often rare) steps generating the crystalline product phase have been achieved, forming a growth nucleus [22]. It further appears that in some reactions the particle assemblage of recrystallized material, the nucleus, is able to retain a proportion of the volatile product [23] and this available water promotes recrystallization of the water-depleted material. This explains the autocatalytic character of interface advance and the loss of water at an intracrystalline reaction zone, rather than from a surface where escape is easier.

Dehydrations are strongly endothermic and many are reversible: both features contribute substantially to the difficulties of interpretation of kinetic measurements and in the formulation of reaction mechanisms. In some reactions, control by the escaping diffusive H₂O product may further complicate behaviour. These uncertainties underlie all work in this field and references to their influences must appear throughout this survey. This short overview is intended to provide a brief, but simplified, perspective across the topic. Greater complications and instances of exceptional behaviour appear below when considering and comparing individual rate processes. In the past, conclu-

sions obtained from careful studies of dehydrations have notably contributed to theory development generally applicable to a wider range of reactions of solids [12]. This choice of dehydration as reactants is, therefore, a potentially profitable foundation from which to explore directions for future advances.

2.5. *Dehydrations and crystal structures*

Hydrates “form an extremely large group of compounds” [24]. Although the structures of many are known, few dehydration studies have compared in detail relationships existing between reactivities and bonding patterns within sets of comparable reactants. The subtleties in bonding, that maximize crystal stability, mean that chemically related hydrates adopt different packing arrangements so that there is no obvious basis for classification of dehydrations through common reactant lattices. A systematic treatment of the subject is made more difficult by formation of crystalline products, so that it is necessary to take into account both phases and their interrelationships. The exception to this generalization is where there is topotaxy, discussed in the Section 2.6 below. In other (non-topotactic) rate processes, it may be that the role of structure may have to be considered individually for each reactant.

The constituent water in hydrates is usually regarded as participating in extensive structural hydrogen bonding and some or all may also be coordinated as a cation ligand. These local linkages must be important in characterizing the first steps towards H₂O release, but the role of the non-volatile constituents of the reactant also must be taken into account. This is conventionally described through preferences shown by chemists who choose to represent behaviour by short-range order, using stoichiometric equations in which the reactant constituents appear in molecular form as (individual) ions, complex ions, water, etc. The kinetic techniques which are then applied to analyze interactions between these species derive from homogeneous reaction models involving an isolated transition state reaction complex, largely uninfluenced by proximate species, materials or structures. This approach must be regarded as only approximately applicable to many reactions of solids, where neighbouring atoms are sufficiently close for several interactions to influence the species undergoing

change. Significant interplay between neighbouring species must occur within interfaces where conditions cooperate, in ways that are not yet understood, to promote or to autocatalyze the reaction. It is, therefore, important when interpreting observations to include consideration of structural features extending beyond immediate neighbours to identify the reactivity controls in solid-state dehydrations.

The stoichiometric proportions of water in crystalline hydrates vary widely [24,25]. Numerous instances of stepwise water loss are known, in which a sequence of hydrates containing progressively smaller proportions of water are formed as the reaction temperature is raised. This may become more obvious during dehydrations in the presence of water vapour: for example, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is dehydrated directly to the monohydrate in vacuum [26] whereas, when H_2O product is available, tetra- and dihydrates intervene during the same overall change [27–29].

Water, a volatile, neutral molecule retained in the crystal by hydrogen bonding, and sometimes also by a coordinate link, is the species most readily lost on heating solid hydrates. Consecutive reactions must proceed with the systematic loss of those water molecules most weakly held and those retained were already, or become, more strongly bonded in the lower hydrate. Dehydration is accompanied by diminution in the total number of (weak) hydrogen bonds present. Elimination of water is accompanied by a density increase with overall increase in close packing, because there is a relative increase in the influence of covalent and/or ionic bonding. Water escape will be more difficult in the more densely packed structures of the lower hydrates, where those H_2O molecules remaining are more strongly linked to the non-volatile crystal constituents than to each other.

2.6. Dehydrations and topotaxy

The crystalline product of a chemical reaction, or of a structural transformation, is said to exhibit a *topotactic relationship* with the reactant if it is formed in one or more orientations that are crystallographically equivalent relative to the parent crystal [30–32]. This change must also proceed through the total volume of the reactant particle. It is believed that, during a topotactic process, the number of strong bonds that are ruptured is minimized and that, during its forma-

tion, the product structure has undergone the least practicable distortion. Less strongly retained components of the reactant are released while stronger features of the reactant lattice persist, perhaps with some modification. Many topotactic dehydrations involve reactant crystals in which the stable, maintained crystallographic features extend in one (linear) or two (planar) dimensions [30].

Topotaxy can be regarded as a solid-state chemical change in which the reactant provides a template for product phase generation. Crystallographic features of the reactant contribute towards the formation of the lower hydrate or anhydrous salt. Two situations can be distinguished. First, the product crystal is a minor modification of the reactant structure, nucleation is effectively unnecessary and water loss is accompanied by the distortion of a pre-existing lattice rather than recrystallization. Second, a crystallographic transformation is required but the energy barrier may be relatively low, because comprehensive rearrangement of all residual constituents is not required. It follows that topotaxy in dehydrations could feature as a factor that facilitates the onset of reaction by eliminating the necessity for the difficult structural recrystallization step; this may include nucleation.

The appearance, or absence, of topotactic relationships provides information of great value in the formulation of reaction mechanisms. The maintenance of various degrees of order can be used to determine the types of change that could have occurred and, more importantly, exclude other possibilities from consideration. Topotaxy is regarded here as providing criteria that are important in the classification of dehydrations.

The dehydration of magnesium hydroxide ($\rightarrow\text{MgO}$) is topotactic [33], but the large volume contraction (ca. 45%) results in product detachment and reaction proceeds through interface advance. Oswald and Gunter [31] demonstrated that the intermediate, $\text{Mg}_2(\text{OH})_2\text{CO}_3$, formed during the dehydration and subsequent decomposition of $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$, conserved structural elements of the reactant finally to yield oriented MgO product.

It appears that the dissociative evaporation theory of decompositions, extensively applied by L'vov et al. [34] to reactions of solids, including $\text{Mg}(\text{OH})_2$ dehydration, retains problems in reconciling topotaxy with a volatilization step. The loss of contact on

evaporation implies destruction of order, unless subsequent condensation involves controls enabling the structural features of the lattice to be restored.

(Further introductory material presented in Section 7).

3. Proposed classification scheme for dehydrations

Table 1 systematically presents the conclusions reached from mechanistic investigations of a representative range of diverse solid-state dehydrations, grouped through chemical similarities identified in the literature reports. This classification scheme includes consideration of the role of extended structural order that is characteristic of all crystalline reactant hydrates and many of the residual products after water loss. Many of the reactant phases included here have been selected because both reactant and product lattice structures are known. However, much less is known, in general, about their contact interactions and their relationships within the active and advancing interface, during the changes that result in elimination of H₂O. In some of the reactions mentioned, features of the reactant structure are preserved in orientation of the product through topotaxy.

The scheme proposed in Table 1 is intended to be a first step towards providing criteria that will enable experimental observations obtained for these reactions to be presented as ordered contributions to a coherent and developing subject. Comparisons of reactivities and other properties, for specific dehydrations, can then be made between processes exhibiting mechanistic similarities and not appear as further, but individual, contributions in a field composed of many and diverse, but unrelated, chemical processes. Consideration of groups of similar reactions together is more likely to lead to the recognition of common features, also more useful in determining reactivity controls and in formulating reaction mechanisms than the previous (implicit) approach that regarded all dehydrations as more-or-less equivalent. A selection of the reaction models mentioned in this scheme include aspects of interface forms and functions that, at present, are only inferred from indirect evidence. However, such assumptions appear to be necessary if the properties of interfaces are to be understood and the concepts and

foundations necessary to further progress the theory require constant reconsideration and investigation in an advancing subject.

3.1. Some structural features of dehydrations

Where the structure of the solid dehydrated product is sufficiently resilient, and there is no cracking, the rate of water release will be determined by the rate of its diffusive transport across this barrier product layer [35,36]. In contrast, where residue cracking permits the immediate escape of the volatile product from its crystal site, dehydration then proceeds as an interface advance reaction [37]. Progressive changes in crystallographic spacings across a reaction zone (thickness ca. 150 μm), together with a metastable intermediate, were detected as participating in Li₂SO₄·H₂O dehydration [38]. During the comparable dehydration of LiHCOO·H₂O, the transformation of the metastable intermediate phase proceeded less readily, confirming the importance of the structural reorganization step in controlling reactivity [39]. Water loss from Li₂SO₄·H₂O and a small density increase (ca. 7%), results in the formation of small particles of the anhydrous salt, 0.2–1.0 μm [40].

From the above experimental observations, it appears that the characterization of interface processes in dehydrations requires consideration and reconciliation of the following complementary features of behaviour:

1. Water must be released from the crystallographic sites in the hydrate, at which it is accommodated, requiring the rupture of hydrogen bonds, possibly coordination links and any other interactions that contribute to hydrate stability. Identification of the dominant (rate controlling) bond redistribution step in dehydration is analogous to the *valence bond* treatment of processes in solids, by focussing attention on local effects of molecular dimensions. This is the approach that is most widely applied in mechanistic discussions, when magnitudes of E_a , and sometimes also A (through entropy) are ascribed to the rupture of a specific link in the reactant. The practice is based on parallels from homogeneous reaction kinetics and is used in the Polanyi–Wigner treatment [11] of dehydration rates in solids.

Table 1
Classification scheme for solid-state dehydrations 'water evolution type' (WET) based on structural criteria^{a,b,c,d,e,f,g}

'Water evolution type' (WET)	Classification criteria	Rate controls	Dimensions	Examples (see text)
<i>WET 1</i>	Crystal structure maintained (no geometric rate controls)	<i>WET 1A</i> Intracrystalline diffusion	Diffusion 1, 2 or 3	Zeolites
<i>WET 2</i>	Diffusion across an adherent barrier layer	<i>WET 1B</i> Surface desorption	Surface (constant)	Uranyl nitrate hexahydrate
<i>WET 3</i>	Interface advance. Nucleation and growth, or contracting envelope	Diffusion and geometric	1, 2 or 3	Muscovite, Vermiculite
<i>WET 4</i>	Homogeneous reactions in crystals	Reaction at interface	1, 2 or 3 (no diffusion)	Alums
<i>WET 4</i>	Homogeneous reactions in crystals	<i>WET 4A</i> Explosive disintegration	–	Colemanite
<i>WET 4</i>	Homogeneous reactions in crystals	<i>WET 4B</i> Progressive structural change	Diffusion 1, 2 or 3	Barium hydrogen oxalate
<i>WET 4</i>	Homogeneous reactions in crystals	<i>WET 4C</i> Homogeneous intracrystalline chemical change	Homogeneous reaction	Calcium hydroxide
<i>WET 5</i>	Melting and formation of impervious outer layer	Atypical kinetic characteristics	Rate may vary with particle size	2-Aminopyridinium chloride hydrate Trehalose dihydrate
<i>WET 6</i>	Comprehensive melting	Chemical steps and/or diffusion	Homogeneous rate process	Many highly hydrated salts

^a The characteristic types of behaviour distinguished in Table 1 have been classified through features based mainly on crystal structures, but also including textural and kinetic criteria. These are individually discussed in greater detail in the paragraphs that follow, including references to some of the most fundamental and influential mechanistic investigations that can be found reported in the literature.

^b The removal of water from the solid almost invariably involves some contraction from the original reactant volume. Unless the reactant structure is exceptionally stable (*WET 1*), there is cracking at the interface, or within a product phase that does not now occupy the reactant volume from which it was derived. Water is lost and there may be a density increase on product recrystallization. Both types of change must be described in any general mechanistic explanation of behaviour.

^c Depending on the symmetry properties of the reactant structure, each type of reaction listed here may be subdivided into processes that proceed with diffusion and/or interface advance in 1, 2 or 3 dimensions.

^d Topotactic reactions in which cracks are generated close to the reaction zone, permitting H₂O escape, means that such rate processes advance at an interface (geometric control) rather than by diffusive losses across a product layer barrier of increasing thickness. The transition from *WET 2* to *WET 3* type mechanisms may, therefore, be sensitive to the mechanical strength and structural change at the interface.

^e In nucleation and growth reactions, the nucleation step is often regarded as being sensitive to numbers and distributions of reactant crystal imperfections, whereas growth appears to be less influenced by defects and interfaces advance at constant rate through the more perfect unreacted material. Enhanced nucleation density, for example by surface abrasion, can profoundly modify the reaction geometry, but there is no evidence that the reactions that occur subsequently at the interface are changed.

^f The possibility that alternative kinetic models, including the participation of melting, local or extensive [9], may account for measured yield–time data must always be remembered in interpreting kinetic data.

^g A limited number of dehydrations proceed by kinetically distinct rate processes in different temperature ranges: rate equations and the magnitudes of Arrhenius parameters are different within each temperature interval. Such reactions might then appear in two of the classes in Table 1. Comparative investigations of the reasons for this variation could be capable of providing valuable insights into reactivity controls and the factors that determine mechanism. These interesting systems appear to merit more detailed investigations than have yet been completed. For example, it could be instructive to determine behaviour during a continuation of reaction in one temperature range after it had been started in the other. It appears that such processes could represent limiting mechanistic types and, therefore, are attractive systems for investigating reasons for the kinetic/mechanistic change. The possible value of work in this area towards advancing understanding of the controls of solid-state dehydrations does not appear to have been fully recognized and exploited.

2. The roles of reactant and product structures in determining reactivity and mechanisms of reactions proceeding in solids are difficult to characterize. It is suggested here that advances in understanding might follow theory developments from inclusion of properties of the extended structure of the reactant. This might be regarded as incorporating features of the *band theory* into solid-state chemistry, an approach that has not, so far, found favour. The release of water from a lattice site may be accompanied, or followed, by reorganization and/or reaction of adjoining species. *Dehydration chemistry*. Various aspects of dehydration chemistry can be schematically represented as follows.

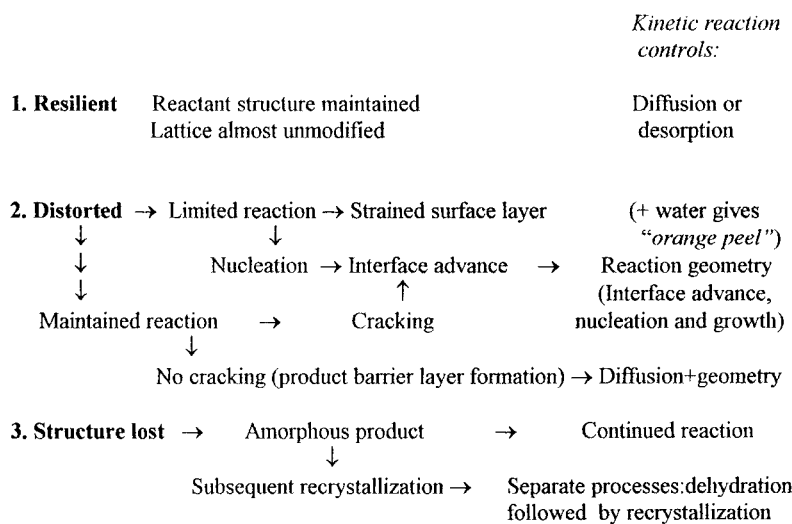
- crystal. Transitory metastable intermediate phases may be formed.
- Reactions are often modified by the presence of water vapour, which can influence sizes and perfections of product phase crystals, etc.
 - Some features of these reaction characteristics are shown in diagrammatic form in Fig. 1, and also illustrated in the descriptions below.

3.2. Types of dehydration reactions

The following general types of dehydration reactions may be distinguished: these are classified in Table 1.

Water elimination (Reactant phase) → Structure strain (Modified lattice, vacant site, etc.) → Recrystallization to product phase (This second step may not necessarily take place)

Properties of the strained structure of the initial product of dehydration.



Notes:

- Dehydration reactions may proceed through interface advance reactions or diffusion in one, two or three dimensions.
 - Solid residual phases may be bonded to and/or topotactically oriented with respect to the reactant
- The reactant structure is maintained or, after water loss, undergoes only the most minor modifications, without recrystallization or cracking. The rate of dehydrations in these most stable crystalline phases is controlled by the rate of outward migration of H₂O, or, if intracrystalline diffusion is rapid, possibly by the water desorption step [41,42].

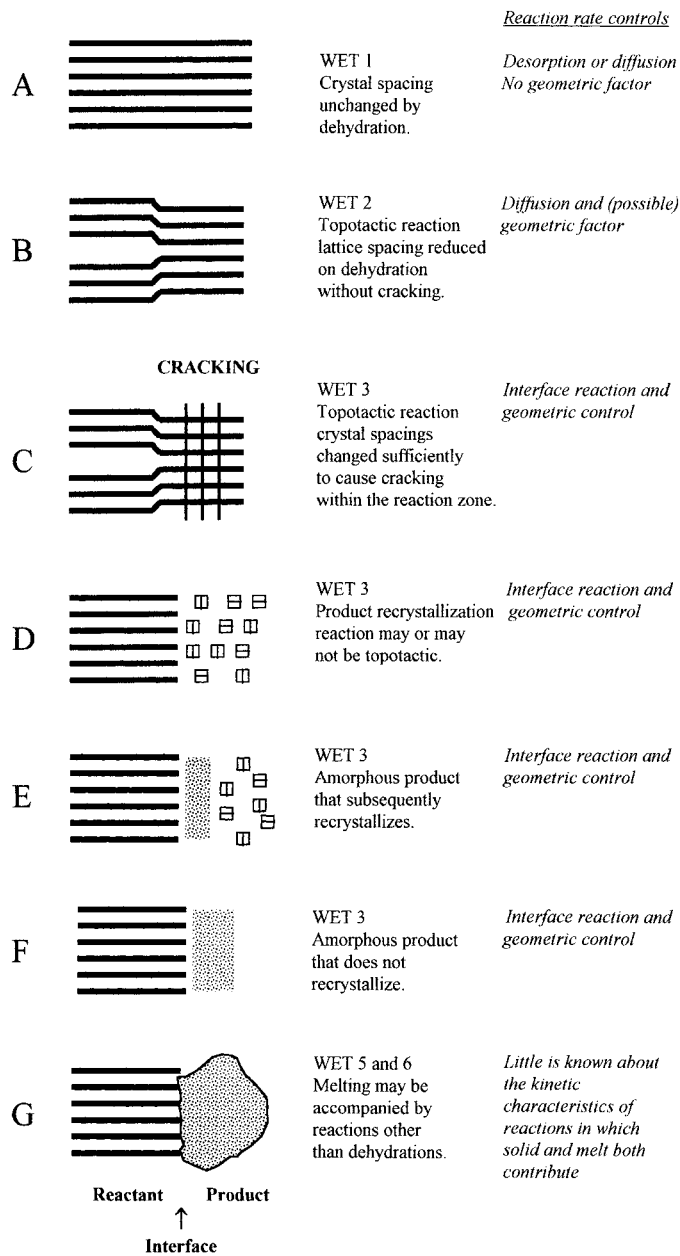


Fig. 1. Schematic representation of interface characteristics envisaged in some of the reaction classes distinguished in Table 1. B and C differ in the important characteristic that the former reaction is not accompanied by cracking (B, water losses are controlled by diffusion across the coherent and adherent product phase) in contrast with the latter (C, interface reaction in which water is lost through cracks generated at or near the advancing reaction zone). Sequences C–F differ in the structures of the product zone, its relationship with reactant at the interface and the delay prior to product recrystallization.

2. The reactant and product lattices are similar, the sharing of specific features often leads to topotaxy, but the structural modification at the reaction zone is sufficient to cause cracking [37], generating channels through which water escape is possible. While limited intracrystalline diffusion may be required for the displaced water to reach these easy outflow paths, the continued generation of fractures means that the interface advances at an effectively constant rate, an essential feature of an interface advance reaction. Whether reaction proceeds by the models (1) or (2) depends, therefore, on whether the crystallographic modification resulting from water loss is sufficient to generate cracks.
3. Reactions in which the recrystallization, reactant to product structure, proceeds relatively easily. Such processes are characterized by high-density nucleation [38–40]. There may be (short distance) intracrystalline diffusion of the water released, across a metastable intermediate phase [38], to the escape channels.
4. Some hydrates, in which the initial recrystallization step to form the product phase is achieved only with difficulty, undergo initial water losses from all crystal surfaces [23,43]. Such losses may be limited in extent due to increasing disorder within the superficial water-depleted layer [44]. Dehydration, continued thereafter in relatively perfect single crystals, often proceeds through the growth of a limited number of separated nuclei; these are typical nucleation and growth reactions. Additional, even large numbers of, nuclei may be induced by abrasion [45], by water vapour [23] or by seed crystals of product [44].
5. In some hydrates, the onset of product recrystallization may not occur immediately following water loss, but is achieved later as different rate processes, so that product phase formation advances at a separate interface. There is also the possibility that recrystallization does not occur and an amorphous product is given.

In such classifications, there is always the possibility of examples of intermediate behaviour or systems capable of reacting in ways other than those represented. For example, the dehydration of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ proceeds to the dihydrate [46,47].

Subsequent concurrent water losses include both water of crystallization and that derived from anion condensation. The course of these changes varies with the size of the reactant crystals, temperature and $p(\text{H}_2\text{O})$. The dehydration of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [46,47] also involves the overlapping reactions, leading to the formation of more than one condensed phosphate anion, together with acid formation and melting. The complexity of these reactions makes the separation of the contributory rate processes difficult and kinetic analyses complicated.

4. Discussion of the proposed classification scheme, Table 1

‘Water Evolution Type’ (WET) classifies patterns of dehydration characteristics on structural, observational and kinetic criteria. Examples are given here, and in Section 8, for the reaction types distinguished in Table 1.

4.1. WET 1: Crystal structure maintained

For a limited range of hydrates, intracrystalline water is lost without significant modification of the reactant structure. Two types of behaviour may be distinguished.

4.1.1. WET 1A: Crystal structure maintained, diffusion control

The kinetics of water losses from zeolites are difficult to interpret. It appears likely that overall these dehydrations contain contributions from more than a single rate process. Interpore water may be desorbed from different sites within the open reactant lattices and there may be concurrent movements between alternative interpore positions, together with intracrystalline interactions. The analysis of rate data is complicated by these overlapping, but incompletely characterized processes and the possible alternative desorption steps with diffusion within the rigid and maintained structure can be identified as an important reaction control. Whether this proceeds in one, two or three dimensions and involves intrapore H_2O redistribution is not clear. Elucidation of the chemistry of these dehydrations has not yet been achieved, but it seems reasonable to suggest that the deceleratory

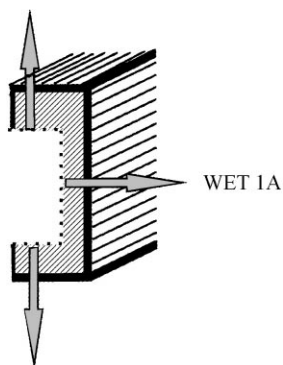


Fig. 2. WET 1A (water elimination type 1A). Crystal shown in section. Intracrystalline water is lost by diffusion in one, two or three dimensions without structural change of the reactant lattice. No geometric factor in rate control.

water loss from the resilient structure of a zeolite crystal is dependent, amongst other factors, on intracrystal H_2O migrations including diffusion control (Fig. 2). Relevant references, which do not extend to a full mechanistic description of kinetic behaviour, include Refs. [48–51]; see also Refs. [52,53].

4.1.2. WET 1B: Crystal structure maintained, surface desorption control

The alternative controlling step is the desorption of water from a surface site. This is only possible for a reactant structure in which H_2O vacancies are highly mobile and water molecules rapidly reoccupy surface sites vacated by desorption (Fig. 3). This behaviour

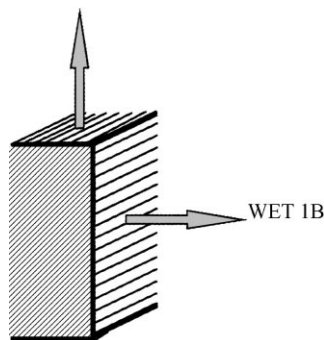


Fig. 3. WET 1B. Loss of the mobile intracrystalline water is controlled by the surface desorption step. H_2O is evolved from all crystal faces. No geometric factor in rate control.

has been described for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dehydration [41,42], the reaction is zero order over a wide range and no geometric control is identified. At present no other examples of such reactions could be found, but this could be because few suitable reactants have been studied under the appropriate (? low-temperature) conditions.

4.2. WET 2: Diffusion across an adherent and coherent barrier layer of product

Where the dehydrated layer forms an adherent and coherent solid product bonded to the reactant comprehensively, water removal is only possible following diffusion-controlled molecular H_2O migration across the crystalline product barrier. This is possible, for example, in topotactic processes where extended, and strongly bonded, structural components of the reactant are retained after water loss. Here, the removal of H_2O results in relatively little modification (and no cracking, leading to pore formation) of the resilient components of the reactant lattice (Fig. 4).

While water migration may, in principle, occur in one, two or three dimensions, many of the examples studied in greatest detail have been concerned with reactants having lamellar structures, where diffusion is in two dimensions. These include the dehydrations and dehydroxylations of clays and other aluminosilicates [35,54–56]. In these reactants, the water is accommodated between extended planar sheets and dehydration is deceleratory. Water evolution rates decrease systematically as the distance to the crystal edge progressively rises, because the progress of reaction increases the thickness across which H_2O

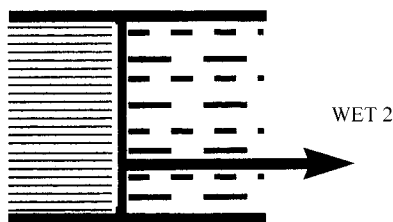


Fig. 4. WET 2. Crystal shown in section. (Two-dimensional layer structure shown). Diffusive water losses across an adherent coherent barrier layer of dehydrated product. Both geometric and diffusion controls, in one, two or three dimensions.

must migrate before volatilization. If cracking in the vicinity of the reaction zone permits water escape directly, then diffusion will no longer control the process and the reaction rate is determined by interface advance (WET 3, Section 4.3). The accumulation of strain, promoting crack formation and propagation, is greatest in large and imperfect crystals and may contribute towards enhancing the reactivity of reactant samples containing defects.

The dehydration of $\text{Na}_2\text{Ca}_5(\text{SO}_4)_6 \cdot 3\text{H}_2\text{O}$ [57], between 453 and 490 K, is an example of a one-dimensional, diffusion-controlled reaction. The magnitudes of E_a increased progressively from 75 to 159 kJ mol^{-1} with rise in the prevailing $p(\text{H}_2\text{O})$ from 10^{-2} to 2.6 kPa. Other examples of the most typical diffusion-controlled dehydrations, from layer-type (two-dimensional) structures, are vermiculite [35], muscovite [54], montmorillonite and illite [55].

4.3. WET 3: Interface advance; nucleation and growth and contracting envelope

Numerous examples of interface reactions, including many dehydrations that have been regarded as the most 'typical', have been described in the literature (Fig. 5). The rate equations applicable [1,5,7,12] are derived from geometric models for two general types: (i) nucleation and growth; and (ii) contracting envelope, each may proceed in one, two or three dimensions. (Diffusion processes are not considered here, because product release is completed within, or very close to, the advancing interface.)

Although rate studies generally report a kinetic fit as an important conclusion from a kinetic analysis, this result should not necessarily be accepted uncritically as a fundamental and unchangeable feature of the chemical change investigated. The nucleation step, initiating reaction and effectively determining subsequent geometric development, is usually sensitive to the numbers and distributions of imperfections within each individual reactant sample studied. Kinetic characteristics can, for some reactants, be changed by mechanical pretreatment of the crystals to be dehydrated. Rubbing the surfaces with product can comprehensively initiate reaction across all surfaces [39,58,59], so that a nucleation and growth reaction may be converted into a contracting envelope process. Thus, both are grouped together within a single class,

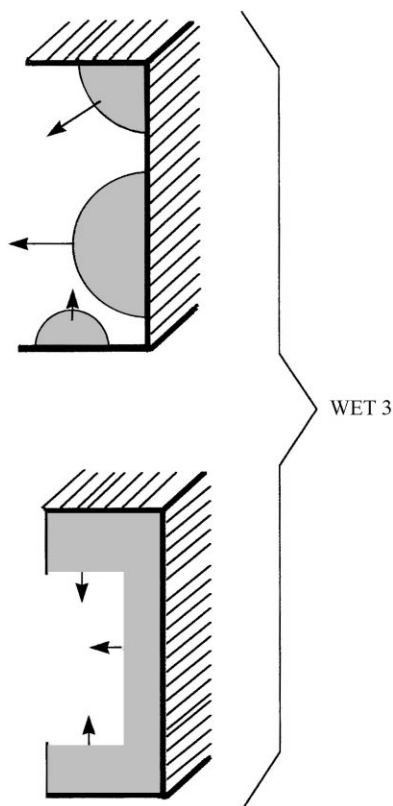


Fig. 5. WET 3 Crystals shown in section. Water is lost from an interface that advances at constant rate into unreacted hydrate in one, two or three dimensions and rate is controlled by geometric parameters. If nucleation is rare event, as in the upper figure, there is a nucleation and growth reaction, proceeding in three dimensions. When nucleation is rapid and dense across all surfaces, reaction proceeds by the three-dimensional contracting envelope model (lower figure).

WET 3. There is no evidence to suggest that the chemical changes taking place within an active interface are appreciably influenced by local defects or the nucleation steps. The interface advances as the dominant mode of chemical change throughout the reactant, including the most perfect regions of crystal. This process may be regarded as the most fundamental characteristic of the chemical change occurring. The interface mechanism is, therefore, identified as sample insensitive, whereas nucleation, and the growth geometry thereby established, can vary between different individual samples of the same compound. [For this reason, it is incorrect to describe the kinetic model as the *reaction mechanism*.]

4.3.1. Interface reactions: three dimensions

The dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is a well-known nucleation and growth reaction [60–63], different nucleus shapes were observed for reaction initiated on different crystallographic faces [64]. The induction period to comprehensive establishment of an active reaction interface across all crystal boundaries could be eliminated by abrading the surface with the dehydration product [58,59]. For a reaction initiated in this way, it was shown that the interface had planar geometry and was parallel to the surface treated.

The dehydrations of alums [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] are also well-studied nucleation and growth reactions [23,60,65]. For chrome alum, a cycle of vacuum, exposure to water vapour followed by reevacuation resulted in a massive enhancement of the nucleation rate [60].

Dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is initiated through the rapid generation of relatively high concentrations of closely spaced nuclei across all surfaces. Consequently there is no induction period, the acceleratory stage is short and the kinetics are well represented by the contracting cube equation [40]. This facile nucleation appears to be a consequence of the relatively minor crystallographic changes required to convert reactant to metastable intermediate and then to product, Li_2SO_4 [39]. Instantaneous nucleation follows surface abrasion. In contrast, the similar transformation of metastable intermediate to the final (anhydrous) product, in the dehydration of $\text{LiHCOO} \cdot \text{H}_2\text{O}$, proceeds much more slowly [39]. This dehydration was not initiated by abrasion alone, rubbing with the anhydrous product was required to form the interface. Presumably the product particles act as seed crystals.

The nucleation and growth dehydration of *d*- $\text{LiK} \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ [44] at 422 K was changed, by rapid initiation, to the contracting envelope kinetic model on placing the reactant crystal in direct contact with dehydrated powder. Abrasion was not required, direct contact was sufficient to ‘seed’ product formation and eliminate the induction period and acceleratory stages of the reaction. The mechanism proposed for this dehydration [44] identifies the interface advance rate during growth as being controlled by diffusive water loss from the reactant layer adjoining the nucleus boundary. Recrystallization of this water-depleted material is then promoted by contact with the anhydrous crystals that comprise the nucleus and

the channels opened enable continued escape of H_2O from the active zone at the nucleus periphery.

4.3.2. Interface reactions: two-dimensions, deceleratory reactions

Reactants in this class of dehydrations usually are composed of extended planar units that are sometimes sufficiently stable to survive the reaction intact to give pseudomorphic product particles. Water accommodated between these large sheets of strongly linked anions and cations is lost and there are modifications of the crystallographic structural parameters. The most obvious change is in the interlayer spacing while most other lattice dimensions undergo relatively less modification.

Transport of water through/across the polymer-like components of the lattice structures is difficult, so that reaction normally starts at the edges of the extended crystal planes and the interface does not advance in the *c*-direction. The nucleation step is either unnecessary, or rapidly achieved, because the formation of a topo-tactic product, retaining much of the reactant structure, requires little reorganization. Two closely related reaction types can be distinguished:

1. If the product remains coherently and comprehensively bonded to the reactant without cracking, then water release is possible only after diffusive transport to the crystal edges. This is mechanism WET 2 described in the Section 4.2.
2. Where strain, accompanying or following H_2O removal, is greater than can be sustained by the product structure, there will be cracking at, or close to, the reaction zone. Cracks provide channels for volatile product escape, the residual solid does not constitute a barrier and the reaction proceeds by an interface advance mechanism (WET 3). There is, of course, the possibility that there is a short diffusion path between the water-vacated site and the nearest escape channel. However, with the maintained generation of cracks, this is an effectively constant delay parameter and later there may be some diminution in the ease of H_2O escape [37]. The ability of intracrystalline strain to modify kinetic characteristics (for a variety of reasons) has been mentioned for several dehydrations [66–69].

Examples of these types of interface reactions [WET 3 as described in (2) above] include the

dehydrations of copper(II) formate tetrahydrate [37] which is topotactic [70], manganese(II) formate dihydrate [71] and (possibly) hydrated molybdenum trioxide (again topotactic) [72,73].

As the solid product does not impede H₂O escape, the influence of $p(\text{H}_2\text{O})$ on kinetic characteristics, for example, in Smith–Topley behaviour [11], is expected to be less than in other interface dehydrations that involve recrystallization. It was shown [37] for $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ dehydration that the rate decreased progressively with increase of $p(\text{H}_2\text{O})$.

4.3.3. Interface reactions: two-dimensions: nucleation and growth

A rapidly completed initial nucleation process was detected [74] during the dehydration of magnesium oxalate dihydrate in nitrogen between 421 to 495 K. Water molecules lie parallel with (1 0 0) planes in the monoclinic reactant (which may undergo reorganization on dehydration). The possibility that nucleation occurs at the edges of the crystals is discussed [74]. Microscopic examinations confirmed that reaction interfaces advance inwards from crystal edges in particles that remain pseudomorphic with those of the original reactant. This is consistent with the fit of kinetic data to the two-dimensional contracting envelope equation.

During the dehydroxylation of cadmium hydroxide between 450 and 473 K, nucleation occurred at apparently randomly distributed sites on the larger surfaces of the plate-like crystals and was not particularly associated with edges [75,76]. Two-dimensional growth of nuclei, at upper and lower crystal faces, advanced predominantly in directions parallel with the larger crystal surfaces. Water loss was accompanied by recrystallization, reaction being completed in two steps: $\text{Cd}(\text{OH})_2$ (hexagonal) \rightarrow $[\text{CdO} \cdot \text{H}_2\text{O}]$ (cubic) \rightarrow $\text{CdO} + \text{H}_2\text{O}$. It seems that the direction of interface advance is controlled by the hexagonal lattice of the reactant and that water release does not proceed to completion [75,76]. This was the only example of this reaction type found in a survey of the literature.

4.3.4. Interface reactions: one dimension

While reactions of this type are to be expected theoretically, only one set of examples was found in the literature [77] and this did not report detailed kinetic data, so that some of the inferences drawn

here are incompletely substantiated. Desolvation of the monohydrates of thymine, cytosine and of 5-nitrouacil were shown to proceed in the crystallographic direction that corresponds to the orientation of structural ‘tunnels’ within which the water is accommodated. The temperatures of onset of reaction (a measure of reactivity) could be correlated with areas of tunnel cross-section and properties of the constituent hydrogen bonds. Some of the reactions appear to involve a nucleation step which was facilitated by contact with product particles. Recrystallization of the product phase may promote the rapid escape of H₂O, which is a characteristic of many interface reactions.

4.3.5. Calcium sulphate dihydrate dehydration: interface advance and diffusion control.

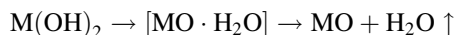
Studies of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dehydration kinetics [36] appear, at first sight, to be inconsistent with the classifications in Table 1 (Types WET 2 and WET 3). This reaction has been described alternatively as subject to diffusion control, in the [0 1 0] direction, or to chemical control, in the [0 0 1] direction. Furthermore, nucleation and growth behaviour was reported [78–81] for reactions below 383 K and diffusion control above this temperature. These differences are reconciled if it is assumed that cracking at the interface is sensitive to reaction conditions. Where reactant and product maintain comprehensive and coherent contact, there is diffusion control. If, however, the strain at the reaction zone is sufficient to generate cracks, then escape of water at an advancing interface is found. These alternatives represent behaviours described by WET 2 and WET 3 of Table 1, respectively. It may be that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (and possibly also $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) will become recognized as reactants useful in the investigation of reaction mechanisms, interface properties and rate controlling parameters.

4.3.6. Interface thicknesses

While many quantitative aspects of interface forms and functions have not been characterized, there have been a few measurements of interface thicknesses. Although the meaning of this parameter is not entirely clear, the following approximate estimations are available: $d\text{-LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ – 10 μm [44], $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ – 150 μm [38] and reaction zone thicknesses may be much greater in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ [82] and $\text{Ca}(\text{OH})_2$ [83] (see also Section 5.4).

4.4. WET 4: Homogeneous dehydration reactions in crystals

The term *homogeneous reaction*, in the present context, is taken to refer to a chemical change that occurs with equal probability for every identical chemical constituent throughout the crystalline reactant (irrespective of its position within the particle). Such reactions resemble those taking place in the liquid or in the gas phase because the kinetic characteristics are expected to be expressed by concentration terms only. Solid-state reaction features, such as the influences of reaction geometry and the autocatalytic promotion of reaction by preferred change at an interface, would not apply. However, the simple observation that dehydration rate data apparently fit a kinetic equation based on reaction order does not confirm that the reaction is homogeneous. Reliable and accurate measurements for the reaction controlling step of interest may not be directly obtainable. It is particularly difficult to measure the rate of only the forward dissociation for identical intracrystalline constituents, which is the 'rate limiting step', in a *reversible* process, under conditions where the product is likely to be retained, at least temporarily, in the immediate vicinity of the site at which it was generated. Such reactions may proceed through two steps:



The rate of water (product) evolution is expected to depend on other factors, including the prevailing water vapour pressure, intracrystalline diffusion rates and, perhaps, breakdown of the coherence of the crystal, due to the increasing numbers of imperfections that result from the chemical change. It must also be remembered that kinetic equations based on reaction orders (particularly first-order) have been shown to apply to certain types of solid-state processes (kinetic models) [1,5,7]. These points are made to emphasize the problems associated with identifying reactions in this class, but it is not intended to review this difficult field here. Previous discussions of the problems have been given, e.g. [33,83].

The evidence available, that can be used to recognize the existence of homogeneous reactions in solids, at present appears to be inconclusive. However, the occurrence of reactions of this type must be remembered as a theoretical possibility and a number of

probable candidates are indicated here. Whether these are truly *homogeneous* or are limiting examples from the other classes mentioned is a decision that may provoke further debate.

4.4.1. WET 4A: Explosive disintegration

The explosive disintegration of colemanite arises, because [84,85] intracrystalline constituent water released on heating is retained within the reactant particle by a particularly resilient structure (Fig. 6A). This cannot escape from the three-dimensional close and strong retaining lattice until the temperature is raised to the characteristic value at which internal pressure literally blasts the crystal apart. Reaction occurs throughout the particle but, in the absence of escape channels (as in Fig. 2) or desorption control (Fig. 3), water release is ultimately catastrophic. Other reactions mentioned in this source [84,85] might also be classified as homogeneous (WET 4A).

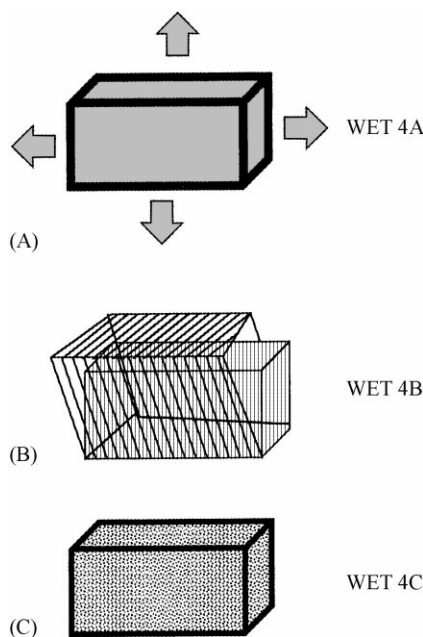


Fig. 6. (A) WET 4A. Water is retained within a strong, impermeable structure until the temperature rise results in an internal pressure sufficient to cause explosive disintegration. (B) WET 4B. Systematic variations of lattice parameters occur with changes in equilibrium $p(\text{H}_2\text{O})$. (Diffusive migration of water within a modified structure.) (C) WET 4C. Crystal constituents react independently of each other and position within the crystal: homogeneous reaction.

4.4.2. WET 4B: Progressive structural change

Equilibrium measurements [86] have shown that lattice parameters of barium hydrogen oxalate hydrate change systematically, and reversibly, with water content determined by $p(\text{H}_2\text{O})$ and temperature. Changes of the lattice show flexibility of structure and the ability of H_2O to redistribute throughout the crystals (Fig. 6B). Although there appear to be no kinetic studies for this reaction, it is likely that movement of water is diffusion controlled (WET 1A or WET 2), so that here behaviour is determined by the ability of the crystal spacings to change, thereby accommodating the available H_2O . It seems that no interface participates.

4.4.3. WET 4C: Homogeneous intracrystalline chemical change

In this class of reaction (Fig. 6C), ‘molecular’ or interionic chemical changes occur throughout each reactant crystal at sites that are randomly distributed amongst crystal constituents, without regard to position or any heterogeneous feature of the solid. $\text{Ca}(\text{OH})_2$ dehydroxylation may be an example of a reaction of this type, aspects of this dehydration have been discussed [33,83]. The authors of a previous work [83] have proposed reaction intermediates of the type $[\text{CaO}\cdot\text{H}_2\text{O}]$ (crystal-retained product), based on thermodynamic considerations rather than from crystallographic evidence. Beruto et al. [87] noted, however, that the $\text{Ca}(\text{OH})_2$ crystal structure is maintained during a large proportion of the dehydration.

4.5. WET 5: Melting and the formation of impervious outer layers

Reactions in a melt sometimes proceed more rapidly than those occurring in the solid state [9]. Reactivity may be enhanced by the loss of the stabilizing, attractive ionic forces existing within the reactant crystal and, in addition, mobility of components may diminish the stereochemical constraints on the formation of the reaction precursor. However, kinetic equations specifically applicable to complex rate processes, involving a melt, have not been formulated because of the problems of allowing for, and measuring the quantity of liquid present and variations of its amount as reaction progresses. The identification of local and temporary melting, particularly within reac-

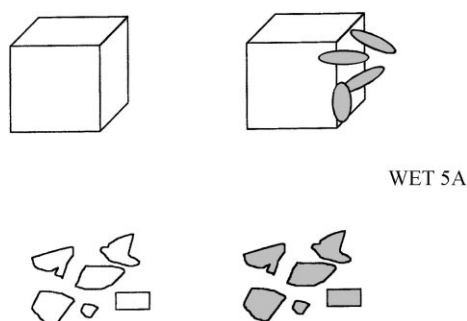


Fig. 7. WET 5A. During reaction of large crystals, water bursts from the surface during rapid reaction. In contrast, dehydration proceeds smoothly in powder, because the escape distances are shorter. (Such reactions probably proceed as types WET 2 or WET 3).

tant particles that form products that are pseudomorphic with those of reactant, is more difficult than is immediately apparent [10]. It follows that the possible participation of melting is not always considered in mechanism formulation and kinetic analysis is not reliably capable of detecting its participation (Figs. 7 and 8).

Melting can be complete (classified as WET 6, below) or partial, which leads to difficulties in interpretation because behaviour is expected to depend on the amounts present, which can vary with the extent of reaction, time, temperature, reaction conditions including $p(\text{H}_2\text{O})$, etc. To approach this problem, in the present state of imperfect development of the subject, some representative reactions are mentioned in which there appears to be partial melting of an initially solid reactant. Under such conditions,

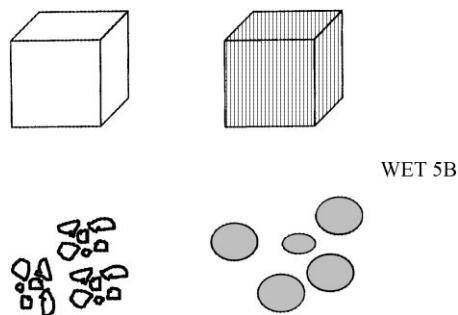


Fig. 8. WET 5B. In contrast with the previous example, reaction of the large crystals proceeds at an interface (WET 3). In powders, an amorphous phase is formed initially which melts before recrystallization to the anhydrous product phase.

impervious or poorly permeable surface layers are sometimes formed that preserve the identities of the individual reactant crystallites [10] and may inhibit the escape of water during dehydrations [88]. The following examples illustrate some reaction types in an incompletely explored field. (It is believed that most of these dehydrations were studied in air or nitrogen: the presence of gas inhibits the escape of product water. The behaviour of these reactants also includes features of the other types of rate processes included in Table 1).

4.5.1. *Nickel sulphate hexahydrate*

The dehydration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in vacuum [26] is a nucleation and growth process (WET 3) in which the monohydrate is formed at an advancing interface. In the presence of an inert atmosphere, the escape of water is inhibited so that dehydrations occur in a higher temperature range and involve the intermediate formation of the tetra- and dihydrates [29]. Microscopic examinations of crystal surfaces during reaction identified [88] the formation of a superficial liquid phase. Later the formation of an impervious and flexible/elastic outer boundary layer resulted in the appearance of bubbles at crystal surfaces, delaying the release of steam.

4.5.2. *2-Aminopyrimidinium [CuCl₃(H₂O)]*

Powder samples of this reactant lose water in a smooth reaction up to 413 K. However, samples in the form of single large crystals, heated to 393 K, burst expelling water-containing dissolved reactant/product, which then crystallized as solvent evaporated (Fig. 7). This is ascribed [67] to the inability of intracrystalline released water to diffuse sufficiently rapidly outwards through structural channels in larger reactant particles when the temperature was rapidly raised. This resembles WET 4A, explosive disintegration.

4.5.3. *Trehalose dihydrate*

The behaviour pattern identified for the dehydration of this reactant [89] contrasts with that described in the previous paragraph. Here, in larger crystals above 353 K, recrystallization follows dehydration, the new phase being formed by a nucleation and growth process, in which restructuring may be promoted by H_2O . The dehydration of powders below 353 K yields an amorphous phase that melts before recrystallization

to the anhydrous solid product (Fig. 8). The amount of water remaining determines whether the structural rearrangement of the solid-solid conversion, catalyzed by water, can occur.

4.5.4. *Calcium nitrate tetrahydrate*

Paulik et al. [90] concluded that this dehydration was not a progressive reaction, but proceeds with melting to form solutions from which water evaporates with crust formation, drying of solids, incongruent melting, evaporation from viscous melts, etc. Rates of dehydration between 320 and 500 K were irreproducible. Inconsistencies in earlier studies were ascribed to the largely physical controls on rates of water release.

4.5.5. *DL- and meso-lithium potassium tartrate hydrates*

Kinetic studies of these dehydrations [91,92] were undertaken initially in vacuum and, subsequently, in the presence of the accumulated water vapour product. For both reactants (mono- and dihydrate, respectively) the greater part of the rate process was zero order, these dehydrations proceeded at constant rate. The changes in extent of melting as reaction proceeded was not determined, but probably represented a large proportion of the reactant and may have approached comprehensive fusion.

4.6. *WET 6: Comprehensive melting*

In some articles, there is no discussion of the possible role of melting in the dehydrations investigated. The acceptance of a kinetic fit, together with calculated Arrhenius parameters, are reported as an (implied) sufficient foundation for mechanistic conclusions based on the assumption that reactions occur exclusively in the solid phase. A central feature of any such reaction description, the phase in which the chemical change occurs is, therefore, not positively identified. The role of melting in dehydrations, in common with most crystallysis reactions [1,4,5,9] is all too often ignored. Nevertheless, melting temperatures are recorded, in tables of physical constants [93,94], for some hydrates that have also been the subject of solid-state dehydration studies. Such entries are sometimes accompanied by the mention of water loss ($-x\text{H}_2\text{O}$) or decomposition(d). For example, one

entry for $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ records the melting point as 89°C and boiling point $-10\text{H}_2\text{O}$ at 100°C and $-12\text{H}_2\text{O}$ at 400°C . These listings may be representative of large samples heated rapidly in air, because dehydration kinetics in vacuum were studied in a much lower temperature interval, 290–340 K [23,95]. A highly hydrated salt, heated under conditions that inhibit water removal, is often capable of dissolving in its own water of crystallization at a temperature that can be regarded as a ‘melting point’. However, the same hydrate, when heated under conditions favouring rapid water removal at low $p(\text{H}_2\text{O})$, may undergo dehydration below the ‘melting point’ without the appearance of a liquid, melt, or solution phase.

Behaviour between these limiting types will be observed for experimental conditions that impose intermediate rates of water escape, which may be determined by one or more of the following parameters: (i) pressure of gas present (opposing the diffusive escape of water); (ii) temperature (controlling volatilization and condensation); (iii) reactant mass and particle sizes (determining ease of water loss from within the particle assemblage); (iv) extent of reaction (influence of product); and (v) size and shape of reaction vessel [$p(\text{H}_2\text{O})$ and ease of product removal], and others including reactant inhomogeneity, inert solids present, possibility of reactant hydrolysis with retained water, etc. Consideration of these possibilities must be included in the design of experiments. Ideally dehydrations should be studied through water losses from a single relatively perfect surface in a good vacuum, sufficiently slowly to avoid self-cooling. Departure from this experimental ideal introduces uncertainty into rate measurements.

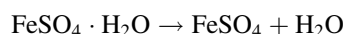
4.7. Hydrolysis and other reactions

A characteristic feature of very many dehydrations is the release unchanged of the very stable H_2O molecule. However, in some compounds water is sufficiently reactive to yield other products through hydrolysis. This is an important aspect of solid-state chemistry that is distinguished here as a group of rate processes about which there is little detailed information. The subject does not seem to have been comprehensively surveyed and, consequently, correlations between these reactions and related dehydrations have not been systematically established. Perhaps many

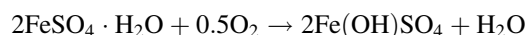
proceed at interfaces and can, therefore, be regarded as a sub-type of WET 3. Alternatively, another possibility is to regard these as a different group of chemical changes. While a review of these processes would be welcomed, the present mention is only for completeness and to include citations for a small number of representative examples found during a limited search of the literature.

4.7.1. Iron(II) sulphate monohydrate

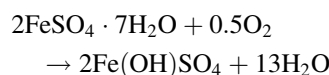
Dehydration of this salt in a reducing atmosphere (carbon monoxide) between 423 and 533 K [96] proceeds directly to the anhydrous salt:



In air there is oxidation, with other reactions [97–99]:



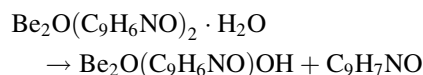
And



Also



Other hydrolysis reactions proceeding in the solid state occur on heating beryllium oxinate hydrate in air [100] and magnesium chloride dihydrate in nitrogen [101]:



(Continued as Section 8).

5. Nucleation and growth reactions

Nucleation and growth reactions (WET 3) constitute the largest, or perhaps the most familiar, group of solid-state decompositions. It is, therefore, appropriate to discuss aspects of these here in the greatest detail. The next stage in classifying these rate processes could be to recognize sub-divisions in the group, WET 3. One potentially valuable approach would be to distinguish reactions by the occurrence or absence of topotaxy and on the number of dimensions

in which the interface advances, as used in the above presentation.

In most crystalolysis reactions, surfaces are identified with the initiation of reaction. Nuclei usually appear on, or near, particle faces where the intracrystalline attractive stabilizing forces are slightly relaxed and from which the product can escape (essential in *reversible* dissociations). During nucleation and growth processes, the subsequent preferred occurrence of the initiated reaction at an *internal* advancing interface, leaving the apparently more reactive superficial material between nuclei temporarily unchanged, is unexpected and requires explanation. For many dehydrations, it has been suggested that the nucleation step can be delayed by the relatively difficult reactant-to-product structural transition. This change, and the accompanying textural modifications including cracking, may mechanically displace reacted material thereby exposing unreacted new surfaces enabling water losses to continue. The contiguous, intranuclear product then promotes recrystallization of water-depleted reactant to its own (product) form, at the active periphery of the expanding nucleus. This ‘seed-crystal’ model is one explanation for the autocatalytic character of the sub-surface, inward-advancing interface [44]. Another explanation is that water, temporarily retained near the active zone, promotes the recrystallization of dehydrated reactant [23]. Either or both of these effects may contribute in any particular reaction, the amount of available, possibly adsorbed, water is expected to reduce at higher reaction temperatures. Forms and functions of nuclei in crystalolysis reactions, generally, have been discussed [1,6,102].

There is convincing evidence that, when subject to dehydration conditions, many hydrates lose water from a superficial layer across *all* reactant crystal faces [43]. This zone is restricted in thickness and these limited initial reactions tend to be deceleratory in character due to increasing structural disorder [44]. Thereafter, reaction only continues inwards, where the transition to the product phase has been achieved (by nucleation) and the difficult recrystallization step is facilitated and maintained. This general representation is consistent with the following observations.

1. When many partially dehydrated crystals are exposed to water vapour, internuclear, apparently unreacted, surfaces retexture (‘orange peel’) [23].

The surface (outer) boundaries of nuclei apparently do not undergo a comparable change. This behaviour is known for many different hydrates [43] and, even when it is not found, as for chrome alum [23], enhanced surface reactivity is apparent through increased nucleation density on resuming dehydration [11,60].

2. A kinetic study of the initial superficial dehydration reaction was reported for *d*-LiKC₄H₄O₆·H₂O [44]. It was also shown, for this hydrate, that the induction period to the subsequent nucleation and growth process was almost entirely eliminated by contact with the anhydrous solid product.
3. Photo-acoustic measurements gave evidence of initial water losses from a superficial crystal layer in chrome alum dehydration [95].
4. Aspects of the various roles of surfaces in dehydrations, and during rehydrations, have been discussed by Guarini et al. [103–105].
5. The inconsistencies between the positions of line dislocation/surface intersections (possible nucleation sites) and the locations of growth nuclei in NiSO₄·6H₂O dehydration [26], could be a consequence of outer layer strain and distortion during initial superficial water losses.

5.1. Nucleation, interface creation

Little is known about the numbers and types of events that culminate in the generation of a growth nucleus [1,7,22]. These are particularly difficult to characterize, because they are usually very rare, in comparison with the number of surface sites on good crystals, perhaps are restricted to ‘molecular-size’ structures and are necessarily destroyed by the nucleation step. The changes preceding nucleation are expected to require movements of the constituents to modify their relationships towards the dispositions and bondings characteristic of the product. Crystals of product may be generated from this structural template. One representation of the nucleation process [106] is based on the formation, accumulation and ordering of site vacancies that leads to the appearance of the product phase.

Solids in which the phase transition, reactant to product, is easily achieved nucleate rapidly and reaction can be initiated across all surface by simple abrasion, e.g. Li₂SO₄·H₂O [39,40], CuSO₄·5H₂O [58]

and $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [45]. Where the transition is more difficult, as for $\text{LiHCOO} \cdot \text{H}_2\text{O}$, the recrystallization is more difficult and abrasion with product, ‘seed crystals’ is required to generate growth nuclei [39]. During diffusion controlled dehydrations (WET 2) and topotactic interface processes (WET 3), in which the product is a modified form of the reactant phase, it may be that no nucleation step is required. Immediate H_2O loss is possible from those faces capable of dehydration. Investigation of the relationships between the ease of nucleation and the nature of the phase change required to form the product phase could contribute towards the advancement of this subject.

Nucleation represents an important control on the overall reaction kinetics by establishing the initial distribution of sites from which interfaces subsequently advance into the reactant bulk. The small amount of reaction required to generate growth nuclei (disproportionately) determines the geometry, and thus kinetic model, of *almost* all the subsequent reaction proceeding at the advancing interface.

5.2. Growth, the advancing interface

In the formulation of kinetic models, based on the developing geometry of reaction interfaces, chemical changes are represented as being completed within a thin reactant–product contact zone. The chemical changes occur preferentially and/or are promoted here (autocatalysis); some reactants yield a finely divided product [11,13,15]. Elucidation of the steps contributing to those changes and their controls are experimentally difficult to characterize so that interpretations must usually be based on indirect evidence, often including the following types of information.

1. *Structural*: X-ray diffraction measurements may indicate detailed changes across the reaction zone [38] and topotaxy [30–32].
2. *Observational*: Microscopic examinations can reveal the textural changes that accompany water elimination [11].
3. *Kinetic*: In common with most crystallographic reactions, dehydrations are well represented by the Arrhenius equation and the concepts of homogeneous kinetic theory are applied to provide models of interface processes. Some features of this approach lack a generally acceptable theoretical foundation [107].

4. Other methods have been used. Dehydrations of hydrates may include two distinct and different rate processes: water elimination and product phase crystallization. The roles of each must be considered in the mechanistic description of any particular reaction.

While reports of dehydrations often describe specific mechanistic features of that particular reaction, there are few discussions of the controls that may generally operate within active interfaces. To contribute to broadening interest in this problem, a consideration of interface phenomena is introduced in Section 5.3.

It was pointed out in Section 5.1 that nucleation, sensitive to the numbers, types and distributions of imperfections in reactant crystals, determines the distribution of sites at which reaction is initiated and, therefore, predetermines the subsequent geometric development of these interfaces. However, there seems to be no indication that the rates of advance of such interfaces are sensitive to (non-nucleating or sub-surface) crystal imperfections. If the interface is regarded as an extended complex imperfection, it is unlikely that its progress will be significantly influenced by the lesser defects and dislocations present within the reactant crystal. Unlike the kinetic model, the interface mechanism appears to be a characteristic and constant feature of the particular chemical change examined, advancing at the same constant rate through the more perfect crystalline regions of the reactant. Different nuclei grow at the same rate [23,45,65]. The properties and chemistry of growth interfaces appear to be independent of whether the original initiation was by inherent nucleation, abrasion or by seed crystals.

5.3. Interface phenomena during chrome alum dehydration (a case study)

In order to consider interface controls, this discussion examines the textures of structures at the chrome alum contact, for which some electron micrographs have revealed details at relatively high magnifications [23,108,109]. The product crystallite assemblage constituting each nucleus is permeated by a regular, divergent pattern of cracks, each about $0.5 \mu\text{m}$ wide. The intercrack spaces, empty in the replica but representing product particles in the nuclei, are often up to $30 \mu\text{m}$ across. Estimations indicated that the cracks

represented, perhaps, 7% of the nucleus volume, compared with the (approximate) 20% weight loss. Without including the possible density increase on dehydration (see Refs. [93,94]), it appears that unreplicated fine channels ($<0.2 \mu\text{m}$) occupy some 20% of the volume of the residual aggregate. The existence of such a microstructure is consistent with the observed [108] roughened texture of the cleaved product surface and support a conclusion arrived at by Cooper and Garner [45] that there was “a loosely packed and somewhat coarsely crystalline product.”

The advancing nucleus edge, seen as the roughened areas in Fig. 2 of [108], is curved outwards, into the reactant. This is strong evidence that water is lost equally easily from zones adjoining or close to the escape channels and from reactant more distant, up to $15 \mu\text{m}$. The intranuclear products offer no impedance [45] to water escape and nucleus growth rates are constant. The textures found [108], together with the cleavage traversing the reaction zone, demonstrate that a strong, close, (topotactic?) contact is maintained between the reactant and the, apparently porous, residue during dehydration. Any strain developed within the interface was insufficient to cause forward crack propagation into unchanged alum (as formerly and incorrectly suggested [23,108]).

Three paths for water migration from interface to intranuclear channels can be envisaged, Fig. 9. Little information is available concerning impedance,

because no experimental measurements seem to have been made of the rates of H_2O diffusive loss through the solid products of dehydrations. Migration parallel to the interface along the contact (A) appears to be the most likely, because the greatest roughening is found here, where reaction is proceeding, Fig. 2c of Ref. [108]. The oblique and vertical diffusive losses (shown in Fig. 9B and C, respectively) would be expected to result in progressively increasing impedance by product, that is not observed [23,45]. Accordingly, it is suggested that, within the active nucleus, a value of $p(\text{H}_2\text{O})$ somewhat below the salt dissociation equilibrium is maintained. This available water promotes the product phase recrystallization. The ability of a lower hydrate to influence rate through $p(\text{H}_2\text{O})$, without contact between solids, has been demonstrated [15,110]. This dynamic model, with self-regulating distribution of water, differs fundamentally from the Polanyi–Wigner representation [11] (Section 10.1), but is not obviously or easily presented in mathematical form. More information is required about the detailed structures of dehydration interfaces.

Quantitative comparative calculations [111] showed that the rate of water evolution from lignite, at 293 K, in which H_2O is not structurally bonded to the organic substrate, was about three times that from chrome alum ($3 \times 10^{-9} \text{ mol mm}^{-2} \text{ s}^{-1}$). These rates were not much lower than those measured for evaporation from liquid water at low pressures, and is

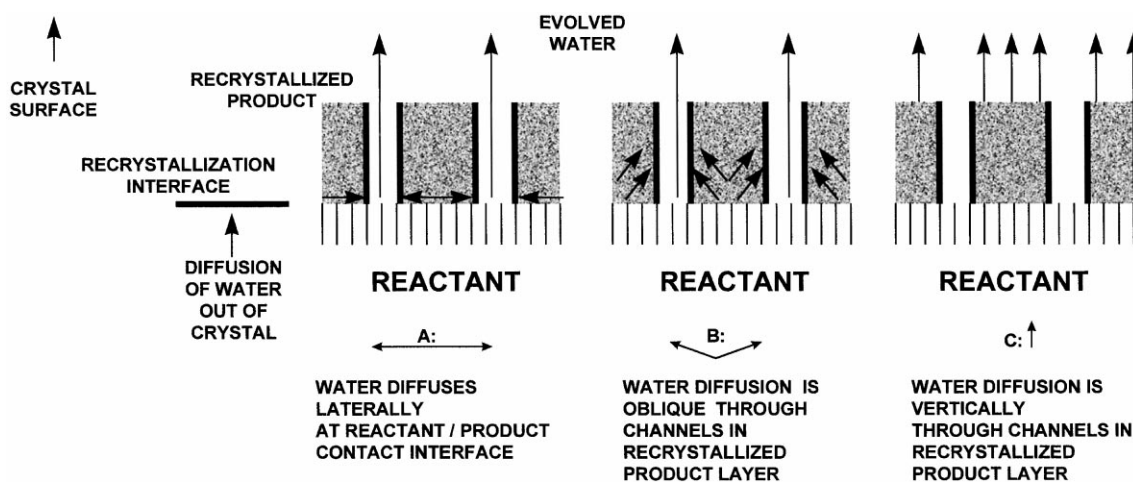


Fig. 9. Diagrammatic representation of possible paths for diffusive release of water from a coherent reactant/product contact across recrystallized product laterally (A), obliquely (B) or vertically (C) during a dehydration reaction.

consistent with expectation from Knudsen diffusion calculations. It is concluded that water losses from within chrome alum nuclei approach those for H₂O volatilization from a liquid free surface. This is entirely consistent with the view [23,95] that, during alum dehydration, a small proportion of intranuclear water is temporarily retained and intranuclear water elimination is facile.

5.4. Thickness of the water loss–product phase recrystallization interface

The interface model described for *d*-LiK-C₄H₄O₆·H₂O dehydration included a water-depletion layer of up to 10 μm thickness followed by a discontinuous advance of the recrystallization zone [44]. In Li₂SO₄·H₂O dehydration, the thickness of the reaction zone, including the formation of a metastable intermediate phase was about 150 μm [38]. In discussing NiSO₄·6H₂O dehydration, Guarini [82] identifies three processes: (i) water release; (ii) migration of H₂O through the water-depleted layer; and (iii) recrystallization to the product phase. It was similarly concluded for Ca(OH)₂ dehydration [83] that the water removal and recrystallization did not occur contiguously. In a number of other hydrates, for example, some transition salts of mellitic acid, the anhydrous dehydration products remain amorphous to X-ray diffraction [112,113]. This is ascribed to the formation of strong (extended and polymeric) bonding between the divalent cations and the multivalent anions which leads to less regular structures that cannot readily reorganize to form crystalline phases.

5.5. The role of strain in dehydrations

There is evidence that strain is generated during some interface dehydrations, particularly in large crystal reactants. It is not known, however, how important are the effects of local distortion in promoting chemical change within the zone of reactant/product mismatch or how many reactants are influenced significantly by strain.

Single crystals of sodium citrate dihydrate release H₂O more rapidly than the powdered reactant, ascribed to enhanced nucleation by strain [66] (also water vapour). There is vigorous disruption (relief of strain?) of barium styphnate monohydrate crystals during

water loss [68,69]. Crystals of pyrimidinium copper chloride hydrate burst to expel liquid during heating, whereas powder underwent a smooth reaction [67]. Reactant cracking in the vicinity of the interface has been identified as a possible factor for the propagation of reaction in the dehydrations of BaCl₂·2H₂O [114], K₂CuCl₄·2H₂O [115,116] and Cu(CH₃-COO)₂·H₂O [117]. Water losses from Li₂SO₄·H₂O were accompanied by structural reorganization [38], reactant cracking and pore formation in advance of reaction zone may arise from strain [40]. The texture of the product of dehydration of CoC₂O₄·2H₂O depended on the reaction temperature [118]. It was shown that, despite the appearance of planar intranuclear channels, crack propagation did not penetrate beyond the interface, to enter the unreacted zones during chrome alum dehydration [108].

6. Kinetic analysis, finding a kinetic fit

The *Kinetic Model*, the rate equation identified as most precisely expressing the yield–time data measured for a particular reaction, provides a valuable means of representing quantitatively the pattern of rate variation. Experimental observations, thus collated and empirically expressed, can be used for many practical purposes, including process design and sometimes a trend may be extrapolated to predict probable behaviour beyond the range of conditions investigated. However, the purpose of many kinetic studies is to gain insights into the controls and mechanisms of chemical changes proceeding in the selected reactant. The present survey is primarily concerned with those fundamental investigations that are undertaken to obtain insights into the chemistry of the steps through which reactants are converted into products. Subsequent ordering of the principles identified as explaining observations may contribute to the development of theory. The representational models formulated may be of value in systematically relating information/results already available and enable useful predictions to be made of the properties of hitherto untested systems. The value of using empirical data to provide (sometimes limited or partial) answers to particular questions is remembered. However, the emphasis here is directed towards theory development, through understanding the widest significance

of the experimental observations and the contributions that these may make towards formulating fundamental theoretical models capable of explaining all features of dehydrations. This is an ambitious target which will require much future effort.

The methods of kinetic analysis are well-known [1,2,5,7,12]. The set of measured values (fractional reaction, α , time, temperature) are determined isothermally or under a controlled regime of temperature change. From these data the kinetic model, $g(\alpha)=kt$, that provides the most acceptable fit for the reaction is identified and (almost invariably) the magnitudes of the Arrhenius parameters calculated. All conclusions reached, together with any other relevant experimental measurements, are taken together to formulate a reaction mechanism, including characterization of both the reaction geometry and/or the controlling (rate-determining) interface step.

It is, of course, essential that all rate measurements used in mechanistic kinetic studies are positively identified with the chemical process of interest and are not modified by other controlling influences, such as self-cooling and/or the availability of water during a reversible dehydration. The rates of many dehydrations are sensitive to $p(\text{H}_2\text{O})$ so that apparent kinetic parameters vary significantly with the procedural variables (gas pressure, reactant particle sizes and packing, etc.). These control the amounts of water remaining in the vicinity of the reactant, which may be inhomogeneously distributed inside the reactant assemblage of particles and be lost by a relatively slow diffusive process. Readsorption of product water vapour, during reversible dehydrations, exerts an important control on the overall kinetic characteristics. The resulting uncertainties in measured kinetic parameters are greatest where product H_2O escape is slowest, e.g. in large samples, at high reaction rates (also, there may be self-cooling), with fine and tightly packed powder reactants, etc. Sensitivity of rate to prevailing conditions [$p(\text{H}_2\text{O})$] may change the kinetic model identified as apparently giving the best kinetic fit and/or the magnitudes of A and E_a (this is one probable explanation for the compensation effects [119] occasionally found for dehydrations [83,120,121]). Measurement of the rate of the forward reaction *only* requires careful experimental technique [122] and interpretation of data [123]. We have little direct information, at a molecular level, of the

chemical steps, and their controls, participating in water release and in the recrystallization of the solid products.

The problems that arise in identifying the ‘best’ kinetic model for sets of measured data, using different reactant samples and variations of experimental technique, both isothermal and rising temperature, are described by House and Ralston [124]. From a series of measurements of ammonium oxalate monohydrate dehydration in nitrogen, it was concluded that useful conclusions can be obtained *only* if a reasonable number of reproducible experiments of the highest quality are completed and the results compared. A second study [125], of $\text{K}_4[\text{Ni}(\text{NO}_2)_6]\cdot 0.75\text{H}_2\text{O}$ dehydration, similarly compared kinetic analyses of experiments carried out under a range of conditions and emphasized the variations in the perceived ‘best fit’ equation that was identified from similarly obtained rate data.

There is no general agreement as to what constitutes an acceptable ‘fit’ in a kinetic analysis. In many reports, statistical tests are applied and, from the set of equations considered, that giving the least deviation is accepted as representing the rate process. Weakness in this approach include the possibility that a kinetic model, not included in the set, may be ‘better’ than those tested. Errors may be random and there may be systematic deviations at limits that are difficult to accommodate into standard statistical tests [126,127]. It appears to the author that the worth of many reported kinetic analyses would be considerably increased if the following types of information were to be provided:

1. The accuracy of reproducibility for successive identical experiments is reported. This error can then be used to estimate the limits of accuracy of the Arrhenius parameters calculated (sometimes given to an unrealistic number of significant figures).
2. The criteria used to recognize a kinetic fit are explained.
3. The α -range across which the ‘fit’ is regarded as acceptable is given.
4. The magnitudes and α -ranges of any deviations from a perfect fit are mentioned.
5. The set of kinetic equations tested in the comparison is specified.

6. The results of investigations of the sensitivity of kinetic behaviour to changes in reaction conditions (procedural variables) are reported.

It was mentioned above that nucleation processes tend to be sample-sensitive, varying between individual crystals, and their contributions can sometimes be changed by mechanical pretreatment (abrasion). The initial distribution of active interfaces controls the subsequent development of reaction geometry which is not, therefore, a fundamental feature of the reaction. In contrast, it would appear that, during nucleus growth, the chemical changes occurring within the interface process are constant, and an essential characteristic of that dehydration. A further complication is that for a number of reactions the kinetic behaviour, and, presumably the reaction mechanisms, are different in different temperature ranges [78–81,128,129].

There is no reason to assume (as sometimes appears to be implicitly accepted) that every rate process must be represented by a *single* rate equation only. For many dehydrations both absolute rates and the shapes of the α -time curves vary between different reactant samples of the same substance (depending on particle sizes, shapes, crystal perfection, etc.), with pretreatment (e.g. abrasion) and with reaction conditions (procedural variables). Moreover, the reaction controls may vary with α , for example the contribution from a nucleation step becomes less significant in the later stages [40,95]. Under accumulatory conditions, the dehydration rate can become increasingly influenced by the reverse process in the approach to dissociation equilibrium [95].

6.1. Kinetic analyses for nucleation and growth reactions

During the literature survey undertaken in the preparation of this review, an inconsistency was identified that appeared not to have been previously noticed or discussed. A high proportion of dehydration reactions have been reported as fitting the Avrami–Erofeev equation [1] with $n=2$ (A2), even though there was microscopic evidence, for at least some of these reactions, that the nuclei grew in *three* dimensions. For these processes the theory [1,5,7,12] predicts that n is 3 (A3) or, if nucleation is maintained, $n=4$ (A4).

The following dehydrations were reported as fitting the A2 rate equation, while observations available describe the growth of three-dimensional nuclei:

$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [11,23,45,95,108]

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ [26]

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ [130]

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [40,120,121] (other kinetic expressions also fitted)

d- $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ [44]

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ [131]

For several other dehydrations the data fitted the A2 equation, but the shapes of nuclei were not reported:

$\text{K}_4[\text{Ni}(\text{NO}_2)_6] \cdot 0.75\text{H}_2\text{O}$ [125]

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [78–81] (below 383 K)

$\text{Cu}(\text{CH}_3\text{-COO})_2 \cdot \text{H}_2\text{O}$ [117] (two-dimensional cracking reported)

$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ [132] (nuclei described as two-dimensional)

$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ [133] (other kinetic characteristics mentioned)

Specific chromium(III) salts [134,135].

The conclusion that reactions, identified as proceeding through the growth of three-dimensional nuclei, do not fit the rate equations specifically derived for these models is an obvious shortcoming of the theory. This is important because these observations provide the foundations for use of the geometry-based rate equations, that are so widely accepted and applied to other crystallysis reactions. Few microscopic investigations have *precisely* compared yield–time data with the rate expressions deduced for each model (see, e.g. the kinetic analysis for NH_4ClO_4 decomposition by Jacobs and Ng [136]). Nevertheless, there is a wide, possibly universal and unquestioning, acceptance of the geometric theory and the equations derived from it [1,5,7,12], including kinetic analyses of dehydrations. The assumptions that provide the foundations for the geometric rate equation theory may now require further critical appraisal. As with so many aspects of this subject, we simply do not know whether these apparent inconsistencies represent a few examples of exceptional behaviour or indicate a more general problem.

It seemed probable, at first sight, that the early (low α) relatively less acceleratory character (the A2 fit) of

these reactions could be due to a contribution from an initial limited evolution of gas, (e.g. [44]). This explanation was tested by the following kinetic analysis. A set of α -time values were calculated from the Avrami–Erofeev equation with $n=3$ (A3) and all values were increased by the addition of the yield of ‘product’ from an initial deceleratory process, representing +4% ‘fast early reaction’ that was completed at about $\alpha=0.2$. Plots of the recalculated (α') data according to the Avrami–Erofeev equations with $n=2$ and 3 (A2 and A3), showed early positive deviation from linearity, due to the ‘initial reaction’. A range of changes in the relative rates and extents of the ‘initial process’ did not resolve this problem.

Acceptably linear Avrami–Erofeev $n=2$ plots (A2), see Fig. 10, were obtained for α'' values, found when the magnitudes of α , (again) calculated by the A3 equation, were modified by subtraction of 0.03 [$\alpha''=(\alpha-0.03)\times 1.031$]. These data fitted the A2 equation between $\alpha=0.03$ and 0.9, whereas with the A3 equation there was an initial deviation to about 0.2

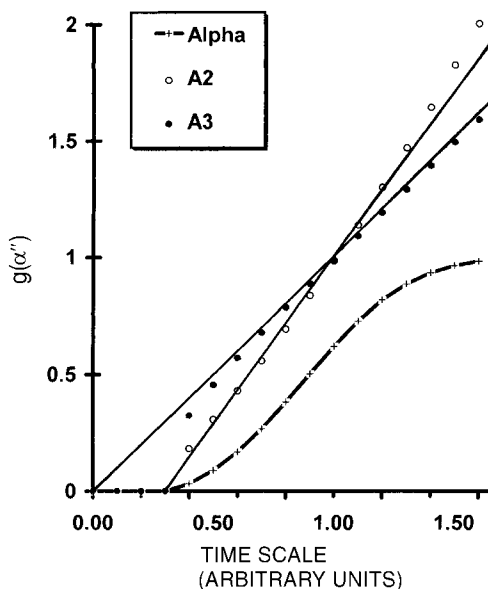


Fig. 10. Comparisons of fit of calculated α'' vs. time data to alternative kinetic models: further explanations given in the text. Values of α were calculated from $[-\ln(1-\alpha)]^{1/3}=t$ and 0.03 was subtracted from each α , which was then rescaled to completion at $\alpha=1.00$ so that: [$\alpha''=(\alpha-0.03)\times 1.031$]. The linearity of plots of $[-\ln(1-\alpha'')]^{1/n}$ against time were sufficiently similar to make it difficult to determine whether the A2 or the A3 equation provides the better fit, that for $n=2$ being preferred when α was <0.9.

after which the fit, not unexpectedly, extended to virtual completion of the ‘reaction’. The kinetic analysis of such a set of data points would make it difficult to decide whether the A2 or the A3 expressions provided the better fit, a problem noted for some of the reactions referred to above [44,124–127].

The unanticipated feature of this explanation of the inconsistency is the apparent ‘disappearance’ of a proportion of the early product. Reasonable explanations can be provided, though more work is clearly required to strengthen the foundations of the important geometric/kinetic theory. ‘Loss’ of initial water could result from adsorption on apparatus walls (glass, in an accumulatory apparatus), dehydration during ageing or from surfaces during evacuation before reaction [23,43] and/or by retention within active nuclei [23,95]. This ‘initial deficit’ model appears to be capable of explaining the inconsistencies between conclusions from kinetic and microscopic observations, Fig. 10.

Other uncertainties, not always adequately considered in kinetic analyses, include the following.

Separate water elimination and product recrystallization interfaces. It has been suggested for some dehydrations that the reaction zone, from which water is lost, may proceed in advance of the solid product formation (recrystallization) interface, e.g. $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ [82] and $\text{Ca}(\text{OH})_2$ [83]. The presence of a ‘thick’ reaction zone from which H_2O is evolved may influence kinetics, a geometric parameter that has not been considered in detail.

Changes in interface advance rates. The initial rate of interface growth may be greater [23] or slower [7] than those subsequently attained. This influences overall kinetic behaviour.

Reactant particle sizes and shapes. Although it is generally accepted that rates of reactions are influenced by reactant particle geometry, quantitative allowances for particle size distributions are not always made (see below).

6.2. Influence of crystal and particle sizes on reaction kinetics

Early studies of dehydrations were often concerned with reactant samples in the form of large single crystals [22], enabling the textural changes accompa-

nying nucleus growth to be characterized. Subsequent work has investigated powders, for which the area on which nucleation can occur has been increased, though crushing is expected to destroy certain types of potential sites for nucleus development while creating others by abrasion. The decrease of particle size circumscribes growth of an individual nucleus within each particle and the progress of reaction depends on whether an active interface can propagate from one nucleated particle to a neighbour. Such ‘seed crystal’ progress through a reactant mass appears possible in at least some dehydrations [39,44]. Little is known about the relative influences of these effects, some of which operate in opposition, and have not been extensively, or quantitatively, characterized. Kinetic behaviour is not easily related to reactant particle sizes and dehydration rates are certainly not directly proportional to the total surface area of the sample. In addition, for powder reactant samples the retention of water in interparticular pores and spaces also contributes to the control of rates in these reversible reactions.

Dehydration rates of alum crystals were somewhat larger (5 times as large) than those for powders, ascribed [95] to the formation of coherent aggregates of particles from which H₂O escape is impeded. Approximate comparisons for NiSO₄·6H₂O dehydrations during vacuum gravimetry (see Figs. 1 and 2 in Ref. [26]) showed that the evolution of water from the powder was about eight times that for large single crystals. Estimations, from the large number of rate measurements available for Li₂SO₄·H₂O, indicate that the H₂O release rate from powder is some 10 times greater than that from larger crystal reactants. The kinetic characteristics of *d*-LiKC₄H₄O₆·H₂O dehydration [44] were complicated by the large extent of the initial reaction in the powder and the ability of the reaction to propagate from one particle to a neighbour. Unusually, the dehydration rate of sodium citrate dihydrate single crystals at 430 K [66] is more rapid than from the powder. This is ascribed to enhancement of nucleation by strain and by water vapour retained in the crystals.

6.3. Different kinetic characteristics in different temperature intervals

Rate studies for a small number of dehydrations have identified different kinetic characteristics for

(often) the same chemical change occurring in different temperature intervals. The dehydration of Cu(CH₃-COO)₂·H₂O fits the nucleation and growth (A2) equation below 371 K [117] whereas above this temperature the contracting envelope (R2) expression provides a better representation of the data and the E_a values are 154 and 76 kJ mol⁻¹, respectively. The low temperature (below 563 K) dehydroxylation of CoO(OH) (→Co₃O₄) is a nucleation and growth process, but is described by the R2 equation above 573 K, and the values of E_a are 214 and 101 kJ mol⁻¹, respectively [129]. The dehydration of NH₄MgCl₃·6H₂O below about 430 K gives the dihydrate by a phase boundary controlled reaction while, at higher temperatures, formation of the anhydrous salt fits the first-order equation [128].

These examples demonstrate that some reactions change mechanism, including the kinetic model, within the temperature interval of investigation and this possibility must, therefore, be remembered when interpreting data. This change is probably more easily detected during isothermal studies. If these mechanistic alterations result from a variation in the parameter controlling the rate determining step (as seems probable), then these systems offer the possibility of gaining direct insights into the controls of interface phenomena. Characterization of the nature of such changes could provide mechanistic insights of a type that is currently not available. It would be interesting to know, for example, whether the mechanism established by starting reaction in one temperature range was maintained during a continuation of the same process in the other temperature interval. Investigations of reactions ‘at the edge’ of conditions appropriate to one mechanism type could provide clues to the factors that determine the adoption of an alternative sequence of interface steps. These (and other) examples could offer an attractive, but hitherto unexploited, potential for probing the interface controls and the essential nature of crysolysis reactions.

7. Introduction (continued)

7.1. Background to this review

One approach towards formulating a chemical theory is to classify the various different patterns of

behaviour that can be distinguished within the range of reaction types found amongst the group of processes identified as being of interest. Any systematic trends recognized for sets of related reactions may then provide insights into the factors that determine reactivity and the mechanisms of the chemical changes that occur. Such systematic ordering can be the first step in establishing the foundations upon which theoretical models can be built. The benefits of such theory can be considerable. The subject is structured around an underlying skeleton about which new advances can be meaningfully positioned, enabling the topic as a whole to enjoy organic growth. Apparent inconsistencies or errors in previous interpretations may be identified in the wider perspective and, if necessary, reconsidered. Properties and behaviour of systems not yet examined can be predicted with some confidence. New directions for useful research effort may be revealed.

The value of theory development in promoting progress in science has been forcefully and succinctly expressed by Gregory [137]. He points out that Mendeleev's Periodic Table "made sense of chemistry, its gaps suggesting where to look for new advances." The ordering of species both in astronomy (kinds of stars) and in biology (plants, animals, etc.) enabled the evolutions of species of both types to be understood. These points were made in a book concerned with the science of seeing, *Eye and Brain*, but the arguments apply equally here. Again, with similar relevance, Laidler [138] stressed the importance of the Arrhenius equation in relating reaction rates to temperature. This expression has particular value because the constants can be ascribed physical significances, whereas the constants arising in possible alternative relationships are empirical, and such equations are 'theoretically sterile'. Thus, generalizations developed from physically realistic models are valuable in classifying observations and capable of separating useful and valid conclusions from misleading analogies. One primary objective of science is to present systematically available information. Another is to extrapolate such conclusions to predict behaviour in hitherto untested situations reliably and to identify directions for potentially significant new research. The objective of the present article is to make a limited contribution towards increasing order and developing theory in the field of decompositions of solids, particularly

dehydrations. The classification scheme proposed in Table 1 is intended to be constructive, wide-ranging and critical. It has been developed through the critical consideration of the information found from the rich harvest of relevant sources. It appears that the subject can only benefit from an attempt to introduce order.

7.1.1. Constructive

The scheme (Table 1) is intended to contribute positively towards advancing a subject-area that at present lacks general theory [1,8]. The approach used is not, of course, the only possibility and is presented here in the hope that it will be adopted. However, if it does not succeed in this, it may be that this attempt will stimulate others to modify the idea or to provide alternatives.

7.1.2. Wide-ranging

The author of a review can reasonably be expected to attempt to locate all relevant sources. Comprehensive coverage of any large subjects is, however, effectively impossible for all but the most restricted topic, and problems must arise in searching a literature as extensive as that devoted to dehydrations of crystalline solids. Sources reviewed in preparation for this survey include *Chemical Abstracts* and all those reports that were located during the writing of Refs. [1,8]. The specific problems of this coverage have been mentioned in Sections 2.1–2.3. and may have discouraged others from exploring this material. Coverage also includes articles found during the several decades (1955–1999) that the author has worked in this field. It is hoped that the presentation here is based on a sufficiently wide-ranging sample of the relevant published material to be representative of the subject as a whole, but it cannot be claimed that the coverage is comprehensive.

7.1.3. Critical

The contents of *all* published articles cannot *always* be accepted as consistent, complete and comprehensible. It is, therefore, essential that the conclusions presented in different sources are compared critically so that similarities are reliably identified and reasons for any differences can be considered. It is a characteristic feature of solid-state dehydrations that the course and speeds of reactions are frequently sensitive to several controlling parameters, the procedural

variables. In many published reports these possible effects are not investigated, not discussed and often not mentioned. Another shortcoming of some research accounts is that the possibility of reactant melting may not be considered. The phase in which a reaction occurs is an essential feature of any mechanism proposed but the detection of melting, particularly when local and temporary, can be difficult to demonstrate or show to be absent [10].

7.1.4. Available theory

Before discussing new concepts, proposed to systematize presentation, it is appropriate to comment on the theory already available. In the past, a number of reaction models have been regarded as successfully representing many solid-state rate processes. However, there seems now to be a diminution in confidence about their applicability and these older theoretical ideas are becoming less frequently employed to explain observations.

1. The concept of reaction occurring preferentially within an active advancing interface was originally proposed to account for the nucleation and growth processes in crystal dehydrations [22]. This model has retained its importance as the common feature underlying the geometry-based kinetic rate equations that appears as the most important unifying theory applied to crystalolysis reactions. However, it now appears that interface chemistry is more complicated than was earlier thought.
2. Rate data for the decompositions of crystalline reactants fit the Arrhenius equation and the magnitudes of calculated activation energies and frequency factors often appear as the principal objective of a kinetic study, or as its most significant result. This arises as a result of perceived parallels with homogeneous reaction rate theory, though the theory has been less reliably applied to the reactions of solids [107]. In addition to these doubts about the theory, measured yield–time data for dehydrations may be influenced by the endothermic character and reversibility of the reactions. It follows that rates measured sometimes vary with prevailing conditions (procedural variables) and are probably not exclusively determined by a *single* chemical step

within a reactant–product contact zone. These points are discussed in detail elsewhere and are simply mentioned here to emphasize the difficulties of interpreting the significance of apparent magnitudes of Arrhenius parameters. Furthermore, their values have provided no criteria for classification of different reaction types.

3. The Polanyi–Wigner equation [11,139–142] was originally accepted as providing a unifying theoretical model capable of describing quantitatively the rates of dehydrations occurring at interfaces. This early promise now appears not to have been realized. The use of this relationship has declined as it has become evident that mechanisms of chemical processes within the active reactant–product contact zone are (much) more complicated than the simple dissociation processes envisaged. As pointed out in (2) above, other secondary controls influence the reaction rates measured so that many reactions are ‘abnormal’ [19].
4. Though not strictly relevant here, it may be pointed that many, but perhaps not all, dehydrations exhibit the Smith–Topley effect [11]. This behaviour pattern may be a consequence of non-equilibrium and/or discontinuities at the reaction interface [20] and self-cooling [21].

7.2. Terminology

7.2.1. Crystalolysis

The investigation of crystalolysis reactions might be regarded as a distinct subject area [1,8]. The prominent unifying characteristics of these reactions are that chemical changes occur at active advancing interfaces and kinetic behaviour is described by geometry-derived rate equations. The types of rate processes encompassed within this discipline are well known to practitioners active in this field and the topic appears to be a recognizable entity. The use of a specific title would confirm the coherence of the subject. This would also, as already pointed out, facilitate literature searches that presently must be based on imprecise, non-specific terms, such as: ‘decomposition’, ‘thermal reaction’, ‘solid’, ‘crystal’, etc. that are inefficient and time-consuming. A further expected benefit of using a term that specifically identifies the reaction as occurring in the solid state

is that authors would be encouraged to declare explicitly the phase in which they identify the reaction as proceeding. At present, many reactions are reported as fitting one of the ‘solid-state type’ equations, but without a positive statement confirming that (the authors believe) the decomposition proceeds without melting.

7.2.2. Mechanism and kinetic model

De Boer [143] considering (in 1960) the meaning to be attached to the word ‘mechanism’, as applied to heterogeneous catalytic reactions, stated that it should “embrace the complex of theories and concepts that give first a picture of the chemical phenomena involved, secondly, an insight into the essentials of the processes, and that thirdly, constitute a proper basis for the mathematical formulation of rate equations.” This is a very much broader view of this word than the narrow meaning found in some of the current literature relating to crystallographic reactions. In these, ‘mechanism’ may simply specify the rate equation, for which the term ‘kinetic model’ is more appropriate and is to be preferred. In general, it is necessary to consider all contributing processes in any study intended to investigate a reaction mechanism: all bond redistribution steps, recrystallizations, etc. Moreover, it must be remembered that overall kinetic characteristics are not an invariable property of a reaction, and can be varied by sample pretreatments, such as surface abrasion [58,59]. Mechanical pretreatment does not, however, necessarily change the chemical processes at the advancing interface, an important, even central feature of the reaction mechanism.

In this field, mechanistic investigations should always include examination of the possibility of melting, perhaps temporary and local, during reaction; this is not always or easily observed [10]. The kinetic properties of rate processes in which both a solid reactant and a liquid phase participate have not been established, because the relative contributions of concurrent reactions are difficult to measure. It follows, therefore, that identification of a solid-state kinetic model as the ‘best fit’ for a particular reaction does not necessarily mean that an alternative model involving at least some melting can be excluded as a possibility. Fusion, and eutectic formation with a product, is always a possibility in thermal reactions and possible

chemical changes in a melt should be remembered in the interpretation of data [9].

7.3. Dehydration reactions

Dehydrations cannot be regarded as a distinct reaction type. Water is accommodated in different lattice environments and bonds of various forms and strengths are ruptured on H₂O release. Water is accommodated by (i) dative coordination, $[M(OH_2)_x]^{n+}$, thereby reducing the effective charge density on a cation, that may be a transition metal ion, and/or (ii) hydrogen bonds to other constituents of the crystal. Many hydrates contain water with bonds of both types. Removal of H₂O changes the stabilizing forces in the crystal, so that dehydration is usually accompanied by recrystallization to the more stable lattice of a lower hydrate and/or to fulfill the coordination requirements of the cation.

A dehydration reaction that involves loss of a coordinated H₂O ligand is, therefore, correctly regarded as the decomposition of a coordination compound. These, and other diverse and numerous water elimination reactions, have often been considered together as a group. This convention, that lacks a chemical justification, will be observed here. Overall dehydrations exhibit dissimilarities of chemical, stoichiometric, kinetic and mechanistic properties that are almost as varied as for those of crystallographic reactions generally. The stable H₂O molecule is a frequent volatile product.

7.4. Theories of dehydration reactions

7.4.1. House dehydration reaction mechanism

House [144] has proposed a general reaction mechanism to account for the elimination of H₂O ligands from coordination compounds. The initial step is a transition state that includes the generation of a lattice point defect in the crystal. Elimination of the (former) ligand, as water that is later volatilized, from a complex ion requires transfer of the species released to an interstitial position, analogous to a Frenkel defect. This dissociation may then either reverse or the defect created will migrate through the crystal. Ligand removal for cobalt(III) and chromium(III) complexes are believed to proceed through the S_N1 mechanism. The rates of these processes are expected

to be influenced by lattice energy and the relative sizes of the ions. Dehydration–anation reactions for several sets of cobalt(III) and chromium(III) complex salts that included H₂O ligands, have been studied by Ribas et al. [134,145]. Results were interpreted according to this reaction model [144], through comparisons of the relative magnitudes of activation energies for the reactions of related coordination compounds. It was concluded that the transition state is determined by the water elimination step and the generation of the non-ionic (H₂O) mobile Frenkel-type defect. The ease of water release and of defect formation depend on the ‘interionic free space’ available in the crystal.

Interpretations based on such reaction models can yield reliable conclusions only if magnitudes of activation energies are measured with sufficient accuracy. Le May and Babich [146] have drawn attention to the poor agreement found between activation parameters reported for some dehydration–anation reactions, due to the sensitivity of kinetics to reaction conditions (procedural variables). Subsequent articles by House et al. [124,125] discuss reproducibility and the variations in results from kinetic analysis that were found from comparative and multiple studies using different experimental procedures for the same dehydration reaction. Values of the Arrhenius parameters could be calculated without knowledge of the kinetic model applicable [147].

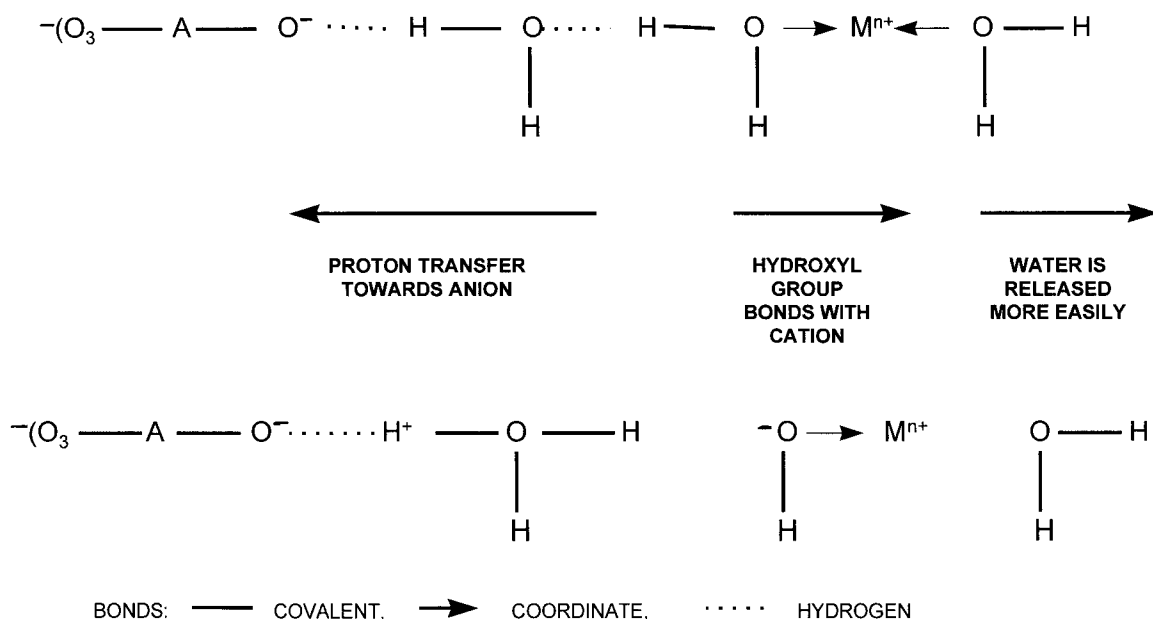
It was concluded from the present survey that this proposed mechanistic model [144] requires further critical examination. The essential steps in this theory appear to be represented as occurring in a zone of perfect crystal, so that this might be treated as a homogeneous reaction, wherein all equivalent ions are presumably regarded as equally reactive (the WET 4C model). However, some of the reactions interpreted according to this theory [134,145], suggest, by reference to nucleation and growth kinetic models (WET 3), that there is an initial period of acceleratory behaviour. Moreover, the kinetic analyses do not appear to have identified a particular rate equation that describes each dehydration, to establish whether or not each reaction occurred at an advancing interface. No microscopic evidence was provided, detecting the participation of a reaction interface. Thus, it appears that the proposed mechanism is incomplete. The following reaction types are

suggested as approaches that might be capable of contributing towards the resolution of the difficulties outstanding. Further work would undoubtedly be required to establish whether either of the proposed models can be applied.

1. A homogeneous reaction (WET 4C) progressing within an increasingly defective crystal structure is expected to be autocatalytic (acceleratory), if a rise in defect concentration facilitates water elimination. This could arise through either a reduction of the energy barrier to reaction or the enhanced mobility and, therefore, ease of removal, of H₂O in the crystal. Characterization of the contributions from these effects would require comparative measurements of E_a and *diffusion coefficients* for water in reactant crystals dehydrated to various extents.
2. The occurrence of reaction at an advancing interface (WET 3) would be most effectively demonstrated by microscopic and diffraction observations, supported from kinetic analyses. It is difficult, however, to reconcile the proposed model [144] with imperfection generation (and interstitial H₂O retention) within an advancing interface where the structures are actively reorganizing as a result of continuing chemical changes and recrystallization. In other dehydrations, it appears that the water released is either volatilized directly from the interface or, where sufficient structure is retained by the coherently bonded product, migrate across the solid phase by diffusion. The reaction model under consideration here apparently does not consider the consequences of topotaxy, including the roles of the crystal lattices at the reactant–product contact discontinuity. At the present state of knowledge, considerable uncertainties arise in attempting to model the energetics of water removal within the interface.

7.4.2. Proton transfer in dehydrations

Thomas et al. measured the values of E_a for the dehydrations of NiSO₄·6H₂O [26] and Mn(HCOO)₂·2H₂O [71] as about 70±16 kJ mol⁻¹ and 74±12 kJ mol⁻¹, respectively. These were described as being close to expectation, if proton transfer controlled the overall rate of interface



Scheme 1. Possible dehydration mechanism in which water loss follows a proton transfer step: schematic, see text for further explanation.

advance. This was based on comparisons of proton motion in kaolinite, about 16 kJ mol^{-1} [148] and the energy ascribed to the coincident rupture of two hydrogen bonds, about 40 kJ mol^{-1} [149].

No detailed description of a dehydration reaction mechanism is provided for either hydrate, but the sequence of changes shown in Scheme 1 appears to be one possibility. The initial proton transfer step results in transitory formation of a hydroxonium ion in the vicinity of the anion. The concurrent formation of the hydroxyl ion reduces the effective cation charge, thereby diminishing the energy barrier for the dissociation of other coordinated ligands. After this $(\text{H}_2\text{O})_n$ loss, the proton transfer step may be reversed and the water depleted components rearrange to redistribute coordination linkages and recrystallize to the product phase. Such transfer steps might be capable of detection by spectroscopic measurements, as interface (energy band) levels [107].

8. Classification scheme for solid-state dehydrations (continued)

Water evolution type (WET) dehydrations grouped through reactant structures and other criteria. Addi-

tional discussion (to that in Section 4) here extends the explanations, and provides further examples of the reaction groups.

8.1. WET 1A: Crystal structure maintained, diffusion control

8.1.1. Zeolites

Water evolution from the ion-exchanged zeolites LiA, NaA, KA, MgA, CaA, CdA and ZnA fitted the first-order equation between about 340 and 400 K [48,49]. Arrhenius plots were non-linear and estimated values of E_a were small, 37–46 kJ mol^{-1} (close to the latent heat for water evaporation, about 40 kJ mol^{-1} [50,51]). X-ray diffraction measurements gave evidence of slight adaptations of zeolite structures at around 380 K, but irreversible changes were found only above 600 K. It was concluded that kinetic parameters were of empirical value and that Arrhenius constants cannot be identified with specific processes. It is believed that this is because water is evolved from more than one type of intracrystalline site and the contributions to product H_2O from different precursor states cannot be distinguished. Magnitudes of E_a and A depend on site

coverage and intrapore interactions between adsorbed H₂O molecules.

8.2. WET 1B: Crystal structure maintained, surface desorption control

8.2.1. Uranyl nitrate hexahydrate

Isothermal kinetic measurements of UO₂(NO₃)₂·6H₂O dehydration (−3H₂O) [41,42] in vacuum between 213 and 243 K showed a close-to-constant rate of water release across the greater part of reaction. There was no induction period and $E_a=46$ kJ mol^{−1}. The dehydration rate diminished linearly with increase in $p(\text{H}_2\text{O})$. These and supporting observations identify rate control as the water desorption step at, or very near to, the crystal surface. The water site vacancies thus generated are mobile and accommodated within the water-depleted crystal that remains pseudomorphic with the original reactant. The surface may, therefore, be identified as a static interface. Although this behaviour appears unusual, this may be a consequence of the few low-temperature dehydration studies that have been concerned with suitable reactants.

8.3. WET 2: Diffusion across a coherent barrier layer of product

The examples mentioned here tend to be concerned with reactants that contain extended two-dimensional constituents because these have attracted the most interest, many minerals containing structures of this type are found in nature. There is no reason why dehydrations proceeding through diffusion in one or in three dimensions should not occur, but such reactants have attracted less attention. Again, many of the reactants studied have been in the form of fine powders, where it is expected that there will be a diminished probability of reactant crystallite cracking.

8.3.1. Muscovite

This mineral KAl(Si₃Al)O₁₀(OH)₂ contains stable, extended planar units that are thermally destroyed only above 1200 K [150]. Dehydroxylation occurred without solid product recrystallization during reaction in vacuum between 818 and 847 K [54]. The rate of water evolution fitted the two-dimensional diffusion

equation, with $E_a=225$ kJ mol^{−1}, ascribed to control by water migration across a growing barrier layer of product.

8.3.2. Vermiculite

This mineral dehydrated, with loss of about half the constituent H₂O, in vacuum (10^{−4} Pa) resulting in a change of spacings of the extended planar units but without recrystallization. The initial rate of water release was constant, 267–290 K, ascribed to control by the desorption step, $E_a=27$ kJ mol^{−1} (WET 1B). Treating the subsequent deceleratory reaction as one-dimensional diffusive loss from a semi-infinite medium, it was shown that dehydration of these small crystallites, 319–359 K was satisfactorily represented by the first-order equation [35].

8.3.3. Montmorillonite and illite

Rates of isothermal dehydration of these reactants in vacuum fitted the first-order equation [55]. The low values of E_a , 18 and 12.5 kJ mol^{−1}, for montmorillonite (363–493 K) and illite (355–573 K), respectively, were ascribed to diffusion control and water retention was ascribed to mechanical collapse of the reactant structures. Reaction in 500 Pa water vapour was relatively slower, E_a values were comparable with the latent heat of H₂O volatilization and ascribed to control by the desorption step.

8.3.4. Kaolinite

Dehydroxylation of kaolinite, 680–750 K, was [56] deceleratory and fitted a diffusion equation. Horvath et al. [151], however, while accepting the diffusion model, regard the second-order equation as providing a more satisfactory kinetic representation. Arrhenius parameters are sensitive to $p(\text{H}_2\text{O})$ and a compensation effect has been found.

8.3.5. Talc

This mineral also has a layered structure, Mg₃(Si₂O₅)₂(OH)₂, and undergoes dehydroxylation by a first-order reaction, $E_a=101$ kJ mol^{−1} between 1100 and 1160 K (→3MgSiO₃+SiO₂+H₂O). From the activation parameters it was concluded [152] that the rate limiting step was Mg-OH bond scission with subsequent migration of magnesium.

8.4. WET 3: Interface advance; nucleation and growth and contracting envelope kinetic models

8.4.1. Interface reactions: three-dimensions

8.4.1.1. *Copper(II) sulphate pentahydrate.* The dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was probably the first reaction to be identified as a nucleation and growth process [22]. This reaction shows the Smith–Topley effect and the generation of ‘orange peel texture’ has also been demonstrated [43]. Reaction in vacuum (1 Pa) at 323 K yields the monohydrate [61,62], whereas above 100 Pa H_2O vapour, the trihydrate is given, for which the nuclei have recognizably different form. Thus, even at low $p(\text{H}_2\text{O})$ the volatile product exerts a significant influence on product texture. (This is consistent with the evidence that intranuclear water influences growth of nuclei in alums by promoting structural reorganization [23]). At very low pressures (10^{-4} Pa), gravimetric studies [58] for dehydration to the monohydrate between 260 and 286 K gave $E_a=74 \text{ kJ mol}^{-1}$, agreeing substantially with a much earlier result [140–142]. Extrapolation of interface advance rates, from Fig. 2 of Ref. [58], gives about $1 \times 10^{-5} \text{ cm s}^{-1}$ at 325 K, which is in accordance with values reported earlier by Lyakhov et al. [61,62].

8.4.1.2. *Alums.* The surface retexturing (‘orange peel texture’ [23]) of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ or the sub-sequentially enhanced nucleation of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, following exposure of partially reacted crystals to water vapour, was identified with boundary-layer strain generated through superficial water losses from *all* reactant faces. The maintained dehydration that occurs during nucleus growth was, therefore, ascribed to facilitated retexturing/recrystallization of water-depleted salt promoted by some product H_2O temporarily retained within each nucleus. Significant water adsorption would be expected to occur on these hydrophilic surfaces at the low reaction temperatures, 287–310 K [95]. The rate of intranuclear water loss is only slightly less than that from lignite [23,111] in which the constituent H_2O is effectively present as a liquid.

8.4.1.3. *Lithium sulphate monohydrate.* Studies of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration have shown this

predominantly deceleratory reaction to be sensitive to the procedural variables [120,153]. The available published data were reviewed by L’vov [154] who applied the dissociative evaporation model and considered quantitatively the effect of water vapour. It was concluded that the apparently diverse reported kinetic results could be reconciled with reactions for which $E_a=86 \text{ kJ mol}^{-1}$ for the ‘pure’ *equimolar mode* and $E_a=192 \text{ kJ mol}^{-1}$ for the ‘pure’ *isobaric mode*.

[In the absence of volatile products, the reaction proceeds by the *equimolar evaporation* process. *Isobaric evaporation* occurs when a constant pressure of product exceeds the equilibrium pressure of the same component released. A more detailed account of the theory is given in [154]. Remaining problems concern the incorporation into the theory of heats of volatilization/condensation.]

Boldyrev et al. [38] have shown that the thickness of the reaction zone involved in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ nucleus growth is about 150 μm . Product phase recrystallization proceeds fairly readily and this is consistent with dehydration characterized by relatively abundant nucleation [39,40] proceeding above ca. 370 K. Product phase recrystallization was relatively more difficult in $\text{LiHCOO} \cdot \text{H}_2\text{O}$ dehydration, a reactant that also exhibited ‘orange peel texture’ formation (possibly representing the intervention of a metastable intermediate that was transformed into product only with some difficulty).

8.4.1.4. *d-Lithium potassium tartrate monohydrate.* The dehydration of *d*- $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ single crystals, between 423 and 463 K, is a nucleation and growth process [44]. A small proportion (4%) of the product water was released in an *initial* deceleratory surface reaction that extended to a depth of about 10 μm . This generated a progressively increasingly disordered superficial layer as the concentration of water-site vacancies increased and $E_a=153 \text{ kJ mol}^{-1}$. Subsequently, at a limited number of points on the surface, there was recrystallization to the product (anhydrous) phase, generating nuclei bounded by active dehydration interfaces that thereafter advanced into the unreacted solid. The product constituting the intranuclear material appears to provide the seed crystals that promote recrystallization of the water-depleted material formed at the reactant side of the

active interface. This crystallization, maintained during interface advance, opens channels permitting continued H₂O escape at a rate similar to that occurring during dehydration of the original surface. Again E_a is 150–160 kJ mol⁻¹ for the nucleation and growth stages of dehydration. The induction and acceleratory processes were eliminated for reactions in which a single crystal had been covered by powdered anhydrous product.

8.4.2. Interface reactions: two-dimensions, deceleratory reactions

8.4.2.1. *Copper(II) formate tetrahydrate*. Water, in this reactant, is retained by hydrogen bonds between relatively stable, extended Cu²⁺–(HCOO)⁻ polymeric ion assemblages [37]. Dehydration resulted in relatively minor alterations of these two-dimensional arrays, but there was modification to their mode of stacking. The maintained topotactic relationship enabled the crystal structure of the product to be deduced [70]. Water was lost from two types of site in a single rate process that was studied [37] in vacuum from 228 to 298 K. Reaction occurred at an interface that advanced inwards at a constant rate, with $E_a=47$ kJ mol⁻¹, slightly less than the dissociation enthalpy. Product solid particles were pseudomorphic with those of the reactant, but there was splitting parallel with the basal plane [70], providing channels for water escape through the dehydrated material. The product did not, therefore, constitute a barrier layer to H₂O escape. The rate of water release decreased with rise in $p(\text{H}_2\text{O})$ and there was no Smith–Topley effect [37], sometimes associated with reactions involving solid product retexturing.

8.4.2.2. *Manganese(II) formate dihydrate*. Dehydration occurs at an interface that advances inwards from {1 1 0} faces of the thin flat crystals [71]. The two-dimensional contracting envelope kinetic process was studied between 335 and 358 K and $E_a=75$ kJ mol⁻¹. Both reaction temperatures and the magnitude of the activation energy were larger than those for copper(II) formate tetrahydrate. This difference is ascribed [37] to the presence, in the manganese salt, of ion bridges, linking planar units, that must be redistributed during water losses.

8.4.3. Interface reactions: two-dimensions, nucleation and growth

8.4.3.1. *Magnesium oxalate dihydrate*. Dehydration of MgC₂O₄·2H₂O in nitrogen between 421 and 495 K resulted in the loss of 2H₂O, disposed parallel with the (1 0 0) planes. The value of E_a for interface advance was 111 kJ mol⁻¹. At the lowest temperatures, below 433 K, the influence of nucleation control became appreciable and brief induction periods and acceleratory processes were detected. The activation energy for nucleation was estimated to be 430 kJ mol⁻¹. There was no indication that the mechanism changed, but there was a systematic variation in the relative significance of the nucleation step with temperature.

8.4.3.2. *Molybdic acid*. MoO₃·2H₂O has an extended planar structure composed of octahedral corner-sharing units [31,72,73]. On heating below 350 K, interlayer water molecules are lost (→MoO₃·H₂O). Above 400 K, water molecules from the octahedra are released but coordination is maintained by aggregation of the layers in pairs to form double sheets of octahedra. Dehydration results in crystal cracking, but the basal plane is retained in the pseudomorphic product particles.

8.4.4. Interface reactions: one-dimension

8.4.4.1. *Purine and pyrimidine hydrates*. Comparative, qualitative studies were undertaken [77] of the dehydrations of the monohydrates of thymine, caffeine, theophylline, 5-nitouracil, cytosine and 2'-deoxyadenosine. These were based on microscopic observations of the progressive development of anhydrous zones within partially dehydrated reactant crystals, conventional kinetic studies were not included. Desolvation was strongly anisotropic, proceeding preferentially in a crystallographic direction that corresponded to the orientation of 'tunnels' occupied by water in the reactant structure. With the exception of thymine, X-ray diffraction data showed that each product structure was different from that of the reactant. Loss of the stabilizing influence of the water was followed by recrystallization. Temperatures of the onset of dehydration (a measure of reactivity), 315–362 K,

were qualitatively correlated with the strengths of H₂O hydrogen bonding and the cross-sectional area of the water ‘tunnels’.

8.5. Some other interface reactions

The reactions mentioned above to illustrate the classification scheme presented in Table 1 have been selected to exemplify the criteria used to characterize each type of behaviour distinguished. Some further dehydrations are described below to show additional features of these reactions, all of which are believed to occur within an active reactant-product contact interface. This anticipates the potential need for the future ordering into sub-divisions within this extensive group of diverse (advancing interface) rate processes, WET 3.

8.5.1. Nickel sulphate hexahydrate

In vacuum, the dehydration of NiSO₄·6H₂O (–5H₂O) is a nucleation and growth process with $E_a=64 \text{ kJ mol}^{-1}$, between about 300 and 317 K [26]. Water is lost from a superficial layer several microns thick and an ‘orange peel texture’ can appear [82]. A tendency for this reactant to generate (under different reaction conditions) an impermeable and elastic superficial layer has also been demonstrated [88]. Guarini interprets the kinetic observations as evidence that three steps control the overall reaction: dehydration, water migration and product recrystallization (the last being the slowest). When recrystallization does not maintain the generation of water escape channels, water transportation becomes rate controlling. Under different reaction conditions [27–29], in the presence of air that opposes water escape, dehydration becomes stepwise and these reactions proceed in a significantly higher temperature range.

8.5.2. Cobalt chloride hexahydrate

Ribas et al. [155] identify lattice ‘free space’ as a dominant feature in dehydration/anation reactions. This is discussed with reference to the structural changes that occur during the stepwise loss of water from CoCl₂·6H₂O (–2H₂O, –2H₂O, –H₂O, –H₂O).

8.5.3. Barium chloride dihydrate

Dehydration of BaCl₂·2H₂O [114] to the crystalline monohydrate, in the temperature interval 313–334 K

was an interface reaction with $E_a=146 \text{ kJ mol}^{-1}$. In the higher temperature interval, 334–346 K, the activation energy for nucleus growth in the [0 1 0] direction was lower, 87 kJ mol^{–1}. There was evidence of topotaxy and indications that water elimination resulted in minimum displacements of the heavy cations, Ba²⁺. Aspects of the structural changes within the reaction zone are discussed in detail.

8.5.4. Potassium copper(II) chloride dihydrate

Studies of K₂CuCl₄·2H₂O dehydration [115,116] complemented TG-DSC measurements in nitrogen with microscopic observations for both single crystal and powder reactant samples. In single crystals, the reaction was initiated by surface nucleation from which interfaces advanced inwards. Subsequently there was further nucleus generation, mainly within intracrystalline regions, somewhat in advance of the active reaction front. Finally, dehydration was completed with water losses by cracks forming to relieve the strain which resulted from solid product recrystallization. It was further concluded that reaction was promoted by the exothermic growth of product crystallites and retexturing in the zones of locally high $p(\text{H}_2\text{O})$. The isothermal dehydration of powder was well described by the contracting envelope equation because low impedance to volatile product escape was offered by the solid product.

8.5.5. Sodium perchlorate monohydrate

Water was lost from NaClO₄·H₂O in two distinct rate processes [156] corresponding to the release of about 0.2H₂O at 363 K and the remainder (0.8H₂O) above 423 K. The two steps are ascribed to the elaborate crystal structure, in which the reactant unit cell contains eight formula units stabilized by extensive hydrogen bonding.

8.5.6. Sodium thiosulphate pentahydrate

The dehydration of Na₂S₂O₃·5H₂O, large single crystals, is an interesting example of a reaction in which the reverse step participates in the condensed phase [157]. Initially, water loss (–5H₂O) produces a superficial layer of anhydrous salt with little retexturing. The accumulation of water at the reaction interface results in nucleation of the dihydrate, thereby generating two interfaces. There is continued inward advance through dehydration at the pentahydrate/

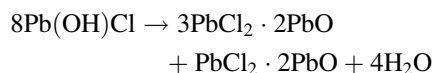
dihydrate contact. There is also concurrent *outward* advance, due to partial rehydration at the dihydrate/anhydrous contact that progresses towards the original crystal surface. Finally, the dihydrate is converted to the anhydrous salt that is the residual product.

8.5.7. Hydrated metal phosphates

Dehydrations of many hydrated metal phosphates proceed by interface reactions [46,47,158–160]. However, the losses of water from acid phosphates, which may also contain water of crystallization [46,47], proceed by more complicated mechanisms. It is not known which of these rate processes should be included here (WET 3), because little is known about the kinetic characteristics and structural aspects of the changes that proceed (sometimes concurrently) within these reactants. For example, the dehydration of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ involves anion condensation: there is melting, the compositions and amounts of intermediates depend on $p(\text{H}_2\text{O})$ and its ease of escape, reactant particle size, rate of heating and other parameters. The reactions contributing are not readily characterized individually in the presence of the other concurrent changes. The occurrence of melting increases the difficulties of experimental investigation and interpretation of observations. Removal of water of crystallization from $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [46,47], by heating in air, was accompanied by both anion disproportionation and condensation, yielding amorphous and acid products. Some of these changes may proceed in a melt. Kinetic studies of dehydrations in the mixture $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [158,159] were interpreted through the use of an extensive set of stoichiometric equations. While characterization of the particular reactions occurring is the essential first step in a mechanistic study, considerable difficulties attend the detailed structural characterization of the environment within which the changes take place in this and related systems. In the absence of kinetic data that can be identified with individual, known reactions and structural information relating to the zone of chemical change, reactions of these types cannot yet be accommodated within the proposed classification.

8.5.8. Lead hydroxychloride

From X-ray diffraction studies [161] it was concluded that:



In dry nitrogen, $E_a = 145 \text{ kJ mol}^{-1}$ and somewhat lower values were found in water vapour ($92\text{--}128 \text{ kJ mol}^{-1}$). Smith–Topley behaviour was noted and, unusually, two minima were identified, which might be ascribed to recrystallizations of the two product phases at different $p(\text{H}_2\text{O})$ values. Kinetic data indicate that this rate process is well-described by the one-dimensional diffusion process equation, suggesting that the products form an effective barrier layer. More detailed structural information is required to establish whether there are orientation relationships between the reactant and product phases. The participation of recrystallization might, in contrast, be associated with an interface process. At present, the evidence appears to be inconclusive so that a final decision cannot yet be made as to whether this reaction should be classified as WET 3 or as WET 2.

8.5.9. Calcium oxalate monohydrate

Although there have been many kinetic studies of the dehydration of this compound [1,5], recent work [162] has shown that water molecules retained within two different types of crystallographic sites are evolved at appreciably different rates. Both rate processes, distinguished and measured by diffuse reflection spectral data, occur within similar temperature intervals. This result invalidates previous kinetic conclusions for this reaction and further investigations are required to characterize individually the two concurrent/overlapping contributory rate processes. This draws attention to the possibility that other, apparently simple dehydrations, may also be complex.

8.5.10. Sodium citrate dihydrate

Unusually the dehydration rates of large single crystals of this reactant are *greater* than for the fine powder [66]. This is ascribed to the promotion of nucleation by strain induced through the growth of established nuclei, an effect that is enhanced by retained water vapour. Microscopic observations confirm that this is a nucleation and growth process (with $-\text{H}_2\text{O}$).

8.5.11. Barium styphnate hydrates

The dehydration of barium styphnate monohydrate was studied [68,69] above about 400 K. After some

initial deviation, the rate of water evolution remained approximately constant during the greater part of the reaction and there was loss of crystallinity. It was concluded that nucleation occurred initially across all crystal faces, but the dehydration interface advanced inwards in only one crystallographic direction. Particle disintegration means that diffusive H₂O escape is not rate controlling. The activation energy ($E_a=108 \text{ kJ mol}^{-1}$) is ascribed to the rupture of hydrogen bonds between H₂O and the anions. In contrast, barium styphnate trihydrate is rapidly and completely dehydrated at about 300 K.

8.6. WET 4: Homogeneous dehydration reactions in crystals

8.6.1. Colemanite (WET 4A)

On heating $\text{Ca}_2\text{B}_6\text{O}_8(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ intracrystalline evolved water is retained [84,85] because escape is both slow and limited in extent within the compact and coherent structure. At a characteristic temperature, 648 K, there is a catastrophic release of this trapped H₂O, giving also an (X-ray) amorphous residue. Other types of related behaviour of certain phosphates and vermiculite are discussed by Stoch [84,85].

8.6.2. Barium hydrogen oxalate hydrate (WET 4B)

Mutin et al. [86] used X-ray diffraction to measure the systematic lattice modifications that occur during the reversible dehydration of $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{BaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$. No discontinuous variations in structure were found as x varied between 0 and 2, crystal cohesion was maintained throughout by strong links between barium and oxygen. Between these extended crystal components, water is accommodated in canal-like structures, along which it can migrate to maintain the equilibrium content, in response to changes of $p(\text{H}_2\text{O})$ and temperature. Transport is by intracrystalline diffusion, there was no mention of a nucleation and growth mechanism. Progressive changes in the degree of hydration, through an infinite sequence of solid solutions, were achieved though systematic variations in unit cell dimensions (contrasting with the constant lattice of a zeolite). It is proposed here that this should be identified as a homogeneous reaction because equilibrium is established *throughout* the crystal. It is also evident, however, that this pattern of behaviour has features in common with diffusion

controlled reactions (WET 2). The properties of strontium oxalates are significantly different [163].

8.7. WET 5 and WET 6: Melting and impervious layer formation during dehydrations of crystalline hydrates

Dehydrations of solutions/melts are outside the scope of the present review but the possibility of liquid formation, and its participation in water elimination on heating initially solid reactants, must be considered in formulating reaction mechanisms. Melting, particularly when local and temporary, can be difficult to detect when the production of an unreactive layer covering original surfaces preserves the shapes and identities of the original reactant particles [10].

Reports, in which reactant melting during dehydration has been identified, often refer to the more highly hydrated, water-soluble salts, heated under conditions that prevent or inhibit H₂O escape. Conditions favouring melting have been described in Sections 4.5 and 4.6. Mechanistic investigations, specifically distinguishing the role of a liquid phase, are relatively few and widely dispersed, and mention of this feature may be embedded within the texts of individual articles. Thus, the available information tends to be inaccessible and, at present, is probably insufficient to allow useful generalizations to be made. Melting, accompanying water release, has been established by microscopic observations for a few systems (see, e.g. [67,88]). It is not improbable that this particular feature of behaviour has remained undetected for many comparable dehydrations which in the absence of evidence to the contrary are, perforce, accepted as proceeding in the solid state.

Liquid was detected on the surfaces of large $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystals at 380–390 K when heated at 4 K min^{-1} in flowing nitrogen [88]. The outer surfaces of crystals became relatively impermeable and elastic, retaining volatilized H₂O under surface layers that swelled up to form remarkable bubbles. Some reinflated and deflated several times, ascribed to intermittent steam escape through temporary perforations of the retentive layer. No such layer, or intermediate hydrates, was described [26] for the reaction in vacuum. Large crystals of pyrimidinium copper chloride hydrate, dehydrated at about 393 K, expelled droplets of a liquid solution that immediately crystal-

lized. At lower temperatures and with powder reactant the reaction proceeded smoothly [67].

9. Experimental: objectives and methods

Any experimental technique capable of determining the stoichiometry and/or measuring the extent of chemical changes in solid reactants can, in principle, be applied to the study of dehydrations (or other crystalolysis reactions). The method selected should ideally yield the most precise data possible for the reactant to be investigated. However, in practice the equipment already available, cost and other pragmatic considerations may determine which technique is employed. Where the data are required to solve a practical problem, such as the operation of a manufacturing plant, a preparation attempted, or other purpose, reaction conditions must be designed to relate, as closely as possible, to those expected to answer the specific questions considered. However, such observations may be empirical and may not be capable of giving information about the fundamental chemistry of the reactions studied.

The present article is concerned with the fundamentals of dehydrations. Interest is, therefore, intentionally directed towards methods capable of obtaining and interpreting data that relate directly to reactivity measurement and the formulation of reaction mechanisms. Because these rate processes are both endothermic and reversible, rates are often sensitive to self-cooling and to $p(\text{H}_2\text{O})$, kinetic behaviour varies with the procedural variables. Consequently, in the absence of confirmatory, comparative kinetic measurements, rate data cannot (and should not) be assumed to be characteristic of a rate determining step. Many papers report measured rates that are applicable under specific conditions only and, because the effects of dependence of rates on conditions have not been examined, may be of empirical value only. Moreover, the relative influences of controlling parameters can vary during the course of reaction. It follows that work intended to elucidate dehydration mechanisms, based on kinetic measurements, may be more difficult to interpret in practice than is evident from many literature reports.

Kinetic measurements directed towards elucidating a particular reaction mechanism are almost invariably

concerned with a *single, identified* chemical change. Contributions to measured rate data from the effects of procedural (and any other contributing) variables must be eliminated or allowed for quantitatively.

9.1. Identified reaction

A reaction mechanism is the theoretical representation of steps whereby a particular reactant is transformed into a product (or products) that is of different (known) structure or composition, or both. Rate data must refer to the target reaction (only) that has been confirmed to occur, by stoichiometric and structural evidence, under the conditions used in the study.

9.2. Single reaction

If kinetic data are to provide information of use in formulating reaction mechanisms, these data must refer exclusively to the target reaction and not include contributions from other concurrent or parallel processes. Kinetic measurements for complex (concurrent and/or consecutive) reactions, for which the individual contributions are not separated, are of empirical value only and may have no mechanistic significance.

The short account of experimental methods that have found wide usage in dehydration studies given below, draws attention to some of the strengths and weaknesses of these techniques. More extensive accounts are to be found within the articles cited. Interpretations based on kinetic information are often supported by complementary structural information (e.g. X-ray diffraction, topotaxy) and by microscopic observations of the textural changes that occur as reaction progresses. Sometimes the measurements are made at reaction temperature (hot-stage diffraction and microscopy). In other work, a dehydrated, or partially reacted, specimen is examined after cooling, when allowances must be made for any changes that result from the temperature reduction (solidification of a melt, phase recrystallization, cracking, etc.). These changes are important because the phase in which the chemical process occurs is of central significance in describing the reaction and in formulating its mechanism. Cooled products are most frequently solids whereas there is a greater probability of melting at elevated reaction temperatures.

A complete mechanistic description of a solid-state dehydration must provide a consistent representation of the chemical and/or structural changes that includes both reaction geometry and interface chemistry. The following experimental techniques have been widely and successfully applied to provide information about these processes. The most valuable conclusions have usually been based on the interpretation of a combination of observational data obtained from diverse, but complementary experimental techniques.

9.3. Water vapour pressure: accumulatory experiments

Measured pressures of evolved water vapour, accumulated after appropriate time intervals for the dehydration reaction, in a sealed, usually preevacuated apparatus, are directly proportional to the amount of H₂O released [164]. However, due to H₂O adsorption onto glass walls of a vacuum apparatus, apparent yields may be appreciably less than expectation from weight loss and the ideal gas law.

Kinetic studies by this method involve the possibility that the reaction rate measured will be influenced by $p(\text{H}_2\text{O})$, as discussed elsewhere, and rates may require correction in accordance with the Smith–Topley curve (see Section 10.2 below). It would appear that allowances for this uncertainty are not usually incorporated in most kinetic analyses. These errors may be (somewhat) reduced by the use of rising temperature experiments which are expected to diminish the relative contribution from adsorption. However, many isothermal, accumulatory studies have been used to determine the kinetic models and the Arrhenius parameters for a variety of dehydrations [44,95].

9.4. Thermogravimetry (TG)

An advantage of using weight loss measurements for kinetic studies is that the atmosphere surrounding the reactant can (in principle) be maintained constant, or varied as required, throughout the experiment. By continual evacuation [122], the contribution from the reverse process can be reduced, though with some particularly sensitive reactants it may be necessary to use a small, spread sample and very low pressure. Alternatively, dehydration rates can be measured at

predetermined, constant $p(\text{H}_2\text{O})$ values to investigate Smith–Topley behaviour or other effects of water vapour. Rate measurements can be made at constant temperature or during a programme of temperature variations.

Non-isothermal TG measurements provide a rapid method of qualitatively characterizing reactions. The approximate temperatures and stoichiometries of two or more rate processes can be determined readily, where dehydration proceeds stepwise. Weight losses should not, however, be used as the sole identification evidence of the chemical change that occurs. This method does not detect melting or phase transitions. Automation enables measurements to be extended to longer time, low-temperature reactions incorporating larger numbers of measured data points than is practicable by manual equipment. Computer analysis of collected values can be used to identify rapidly the (relatively) most precise kinetic model to describe the reaction. The quartz crystal microbalance has been successfully applied in kinetic studies of dehydrations at very low pressures [58], but is not suitable for use in controlled atmospheres.

9.5. Differential scanning calorimetry (DSC)

DSC is used to measure reaction rates in both the isothermal and programmed temperature modes and (as with TG) can be extended to automatic computer recording followed by analysis of the data. Again rapid experiments can usefully characterize the steps in a sequence of thermal reactions occurring in different temperature intervals. DSC has also provided information about the initial reactions, associated with surfaces, that occur during the early stages of many dehydrations [43,103,104].

The presence of an atmosphere during these reactions promotes thermal equilibration within the reactant sample, but also acts as a barrier opposing H₂O escape. Controlled amounts of water in the inert gas passing through the reactant chamber can be used to investigate the dependence of H₂O release rate on the pressure of water vapour present. Using a gas flow will promote product removal though it may be difficult to measure quantitatively the influence of water vapour in controlling reaction rates.

The DSC responses include contributions from melting, solidification, phase transitions and also

the recrystallization of any finely divided solid products, that are formed during some dehydrations [13,115,116]. The contributions from such processes must be allowed for in kinetic analyses. It is usually (implicitly) assumed, but not so easily or frequently confirmed, that the total heat absorption is *directly* proportional to the fractional reaction. Thermal measurements (both DSC and DTA) provide thermochemical information, the reaction enthalpy, etc., which may be of value in the discussion of reactant stability.

9.6. X-ray diffraction measurements

X-ray diffraction measurements characterize unambiguously and may further be used to measure the amounts present of all crystalline phases participating in the reaction: reactant, product and any solid intermediates. This method allows the reactant to be authenticated and the products to be positively identified in samples reacted to known extents. Diffraction methods of kinetic investigation are of particular value for rate processes that yield no volatile product. Amorphous materials are not detected but, in favourable systems, the total amounts present can be determined or estimated by difference. Diffraction studies can be made for reactants at reaction temperature [86,165] whereas, after sample cooling, the possibility of solidification of a melt or of recrystallization must be considered.

Characterization of the structural changes that accompany, or follow, water loss are an essential objective of dehydration studies. Garner [11] distinguished three possible consequences of water removal from a crystalline hydrate:

1. Little change, the lattice remains closely similar to that of the reactant [63] (the residual material is regarded as closely resembling a zeolite).
2. Loss of crystalline order, to give a phase that is amorphous to X-rays.
3. Recrystallization to the product phase.

Water vapour often promotes recrystallization, whereas in vacuum an amorphous product may be given.

X-ray diffraction is invaluable in detecting topotaxy [30–32,166], providing information useful in the formulation of reaction mechanisms. X-ray topography is capable of detecting the numbers and distributions of

line imperfections, dislocations, in large crystals. These measurements also enable the role of crystal dislocations in initiating reaction to be determined, as already demonstrated [167] for some reactions other than dehydrations.

A potentially very powerful investigative technique in solid-state chemistry, is through the use of bursts of high-energy synchrotron radiation to give diffraction patterns for selected small volumes of reactant [38]. If a serial sequence of sites is selected to traverse a reaction interface, the systematic changes in crystal structure that occur during reaction can be established. Using this method, it has been shown that the thickness of the reaction zone during $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration is about 150 μm , within which a metastable intermediate phase is formed. This method has been used to compare the reactivities of the two salts $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{LiHCOO} \cdot \text{H}_2\text{O}$ which contain equivalent water sub-lattices [39]. The (expensive) equipment required for such experiments is not widely available, but the method is potentially of the greatest value in elucidating the structural changes that occur within an advancing active interface.

9.7. Microscopy

Microscopy allows direct observations to be made of the textural changes that accompany reaction, giving information of a qualitative type that is never available for homogeneous processes. This ability to identify the particle modifications that are a consequence of chemical changes in crystals sometimes provides insights or clues to the nature of the often complicated interface processes. The potential value of this approach does not always appear to be realized. Microscopy is capable (for suitable reactions) of establishing or confirming the distribution of reaction zones and, thus, complementing the geometric interpretation of kinetic measurements. In addition, examination of the interface can provide evidence about the structures within which reactivity is locally enhanced. For some reactants, the textural changes across interface sections can be determined [108].

Microscopy provides the most direct method of measuring individually the kinetic characteristics both for nucleation rates and for interface advance. Measurements of this type constitute the experimental foundation for the formulation of the geometric rate

equations that are the kinetic models applied to crystallization reactions [1,2,5,7,8,11,13,23,45,60,65]. This is possible where the reactant and product phase can be distinguished, often most obvious when recrystallization yields a finely divided product. In some dehydrations the water elimination and product recrystallization processes are (apparently) closely interlinked so that reaction is completed within a thin laminar zone. However, in other reactants these steps are not so closely linked, but may be appreciably separated in space and time [82,83] and correlation of kinetic and microscopic observations must take account of this feature. Microscopic evidence may be capable of providing confirmation of kinetic interpretations based on 'best-fit' to an appropriate rate equation (but such confirmation is not always provided: see also Section 6.1).

Using higher magnifications, it may be possible to recognize fine textural details of the structures of germ nuclei and inside reaction zones, particularly by sectioning growth nuclei [23,44,108]. A problem in investigating nucleation [12] is that any precursor structures may be unrecognizably changed by onset of reaction which is the only reliable proof that the site was capable of generating a nucleus. Microscopic observations have also been important in identifying the changes that occur on exposing dehydrated surfaces to water vapour: the development of the 'orange peel texture' has been shown to be characteristic of many crystalline hydrates [23,43]. The occurrence of melting at surfaces [88], or more generally [67], and the detection of other structures, such as bubbles [88] can be achieved by optical microscopy.

In order to observe the textures of unstable substances likely to deteriorate during inspection or in the vacuum conditions of an electron microscope, it may be useful to prepare a replica [108,109] before examination. The atomic force microscope offers the interesting possibility of enabling detailed textures to be observed at even higher resolutions, but the potential of the technique does not yet appear to have been exploited.

9.8. Other experimental methods

In addition to the more familiar techniques referred to above, a variety of other experimental methods have contributed in investigations of the kinetics and

mechanisms of dehydrations [1,2,5,7,11,13]. Often these complement the more traditional measurements. Magnetic, and sometimes electrical, properties are determined [1,5] to obtain information about coordination or oxidation states that change during reaction. Infrared spectra, used for the qualitative identification of participating compounds, can have particular value in kinetic studies [162]. This type of measurement is potentially capable of detecting any specialized interface energy levels that may participate in controlling chemical changes within the active, advancing reaction zones [107]. Methods based on volatile product analysis (e.g. MS and GC) are of less value for simple reactions yielding H₂O only, though these could be useful in detecting other (perhaps unsuspected) products.

9.9. Comment

The experimental methods used to study dehydrations must include a confirmation of reactant identity and the stoichiometry of the chemical changes with which the research is concerned. Kinetic analysis should include consideration of all contributions incorporated into the measurements from concurrent processes (e.g. any heat of fusion, sintering, etc. when using the DSC or DTA methods). The possibility that rates may be influenced by heat or gas (H₂O) transfer should be investigated and the roles of diffusion established. It is important to investigate the accuracy of reproducibility, preferably using more than a single preparation of reactant. The extent (α range) of reaction across which the kinetic fit identified is considered to be acceptable should be stated. Similarly, the temperature range for which Arrhenius parameters were calculated may be given, together with values reported to a realistic number of significant figures and accuracy limits. Vigilance is necessary to detect unusual behaviour so that a change of reaction mechanism, perhaps in different temperature ranges, or contributions from overlapping processes will be recognized.

Results using automated data collection techniques, directly linked for subsequent kinetic analysis, must be considered critically in the context of the limitations of both detection ability and programme capability. Sophisticated equipment, while capable of rapidly recording data, may, at the same time, conceal

(or fail to reveal) essential features of the reaction in the final print-out of apparently very accurate results. There still remains the need for confirmatory experiments to test conclusions and interpretations. Partial studies of an increasingly diverse range of reactants, as appears fashionable in the recent literature, does not substantially increase general understanding or order amongst the numerous studies already published and does not usually contribute towards the development of theory.

10. Chemistry and mechanisms

This Section is concerned with interface phenomena and product retexturing, features most usually identified with interface advance dehydrations (WET 3). Typical examples and theoretical principles that are characteristic of this most familiar type of reaction resulting in water elimination from crystalline hydrates are discussed with reference to mechanisms.

No simple or consistent pattern of mechanistic behaviour was found in the literature concerned with dehydrations. The evolution of water from crystalline hydrates is invariably endothermic and frequently reversible; both properties can exert some influence on the rates of the chemical processes occurring [20]. Reactivities and apparent kinetic characteristics measured for many, perhaps most, dehydrations vary appreciably with conditions prevailing in the immediate vicinity of the reactant, particularly the availability of water vapour within the active zone of chemical change. Water accessible to the reacting sites is often capable of diminishing the dehydration rate, the 'forward' reaction. This control may operate inhomogeneously within the mass of a powdered reactant, in which the water distribution throughout the assemblage becomes controlled by diffusion and its removal/escape is opposed by any other gases present. The product H₂O may also promote recrystallization of solid products and this further influences its distribution and ease of escape. Consequently, measured kinetic data are sensitive to both reactant environment and the course of reactant retexturing. Apparently irreproducible or inconsistent measurements for the same rate process are sometimes obtained by different workers or through the use of different experimental

techniques. Relatively few kinetic studies [122] have intentionally designed conditions that can be used to determine the rate of the forward dissociation step *only* and thus measure *dehydration*. It appears also that the reactivities and properties, including dependence of kinetic characteristics on experimental conditions, vary differently for different reactants. These complications in understanding kinetic data increase the problems of identifying trends of reactivities between reactants and of chemical controls within groups of related reactions and in recognizing order within the subject.

10.1. The Polanyi–Wigner (P–W) equation

For completeness, this theory is briefly described here but more comprehensive accounts are available [11,13,139]. The rate of a dehydration reaction, the dissociative desorption step for a constituent water molecule in a hydrate, volatilized at an active interface, is represented in the language of transition state theory by [13]:

$$\left(\frac{dx}{dt}\right) = x_0 \left(\frac{kT}{h}\right) \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right) \times \left[1 - \exp\left(\frac{\Delta G}{RT}\right)\right]$$

where (dx/dt) is the linear rate of interface advance (corrected for geometric effects), x_0 the incremental forward advance distance for unit reaction, k the Boltzmann constant and h the Planck constant. The thermodynamic symbols have their usual meanings and refer to precursor activation to the transition state which then can dissociate along the reaction coordinate to yield product. It is assumed that these reactions occur individually at an array of identical sites and are not influenced by the occupancy of neighbouring sites. Various aspects of the application of this treatment to solid-state processes have been quantitatively examined [18,168].

It appears that the P–W representation of dehydration kinetics has found relatively fewer applications in the recent literature than formerly. The following reasons may account for this. Measured values of E_a (taken to be equal to reaction enthalpy [11]) cannot now be accepted as representing the interface rate limiting step (transition state theory), but are

recognized as possibly containing contributions from other controls through the reverse reaction (see Ref. [123]), self-cooling or other effects. Aspects of the magnitudes of Arrhenius parameters (for a range of crystallization reactions) have been discussed [19]. Many interface processes are undoubtedly more complicated than appears from this very simple model, indeed little is known about the detailed mechanisms for most reactions of interest. It also might be mentioned that the basic P–W representation provides few mechanistic insights [138] into the factors controlling mechanisms of dehydrations at interfaces.

10.2. The Smith–Topley effect

The Smith–Topley (S–T) effect [1,2,5,8,11,21,140–142,169] describes a characteristic pattern of dehydration rate variations with $p(\text{H}_2\text{O})$ that has been found for a number of crystalline hydrates. This is shown schematically in Fig. 11. L'vov et al. [21] cite 20 examples of reactions exhibiting S–T behaviour, reported between 1931 and 1995. The majority of reactants mentioned are transition metal sulphates, but S–T effects are known for salts of other cations (Ca^{2+} , Mg^{2+} , Na^+) and anions (oxalate, formate, chloride, nitrate) and amounts of water in the reactants vary from 0.5 to $8\text{H}_2\text{O}$. There appear to be no obvious chemical characteristics that particularly distinguish the reactions that show this effect (Table 1 of Ref.

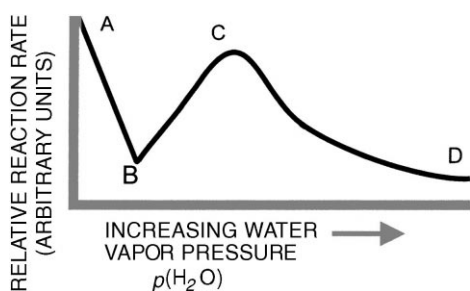


Fig. 11. Schematic representation of the pattern of systematic changes of dehydration rates with water vapour pressure, $p(\text{H}_2\text{O})$, referred to as the Smith–Topley effect [1,2,5,8,11,21,140–142,169]. At low pressures (AB) there is an initial sharp diminution of rate. On further increase of water vapour pressure there is an increase in dehydration rate (BC), often ascribed to promotion of product recrystallization that facilitates H_2O escape. As the water vapour pressure approaches the dissociation equilibrium pressure, the rate of water loss diminishes (CD). Further explanation in text and Fig. 12.

[21]). Those mentioned here are interface processes (WET 3) but other reactions, also of this type, are described as not giving S–T behaviour [37,45].

The explanation of the S–T pattern of reactivity, Fig. 11, given most frequently [21] is due to Volmer and Seydel [169]. This is represented schematically, derived from literature descriptions, in Fig. 12 referring to sections across advancing interfaces. An alternative explanation of S–T behaviour by Bertrand et al. [20] was based on comparative kinetic measurements for five diverse inorganic hydrates. The characteristic variations in rates measured were ascribed to physical discontinuities at the interface, overall water evolution being dependent on intracrystalline heat and gas (H_2O) transfer processes. These influences occurred for the different reactants within well-defined temperature and pressure ranges, identifying S–T phenomena as being *physical* in character and independent of the chemical differences between the five reactants studied. (The S–T effect was also shown to occur for evaporation of liquids, including water [170,171].) This pattern of reactivity was believed to occur because thermal equilibrium is not maintained throughout the reactant solid. The S–T behaviour [20] arises through the coupling of irreversible processes within the reaction zone: there are chemical potential discontinuities and temperature irregularities at the active interface. These conclusions, despite the supporting experimental evidence, have hitherto been accorded surprisingly little recognition. However, recent calculations [21,34] have given support to this work by showing that the self-cooling during dehydration reactions is larger than appears to have been generally accepted. Quantitative (computer-modelled) representation of temperature distributions within crystals during $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration accounts for the main features of the S–T effect shown by this (and some other) reactions [21].

Some variations on the reactivity pattern represented in Fig. 11 have been described. For example, S–T plots for dehydrations of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ [21,172] and of $\text{Pb}(\text{OH})\text{Cl}$ [161] show two maxima. The rate of nucleus growth in $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ dehydration increased somewhat ($\times 1.25$) when $p(\text{H}_2\text{O})$ rose from 12 to 60 Pa, compared with the vacuum reaction [45]. Thereafter, the rate progressively diminished to zero at equilibrium dissociation (about 1 kPa H_2O). A generally similar pattern was found [173,174] for borax.

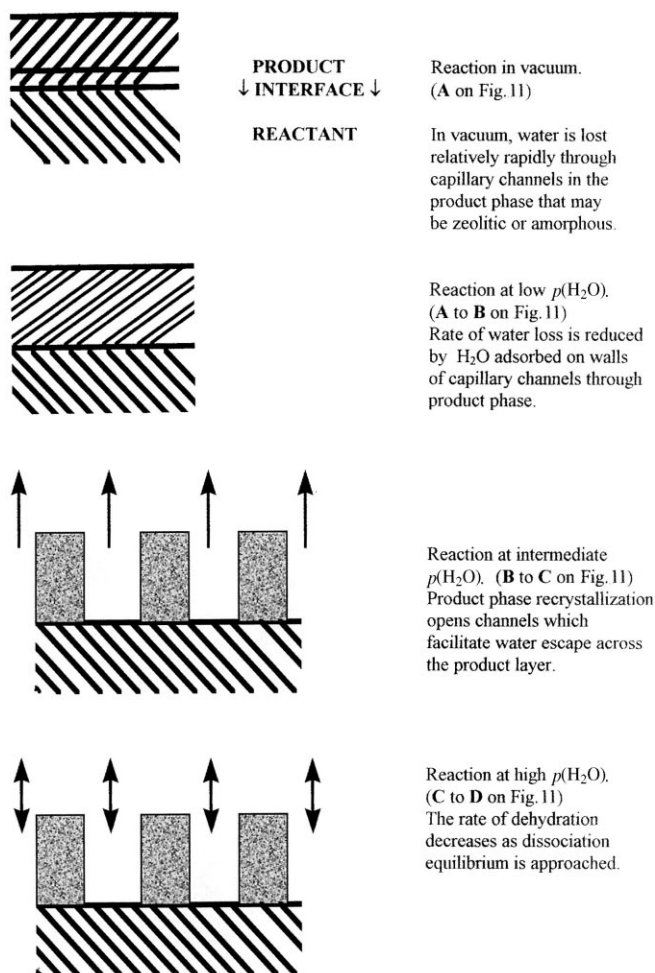


Fig. 12. Model widely used to explain Smith–Topley effect [1,2,5,8,11,21,140–142,169]. Interfaces shown in section.

The rate of dehydration of copper formate tetrahydrate systematically decreased with rise in $p(\text{H}_2\text{O})$, ascribed [37] to the absence of product phase recrystallization in water vapour. Finally, it may be mentioned that the stoichiometric reaction that occurs often depends on $p(\text{H}_2\text{O})$; the numbers of water molecules lost change with $p(\text{H}_2\text{O})$ in the different dehydrations possible of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ [175], etc.

10.3. Influence of water vapour pressure on dehydration rates

Water vapour within the reaction zone may be adsorbed on the hydrophilic phases that are participat-

ing in the dehydration. In principle, the following types of influences may be expected: (i) H_2O retained at the *active* surface of the reactant, constituting one side of the interface and entering surface equilibria, will be expected to reduce the overall rate of the forward dissociation. (Readsorbed water represents a contribution to the *back* reaction.) (ii) It is also probable that adsorbed surface water will be capable of increasing mobility of the constituents of all solid phases participating, and thus promote recrystallization of a metastable water-depleted hydrate. (iii) Surface retained water is similarly expected to facilitate the crystallization of an anhydrous, or lower hydrate, residual product. Sintering, similarly promoted, will result in increases in sizes and perfection of initially

finely-divided particles of the product phase, with concurrent formation of wider channels between such crystals, permitting greater ease of escape of the H₂O released (Figs. 11 and 12). While there is experimental evidence in support of (or, at least, consistent with the operation of) these effects, it is not known how widely they apply nor how widely the magnitudes of their influences differ between different reactants. Distinguishing the relative significances of the effects mentioned poses considerable experimental and interpretational problems. The markedly different sensitivities of rates of dehydrations to $p(\text{H}_2\text{O})$ are illustrated by the following examples.

10.3.1. Nickel oxalate dihydrate

The dehydration of NiC₂O₄·2H₂O was studied by Flanagan et al. [122] under conditions carefully designed to minimize contact between the reactant and the H₂O evolved. It was shown that the reaction rate at 383 K was reduced $\times 0.04$ by the small $p(\text{H}_2\text{O})=5 \text{ N m}^{-2}$. The apparent magnitude of E_a was relatively large (129 kJ mol⁻¹ between 358 to 397 K) and was sensitive to the pressure of water vapour in the reaction vessel. The probable role of atmosphere (air, nitrogen, etc.) in hindering the escape of product water is also emphasized. Very few studies have taken such care to eliminate contributions from the 'back' reaction: the results show, for this reactant, the considerable sensitivity of kinetic characteristics to experimental conditions. Much more work using this type of approach is required to determine whether similar patterns of behaviour are of common occurrence or whether this reactant is unusual, even exceptional. Surprisingly few studies of this type have been reported.

10.3.2. Chrome alum

The results presented in the previous paragraph contrast markedly with the dehydration of KCr(SO₄)₂·12H₂O, where the rate of interface advance at 290 K showed a small maximum (+about 25%) between vacuum and 100 Pa H₂O [45]. Under accumulatory reaction conditions [95], up to about 800 Pa H₂O, dehydration rates of large crystals were similar to those measured at 10⁻² Pa H₂O [23]. Nucleation rates were, however, much more sensitive to the availability and the variations of water vapour [11,23]. This relative insensitivity of rates of alum

dehydration to $p(\text{H}_2\text{O})$ is consistent with the conclusion [23] that intranuclear, retained water is an essential feature of the reaction mechanism.

10.3.3. Yttrium formate dihydrate

The rate of this reaction, which fitted the contracting envelope equation, at first increased with $p(\text{H}_2\text{O})$, passed through a maximum and finally decreased thereafter. The S-T character of this behaviour was ascribed to product phase recrystallization, confirmed by X-ray diffraction [176].

10.3.4. Ammonium magnesium chloride hexahydrate

This dehydration was studied between 373 to 473 K and from 10⁻⁶ to 2.7 kN m⁻². At low temperatures the dihydrate was formed by a phase boundary process but above about 430 K the anhydrous salt was given by a first-order reaction [128].

10.3.5. Calcium sulphate dihydrate

The kinetics of the dehydrations of CaSO₄·2H₂O and of CaSO₄·0.5H₂O were influenced by variations in $p(\text{H}_2\text{O})$, values of E_a for nucleation were reduced [78–81,177]. The dehydration of Na₂Ca₂(SO₄)₃·6H₂O fitted the parabolic law, identified as being due to one-dimensional diffusion. The magnitude of E_a increased from 75 to 159 kJ mol⁻¹ as $p(\text{H}_2\text{O})$ rose from 10⁻⁵ to 2.6 kN m⁻² [57].

10.3.6. Sodium carbonate monohydrate

The rate of dehydration diminished systematically with rise in $p(\text{H}_2\text{O})$ due to a contribution from the back reaction [132].

10.3.7. Sodium citrate dihydrate

The (unusual) greater rate of dehydration of single crystals than that of powder was ascribed to the retention of water vapour, recognized as promoting both nucleation and growth processes [66].

10.3.8. Reaction stoichiometry

At higher $p(\text{H}_2\text{O})$ values the reaction stoichiometry may change, as illustrated by the following examples. CuSO₄·5H₂O dehydration in vacuum yields the monohydrate whereas above 130 Pa H₂O the trihydrate begins to appear [61,62]. Different stoichiometries and kinetics were found on heating NiSO₄·6H₂O, under different conditions that change the ease with

which the water volatilized can escape [26–29]. The sequence of steps found in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dehydration [178,179] depends on $p(\text{H}_2\text{O})$: one of these reactions (tetra- to dihydrate) was used in the comparative investigation of the S–T effect [20]. Any mechanistic study of any such reaction must use conditions under which there is only a single rate process occurring.

10.3.9. Comment

The significance of $p(\text{H}_2\text{O})$ must always be considered in the mechanistic interpretations of dehydration rate measurements undertaken to determine absolute reactivities or to characterize a rate limiting step. Dehydrations of powdered reactant, large samples, in a gas atmosphere are particularly susceptible to influences from self-generated, and possibly inhomogeneous, distributions of H_2O throughout the reactant mass. At higher $p(\text{H}_2\text{O})$ the rates of water expulsion may be determined by displacement of a gas-hydrate equilibrium [26–29].

10.4. Influence of water vapour pressure on crystal sizes of dehydrated product

This topic is conveniently discussed with reference to the Smith–Topley effect to which it is often related in the literature (though the points made in Section 10.2. above show that theoretical models proposed to explain this widely accepted relationship now require critical reconsideration [21]. This must be remembered as an unresolved problem in the literature reviewed here). Some mechanistic discussions have assumed [11] that the initial solid products of dehydration are zeolitic, amorphous or microcrystalline. Subsequently, such products may be reorganized to crystalline phases, the energy changes of some of these have been discussed [13]. Recrystallization to larger particles may be promoted by H_2O and the intercrystalline channels, opened by product reorganization, decrease water impedance, thereby accelerating the reaction rate overall.

10.4.1. Low water vapour pressure

S–T behaviour includes a sharp decrease in dehydration rates with the initial small rise in $p(\text{H}_2\text{O})$ from zero to about 40 Pa. This has been ascribed [13] to reduced ease of H_2O escape in unreorganized product, see also: [122]. From studies of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dehydrations, it was suggested [180] that polarization effects may also contribute.

10.4.2. Intermediate water vapour pressure

The dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [61–63] in vacuum (1 Pa) between 320 and 330 K gives X-shaped nuclei having the composition of the monohydrate but a structure closer to that of the reactant pentahydrate. This is converted to an amorphous phase that recrystallizes to the monohydrate. Above $p(\text{H}_2\text{O})$ values of 130 Pa, ellipsoidal nuclei are formed in which the trihydrate structure is orientated with respect to the reactant pentahydrate lattice. Discussion of these observations takes into account the metastable intervention of the trihydrate and S–T behaviour.

The residual product from $\text{Zn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ dehydration in vacuum was amorphous but in water vapour was crystalline [181–183]. As the reaction temperature was increased from 370 to 400 K, the magnitude of $p(\text{H}_2\text{O})$ required to form the crystalline hydrate decreased from 80 to 13 Pa. Similarly, $\text{Y}(\text{HCOO})_3 \cdot 2\text{H}_2\text{O}$ [176] dehydrated in vacuum (0.1 Pa) to give a product that was amorphous to X-rays while the crystalline anhydrous salt was given in the self-generated atmosphere at 396 K.

10.4.3. High water vapour pressure

The diminution of dehydration rates at relatively high $p(\text{H}_2\text{O})$ is usually ascribed to a progressively increasing contribution from the reverse reaction as equilibrium is approached. Kinetic studies of alum dehydrations [95] showed that the rate diminished when $p(\text{H}_2\text{O})$ exceeded $0.3P_e$ (the equilibrium dissociation pressure). Above $0.5P_e$ dehydration rates were well represented by:

$$\ln \left[1 - \left(\frac{p}{P_e} \right) \right] = kt$$

which can be regarded as a ‘first-order’ approach to equilibrium, entirely consistent with the S–T diminution in rate at high $p(\text{H}_2\text{O})$.

10.4.4. Inert atmosphere

The dehydration of a large sample of fine powder hydrate, packed in a reaction vessel, may be effectively prevented, at least during short time intervals, by an inert atmosphere. Water losses will proceed only as rapidly as the released H_2O can diffuse outward

through gas-filled channels to the sample boundaries and beyond. When the temperature is raised sufficiently, $p(\text{H}_2\text{O})$ will achieve equilibrium with salt and lower hydrate throughout the reactant mass, perhaps with some escape through the outer edges. Water losses can only become rapid when the temperature has risen sufficiently for $p(\text{H}_2\text{O})$ to overcome the confining atmosphere. Thereafter the product H_2O is effectively 'boiled' from the reactant mass. 'Dehydration temperatures' are then determined by dissociation equilibrium displacement, rather than by kinetic controls. Kinetic interpretations must include consideration of this possibility. The significances of equimolar and isobaric reaction conditions in the interpretation of kinetic observations for $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ dehydration have been discussed by L'vov [154].

The participation of this atmosphere displacement model accounts for the considerable inconsistencies that have been reported for $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ dehydration [26–29]. For the same salt, reaction in vacuum proceeded at a low temperature, above 308 K, yielding ($-5\text{H}_2\text{O}$) the monohydrate in a single rate process

[26]. A subsequent kinetic study [27,28] (which did not describe the reaction conditions in detail) reported stepwise water losses of -1 , -2 , -2 , $-1\text{H}_2\text{O}$ at the considerably higher reaction temperatures, 416, 453, 503 and 613 K, respectively. Intermediates inferred were the penta-, tri- and monohydrates. A more recent report [29], where the reactant was heated at 8 K min^{-1} in air, positively characterized by X-ray measurements, the intermediates formed in the reaction sequence as tetra-, di-, and monohydrates. Impedance of H_2O escape enables intervention of the lower hydrates, otherwise the monohydrate appears in a single rate process [26].

10.5. Aspects of nucleation

Some aspects of nucleation, based on two dehydration studies [23,44], are presented in diagrammatic form in Fig. 13. This model identifies water losses from crack surface area followed by recrystallization exposing further surface at which the H_2O release process is maintained.

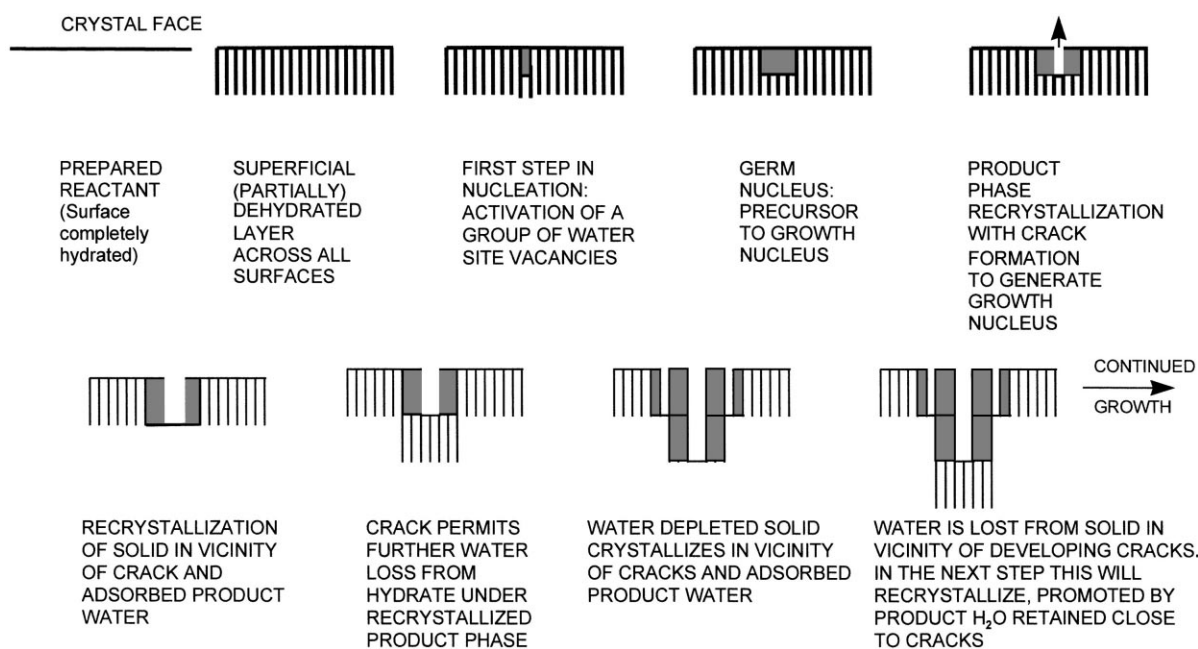


Fig. 13. Diagrammatic representation of growth of dehydration nucleus. This is based on proposals that water product, temporarily retained at or near propagating cracks in the solid product phase promotes the difficult recrystallization process [23] and there may be stepwise advance of reaction zone [44].

11. Some other aspects of dehydrations

Some other important features of dehydrations, not specifically discussed elsewhere in this review, merit brief mention here.

11.1. Solid-state reaction or participation of melting

The *phase* in which a chemical reaction proceeds is an indispensable feature in the formulation of a reaction mechanism, yet is rarely identified explicitly when describing possible crystalolysis reactions. The participation of melting in a thermal rate process is probably more widespread than appears from the literature, or is appreciated. The positive characterization of melting, perhaps local and temporary within the reactant mass, is sometimes difficult [10]. In some reports the fit of data to a geometry-derived rate expression appears as an implicit indication that the reaction proceeds in the solid state. In other articles, kinetic behaviour is described by reaction-order expressions only and no comment is made about whether the chemical process is heterogeneous or homogeneous. The reaction and reactivity controls in reactions of the two types are not necessarily identical. A clear identification of those chemical changes that proceed in the solid state would benefit immensely the literature that is intended to be specifically concerned with crystalolysis reactions.

11.2. Close agreement of kinetic characteristics

The close agreement of kinetic characteristics for related, but different, rate processes may be a simple coincidence or evidence for the operation of identical controlling steps. The latter possibility offers a valuable approach to gaining insights into the parameters that determine rates of reactions. For this reason the following similarities, where common mechanistic features are not immediately obvious, are mentioned as meriting further consideration.

The dehydration rates of $\text{Ca}(\text{OH})_2$ and of $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ were remarkably close within comparable temperature intervals, and values of E_a were virtually identical, 174 and 173 kJ mol^{-1} , between 633–683 and 573–673 K, respectively [83,184]. The shapes of the α vs. time curves were, however, significantly different. This is an unusually high

temperature for elimination of water from a crystalline hydrate ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$) and evidence was provided to suggest that calcium hydroxide was not a probable intermediate. While a coincidence of reactivities cannot be excluded, the possibility of common mechanistic controls operating for both reactions was discussed. This close similarity did not extend to reactions of the calcium sulphate hydrates. Dehydrations of calcium sulphate hemihydrate, α - and β -forms (or 0.67 and 0.50 H_2O [36]) [78–81,177], and of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were studied in lower temperature intervals (below 450 K) and at low $p(\text{H}_2\text{O})$: the E_a values were smaller.

Another enigmatic example of virtually identical kinetic characteristics was found for $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ dehydration [101] and the reaction of MgCl_2 with oxygen ($\rightarrow\text{MgO}$) [185]. Again it is not known whether this is due to a common, but as yet unidentified, rate control or is simply a coincidence.

At very much lower temperatures, water is evolved from lignite [111] and from chrome alum [23]: this similarity is more readily explained. Water in lignite is retained by physical bonding only and it is believed that intranuclear water, temporarily retained adsorbed on the solid product, may promote the difficult recrystallization step in alum dehydration. Few quantitative measurements have been made of the impedance offered by solid dehydration products to H_2O diffusive escape.

11.3. Dehydration by laser irradiation

Heating results in H_2O release when the thermal energy is sufficient to cause bond dissociation, as a stepwise series of processes in reactants for which the water is, or can be, retained in the different structures of lower hydrates. Popescu et al. [186] have shown that laser irradiation can result in complete dehydration as a single process for H_3BO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$, which contrasts with the stepwise thermal dehydrations of these reactants.

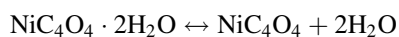
11.4. Dehydrations as precursor reactions

Reactants, to be used for studies of crystalolysis reactions other than dehydrations, are often prepared originally in the form of a hydrate. On heating, the first step is usually water loss, with recrystallization, but

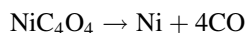
sometimes yielding an anhydrous reactant that is amorphous to X-ray diffraction [112,113]. It is generally assumed that H₂O expulsion is completed before the onset of the subsequent reaction of interest. Dehydration should, however, be regarded as the final step in reactant preparation and is accompanied by changes in crystallite sizes and shapes, together with the reorganization of types, numbers and distributions of imperfections. If these are significant in controlling the crystallization process of interest, then appropriate measurements must be made to characterize the anhydrous reactant, not the precursor hydrate. Similarly, the *reactant* in the second, and subsequent, processes in a stepwise dehydration is the *product* of the previous rate process.

Dehydration of CoC₂O₄·2H₂O at 423 K [118] gave a high area (over 30 m² g⁻¹) form of the oxalate that subsequently decomposed (above 570 K) and initially fitted an exponential law, but reacted thereafter at an almost constant rate. The same hydrate, dehydrated at 473 K, gave a lower area (15–27 m² g⁻¹) anhydrous salt and its decomposition was represented by the Prout–Tompkins equation (B2) [1] between 578 and 593 K. Variation of precursor dehydration conditions can, therefore, significantly influence the kinetics of a subsequent decomposition.

The thermal reactions of nickel squarate dihydrate [187], including kinetic characteristics, were sensitive to conditions within the reactant sample, particularly salt mass and disposition. The reversible dehydration:



was rapidly followed, within the same temperature interval, by decomposition:



11.5. Reactant water

In addition to the constituent water, structural, ligand and hydroxyl, water may be present in the reactant [14], in other forms, including H₂O adsorbed (weakly to strongly) at surfaces and within included droplets of liquid (solution). At surfaces it may be difficult to distinguish between molecules strongly adsorbed and the outer layers of structural water in the hydrate: both are retained by hydrogen bonds.

12. Conclusions

Presentation throughout is intended to examine fully all relevant features of dehydration phenomena as presented in the literature and to discuss how all available information can be classified and systematized. The interface advance/nucleation and growth mechanisms (WET 3) have been emphasized here because these appear to constitute the largest and best-studied group. Some of the points made about these are equally applicable to dehydrations of the other types listed in Table 1. It remains now to identify the important aspects of the subject, to determine whether there are useful links between these and to look to the future.

12.1. Classification

The primary motivation for this review was to propose criteria whereby dehydrations can be systematically classified. Whether or not the classes distinguished in Table 1 will prove to be acceptable and useful remains to be seen. However, perhaps this attempt will (at least) encourage others to recognize the value of order within the subject and to refine, develop, extend or even replace this scheme.

The benefits of subject ordering cannot be predicted but these could be large. Grouping reactions on the basis of behavioural similarities could lead to the identification of trends and these are the first steps in theory formulation. The recognition of common features provides a common basis for quantitative comparisons within sets of reactions, enabling apparent instances of exceptional properties to be recognized and further investigated. Once controlling parameters have been recognized, it may be possible to predict the properties and characteristics for other, hitherto untested, reactions. Order and theory development provides the framework for progress [138].

12.2. Kinetic analysis

It appears from the reports for many dehydration studies that characterization of the kinetic model (rate equation), together with determination of the magnitudes of *A* and of *E_a*, have often been the principal motivation for undertaking the research. While these results undoubtedly have intrinsic value, the data

obtained for the particular substance are not usually correlated quantitatively with similar observations for other reactants. Thus, many studies remain individual because these are not related to other reactions and do not contribute to the subject as a whole by not extending the wider systematic understanding of chemical behaviour.

The fit of yield–time measurements to a particular rate expression does not identify a *fundamental* property of that reaction. The shapes of α vs. time curves overall can be sensitive to the initial nucleus distribution, controlled by a small amount of a (probably) atypical reaction that occurs at imperfections and for some reactants is influenced by mechanical pretreatment (abrasion). The subsequent interface reaction, responsible for almost the total chemical change, is probably a fundamental and constant feature of the process, but the detailed mechanism may not be easily investigated. Measured rates of endothermic and reversible dehydrations are influenced by self-cooling and $p(\text{H}_2\text{O})$ as discussed above [20,122]. The calculated, apparent magnitudes of Arrhenius parameters cannot be assumed to provide quantitative information from which the rate limiting step can be identified [123]. Kinetic characteristics for many dehydrations are markedly influenced by the procedural variables. Other difficulties in interpreting α vs. time data concern the possible contributions from early (possibly surface) reactions, including the points of onset and completion of the ‘main’ rate process.

It appears, for these reasons, that the kinetic analysis of any set of measured data for solid-state dehydrations is *much* more difficult than appears to have been appreciated in many research reports. Rate data that may have empirical value in designing technological processes can be directly used for the envisaged purpose. However, if experimental measurements are to be interpreted to obtain absolute reactivities or to formulate reaction mechanisms, then the kinetic observations can only be considered to be suitable if shown to be uninfluenced by secondary controls, or that appropriate corrections have been made. Solid-state dehydrations have been recommended [188] as systems suitable for laboratory teaching, in particular the use of microscopy to characterize the fundamental features of solid-state reaction kinetics, including nucleation and growth behaviour.

12.3. Structure

Previous discussions, that considered interrelationships between the characteristics of solid-state dehydrations (also other crystalolysis reactions) and the individual chemical constituents of the reactants, have (at best) met with only moderate success in providing a basis for systematizing the subject. However, it is obvious that, in many of these reactions, features of the extended crystal lattice influence the course of the chemical changes occurring. In topotactic processes, for example, structural elements remain largely unmodified across a reaction interface, whereas within other types of active zones the reactant phase is recrystallized to the distinct product phase. The reactant lattice, and its interrelationship with that of the product, determines the number of dimensions in which the reaction propagates.

It appears that the identities of chemical constituents in the reactant do not provide a sufficient foundation for the comprehensive classification of solid-state decompositions/crystalolysis reactions. As pointed out in the Section 1, this approach is analogous to the *valence bond* theory. It is, therefore, suggested, from the observations indicating that extended structural features of each reactant influence, or possibly control, the course of its reactions, that these lattice properties should be explored as possible classification criteria. This is the analogue of *band theory*. This is used in the proposed ordering scheme presented in Table 1. If, as seems reasonable, the rate processes grouped within each class exhibit common mechanistic features (including the number of dimensions of reaction development), then it may be that these are controlled by similar chemical (rate determining) steps. Direct comparisons of reactions within each group distinguished by these criteria, rather than across all dehydrations, then can be expected to reveal trends based on systematic changes of structural elements, composition, (etc.) with the stoichiometry and with the kinetic characteristics such as rate equation, A and E_a for the dehydrations. By restricting comparisons to groups of like reactions, greater insights into reaction controls can be expected. The relationships and differences between the various groups so distinguished could then be explored.

There is ample evidence that dehydrations are not always one-step dissociations (the Polanyi–Wigner

model) and (at least) three distinguishable processes may contribute to the overall chemical change. This is a further good reason for considering the role of extended structures when comparing the behaviours of different solid reactants. Water must first be released, by rupture of the bonds retaining it at its lattice site. Second, it must diffuse to the crystal edge, where desorption may be a further difficult step. These processes may continue to completion of reaction or be restricted in extent, perhaps to a surface layer, during which losses can be progressively inhibited by increasing structural disorder [44]. Where restricted, or no, surface dehydration occurs, the continuation of reaction, by interface processes, requires the generation of solid product, nucleation, which may, or may not involve product phase recrystallization, is often regarded as a difficult step. Once the interface has been established, reaction continues preferentially within this active advancing zone. The difficult nucleation step can be promoted in different reactants by one or more of the following: crystal imperfections, seed crystals, water vapour, strain, abrasion, irradiation and possibly others. In some reactions, particularly topotactic processes, nucleation may be unnecessary or rapidly completed very soon after the commencement of reaction. The relative significances of the various steps mentioned, H₂O release, transport/diffusion, desorption and residual product recrystallization, vary markedly between different reactants for reasons that are not yet understood, but may be determined by lattice properties. However, this approach based on extended structures and recognizing greater complexity of interface chemistry, is likely to provide a more realistic representation of solid-state reactions than the Polanyi–Wigner model.

When the writing of this review had almost been completed, the author became aware of the ‘Unified Model of Dehydration of Molecular Crystals’ published by Petit and Coquerel [189]. The content of this valuable and timely article overlaps significantly with the present review. It is a matter of regret to the present author that a knowledge of the content of this paper was not known and, therefore, was not incorporated into this survey from its inception. However, in the belief that the points of general agreement in the two articles far outweigh any differences, the above analyses are presented as a separate and independent

approach intended to systematize the subject. The coverages in the two papers are different in scope, but evidently share the same objective of providing explanations of observed behaviour that have general applicability. There is also a common interest in identifying the role of long-range order in controlling the changes that participate in water elimination reactions.

12.4. Towards the future

From the literature perspectives identified above, there appears to be ample evidence that the theory of crystalolysis reactions, including, in particular, dehydrations, is in urgent need of wide and critical reappraisal and renewal. Two possible ways forward are to be contrasted. We can maintain a dominant trend evident in the recent literature by continuing to amass further separate contributions that will extend even further an already very large assemblage of articles that together form an unrelated (or, at best, loosely related) set of essentially individual research reports. Published kinetic results, such as A and E_a magnitudes for selected reactions, have not been found to form any recognizable pattern. Some rate processes, at least, are highly sensitive to reaction conditions, thus apparent magnitudes of Arrhenius parameters of an unknown proportion of these are of empirical value only. Furthermore, it is argued above that kinetic models, carefully analyzed for specific reactions, can be reactant-sensitive, so that another widely reported conclusion may be of doubtful mechanistic significance and value. Therefore, the continued collection of kinetic data, even using the most recent techniques (more data points, improved accuracy) does not necessarily yield data of enhanced theoretical value or fundamental significance.

The alternative approach, strongly advocated here, is to reconsider critically the information already available to seek to reconcile the differences and inconsistencies apparent. Progress may be possible towards developing mechanistic explanations of behaviour by using experimental methods carefully designed to eliminate the influences of secondary controls. L'vov [21,154] has shown the value of comparative reanalysis of published information and his work extends to a variety of other crystalolysis reactions. The value of systematic structuring of the

subject has also been recognized by Petit and Coquerel [189], as mentioned in the previous section. It is hoped that the case made here will encourage others to look at this subject from the wider perspective and expand these first signs of a renaissance in the theory of solid-state decompositions. History might even repeat itself and once again dehydrations will serve as model systems in developing understanding of a wider range of chemical changes that take place in crystalline reactants.

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Appendix A. Note added after completion of above review:

Korobov [190] has recently published an article that presents a comprehensive reappraisal of the theoretical models used in the derivation of the rate expressions applied to kinetic analyses of solid-state decompositions. In this paper the geometric and probabilistic concepts, upon which the currently used kinetic equations are founded, are critically reexamined. This reconsideration of the assumptions that underlie the principal approaches now in use enables the derivation of kinetic models to be reformulated so as to include chemical features of the changes occurring. It would appear that both this review [190] and the present survey share the opinion that it is now necessary and timely to move towards (to emphasize,

to reconsider, to introduce) more chemical features in the description of solid-state decomposition (cristolysis) reactions. However, the two approaches given, to this (apparently) common objective, are somewhat different. Time alone will show which of these alternative methods of representing reactions will be of the greater value. Both appear to be complementary and perhaps might together indicate ways towards increasing our understanding of the inner mysteries of this interesting class of chemical changes.

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