SOME RECENT STUDIES OF THE MECHANISMS OF DEHYDRATION REACTIONS OF SOLIDS

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Thermal Analysis, the central topic of this conference, is a technique that is widely used for the measurement of reaction rates and from which deductions can be made concerning the identity of the bond redistribution steps contributing to the chemical change being investigated. The mechanistic insights obtained from such studies enable us to identify the factors that determine reactivity and to understand theoretically the controls operating in chemical reactions. The present article points out, however, that kinetic data alone do not usually provide sufficient information to enable detailed identification of the sequence of steps through which reactants are converted into products.

This review discusses recent research concerned with characterizing mechanisms within a group of solid state processes that has been the subject of extensive kinetic investigations (including thermal analyses): the dehydrations of crystalline hydrates. Conclusions from previous studies of reactions of this type have contributed extensively to the more general understanding of solid-state reactions. Here we discuss some mechanistic conclusions from a number of recent studies in the field and emphasize the value of complementing rate measurements with other relevant observations, including microscopic examinations of the textural modifications that accompany chemical changes.

Keywords: dehydration reactions, mechanism of dehydration, reactions of solids

Dehydration reactions

Dehydration reactions of solids are often regarded as a distinct class of rate processes and as such have been the subject of many intensive kinetic and mechanistic studies [1]. Investigations of chemical steps participating in water elimination from these crystalline reactants have notably contributed towards advancing our theoretical understanding of reactions of solids, including recognition of the importance of the interface in nucleation and growth processes [2, 3]. The characteristic autocatalytic behaviour identified as occurring within such interfaces is ascribed to enhancement of the ease of

bond rearrangement steps within a modified zone associated with and in the immediate vicinity of the advancing contact at which reactant to product recrystallization occurs. Such local promotion of reactivity has been ascribed to stress-induced crystal perturbation resulting in a diminution of the energy barrier to reaction and/or a relaxation of the stereochemical constraints to structural reorganization necessary to permit chemical change.

Hydrates, however, although often discussed together as a group, are neither a unique nor a uniform set of chemical compounds and may be alternatively classified under a variety of other headings. For example, water of crystallization in solids may be retained in the form of ligands, as metal coordination compounds, as constituents of the crystal structure, or in alternative chemical forms such as hydroxyl groups in hydroxides, silicates, etc. One possible measure of the strength of water retention in the solid is provided by the temperature required for its removal.

The present article discusses studies of representative dehydrations of solids to compare the reactivities of diverse hydrates and to review recent mechanistic proposals in the field. As in the past, these observations increase our theoretical understanding of the chemistry of solid-state dehydrations and again provide model systems that contribute towards the more general understanding of the chemical characteristics of crystals.

From our literature survey we conclude that meaningful mechanistic conclusions must be based on diverse and complementary types of experimental observations. This point is mentioned here to justify the incorporation of this paper within the stated objectives of the 5th ESTAC Conference. Kinetic data, the valuable experimental observations obtained from thermoanalytical measurements, are by themselves not capable of characterizing completely the chemical changes that occur in crystals. Interpretations of kinetic data always benefit from support through other types of complementary evidence, particularly including stoichiometric information and microscopic observations that characterize the textural changes that occur as reaction proceeds, together with all other relevant information. The problems inherent in obtaining meaningful kinetic parameters using non-isothermal data have already been stressed [4].

Reaction mechanisms

Homogeneous reactions proceed through intermolecular and/or intramolecular bond rearrangements that follow activation through energetic collisional encounters. Chemical changes involving crystalline participants,

heterogeneous reactions, are often regarded as being more complicated and may involve, in addition to the evolution of molecular and crystalline products, diffusive migrations and structural reorganization (recrystalliza- tions). Recent work, including references cited below, has concluded that the interface in a reacting solid is not an advancing surface of monomolecular thickness within which the overall chemical transformation is completed. In- creasing experimental evidence is becoming available that characterizes in detail the structural features within such active zones. These are physically more extensive and involve chemical behaviour that now appears to be more complicated than has been recognized hitherto.

Important aspects of reactivity in the solid state that undoubtably merit further critical consideration are the consequences of repetitive collisions (multiple vibrational interactions) between reactant species that are effec- tively immobilized or have restricted mobility. Theories of reaction rates, developed for homogeneous processes, are based largely on the model that bond redistributions occur after and as a consequence of transitory but often energetic encounters between two mobile entities. In reactions involving solids there are (at least) two fundamental differences from this model that can be expected, whether these proceed at an interface (decompositions) or occur between chemisorbed surface species (heterogeneous catalysis).

(i) Energy exchange is not necessarily the result of individually separate transitory collisions but, for any specific constituent component of the reac- tant, may involve numerous and repeated vibrational exchanges with one or more immediate neighbours.

(ii) Reactant immobilization within a structured interface enables an over- all chemical change to proceed through a sequence of interlinked steps. An intermediate retained at a specific site within the interface structure has a high probability of encountering other reactive entities present within the same active zone. This enables reaction to proceed through a mechanism that involves a series of energetic interactions between participants present only in small quantities, because these are localized within the active regions of the organized crystal structure in suitable proximity and spatial dispositions. Similarly, stereochemical constraints arising from the lattice structure may enable termolecular (or higher molecularity) multiple collisions to be effec- tive in promoting change. Restrictions on the mobilities of reactant entities enable 'co-operative' mechanisms of chemical change that are excluded (as highly improbable) from collision-controlled homogeneous reactions. When reactive entities or potential intermediates have low probability of interac- tion, as in the gas phase or in solution, certain routes to chemical change are

thereby excluded but these may be possible under the special conditions that obtain within a reaction interface.

The chemistry of selected and representative solid state dehydrations are discussed in the paragraphs that follow.

Kinetics and mechanisms of selected dehydrations: interface reactions

Alums: $KAl(SO_4)_2 \cdot 12H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$

Water elimination in alum crystals is identified [5, 6] as proceeding predominantly at, or near, the interface that constitutes the contact between the reactant alum phase and the recrystallized lower hydrate product(s). This advancing interface is the peripheral and reactive boundary of each product growth nuclei. It was concluded [5] that the process controlling the overall rate of chemical change is the structural reorganization of the crystalline reactant, following depletion of the constituent water within the reaction zone. Promotion of this difficult recrystallization step is ascribed to autocatalytic behaviour involving the participation of product water temporarily retained in the immediate vicinity of the reactant-solid product contact. The ability of water, adsorbed from the vapour, to modify partially dehydrated alum surfaces has been demonstrated [5] for cleaved crystal faces of alums where $KAl(SO_4)_2 \cdot 12H_2O$ developed the 'orange peel' texture and $KCr(SO_4)_2 \cdot 12H_2O$ exhibited markedly enhanced nucleus formation. (Comparable behaviour has since been demonstrated for several further hydrates [7]). Thus the maintenance of a significant, but subsaturated, intranuclear water vapour pressure explains the preferred occurrence of reaction at the intracrystalline advancing nucleus boundary.

This model contrasts with the simple expectation that water will be lost most readily from original, external, crystal faces. Previous discussions [1] have emphasized the view that the residual solid material of the nucleus does not oppose the escape of product water. This observational result does not, however, account for the preferred loss of water from a subsurface active interface. However, the present explanation of nucleus function identifies structural reorganization of the water-depleted crystal zones as being promoted by adsorbed water that is retained through slightly impeded volatile product escape. Interface advance is, therefore, autocatalytic, the essential mechanistic feature of nucleation and growth behaviour.

Lithium sulphate monohydrate: Li₂SO₄·H₂O

Several kinetic studies and mechanistic discussions of this dehydration have been reported: the reaction has been identified [8] as occurring at an interface, again this is a nucleation and growth process. Nucleation is rapid and extensive initially so that a coherent and comprehensive product boundary layer is developed rapidly after the establishment of reaction conditions. The acceleratory process is completed by coalesence of neighbouring nuclei before 5% dehydration. The interesting mechanistic conclusion reached for the dehydration of this salt was that significant water losses occur from a zone of appreciable thickness located in advance of the progressing recrystallization interface. There is evidence from electron microscopic examinations that pore development occurs beyond the recrystallization domain [8] and changes in lattice spacing show that the thickness of the water depleted zone is ca. $150\,\mu$m [9]. This model differs from that described above for alums but is consistent with dehydration in the higher reaction temperature interval $(360-400$ K [8] where less (compared with alums) water retention is expected within the nucleus.

Kirdyashkina and Okhotnikov [10] showed that during $Li_2SO_4·H_2O$ dehydration the rate of interface advance is constant: the accumulating residual product does not increasingly oppose water loss. Gaponov *et al.* [11] contrast the small amount of prereaction structure modification, in this reaction, with the production of a metastable intermediate during lithium formate monohydrate dehydration.

Sodium thiosulphate pentahydrate, Na₂S₂O₃·5H₂O

From microscopic and kinetic evidence [12] it is concluded that $Na_2S_2O_3·5H_2O$ dehydration yields a dihydrate intermediate. Nucleation of the product phase requires crystallization within already reacted material. The aggregate volume of the product nuclei does not, therefore, provide a measure of the extent of reaction (water loss) because the structural reorganization is occurring within already dehydrated material. This measurement of total water loss cannot, therefore, be correctly used to characterize reaction kinetics.

Calcium sulphate dihydrate, CaSO₄·2H₂O

Okhotnikov *et al.* [13] report a kinetic study of $CaSO_4·2H_2O$ dehydration in which rates of interface advance in selected crystallographic directions were measured. The migration rate of the reactant-product contact was con-

stant in the [100] direction, parallel to the water layers in the structure. Water losses in the direction normal to the water molecule layers were, however, subject to control by diffusion through the pores of the solid product. The importance of the vacancy structure in the crystalline reactant adjoining the interface was considered [13, 14] in formulating the reaction mechanism.

Magnesium chloride dihydrate, MgCl2·2H2O

The thermal dehydration of $MgCl_2 \cdot 2H_2O$ can be alternatively regarded [15] as a salt decomposition because the constituent water reacts with the anion:

$$MgCl_2 \cdot 2H_2O \rightarrow MgO + 2HCl + H_2O$$

This reaction obeys the contracting area rate equation [1] and is identified as an interface process. The interpretation of the kinetic data is, however, incomplete because the small particle size precluded microscopic confirmation of these mechanistic conclusions and a reliable determination of the reaction frequency factor. Although the chemical changes suggest the participation of proton transfer steps, it is concluded that the reaction does not proceed through intermediate formation of the relatively more reactive magnesium hydroxide. The high thermal stability of this hydrate is ascribed to control by the chemical properties of $MgCl_2$ and/or MgO.

Lignite

The drying of lignite [16] does not involve a chemical reaction but was identified as the evaporative loss of free (liquid) constituent water from a natural coherent carbonaceous matrix within which it was immobilized. Interestingly the kinetic data fitted the contracting cube rate expression [1], modified by a term incorporating the contribution from the reverse process (water condensation) at higher humidities. Thus the rate characteristics of water evolution were comparable with the reaction of a solid and, as such, the system provides a useful measure of the rate of water evolution from a porous matrix within which it is not chemically bonded. This study was, however, restricted to the low temperature interval within which only the free water was evolved.

Diffusion controlled reactions

Okhotnikov and coworkers [13, 17−20] have used the quartz crystal microbalance in rate studies concerned with the earliest stages of water loss from the selected face of a large single crystal of reactant. Any influence of the reverse reaction is effectively eliminated by the use of very low pressures (dynamic vacuum ca. 10^{-4} Pa). Evidence has been obtained that the initial stages of water losses from the reactants studied are subject to intracrystalline diffusion control [13, 18−20]. These discussions concern the theoretical treatment of water volatilization rates following this diffusive migration within a developing water-site vacancy structure.

This reaction model may be applicable throughout the completed dehydration if the residual phase does not undergo recrystallization. Such retention of structure occurs, for example, in the dehydration of vermiculite [18], for which kinetic studies of the low temperature (267−290 K) reaction gave the activation energy 27 ±3 kJ mol^{-1}.

The early stages of lithium potassium tartrate monohydrate dehydration [19] were also controlled by diffusion between 392−453 K and the activation energy was relatively larger, 155 ±5 kJ mol^{-1}. This initial deceleratory process is believed to occur within a developing vacancy structure, water losses being limited to a thin outer superficial layer of the reactant crystals. After the rate of this diffusive loss has diminished, an acceleratory process is established, growth nuclei appear and subsequent dehydration is completed by a nucleation and growth reaction that exhibits the characteristic sigmoid shaped isothermal α-time curve.

Mechanisms of dehydrations of crystalline solids

In an earlier review [1] of mechanisms of solid state reactions, the following types of process were distinguished and the kinetic characteristics individually considered.

(i) Interface Advance,
(ii) Chain Type and
(iii) Diffusion Limited.

An important objective of the present review is to advance our current theoretical perspective of these reactions by recognizing now that these classes of behaviour are not necessarily mutually exclusive. Interface advance and diffusion limited processes together can contribute in a complementary manner during water elimination. Diffusive loss of water from solids occurs in the

reactant zone adjoining the boundary of the advancing nucleus. A vacancy structure is developed within reactant beyond the recrystallization interface that constitutes the most obvious textural feature of a nucleation and growth reaction, the reactant-product contact. Evidence has been referred to above that indicates the occurrence of significant water losses at the onset of dehydration and before any solid product phase can be detected. Moreover, where the anionic structure shows particular stability, e.g. in silicates, lattice modification following dehydration may not involve recrystallization and thus diffusion control is maintained throughout. (We note that the third class of reaction, Chain Type, based on an earlier view of energy transfer, is no longer regarded as valid theoretically [1]. Kinetic expressions based on this model are now ascribed to branching crack propagation. Such behaviour has never found extensive applications to dehydrations and this mechanism will not be considered further here.)

Interface structure

From the representative dehydrations mentioned above, and other similar studies, we identify the following processes as participating in the dehydrations of solids: see also Scheme 1.
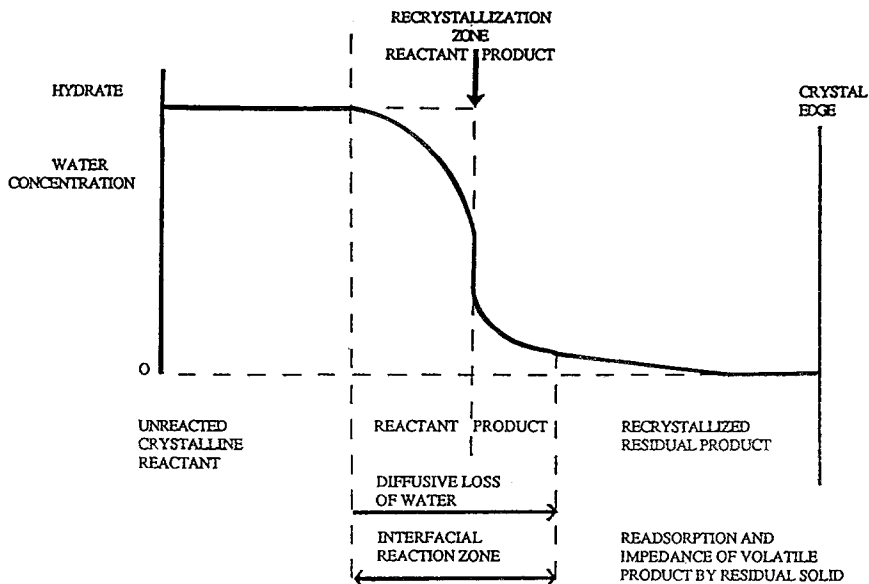
Scheme 1 Diagrammatic section giving a generalized representation of interface structure for dehydration reactions

1. Water mobility within the crystalline reactant. (Intersite movements involve vacancies.)

2. Diffusive migration of water to crystal edge or reaction interface. (Water losses will result in vacancy concentration increase.)

3. Water volatilization at the crystal edge or interface (desorption).

4. Chemical reactions (see $MgCl_2 \cdot 2H_2O$ above), if any.

5. Recrystallization of solid reactant to product structure.

6. Water vapour adsorption/desorption on product solid.

7. Intranuclear diffusive escape of water and loss beyond crystal.

The sequence and relative significances of these steps will vary between different reactions: in addition, there may be overlap or intermediate behaviour. Not all may occur in any selected dehydration. A similar pattern of steps may be applicable in reactions other than dehydrations.

Where the diffusion process is dominant, the rate controlling step may be the migratory escape of water through an unrecrystallized product layer of progressively increasing thickness. The diffusion controlled rate expression obeyed may also include a contribution from geometric factors [1]. For reactions in which the reaction zone is thin, interfacial behaviour is observed and the geometric factors are dominant in determining the kinetic characteristics. If nucleation is slow, a sigmoid-shaped α-time curve is given and the Avrami-Erofe'ev equations are obeyed [1]. Rapid and extensive initial nucleation, in contrast, gives deceleratory behaviour and obedience to either the contracting volume (or area) rate expression. When the volatile product (water) is extensively readsorbed, or reaction is reversible, kinetic behaviour will be modified accordingly and there may be a Smith-Topley effect [1].

The active reaction interface may, therefore, be represented as being composed of up to three zones, specified in sequence outwards as:

(i) a vacancy structure from which there is diffusive (outward) loss of water,

(ii) a recrystallization zone and

(iii) a product layer which may reduce the rate of water losses.

Recrystallization does not necessarily occur, as in the case of vermiculite mentioned above [18].Kinetic data for the rates of interface reactions from the present set of reactants are summarized below in the Table. Observations for the diffusion controlled processes are not directly comparable with interface advance controlled reactions and are not, therefore, included.

Within the small sample of representative dehydrations tabulated here, the measured values of the activation energies are predominantly in the relatively restricted interval 90 ± 20 kJ mol^{-1} with the exception of the value for

Table 1 Dehydrations controlled by an interface mechanism. Summary of kinetic data for reactions mentioned in the text

Reactant solid	Activation energy / kJmol⁻¹	Log Pre-exponential factor/mm s⁻¹	Temperature interval studied /K	Rate of Interface Advance / mm s⁻¹	at K	(Ref.)
$KAl(SO_4)_2 \cdot 12H_2O$	108 ±2	14.1	292–302	3.4×10^{-5}	305	(5)
$KCr(SO_4)_2 \cdot 12H_2O$	70 ±10	8.0	287–310	13.2×10^{-5}	305	(5)
$Li_2SO_4 \cdot H_2O$	80 ±3	7.5	360–400	1.5×10^{-5} (E)	343	(8)
$CaSO_4 \cdot 2H_2O$	82 ±2	7.9	324–371	1.7×10^{-5} (E)	343	(13)
$MgCl_2 \cdot 2H_2O$	110 ±5	1.5	623–703	0.004×10^{-5} (E)	653	(15)
Lignite	24 ±18	0.88	273–293	33×10^{-5}	291	(16)

(E) Value estimated from data in reference cited. (For $MgCl_2 \cdot 2H_2O$ the reactant particle size was assumed to be 1 μm diameter.)

lignite which was (unexpectedly) appreciably less than the enthalpy of water vapourization. (See also data in Table 10 in [1]). No trend of rise in activation energy with increase reaction temperature is evident. This is entirely consistent with the similarities of the interface processes participating: diffusion in a changing vacancy structure, recrystallization and water desorption, perhaps with a contribution from readsorption. The calculated activation energy cannot be identified with a specific rate limiting step and, therefore, the pre-exponential term is similarly uncharacterized. (Assuming a vibration frequency of $10^{12}s^{-1}$ and an interface advance step of 1 nm/molecule of water loss (lattice unit) the calculated frequency factor is $1 \text{ nm} \times 10^{12}s^{-1} = 10^6 \text{ mm s}^{-1}$. This is comparable with some of the values listed here.)

From these comparisons we note that absolute rates of interface advance in alum dehydration (3.4 and $13.2 \times 10^{-5} \text{ mm s}^{-1}$ at 305 K, Table 1) where it is believed that water is temporarily retained at the interface, are close to the value ($33 \times 10^{-5} \text{ mm s}^{-1}$ at 291 K) for the release of the free constituent water from lignite. This comparison is consistent with the mechanistic discussion in which alum dehydration is identified with evolution of loosely retained surface water [5]. Other hydrates, in which water is more strongly held, are dehydrated more slowly.

We conclude that diffusion and interface controls in the overall mechanism are complementary, recent investigations indicate that both reaction processes together contribute towards the release of water from the crystalline hydrate.

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Zusammenfassung — Die Thermoanalyse ist ein Verfahren, welches bei der Messung von Reaktionsgeschwindigkeiten breite Anwendung findet und mit deren Hilfe Schlußfolgerungen bezüglich von Bindungsumlagerungsschritten gezogen werden können, die für die untersuchten chemischen Umwandlungen charakteristisch sind. Die aus derartigen Untersuchungen gewonnenen mechanistischen Erkenntnisse ermöglichen uns, die reaktivitätsbestimmenden Faktoren zu identifizieren und ein theoretisches Verständnis für die Beherrschung chemischer Reaktionen zu entwickeln. Vorliegender Artikel zeigt, daß kinetische Daten allein nicht immer genügend Informationen liefern, um die Reihenfolge der einzelnen Reaktionsteilschritte von Reaktionspartnern zu Reaktionsprodukten ausreichend zu identifizieren.

In vorliegendem Überblick werden die jüngste Forschungen diskutiert, die den Reaktionsmechanismus für eine Gruppe von Feststoffreaktionen bei extensiven kinetischen Untersuchungen (einschließlich Thermoanalyse) charakterisieren: die Dehydratation von kristallinen Hydraten. Schlußfolgerungen aus der bisherigen Untersuchung solcher Reaktionen haben in großem Maße für ein allgemeineres Verständnis von Feststoffreaktionen beigetragen. Es werden hier einige mechanistische Studien auf diesem Gebiet diskutiert und die Wichtigkeit betont, Geschwindigkeitsmessungen durch andere relevante Methoden zu ergänzen, z.B. durch mikroskopische Untersuchungen der Gefügeveränderungen, von denen chemische Umwandlungen begleitet werden.