

# **THERMAL REACTIONS OF SELECTED SOLIDS INCLUDING REACTANTS THAT MELT DURING CHEMICAL CHANGE**

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## **Abstract**

Selected kinetic and mechanistic studies of thermal reactions of initially solid substances are reviewed with emphasis on the evidence that some of these chemical changes proceed with the essential participation of melting. The reactions considered are classified on the extent and the role of such melting and the various types of behaviour observed are discussed with reference to solid state rate processes in crystals.

It is stressed that melting is an important feature in theoretical considerations of crystal reactivity because chemical changes often proceed more rapidly in a melt than in the solid state. However, literature reports concerned with reactions of solids do not always explicitly mention the possibility of melting during discussions of reaction mechanisms. The present paper comments on methods capable of detecting liquefaction during reaction, a feature of behaviour that is not always easily identified experimentally. Also considered here is the recognition of reaction intermediates, which provide important evidence concerning the course of the chemical changes through which the reactant is transformed into product.

This short review draws attention to the considerable value of chemical evidence in elucidating mechanisms of reactions of solids including the necessity for identifying intermediates and the role of any melt or liquid participating.

**Keywords:** solid state decomposition kinetics, thermal reactions of solids, reaction intermediates

## **Introduction**

On heating, some solids melt, others decompose. There are also the possibilities that decompositions may occur during melting or that melting may accompany decomposition. The present article discusses the kinetics and mechanisms of thermal reactions of initially solid reactants, for some of which there is evidence of liquid or melt participation.

Thermal decompositions of diverse crystalline reactants have been studied [1] and many of these have been identified as proceeding exclusively in the

solid state: crysolysis reactions [2]. In contrast, much less effort has been directed towards the investigation of condensed phase processes in which both solids and liquid may be present during the chemical changes. This article, therefore, discusses the following aspects of reactions that occur on heating initially solid reactants:

- (i) the role of melting, if any, in reaction; this may be local and temporary,
- (ii) the kinetic characteristics of reactions proceeding in completely melted reactant (crystal order has been lost: this may alternatively be regarded as a solvent-free homogeneous rate process),
- (iii) specific examples of reactions involving both solid and liquid phases,
- (iv) the detection of melting during thermal reactions of solids, and
- (v) the detection and identification of intermediates in condensed phase reactions.

In summary, we are here concerned with the relatively undeveloped topic: recognition and characterization of the roles of melt/liquids during thermal reactions of initially solid reactants.

### *Melting*

Melting during a thermal reaction of a solid is of interest because the inherent loss of crystal cohesion may result in an increase in reactivity of the lattice components, as discussed previously [3]. This is a consequence of the relaxation of the regular structural, and stabilizing, bonding forces together with the enhancement of stereochemical freedom that permits a wider range of chemical interactions in the melt, between the formerly immobilized constituents of the crystal.

Melting is probably the most frequently observed consequence of the continued heating of a pure solid compound. Melting to an unchanged liquid occurs at a constant temperature and at a rate that is controlled by heat flow. Primary bonding forces are not involved and kinetic investigation is difficult. In contrast, most chemical reactions of solids are amenable to kinetic study and many such investigations have been concerned with decompositions of crystalline reactants [1]. These crysolysis [2] reactions have been accepted as relatively uncomplicated chemical changes and, therefore, most suitable for study. Particular interest has been focussed on a restricted range of reactant types, the most important being [1] hydrates (that evolve water of crystallization) and metal salts containing unstable anions, some of which are highly oxygenated species (azides, oxalates, perchlorates, permanganates, etc). Observations from such studies have notably contributed to the theory of the chemistry of solids. It is, however, frequently difficult to establish conclusively whether or not there has been melting, perhaps local and temporary, during these decompositions.

### *Reaction mechanisms*

Reaction mechanisms are the detailed sequences of physical and chemical steps used to describe the conversion of reactants into products. In the elucidation of the mechanism of a solid state reaction it is, therefore, essential to determine whether or not there has been melting. Knowledge of reaction mechanisms enables correlations to be made between related rate processes, thereby extending theoretical understanding of the subject. Such insights permit useful predictions of behaviour in hitherto untested systems and may introduce the possibility of exerting some control over reactivity by appropriate selection of reaction conditions or through the use of additives. Identifications of rate limiting steps can be expected to contribute to theory development and/or the identification of practical applications.

### **Solid state decomposition kinetics [1]**

Because the reactants with which this review is concerned are initially crystalline, it is appropriate first to refer to the well-established theory and to the specialist methods of kinetic analyses used in studies of solid-state decompositions [1]. Applicable reaction models identify the chemical change as occurring preferentially and predominantly (perhaps exclusively) at reaction interfaces that progressively advance into unchanged reactant. There is, therefore, a systematic development of the changing spatial dispositions of these migratory zones within which reaction occurs completely. This model contrasts with the circumstances obtaining in homogeneous rate processes, where all equivalent reactant entities possess an equal probability of reaction. Rates of reactions in gases and in solutions are controlled by reactant concentrations. In contrast, concentration terms are regarded as inapplicable to the kinetic analyses of most reactions of solids (though first- and second-order equations have found applications, sometimes on an empirical basis). Thus, for solids, the concentration terms of rate equations are replaced by parameters representing the progressive changes of areas of effective, active interfaces during their advance. Accordingly, two different, but complementary, characteristics of chemical change claim consideration here:

1. Geometry of systematic interface advance
2. Chemistry of the interface reactions.

### *Geometry of interface advance*

Rate equations {of the form:  $f(\alpha) = kt$ , where  $\alpha$  is the fractional reaction}, applicable to solid-state decomposition [1], are derived from quantitative con-

sideration of the systematic changes in geometry of reactant/product contact as these active reaction zones traverse each entire reactant particle. Such interfaces are generated by nucleation [4] (the initiation of a particle of the solid product) which is accompanied by the formation of the reactant/product interface that subsequently advances as growth [5, 6].

In any kinetic analysis, that rate equation identified as most accurately and satisfactorily describing [7] a measured set of yield-time data, is often accepted as sufficient evidence to characterize conclusively the geometry of the interface advance reaction. Such treatments do not always, however, express the perceived 'excellence of fit' or  $\alpha$  range of fit in quantitative terms. There are, moreover, a variety of ambiguities and uncertainties inherent in this approach to kinetic analysis [1], including (inter alia) a sensitivity of rate behaviour to the presence of imperfections and impurities in the reactant, to particle-size effects, to the reversibility of reaction, and to temperature variations and inhomogeneities within the reactant mass due to the enthalpy of reaction. Accordingly, deductions from kinetic analyses about reaction geometry should always (in the strongly held view of the author) be complemented where possible, by other experimental observations. Particularly valuable are (optical and/or electron) microscopic examinations of the textural changes that accompany reaction, from which deductions may be made concerning the systematic changes of interface dispositions that occur as reaction proceeds.

### *Chemistry of the interface reactions*

Identification of the bond redistribution steps by which reactant is converted into products, within the specialized, inaccessible reaction interfacial zone, having a thickness of perhaps molecular dimensions, is experimentally very difficult. Conclusions are usually based on indirect evidence. Sometimes the rate limiting step can be inferred from a measured activation energy ( $E$ ) on the assumption that reactions of solids obey the Arrhenius equation:

$$f(\alpha) = kt = A \exp(-E/RT) \cdot t$$

Objections to this approach for the measurement of the energy barrier to reaction are based on the recognition that the energy distribution function for solids (Fermi-Dirac statistics) is different from that applicable to homogeneous reactions (the Maxwell-Boltzmann equation). Accordingly there are doubts as to whether the theory of homogeneous kinetics and, in particular, the usual interpretation of the significance of the activation energy, can be satisfactorily applied to chemical changes proceeding within a crystalline structure.

## Thermal reactions of solids (including the possible participation of liquids and melting)

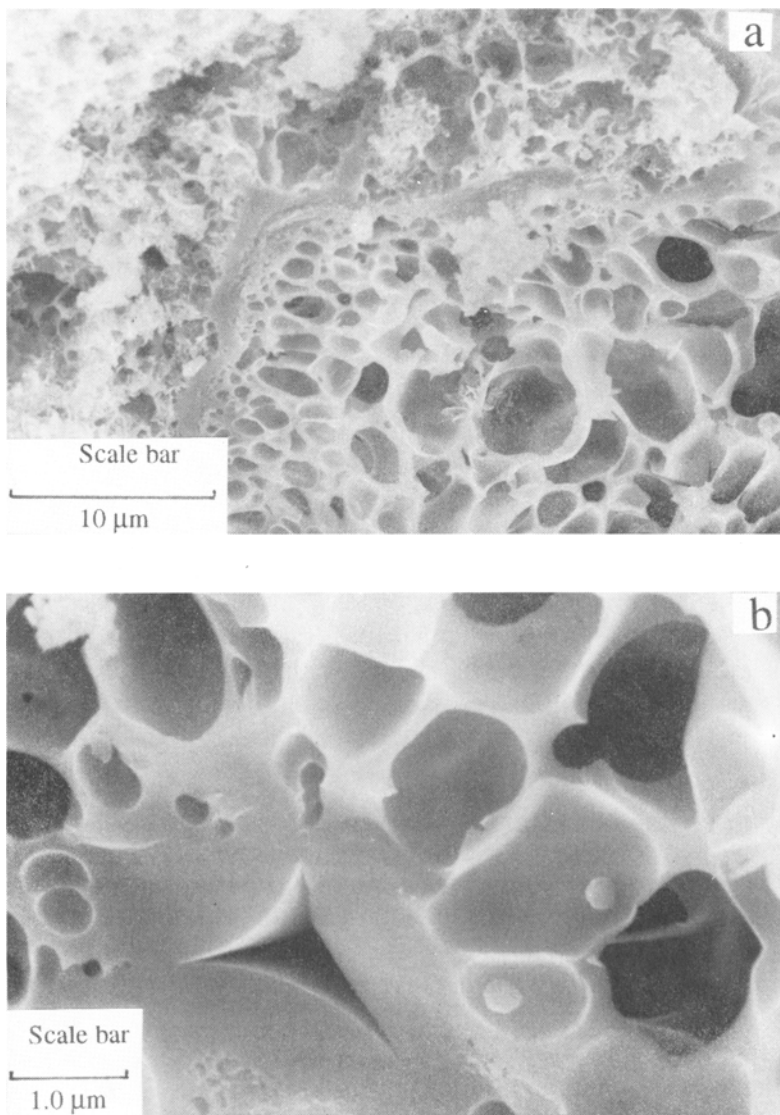
Here we consider a wider range of reaction mechanisms than is usual in this field [1] and examine critically the possibility that chemical changes proceed in solid-liquid reaction zones of thicknesses greater than those envisaged at most solid-solid active interfaces. We conclude that some condensed-phase reactions are accompanied by extensive melting. The variety of thermal reactions reviewed here include diverse reactants that are initially solid and in which the possible participation of a liquid or of a melt has been carefully investigated. Selected kinetic studies of decompositions of solids, gas-solid and solid-solid reactions are grouped below on the basis of similarities in mechanistic behaviour. This classification provides a systematic framework for the elucidation of mechanisms of rate processes in the condensed phase and draws attention to the types of reaction models that merit consideration in the developing theory of the subject.

For each reaction, only those aspects of behaviour that relate to the participation of a melt or of a liquid in the chemical change are discussed here. More detailed descriptions of the individual reactions are given in the references cited, including observational data and mechanistic discussions. The generalized perspective presented below is based on an overall consideration of the specific conclusions reached for the various different reactions studied.

### Melting of a reaction intermediate

Several reactions have been identified in which the chemical changes are accompanied by melting ascribed to the participation of an intermediate that is either molten at reaction temperature or melts in contact with the (chemically similar) reactant, perhaps through eutectic formation. Enhanced reactivity in the melt results in autocatalytic behaviour, but yield-time data are not necessarily represented satisfactorily by rate expressions based on advancing-interface reaction models [1].

Copper(II) malonate decomposition proceeds [8] with the participation of a melt (possibly a eutectic) containing ( $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ , malonate and acetate). Intracrystalline froth formation, observed microscopically, Fig. 1, is evidence of fusion. The exponential rate equation is obeyed. The rate is believed to be directly proportional to the quantity of melt present and thus to the extent of reaction:  $d\alpha/dt = k\alpha$ . Copper metal is not an effective catalyst for carboxylate anion breakdown.



**Fig. 1a, b** Thermal decomposition of copper(II) malonate [8]. Scanning electron micrographs of crystal sections exposed by light crushing of salt after partial decomposition ( $\alpha = 0.4$ ). The froth-like texture is ascribed to product gas evolution within melted zones. No regular aligned or flat surface features associated with crystal lattice structures are evident: the rounded pores are ascribed to surface tension control that minimizes the boundary area of the fused material. Scale bars: a - 10  $\mu\text{m}$ , b - 1.0  $\mu\text{m}$

Copper(II) maleate exhibits a pattern of behaviour that is closely similar [9] to that of copper(II) malonate, but here fusion is ascribed to anion isomerization to give the active reaction melt containing the ions ( $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ , maleate and fumarate). There was no evidence of melting [8, 9] during the decompositions of the relatively more stable salts: copper(II) fumarate, copper(I) malonate, copper(I) maleate and copper(I) fumarate.

Ammonium dichromate decomposition [10] proceeds with extensive melting that is identified as including  $\text{CrO}_3$ , known to melt close to the decomposition temperature of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . Various concurrent reactions contribute to the oxidation of ammonia.

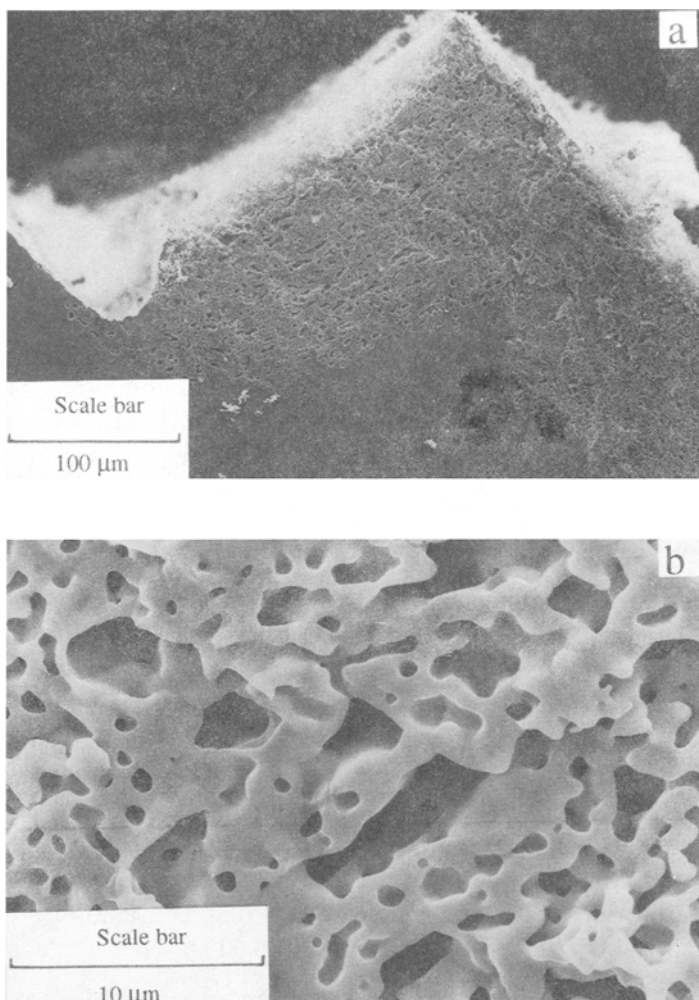
Silver salts catalyse the decomposition of ammonium perchlorate, ascribed [11] to the intervention of the complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$  and melting:  $[\text{Ag}(\text{NH}_3)_2]\text{ClO}_4$  melts below the temperature of the reactions studied.

### **Molten, mobile, highly reactive intermediate**

Ammonium perchlorate decomposition exhibits several unusual (probably unique) features and has been the subject of particularly extensive investigations. Unresolved problems concerned with chemistry of this reaction were recently reconsidered [12]. This analysis led to the novel mechanistic proposal that reaction occurred in molten droplets of the highly reactive intermediate,  $\text{NO}_2\text{ClO}_4$ , that were mobile within the reactant crystal. Ammonia is oxidized to the nitryl ion after anion breakdown within the fluid particles that constitute the zones of chemical change. These fluid droplets migrate into unreacted salt as an irregular and discontinuous approximate interface. This model explains the sigmoid yield–time curve and the cessation of decomposition after breakdown of only a proportion (28%) of the reactant solid [13]. The residual product is highly porous, Fig. 2.

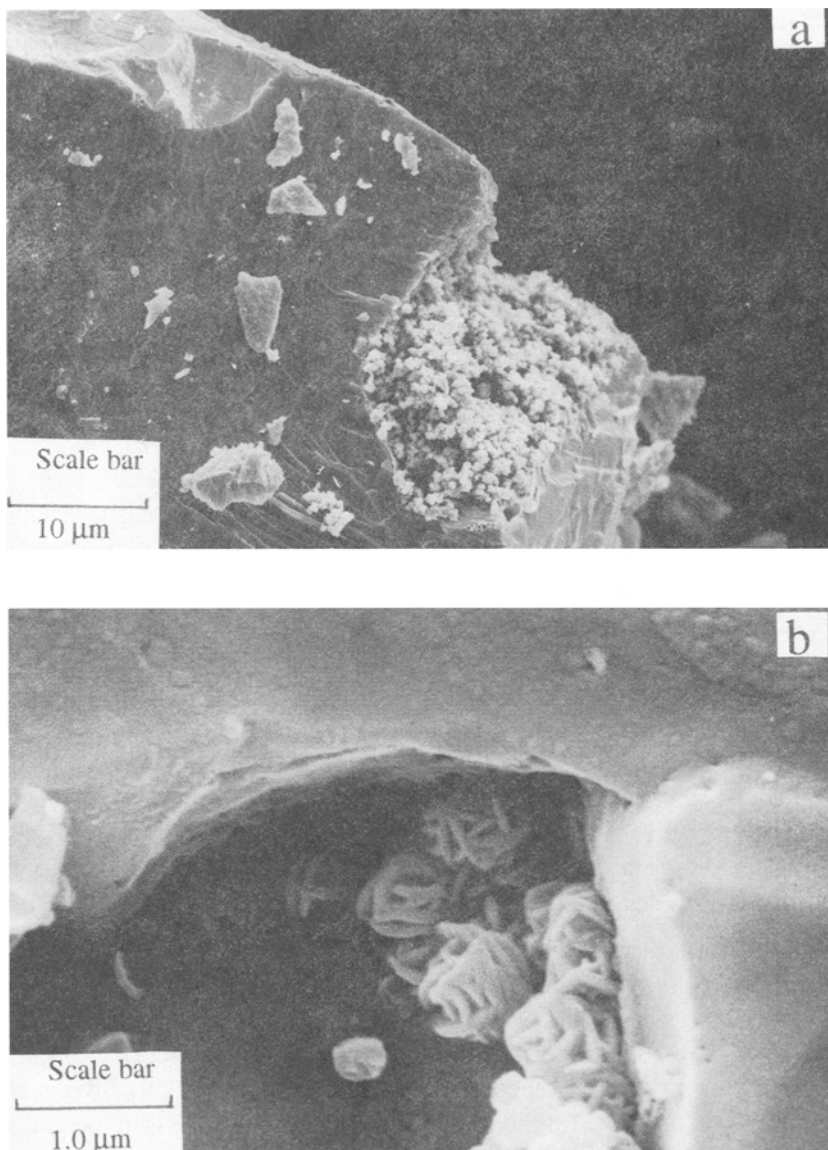
### **Highly localized temporary melting**

Caesium permanganate. The textural changes accompanying decomposition [14] of this salt are difficult to identify by electron microscopy because these are obscured by an outer unreactive layer. This layer constitutes the original crystallite surfaces and does not undergo textural change during reaction. Intracrystalline modifications, revealed on crushing after reaction, however, showed the product to be composed of aggregates of rounded particles rather than the irregularly disintegrated product of decomposition with cracking. The most satisfactory explanation of the observations is the occurrence of localized, temporary liquefaction within the reaction zone during decomposition: this is,



**Fig. 2a, b** Decomposition of ammonium perchlorate [12]. Scanning electron micrographs, at two magnifications, of sections across reacted zones of a partially decomposed ( $\alpha = 0.10$ ) ammonium perchlorate crystal. This is a nucleation and growth process. Reaction is initiated at crystal faces and regions of product nuclei (the residual solid is  $\text{NH}_4\text{ClO}_4$ : chemically identical with reactant) grow by the inward advance of an irregular boundary (a discontinuous interface) between unchanged reactant and the highly porous product. About 28% of the salt is decomposed leaving an open structure penetrated by irregular cavities ascribed [12] to reactions within randomly progressing droplets containing the highly unstable reaction intermediate,  $\text{NO}_2\text{ClO}_4$ . Scale bars: a - 100  $\mu\text{m}$ , b - 10  $\mu\text{m}$





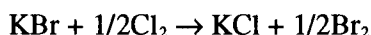
**Fig. 3a, b** Thermal decomposition of potassium permanganate (to be published). During the early stages of  $\text{KMnO}_4$  decomposition ( $\alpha = 0.05$ ) product nuclei are formed, composed of bent acicular crystals grouped into approximately spherical aggregates. It seems unlikely that any melting or sintering occurred during what is identified as a solid state reaction. Scale bars: a - 10  $\mu\text{m}$ , b - 1.0  $\mu\text{m}$

however, difficult to confirm conclusively by microscopic observations. In contrast, it appears that potassium permanganate decomposes in the solid state, Fig. 3.

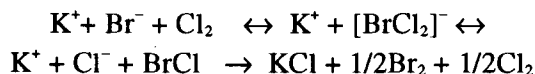
### Reaction within retained liquid product

Reactions included in this group yield and retain a liquid or molten product, within which the controlling chemical changes proceed more readily than in the solid reactant.

Potassium bromide reacts with chlorine gas [15] as follows:



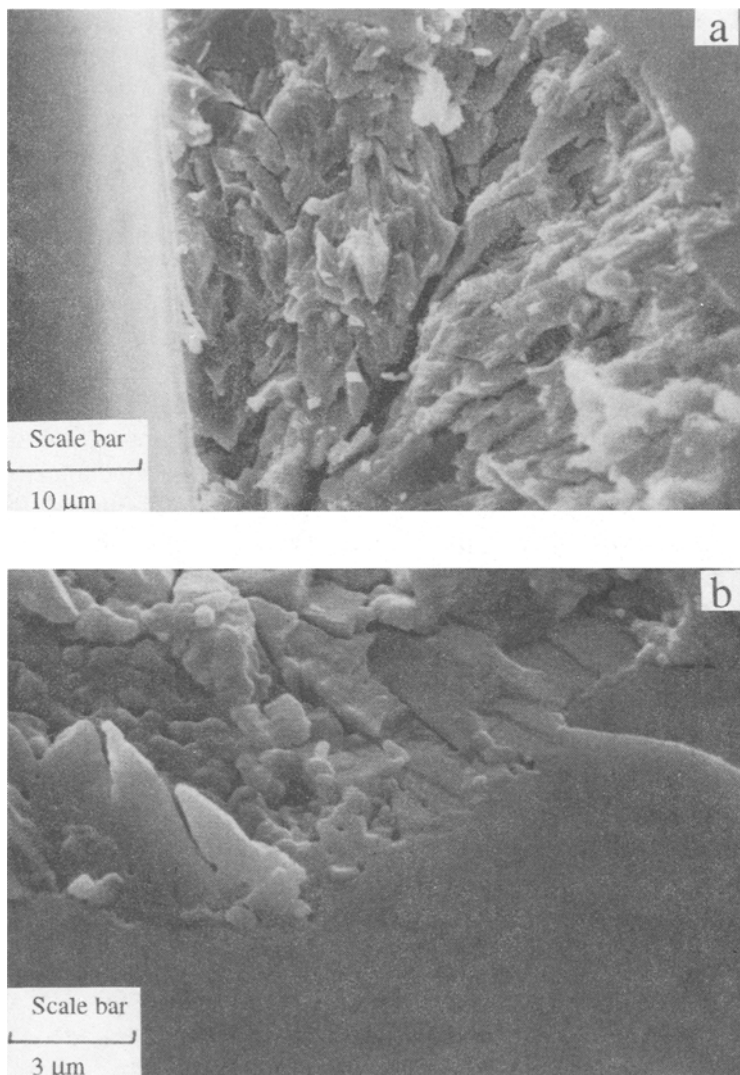
This solid + gas reaction exhibits the important characteristic that, like many solid state decompositions, it is an interface advance process based on nucleation and growth, Fig. 4. During the low temperature (< 400 K) reaction, nuclei retain liquid bromine product that is identified as the medium in which reaction proceeds by the ionic mechanism:



Evaporation of the intranuclear liquid ( $\text{Br}_2$ ) by evacuation, or on heating, resulted in the cessation of nucleus growth. At higher temperatures, reaction again proceeded by a nucleation and growth mechanism, but the rate was apparently controlled by different chemical steps, not involving a liquid.

Decomposition of lithium potassium tartrate. Decompositions of the various forms of  $\text{LiKC}_4\text{H}_4\text{O}_6$  [16] can be described by the Avrami-Erofeev equation [1] but microscopic observations showed the formation of molten salt/liquid reaction zones. It was concluded that the chemical changes occurred principally within the melt portion of a reaction interface that progressively advances into each reactant crystal. As with the group of reactions classified (in the following section) under the heading 'Comprehensive melting before reaction', the activation energies for these salt decompositions were relatively large,  $220 \pm 20 \text{ kJ}\cdot\text{mol}^{-1}$ . Melting was more extensive in crushed powder reactants, where the kinetic behaviour was more complicated.

Chrome alum reaction with ammonia gas [17] proceeds through ligand replacement ( $\text{H}_2\text{O}$  by  $\text{NH}_3$ ) in the  $\text{Cr}^{3+}$  co-ordination sphere, and the displaced water of crystallization forms a viscous solution within which reaction continues.



**Fig. 4a, b** Reaction of potassium bromide with chlorine gas [15]. Scanning electron micrographs of crystal surfaces exposed by sectioning after reaction to reveal the internal structure of growth nuclei. At the lower magnification the outline of the product assemblage, KCl crystallites comprising a growth nucleus, are seen in contact with the unchanged KBr. Bromine liquid, in which the reaction is believed to occur [15], is accommodated within the diagonal cracks that extend from the outer crystal surface to the innermost corners of the approximately rectangular nuclei. The complicated structure of the reactant/product (KBr/KCl contact) interface is seen in greater detail in the higher magnification micrograph. Scale bars: a - 10  $\mu\text{m}$ , b - 3.0  $\mu\text{m}$

Copper(II) malonate decomposition is promoted by copper(II) bromide [18] with the intervention and probable participation of a liquid, perhaps involving the formation of  $\text{CH}_2\text{Br}_2$  and related compounds.

### Comprehensive melting before reaction

There have been relatively few detailed investigations of chemical reactions occurring at temperatures just above the melting point of the solid and in the absence of solvent. When the heterogeneity associated with the crystalline state is lost, it is to be expected that such reactions will obey rate laws characteristic of homogeneous rate processes. If a mixture of liquid and dissolved product is formed, the reactant concentration will decrease progressively during reaction, though this effect may be offset to a greater or lesser extent by a diminution in reactant amount as a consequence of the chemical change. In contrast, if the reaction yields no condensed product, the reactant concentration will remain unchanged but its quantity will progressively diminish. The kinetics of dehydration of the fused salt, *dl* lithium potassium tartrate monohydrate have been discussed in detail [19].

*dl* and *meso*  $\text{LiKC}_4\text{H}_4\text{O}_6$  hydrates. There were, not unexpectedly, points of similarity in the dehydrations of these similar reactants: *dl*  $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$  [19] and *meso*  $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$  [20]. Both salts melted before dehydration. Rates of water evolution were approximately constant (zero-order kinetics) over the greater part of reaction (although there were also small but irregular variations in rate) and activation energy values were large (330 and 230  $\text{kJ} \cdot \text{mol}^{-1}$  respectively) for the two salts mentioned.

Sodium percarbonate decomposition. This example differs from the other systems described in the present article in that sodium percarbonate ( $\text{Na}_2\text{CO}_3 \cdot 1/2\text{H}_2\text{O}_2$ ) decomposition was studied in the presence and in the absence of the liquid product, water. Reaction,  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2$ , in aqueous solution proceeds more rapidly and at a lower temperature, apparently by a mechanism different from that proceeding in the dry crystalline solid [21, 22].

Comment. Kinetic characteristics of reactions in this class are not adequately or comprehensively described by these three examples. They can only represent 'samples' of the types of behaviour that may be observed. More work is clearly necessary to identify all patterns of reactivity characteristic of reactions in such melts. This information is, however, an essential requirement to enable progress to be made in distinguishing such processes from solid-state reactions, some of which also exhibit zero-order kinetic behaviour [1].

## Evaporation of liquid immobilized in a coherent matrix

Lignite (brown coal) dehydration [23] has been identified as the volatilization of liquid water that is retained in a coherent matrix. No chemical reaction is involved in drying. The liquid that permeates the retaining, semi-rigid carbonaceous non-volatile material evaporates. A water evaporation interface is established that advances inwards from original particle surfaces and water evolution obeys the contracting-volume kinetic expression, in this respect resembling a solid-state rate process.

## No melting during reaction

Reactions described as proceeding without melting are included here to provide comparisons and contrasts with the various classes of melt/liquid participation rate processes described above. The examples of crystallysis reactions, selected from this well-developed subject [1] as being relevant here, were studies in which evidence of melting had been specifically sought and for which the possibility of melting had been excluded only after careful consideration.

Silver malonate decomposes [2] by a nucleation and growth process in which it is concluded that the carboxylate anion group breakdown is catalysed by the silver metal product. Irradiation increases the number of decomposition nuclei that participate in reaction [24]. (Similar metal-catalysed anion decompositions are probably essential steps in the breakdown of various other metal carboxylates [1], for example nickel formate [25].)

Nickel squarate dihydrate decomposition [26] has also been recognized as an interface reaction, possibly involving the intervention of nickel carbonyl as an intermediate. Kinetic analyses were complicated by the evidence that anion ( $C_4O_4^{2-}$ ) breakdown rapidly followed the dehydration step and that release of  $H_2O$  was sensitive to the prevailing water vapour pressure.

Ammonium chromate dissociation [27] (to yield the dichromate, ammonia and water) proceeded in vacuum by a contracting-interface model and the rate was increased by crushing. Reaction was not reversible under the conditions studied, but accumulation of volatile product decreased the rate.

Calcium sulphite hemihydrate dehydration [28] proceeds by a sigmoid yield-time curve and is identified as a solid-state reaction that occurs at a temperature well above the range in which volatile product condensation is possible. Magnitudes of the Arrhenius parameters were closely similar to the values measured for the dehydroxylation of calcium hydroxide [29] in the same temperature range. It is suggested that identical chemical steps, perhaps proton transfer or  $Ca^{2+} \cdots O$  bond rupture, control the rates of both reactions.

Magnesium chloride dihydrate, when heated, reacts [30] to form residual MgO and volatile HCl (+H<sub>2</sub>O) by an advancing interface mechanism. This behaviour contrasts with most dehydrations where the water molecules are released unchanged.

## Reactions of solids involving adsorbed products

The solid-state reactions classified under this heading are believed to proceed without melting, but with the participation of a volatile product retained on reactant surfaces. The examples described are dehydrations that occur at low temperature and at low prevailing H<sub>2</sub>O pressures, where the water product is inherently volatile, but a proportion is adsorbed on the hydrophilic surface and may participate in restructuring of the solid. While such surface bonded H<sub>2</sub>O may be mobile in the adsorbed state, there is no evidence that there was appreciable liquid formation or retention. Such reactions are, therefore, regarded as proceeding in the solid state.

Dehydrations of crystalline hydrates. Studies of the dehydrations of alums [31, 32], Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O [33] and related hydrates [34, 35] have led to the mechanistic proposal that two distinct steps are involved in the overall elimination of water from these crystalline reactants. Water is first evolved from the hydrate structure and this is followed by a phase change of the water depleted reactant to the structure of the product, anhydrous or lower hydrate, as recently discussed for alum dehydrations [32]. Direct investigations were made [31] of the effects of exposure of partially dehydrated alum crystals to water vapour on the kinetics of subsequent water loss. From these observations it was concluded that product H<sub>2</sub>O, temporarily retained within dehydration growth nuclei, promoted the recrystallization step. Amounts of intranuclear water must be much less than those required for salt dissolution: the alums concerned (KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O) are not particularly soluble. Retained intranuclear superficial water may, however, be expected to enhance the mobility of surface ions sufficiently to promote the reorganization essential to transform the reactant structure into that of the product.

## Detection of melting during thermal reactions of solids

Mechanistic discussions in the papers referred to in the above classification provide substantial evidence that the thermal reactions of many, but not all, initially solid reactants involve melting or liquid participation. In several examples, zones of preferred/enhanced reactivity are identified with loss of stability on melting or with catalytic promotion of chemical change by the solid product.

Positive characterization of the role (if any) of liquids in the reaction mechanism for a particular system is sometimes relatively straightforward, but often this is difficult and it may remain unresolved by the investigative techniques available. In the experience of the author, the following experimental methods, singly or in combination, have been identified as being the most useful.

### *Microscopic observations*

The identification of melting by optical or electron microscopy is straightforward if melting occurs before, or during, reaction to yield a single coherent product droplet (that solidifies on cooling) filling the container and sometimes adhering to its walls. Less easily recognized, however, is the occurrence of local, perhaps temporary, melting within restricted intraparticle reaction zones. The difficulties of melt detection are conveniently illustrated by reference to our [8] observations for copper(II) malonate decomposition, shown to occur in a melt (or eutectic) containing ( $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ , malonate and acetate). The internal textures of the reactant crystallites, exposed by crushing after partial decomposition, included rounded cavities ascribed to gas evolution within a fluid matrix, with texture control by surface tension forces, Fig. 1. On commencement of reaction, the original crystallite surfaces are rapidly rendered unreactive by an initial superficial decomposition. This boundary skin inhibits particle sintering so that the identities of the individual reactant crystallites are preserved and the product particles are pseudomorphic with those of the reactant.

Microscopic examinations must, therefore, include observations of the intraparticle textures of reactant crystals, partially decomposed to appropriate and known extents. The generation of rounded features (bubbles, sintering etc.) is evidence that surface free-energy (liquid) forces control textural features resulting in surface area minimisation. Such textures contrast with control by crystallographic characteristics that are expected, through cleavage cracking, to yield crystallites having symmetrical geometric shapes bounded by flat faces meeting at linear edges, together with features oriented at linear or characteristic angular arrays.

### *Thermal measurements*

Because DSC and DTA measurements are based on total heat flux, a melting endotherm can only be recognized as such if it is separate and distinguishable from a thermal response due to a reaction. Again referring to copper(II) malonate [36], no melting endotherm could be recognized during salt decomposition, though by cooling, an exotherm, identified as solidification, was found. Thermal measurements can, therefore, be used to detect melting where behaviour enables the response to be separated from other thermal events.

### *Chemical analysis*

Although not providing direct evidence of a phase change, the identification of an intermediate that is molten at reaction temperature strongly suggests the participation of a liquid [10, 12, 15]. Moreover, progressive changes in reactant composition may be indicative of mobility, melting or eutectic formation [8].

### *Kinetic analysis*

The accurate fit [7] of a set of  $\alpha$ -time data to a rate expression based on a crystallization reaction model [1, 2] does not, of itself, demonstrate that the reaction concerned proceeds in the solid state. The active interface, common to all such reaction models, could, in principle, be a thin layer of liquid.\* For example, the decompositions of  $\text{NH}_4\text{ClO}_4$  [12] and of  $\text{LiKC}_4\text{H}_4\text{O}_6$  [16], both of which appear to involve liquids, have also been shown to obey the Avrami-Erfe'ev equations [1]. It is appropriate, therefore, to consider the possible participation of a liquid or melt in formulating a reaction mechanism, even for a rate process satisfactorily represented by a kinetic expression derived from a solid-state reaction model.

Several of the reactions mentioned above exhibit kinetic characteristics that differ significantly from those applicable to solids. The decomposition of copper(II) malonate [8] is accurately represented almost to completion (yielding copper(I) malonate) by the autocatalytic expression ( $d\alpha/dt = k\alpha$ ), the exponential rate equation. The first part of the  $\alpha$ -time curve for  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  decomposition [10] is approximately sigmoid, but completion is reached only after a distinguishable second rate process. Much more extensive rate investigations

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\* It is relevant to discuss the criteria that can be used here to define the molten state and to consider the size of the minimum accumulation of such material that can be regarded as molten. This type of application of a widely used term to a particular limited situation requires a specialist definition.

In the present context we regard molten reactant as a region of liquid material within which crystal order has been lost. Within this zone of resulting disorder, the regular intracrystalline cohesive forces that lend stability to the constituent components of the solid are absent. In addition, these crystal components attain the ability to move relative to each other and are thereby enabled to adopt the stereochemical configuration that is the most effective precursor to chemical reaction. On melting, order is decreased and mobility is increased.

Within an interface of molecular dimensions it is possible to envisage a monolayer of species interposed between and influenced by the lattice forces of adjacent reactant and product crystals that are, however, unconformable. Material within this layer may be disordered and mobile, and regarded as a two-dimensional liquid. Thicker layers may, however, retain peripheral zones partially structured by the crystals to which they adhere. There must, in such systems, be several or many layers before a thickness of liquid can be regarded as being present.



are required to characterize conclusively the types of kinetic behaviour that are representative of all solid-liquid reactant systems.

Zero-order and first-order rate equations have been widely used in kinetic analyses of reactions of solids. While these equations can represent, to greater or lesser accuracy, rate processes proceeding in the solid state, such behaviour cannot be regarded as the demonstration of a crystallization reaction in the absence of direct supporting evidence. Microscopic observations of textural changes during reactions may provide the most reliable and direct evidence in confirmation of an interpretation of kinetic data concerning the geometry of interface development, or the participation of a phase change in the reaction investigated.

### **Reaction intermediates in thermal reactions**

Whereas investigations of homogeneous reactions often include consideration of, and indeed identification of, participating intermediates, similar studies of solids frequently ignore this possibility [37] and stoichiometric characterizations are, therefore, often incomplete. Reasons for this omission may include the belief that at an advancing interface, the chemical transformation of reactant to product is effectively instantaneous, which implies minuscule concentrations of any intermediates involved. This apparent paucity of successful identifications of intermediates does not encourage other workers to focus effort in this direction.

There is, however, the important alternative view, implicit in the articles cited in the above survey, that significant amounts of qualitatively and quantitatively identifiable intermediates participate in some thermal reactions of solids. It is also considered significant that several of these chemical changes may involve melting at reaction temperature or through eutectic formation.

We regard the characterization of reaction intermediates as an essential part of each stoichiometric investigation and of the formulation of a reaction mechanism. The examples listed below are regarded as providing useful insights into the chemistry of the solid and the solid-liquid reactions mentioned. Methods used for the identifications of intermediates include the analyses of partially-reacted samples by appropriate chemical, spectral, X-ray diffraction and thermal analysis techniques [37].

### **Examples: (Intermediate: Reactant)**

Acetate: Metal malonates. Acetate has been identified as an intermediate/participant/product in the decompositions of several malonates, following hydrogen transfer and/or with the intervention of ketene ( $\text{CH}_2\text{CO}$ ): copper(II) [8],

silver [2], nickel [38] and calcium [39] malonates. (The  $\text{Cu}^{2+}$  salt melts in contrast with the solid-state reaction of the  $\text{Ag}^+$  salt.)

Copper(I): Copper(II) carboxylates.  $\text{Cu}^+$  salts have been identified as intermediates in the decompositions of several copper(II) salts. Cation reduction proceeds to completion in two steps ( $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$ ) and often there is appreciable overlap of the consecutive rate processes: Copper(II) formate [40], oxalate [41], malonate [8], maleate [9], fumarate [9] and squarate [42].

Copper metal is not an effective catalyst for carboxylate group breakdown or hydrogen transfer. Other transition-metal carboxylates undergo stepwise decomposition, sometimes with more widely separated reactions as, for example, in: iron(III) oxalate  $\rightarrow$  iron(II) oxalate  $\rightarrow$  iron and iron oxides [43].

Specific intermediates. Other more specific intermediates have been identified in the following reactions.

$\text{NO}_2\text{ClO}_4$  has been recognized as the highly unstable intermediate that explains unusual features of  $\text{NH}_4\text{ClO}_4$  decomposition [12].

$\text{CrO}_3$  is believed to be the molten intermediate formed during thermal reactions of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  that also involve ammonia oxidation [10].

$[\text{BrCl}_2]^-$  dissolved in liquid bromine explains the low temperature  $\text{KBr} + \text{Cl}_2$  reaction by providing a facile ionic reaction sequence [15].

Lower oxides are formed as intermediates in the decompositions of  $\text{CuC}_4\text{O}_4$  ( $\text{Cu}_2\text{O}$ ) [42] and of  $\text{AgC}_4\text{O}_4$  ( $\text{Ag}_2\text{O}$ ) [44].

$\text{Ni}(\text{CO})_4$  may be an intermediate in  $\text{NiC}_4\text{O}_4$  decomposition [26].

## Comment

Together the studies classified above provide substantial evidence that many thermal reactions of solids involve melting, perhaps local and temporary, or liquid retention. The fluid provides a zone of enhanced chemical reactivity wherein reactions proceed preferentially. This review is intended to draw attention to this important possibility and also to point out that the participation of a melt in such condensed phase reactions is not always easily detected.

Determination of the rate characteristics of solid-state crystallization reactions has been widely accepted as a specialized topic in chemical kinetics [1]. In contrast, very much less is known about the types of rate behaviour that may characterize reactions in solid/liquid and liquid (solvent free) systems. Because this field is so closely related to solid-state chemistry, it is now appropriate to identify criteria that can be used to recognize whether reactions proceeding in the condensed phase do or do not involve the essential participation of a fluid. Such knowledge is important to enable the chemical changes concerned to be correctly classified and permit the formulation of meaningful reaction mechanisms.

The present article also emphasizes the value of a more 'chemical' approach to the elucidation of solid-state reactions. In addition to establishing the stoichiometry of the overall change, the identification of intermediates (where this is possible) provides information essential for the elucidation of the chemical steps through which the reactants are converted into products, the reaction mechanism.

\* \* \*

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**Zusammenfassung** — Es wird ein Überblick über ausgewählte kinetische und mechanistische Untersuchungen der thermischen Reaktionen von ursprünglich festen Substanzen gegeben, wobei die Aussage betont wird, daß einige dieser Reaktionen mit essentieller Teilnahme des Schmelzvorganges verlaufen. Die fraglichen Reaktionen wurden nach Ausmaß und der Rolle eines solchen Schmelzens klassifiziert und die verschiedenen beobachteten Verhaltenstypen unter Bezugnahme auf Feststoffprozesse in Kristallen diskutiert.

Es wird betont, daß das Schmelzen ein wichtiger Fakt bei der theoretischen Beurteilung der Kristallreaktivität ist, da chemische Umsetzungen in der Schmelze oft schneller ablaufen als im festen Zustand. In zahlreichen Berichten über Feststoffreaktionen wird bei der Diskussion des Reaktionsmechanismus die Möglichkeit des Schmelzens nicht immer explizit erwähnt. Vorliegende Arbeit befaßt sich mit Methoden, die sich zum Nachweis des Schmelzens während der Reaktion eignen, eines Verhaltens, das experimentell nicht immer leicht identifiziert werden kann. Ebenso berücksichtigt wird das Erkennen von Reaktionszwischenprodukten, die wichtige Beweise für den Umwandlungsweg liefern, auf dem die Reaktanden zu Reaktionsprodukten umgesetzt werden.

Dieser kurze Überblick macht auf den großen Wert chemischer Beweise bei der Lösung von Reaktionsmechanismen von Feststoffen, einschließlich der Notwendigkeit des Erkennens von Zwischenprodukten und der Rolle der Beteiligung jeglicher Schmelzen oder Flüssigkeiten.