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On a model of thermal internal decomposition of solids

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Abstract

Thermal decomposition reactions of solids connected with the rebuilding of their internal structure are considered. The mechanism of such a decomposition is presented using the example of the dehydration and dehydroxylation reactions. A sealed box containing a compressed gaseous product is proposed as a model of the internal decomposition.

INTRODUCTION

Theoretical models play an important role in the development of science. They facilitate the understanding of the essence of phenomena and processes, and also enable their quantitative mathematical description to be represented. They provide a description of the most important parameters which determine their progress. They may even become the beginning of a new branch of research. Occasionally, models which proved effective in the description of certain phenomena are extended to cover other phenomena which may be quite different from those for which the given model was developed. An example here is the Arrhenius equation derived for chemical reactions in gases and also used in the investigations of reactions of solids although the correctness of such a procedure has been questioned [1].

The thermal decomposition reactions of solids are usually explained using the model of a contracting disc or sphere. This model, however, does not account for the reactions taking place in the reconstruction of the internal structure of the precursor. A general concept of the structural mechanism of these reactions has not yet been developed. Some remarks on this subject are presented in this paper using the example of dehydration and dehydroxylation reactions. They are of a preliminary, qualitative nature. A mathematical model will be developed when more experimental data are available.

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

REACTIONS OF THE REBUILDING OF THE INTERNAL STRUCTURE OF SOLIDS

In the commonly accepted model of thermal decomposition reactions or oxidation reactions of solids, it is assumed that this process takes place at the interface boundary between the reacting substance and the solid products of reaction. The latter form a compact layer around the substrate grain. Diffusion through a layer of products is usually the factor determining the progress of the reaction. A contracting sphere or disc illustrates the course of such a process. Depending on the character of this diffusion the degree of reaction completion as a function of time is expressed by various equations: the parabolic equation, Jander's equation, Ginstling and Brounshtein's equation, etc. It may also be expressed by Sharp and Brindley's equation [2] in which the rate of the interface shifting when the process is limited by a reaction at the boundary has been taken into consideration. On account of the model of the formation and the location of a solid product with respect to the parent substance, it seems correct to refer to those reactions as topochemical reactions. In these reactions the product and the parent substance usually remain in epitaxial relation. However, this is not the only possible topological relationship between the solid product and the precursor.

In solid bodies we can also observe reactions occurring within the bulk of the crystal grain, occasionally even without any visible changes in their outer shape. A solid product structure is formed by the rearrangement of the elements of the precursor's structure, or the structural framework of the parent substance remains preserved after the completion of the process or is only partly damaged. The solid products of these processes are located inside the grains of the precursor, usually remaining in a toptactic relation with respect to their primary structure.

The author has been prompted to distinguish this group of reactions from the results obtained in the investigations of thermal reactions in layer silicates [3] and borates [4]. For these, the term intra-framework or internal reactions has been proposed.

Internal reactions take place through the displacement of atoms, ions or molecules inside the precursor structure. Diffusional transport in solids is slow and it is directional depending on the anisotropy of their internal structure. The results is a multi stage course of reaction and a step-by-step mode of establishing a state of equilibrium. The rate of transport is the factor which usually determines the kinetics of the internal reaction.

The existence of various but defined positions of the product with respect to the precursor is the consequence of the fact that the reaction centres of solids are located within the rigid framework as distinct from delocalized reactions in gases and fluids.

The number of substances undergoing thermal reactions of internal character is considerable, particularly among those whose structure contains elements formed from polymerized coordination polyhedra with strong bonds, such as silicates, borates, phosphates and others.

The internal thermal reactions include, among others the following.

(1) Breaking of some of the bonds with a splitting off and subsequent liberation of molecules of gaseous products (thermal decomposition and dehydroxylation of hydroborates, hydrophosphates, layer silicates, zeolites etc.).

(2) Diffusional displacement of atoms and ions over distances greater than the interatomic intervals. This leads to formation of new structures (polymorphic transformations of reconstructive and order–disorder type of silicates) and redistribution of chemical components leading to their segregation and the synthesis of new compounds (recrystallization, crystallization of amorphous solids and multicomponent glasses, exsolution of solid solutions, liquation or spinoidal effect in glasses).

(3) Incorporation of ions and molecules into the structure, including the formation of new structural layers (ion exchange in silicates, formation of intercalation compounds of graphite, alumina and others).

(4) Change of valency of ions in the structure (oxidation and reduction reactions), sometimes accompanied by change in colour.

In some reactions the reaction front propagates from the edges to the crystal centre, but the elements of the structural framework and the outer shape of the parent substance are preserved; this is the main characteristic feature of the internal process.

The internal thermal decomposition processes will be the subject of further considerations.

MODE OF INTERNAL THERMAL DECOMPOSITION

Reactions proceeding within the bulk volume of crystal grains have been reported for quite a long time. The decomposition of many copper compounds is accompanied by a change in colour within the whole crystal. Intrinsic hydrolysis of $Na_3P_3O \cdot H_2O$ was described in ref. 5. During the decomposition of hydrated phosphates there occurs a peculiar phenomenon connected with the internal decomposition: bubbles filled with the liquid and gaseous reaction products from within the crystal volume [6].

Among the internal thermal decomposition reactions, the most extensively studied are the dehydroxylation and dehydration reactions of layer silicates and borates; the data published on this subject so far as well as the results of the author's investigations [4,7,8] indicate that they have a specific nature.

From the thermal investigations of the borates colemanite $Ca_2B_6(OH)_6 \cdot 2H_2O$, pandermite $Ca_2B_5O_8(OH)_3 \cdot 2H_2O$, caliborite $HKMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O$ and ulexite $NaCaB_5O_6(OH)_6 \cdot 5H_2O$ (Scheme 1), it follows that the thermal decomposition of these substances proceeds through a number of distinguishable stages:

(1) the removal of H_2O molecules bound to a boro-oxygen anion and those coordinating metal cations;

(2) the removal of OH groups and protons from borate anions and the formation of water molecules from them;

(3) the release of water molecules formed as a result of both the above processes, which after they have been formed remain enclosed as intra-framework water or fill the pores in the grains of the parent substance;

(4) the rebuilding of the structure accompanying the removal of water and OH groups;

(5) the amorphization and densification of the structure following dehydration and dehydroxylation. This process is accompanied by slow removal of the remaining water molecules or OH groups preserved in the framework [3,4,9].

Similar phenomena are observed during the decomposition of hydrated silicates [10].

It follows from these data that the thermal decomposition comprises two separate processes, namely (1) formation of free H_2O molecules by the loss of water molecules of hydrates from their structural framework or formation of such molecules from the OH groups (dehydroxylation) and (2) moving of water molecules towards the outside of the framework.

These processes do not necessarily take place simultaneously as was believed. They are often independent processes occurring at different temperatures or coinciding only in part or even proceeding quite independently.

The thermal decomposition of hydrated borates, especially that of colemanite $Ca_2B_6O_8(OH)_6$ is an example of a case in which these processes take place independently at different temperatures. The H_2O molecules formed during the first stage remain confined within the empty places of the framework (voids) or accumulate forming gas bubbles (internal water). With increasing temperature, the pressure of the confined gas molecules increases which results in the breaking of the framework and the liberation of the molecules (internal pressure) [7].

The process of liberation of the gas components occasionally induces an increase in the sample volume due to the exfoliation of the crystals along their cleavage planes etc., the consequence being the secondary porosity of the grains. Sometimes the escape of vapour has a sudden, explosive character (explosive dehydration). The decomposition of colemanite, ulexite and dickite, and the dehydration of vermiculite are examples [9].

The dehydroxylation process consists of the dissociation of some of the OH groups with the separation of protons which join the other OH groups. This is preceded by the state of intensified mobility of protons—the pre-dehydroxylation state. The existence of this stage has been well investi-

$$\underset{\text{ulexite}}{\mathrm{NaCaB_5O_6(OH)_6 \cdot 5H_2O}} \xrightarrow[\text{endo}]{110°\mathrm{C}} \underset{\text{cryst.}}{\mathrm{NaCaB_5O_6(OH)_6}} |0.5\mathrm{H_2O_{int}}| \cdot 3\mathrm{H_2O} + 1.5\mathrm{H_2O}\uparrow \xrightarrow[\text{endo}]{144°\mathrm{C}}$$

$$\underset{\text{cryst.}}{\mathrm{NaCaB_5O_6(OH)_6 \cdot 3H_2O}} + 0.5\mathrm{H_2O}\uparrow \xrightarrow[\text{endo}]{152°\mathrm{C}} \underset{\text{cryst.}}{\mathrm{NaCaB_5O_6(OH)_6 \cdot 0.5H_2O}} + 2.5\mathrm{H_2O}\uparrow \xrightarrow[\text{endo}]{152\text{–}260°\mathrm{C}}$$

$$\left[|\underset{\text{cryst.}}{0.5\mathrm{CaB_2O_4}} + \underset{\text{cryst.}}{0.25\mathrm{Ca_2B_2O_5}} \| \underset{\text{amorph. matrix}}{\mathrm{NaB_{3.7}(OH)_{3.8}}}| \right] + 1.5\mathrm{H_2O}\uparrow \xrightarrow[\text{endo,exo}]{550°\mathrm{C}}$$

$$\left[|\underset{\text{cryst.}}{\mathrm{NaB_3O_5}} \| \underset{\text{amorph. matrix}}{\mathrm{(Ca_2B_2O_4)_{0.5}(Ca_2B_2O_5)_{0.5}(B_2O_3)_{0.25}}}| \right] + 2\mathrm{H_2O}\uparrow \xrightarrow{700°\mathrm{C}}$$

$$\left[|\underset{\text{cryst.}}{\mathrm{NaCaBO_3}} \| \underset{\text{amorph.}}{\mathrm{(B_2O_3)_2}}| \right] \xrightarrow[\text{endo}]{854°\mathrm{C}} \underset{\text{melt}}{\mathrm{NaCaB_5O_9}}$$

Scheme 1. Stages of the thermal decomposition of ulexite. For experimental data, see ref. 8.

gated by various methods in the case of kaolinite. It is accompanied by changes in the electrical conductance and in other physical properties of the substance.

This process and other processes of the formation of the molecules of the gaseous product consist of single events in which single ions or atoms take part. It can be assumed that the atoms participating in the events are located more or less uniformly in the whole volume of the solid or in large regions of it, and that possible deviations from this uniformity are only due to the anisotropy of the location of the OH groups in the body structure. This stage of thermal decomposition in analogous to reactions in homogeneous systems with the difference that it takes place in a solid body which plays the role of a medium in which the atoms or ions participating in the reaction undergo displacements. This medium (matrix) moderates the velocity and also occasionally the directions of the displacements of atoms or ions participating in the unit events. This stage of decomposition should have the character of a reversible reaction; it may be defined as a homogeneous stage of a heterogeneous reaction of internal decomposition.

The subsequent stage can be defined as the stage of phase separation (solid phase and gaseous phase) and the removal of the gaseous products. The newly formed molecules of the gaseous reaction product are located in the empty spaces of the framework; they accumulate along the macro- and micro-defects of the grains, trying to escape outwards. In substances of uniform structure with a small number of defects (usually substances with a high degree of crystallinity), such escape routes are not available and the pressure of the confined gaseous products (internal pressure) increases with temperature. When the pressure exceeds the critical value, the weakest framework bonds burst, e.g. along the cleavage planes, and the enclosed gaseous products are liberated in a sudden way. This is referred to as a heterogeneous stage of the decomposition reaction.

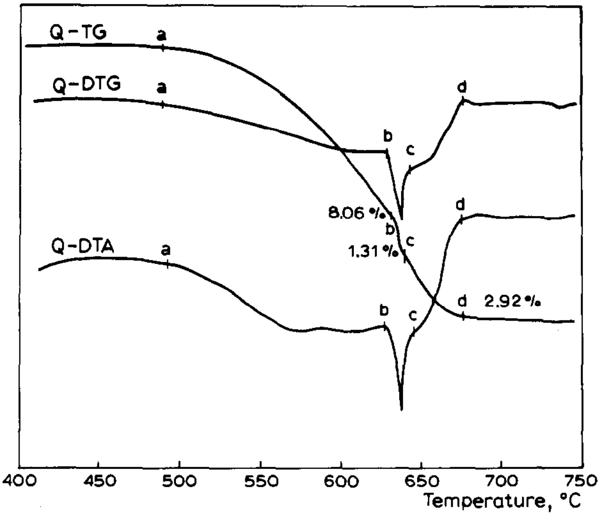

Fig. 1. Q-TG, Q-DTG, and Q-DTA curves of the thermal dehydroxylation of dickite.

The solid matrix remaining exhibits numerous pores which with increasing temperature become closed and scarred over in the sintering process. In this process the residual water molecules left after the reaction and the undecomposed OH groups are trapped (Scheme 1). With further increase in temperature they penetrate by way of diffusion through the matrix outwards. This is the stage of removal of the remaining gaseous components. Its velocity usually diminishes with the thermal densification of the matrix. Both the heterogeneous and the diffusional stage are irreversible.

Constant rate thermal analysis is helpful in determining the stages of internal dehydroxylation mentioned above. In this method the parameter controlling the decomposition and maintaining its constant rate is the pressure of the evolved gas or the loss of the sample mass as in the Q-derivatograph. This will be demonstrated by the example of the Q-derivatograph of dickite which represents a well crystallized polymorphous variety of kaolinite, $Al_4Si_4O_{10}(OH)_8$ (Fig. 1).

The section a-b of the TG and DTG curves corresponds to the stage of the formation of water molecules and their gradual escape through the discontinuities of the crystal lattice, and water evaporation from the surface layers in contact with the atmosphere.

Part of the water, however, becomes confined as intra-framework water and it escapes in an explosive way at 638°C. This is indicated by the vertical section b-c of the TG curve and the peak of the Q-DTG curve.

The section c-d corresponds to the diffusion stage of the removal of residual water from the gradually condensing amorphous anhydrous matrix. Its collapse due to sintering causes a change in the thermal conductivity of the sample, seen in the section c-d on the Q-DTA curve.

Therefore the mode of the removal of the gaseous products changes with the progress of the thermal decomposition. It may have the following stages: (1) escape through the structural discontinuities; (2) explosive outburst; (3) diffusional migration.

For this reason the progress of thermal decomposition determined on the basis of TG cannot often be expressed by a single kinetic equation: its initial and final stages are expressed by different equations. An example of this is the decomposition of kaolinite, as confirmed by the investigations of various authors [10,11].

Depending on the degree of crystallinity and the character of the structural defects the above stages may overlap. In fine grained materials with structures that have many defects, the stage of explosive gas outburst does not occur.

THE "SEALED BOX" AS A MODEL OF INTERNAL DECOMPOSITION

The specific mechanism and progress of the internal decomposition can be visualized if we assume a sealed box as a model of this process.

The homogeneous part of the decomposing substance may be compared with a box with walls that are completely impermeable or only partly permeable to the gaseous decomposition products. Partial permeability may be exhibited by all or only some of the walls (directional permeability).

In the box, there is a definite pressure of the gaseous decomposition products (internal or intra-framework pressure). The walls of the hypothetical box do not, of course, exist in fact: they represent the forces of the diffusional resistance counteracting the migration of the molecules of the gaseous components outwards. They may be so great that the duration time of the reaction will not be long enough for a considerable, measurable part of the gaseous reaction products to leave the inside of the box, and then we say that the walls of the box are impermeable. If the reaction products escape outwards at a low but measurable rate, then the walls are regarded as partly penetrable.

Inside the box there is the internal pressure of the gaseous decomposition products produced by the molecules of the gaseous decomposition products found in the voids of the structural framework (intra-framework pressure) and gathered in the gas bubbles.

The space occupied by the sealed box corresponds approximately to the space of the uniform part of a solid grain, free from structural imperfections, bordered by boundaries of mosaic blocks, dislocations and other discontinuities along which the gaseous products of reaction may escape. These spaces may be termed thermochemical domains. An ideal crystal represents one domain; real crystals are a set of domains.

Thermal decomposition begins with thermal dissociation and formation of molecules of the gaseous products of the reaction. If the domains are large enough and satisfy the conditions of a sealed box, the molecules remain there and are located in the voids of the intra-framework, some of them forming and filling the pores. When the internal pressure exceeds the tensile strength of the walls of the sealed box, which may be assumed to be a function of the weakest chemical bonds, the sealed box is torn open and the gases are liberated. This may have an explosive character and cause the disintegration or exfoliation of solid grains.

Usually the formation stage of the molecules of the gaseous component is already accompanied by some loss of sample mass, increasing with temperature increase. This is caused by the volatilization of the gaseous component from the surface layers and cracks and other discontinuities of the internal structure that are in direct contact with the surrounding atmosphere; and they escape from such a depth that the diffusion resistance is too small there to prevent their escape.

In the case where the volumes of the domains are too small to function as a sealed box, the thermal dissociation and escape of the gaseous decomposition products occur simultaneously. Then it should be easy to describe the reaction kinetics on the basis of the rate of mass losses using well-known equations such as the Arrhenius equation. In this case, the decomposition becomes close to that which occurs in a homogeneous system. This takes place when the substance is very finely grained or has a structure that is full of defects.

There are also numerous possible instances of intermediate character, depending on the distribution of the size of the domains in the decomposing substance. An example here is the decomposition of kaolinite [10,11].

The liberation of molecules of the gaseous products from outside the regions behaving like a sealed box depends on their partial pressure in the surrounding atmosphere. The tearing open of these regions under the influence of internal pressure, however, may be hampered by very high pressures, comparable to the pressure of these gases at the decomposition temperature.

The presented "sealed box" model of internal decomposition accounts for the discrepancies in the results obtained in the investigations of the kinetics of samples of the same substances but of various origins observed by many authors, as well as the effect of the grain size or structural factors on the values of the kinetic parameters.

The model also explains why it is difficult to present the decomposition kinetics of solids in the form of a single function of decomposition degree versus time, which would be characteristic not only for the given sample of the substance but valid for each instance.

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