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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60^{th} birthday

EXPLOSIVE THERMAL DEHYDRATION OF SOLIDS

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Selected examples of dehydration, accompanied by violent disintegration or bloating of the decomposing solid substance are presented. This phenomenon has been explained as a specific case of internal decomposition of solids. A sealed box with compressed gaseous products is proposed as a model of the process. The practical applications of this phenomenon are discussed.

Thermal dehydration and dehydroxylation of inorganic compounds and minerals have been the subject of interest and investigations for centuries. In spite of this their mechanisms have not been sufficiently explained as yet. Of particular interest are the processes of dehydration that are accompanied by a rapid increase of the volume of sample or even its disintegration. Some of these processes such as the thermal bloating of vermiculite and certain volcanice glasses have found practical application in the production of heat-insulating porous materials. They are obtained by an appropriate heat treatment of these minerals.

The mechanisms of dehydration and dehydroxylation taking an explosive course cannot be explained on the basis of the traditional concept of topochemical reactions and models of thermal decomposition of solids developed so far.

The aim of the present study is to discuss some specific features of explosive dehydration and dehydroxylation on the basis of the author's investigations and data from current publications of other researchers. A concept for a model explaining the structural mechanism of thermal decomposition of solids, including the processes of explosive character is proposed.

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Internal thermal dehydroxylation

The kinetics of heterogenous reactions is now oriented chiefly toward the investigation of reactions localized on the surface of solid. This refers in particular to the reaction of thermal decomposition. The mathematical equations developed so far are concerned with decomposition taking place on the crystal faces where the solid products form a layer, separated by the interface boundary from the decomposing substance. The contracting sphere or disc are models of the reaction.

It is known, however, that in solid bodies processes also occur in the bulk of the reacting solid substance. Here belong the phase transformations such as recrystallization and crystallization of amorphous solids. The mechanisms of these processes have become the object of numerous and extensive studies and their theory is the subject of several publications.

The data concerning the decomposition of many solids have revealed that some of these processes proceed also in the bulk of grain of the reacting solid substance. Here belong also the reactions of ion exchange and the intercalation processes. Some oxidation and reduction processes have internal character too.

These facts prompted the author to put forward a proposal to use the localization of the reaction and mutual topological and structural relationship between the parent substance and the solid product of the process as a criterion for classification of the chemical reactions of solids [1, 2]. According to this criterion two types of the chemical reactions in solid bodies can be distinguished:

1. topochemical surface localized reactions,

2. internal or intracrystal reactions.

A characteristic feature of the internal reactions is the evident interrelation between the structure of the parent substance (precursor) and the structure of the solid product. In case of reactions proceeding by rearrangement of the structural framework of the precursor (intraframework reactions) the structure of the solid product contains elements of this framework, or even the precursor framework is retained or only partially destroyed. The thermal decomposition of many silicates, phosphates and borates are examples of such intraframework reaction.

In the case of surface localized reactions the solid product and substrate are in epitaxial relation. The consequence of the internal reaction is a topotactic relation between the structure of the precursor (matrix) and that of the solid product.

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

The division of the reactions of solids into surface localized and those localized in the bulk of crystals has been also used by Prodan in his recent studies [3, 4]. As a criterion for this distinction he assumed the mode of the distribution of the reaction centres or of the nuclei of a new phase visible in an optical or an electron microscope. He pointed out the fact that the reaction centres and the nuclei can be distributed inside the crystals in a uniform way (homogenous reaction) or grouped in some definite areas or crystallographic directions (heterogeneous reaction). The initial stage of the reaction, especially prereaction stage of breaking some of the bonds has often the character of a homogeneous process. The latter reaction stages may have the heterogeneous course. Under favourable conditions of the course of a reaction localized in the bulk may even change into that of a surface localized reaction [4].

The phenomenon of internal decomposition of solids has been observed for quite a long time. It had been observed e. g. that the decomposition of a number of copper compounds $\{Cu(OH)_2$, $Cu(HCOO)_2$, $3Cu(OH)_2 \cdot Cu(NO_2)_2\}$ accompanied by a change in colour, proceeds in such a way that the colour of the compound changes simultaneously in the whole crystal.

An interesting example of internal process can be found in the work by Thilo and Wallis [5] on the thermal decomposition of sodium cyclotriphosphate monohydrate ($Na_3P_3O_9 \cdot H_2O$). In the structure of this compound there occur phosphate rings each accompanied by one water molecule. In the course of heating the process termed intrinsic hydrolysis takes place. The anion ring is broken, changing into a chain with two OH groups obtained from the water molecule. No gaseous or liquid products are formed in this process. In the next stage water is removed from the OH groups and the newly formed anhydride retains the basic anion structure of its precursor.

An intersting phenomenon connected with the process of internal decomposition is the formation of bubbles in the bulk crystal, filled with liquid and gaseous reaction products, which occurs in the course of decomposition of hydrated acid phosphates [3]. An example is the reaction:

$$5MnHPO_4 \cdot 3H_2O \rightarrow Mn_5(HPO_4)_2\,(PO_4)_2 \cdot 4H_2O + H_3PO_4 + 11H_2O$$

Part of the water together with the phosphoric acid form inclusions in the grains of the reaction products with $Mn_5(HPO_4)_2(PO_4)_2 \cdot 4H_2O$ crystals precipitating occasionally into them. The remaining water escapes outside through the domain boundaries and other defects [4].

Worzala and Jost [6] carried out systematic investigations of the thermal dehydration of $Pb_2P_4O_{12} \cdot 4H_2O$ and $Pb(H_2PO_4)_2$. The decomposition of these compounds runs through the formation of a number of intermediate compounds. They lead to the formation of the same final product, i. e. the polyphosphate $\{Pb(PO_3)_2\}_x$. The reactions are taking place throughout the entire volume of the crystal. There exists a definite and reproducible orientation relation between the unit cells of the starting compound and the solid product. According to these authors the observed orientation relation of the solid substrate and product structures is attributed to the fact that whole pieces of the structural elements (chains, layers etc.) are displaced from the structure of the substrate into the structure of the product. On account of both geometrical and genetic relations between these structure they have proposed the term topotactic reactions for reactions of this type.

Explosive dehydratation phenomena

Calcium borates

There are known several cases of the decomposition of hydrated calcium borates accompanied by rapid escape of water vapour and bloating or even explosive disintegration of the sample. These phenomena are more or less independent of the heating rate of the sample even if it is heated at a standard rate of 10–5 deg/min or much more slowly. Fast heating enhances this effect.

A particularly strong effect of explosive dehydration connected with desintegration and sputtering of the sample can be observed when the mineral colemanite is heated. This phenomenon has been studied by many authors, however their opinions about its mechanism were divergent. Our investigations by means of thermal methods, X-ray analysis, IR and electron or optical microscopy [7] prompted us to assume the following course of the process.

Colemanite $\{Ca_2B_6O_8(OH)_6 \cdot 2H_2O\}$ structure consists of infinite boronoxygen chains parallel to the *a* axis. Each chain is built of units combining two BO_4 tetrahedra and a ring $\{B_3O_4(OH)_3\}^{2-}$. The chains are linked to each other by Ca^{2+} ions to form sheets extending parallel to 010. A system of hydrogen bonds involving the hydroxyl group of the chains and water molecules ties the sheets together.

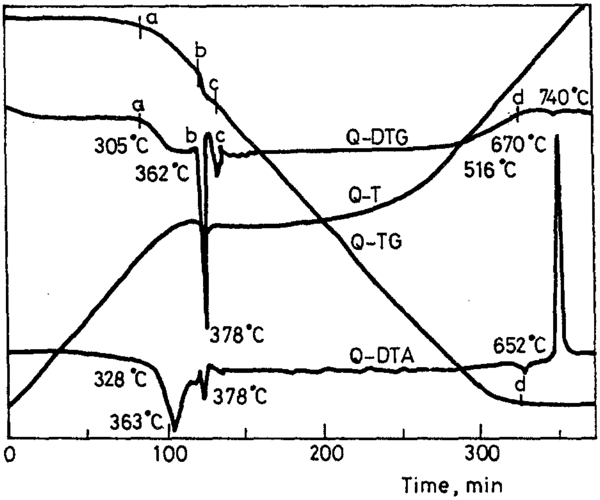

Fig. 1 Q-T, Q-DTA, Q-TG and Q-DTG of colemanite [7]

The decomposition of colemanite is an example of the multi-stage thermal decomposition (Fig. 1). It begins with the splitting-off of the OH groups and the formation of H_2O molecules. Next, the bonds of molcular water with the borate rings become broken. Each process takes place independently, hence the first endothermic peak of colemanite is a double one. The molecular water is bound by relatively strong hydrogen bonds within the borate framework. This accounts for the relatively high temperature at which this process occurs, higher than that of the splitting-off of the OH groups.

In spite of these changes the essential framework of the colemanite structure is retained. At 360° the bonds of the H_2O molecules become broken. A small part of the newly formed water molecules escapes in the course of these processes. The resulting loss of the sample mass is about 3 wt% and it proceeds gradually.

At the temperature 375° there occurs a violent outburst of water vapour (1.5 wt%) resulting in the sputtering and disintegration of the sample. The material left back is X-ray amorphous. In the scanning electron microscope bubbles can be seen in which the released water molecules were gathered

(Fig. 2). When the pressure of the water vapour accumulated in the bubbles exceeds the critical value the mineral grain breaks apart and the vapour is violently released.

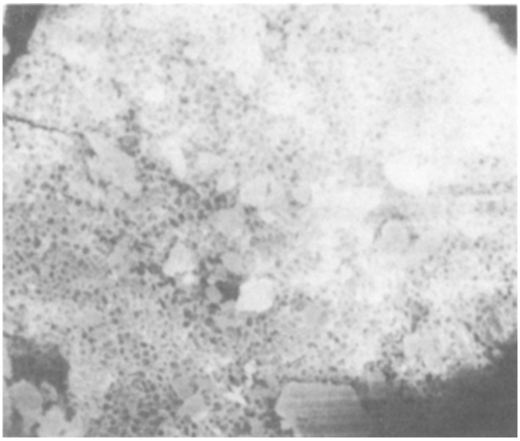

Fig. 2 Scanning electron micrograph showing the water bubbles in the colemanite heated at 400°C

The presented data show that in case of an internal endothermic process, e. g. the decomposition of colemanite, which comprises the formation of gaseous molecules (in this case H_2O) and their release from the inside of the solid substrate (an endothermal process involving a loss of the sample mass) may proceed at various temperatures.

The water molecules formed from the OH groups and from H_2O molecules split off the borate framework, become localized in the voids between the chains, and accumulate at defects of the structure eventually forming the bubbles which were mentioned above. This water can be termed intrastructure or internal (H_2O int.). The water in the bubbles (1.5 wt%) becomes released when its pressure breaks the borate crystal.

The remaining water molecules (about 20 wt%) are released gradually up to the temperature 600°. These are individual molecules trapped inside the framework. Their release is hampered by the diffusional resistance of the solid matrix.

The process of colemanite decomposition can be described as follows:

$$\longrightarrow \underset{\text{cryst.}}{Ca_2B_6O_8(OH)_6\cdot 2H_2O} \xrightarrow{340^\circ} \underset{\text{cryst.}}{Ca_2B_6O_{11}\cdot 2H_2O\ |3H_2O_{int.}|} \xrightarrow{363^\circ}$$

$$\underset{\text{cryst.}}{Ca_2B_6O_{11}\ |5H_2O_{int.}|} \xrightarrow[\text{expl.}]{378^\circ} \underset{\text{cryst.}}{Ca_2B_6O_{11}\ |4.5H_2O_{int.}|} + 0.5H_2O \xrightarrow{378-650^\circ}$$

$$\uparrow \underset{\text{amorph.}}{Ca_2B_6O_{11} + 4.5H_2O} \uparrow$$

The decomposition of pandermite $Ca_2B_5O_8(OH)_3\cdot 2H_2O$, a borate with a layer structure, takes also a multi-stage course. The process begins with the removal of water molecules from the structure. It has two stages. In the range 200° to 380° a slow dehydration takes place with a rapid escape of the portion of the water at 284° visible as the Q-DTA and Q-DTG peaks. It causes the exfoliation of pandermite crystals according to their cleavage.

Breaking of the bonds of molecular water with borate rings causes the rearrangement of the framework and at 400° the peak of recrystallization appears. It facilitates the removal of the water molecules.

The next stage of dehydration is violent and accompanied by splitting of the crystals into thin lamellae (Fig. 3).

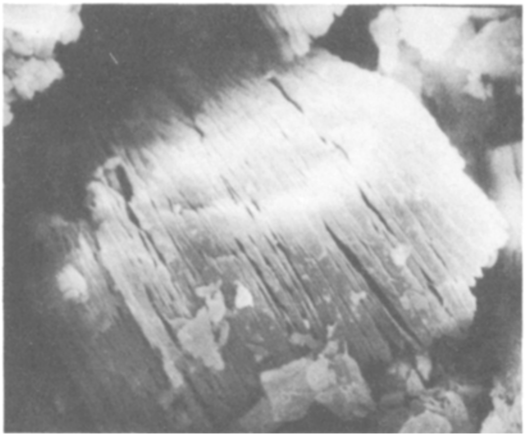

Fig. 3 Scanning electron micrograph of the pandermite exfoliated at the 438°C

At higher temperatures OH groups are removed. The dehydroxylation causes the damage of the internal structure of the mineral, which then becomes amorphous. The newly formed amorphous substance shows the spherical pores in which H_2O molecules were accumulated. It contains further a number of confined OH groups left, which gradually escape until the temperature reaches 580°.

The course of these processes is as follows:

$$2\,|\underset{\text{cryst. I}}{Ca_2B_5O_8(OH)_3\,2H_2O}|\xrightarrow{200-380^{\circ}}2\,|\underset{\text{cryst. I}}{Ca_2B_5O_8(OH)_3|H_2O_{int.}|}\,|+2H_2O\uparrow$$

$$\xrightarrow[\text{exfol.}]{284^{\circ}}2\,|\underset{\text{cryst. I}}{Ca_2B_5O_8(OH)_3\;|0.25H_2O_{int.}||}\;+1.5H_2O\uparrow\xrightarrow[\text{exfol.}]{438^{\circ}}$$

$$2\,|\underset{\text{cryst. II}}{Ca_2B_5O_8(OH)_3|}+0.5H_2O\uparrow.\xrightarrow{438-580^{\circ}}\underset{\text{amorph.}}{Ca_4B_{10}O_{19}}+3H_2O\uparrow$$

Layer silicates

The structural mechanism of thermal reactions of layer silicates allows to include a number of them among typical processes of internal structure rebuilding. Their dehydroxylation is also a process of the internal nature.

The structural mechanism and the kinetics of dehydroxylation of kaolinite and its polytypes have been thoroughly investigated [1, 8].

The process begins with an increase in the mobility of the protons and their displacement. It is detectable above 300° and it proceeds in a homogeneous way through the entire volume of the crystal. The loss of mass due to the escape of water formed from the OH groups begins at a somewhat higher temperature. The studies of numerous authors on the dehydroxylation of kaolinite carried out under various experimental conditions have revelated that at a decomposition degree exceeding 50–70% the kinetics of the process changes.

The first step of dehydration is the release of newly formed water molecules through the interlayer space. The final step consists of a gradual removal of the remaining water molecules confined in the voids of the colapsed, X-ray amorphous structure of metakaolinite and escape of water from the preserved OH groups coordinating Al^{3+}. The longer the time or temperature interval of the second dehydration stage, the larger are the plate crystals of kaolinite and the higher is the degree of their structure perfection. In accordance with this the DTG and DTA peaks of dehydration have more or less narrow shape or are double. At the peak temperature both processes run simultaneously but the first one is still predominant.

The dehydration is accompanied by a considerable decrease in density of the crystals as they become micropours.

Double DTA peaks of kaolinite (Keokuk kaolinite), dickite and nacrite which are distinguished by their perfect crystallinity become single when the grain size of these minerals is less than 1 μm.

The double DTA peak of dehydroxylation or the broadening of the single peak is the consequence of the separation of the splitting of OH groups and H_2O formation stage from that of the release of the H_2O molecules. In fine-grained clay minerals they are not so distinctly separated from each other as for the well shaped crystals of colemanite and overlap to a smaller or greater extent. Some of the water molecules escape immediately after they have been formed through the cracks and structural discontinuities of kaolinites.

The second DTA and DTG peak is accompanied by a sharp peak on the dilatometric TD and DTD curves [1]. It is caused by a rapid separation of the layers in the structure and the relase of water vapour escaping through the open interlayer spaces.

The finer the kaolinite and the greater the defectiveness of its structure, the more pronounced is the overlapping of the stages of water molecule formation and its release, consequently the DTA and DTG peaks become single and narrower. The bloating effect observed on the dilatometric curves does not occur here.

The rapid increase in volume caused by the delamination of the layers under the action of the evolving vapour is a phenomenon often observed among layer silicates.

In Schomburg's catalogue of dilatometric curves [9] one can find chlorites characterized by a rapid increase in volume accompanying dehydroxylation.

A great increase in volume accompanies the dehydroxylation of muscovite. This phenomenon becomes very distinct when the mica lamellae are large enough (Fig. 4).

The heating of vermiculite causes strong delamination and bloating of its plates so that it becomes transformed into a porous material valuable because of its various applications. It occurs only when its lamellae are sufficiently large and their internal structure well ordered.

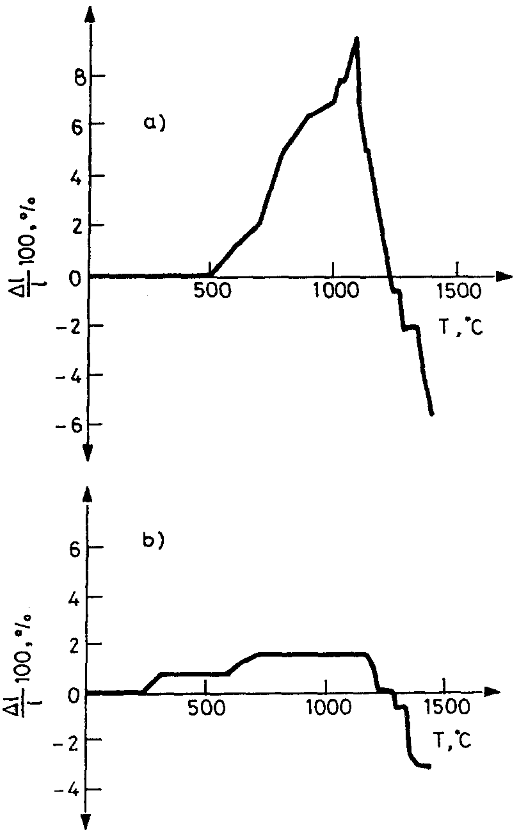

Fig. 4 Change of the dimension of samples of muscovite with temperature, measured in the heating microscope, rate of heating 5°C per minute, (*a*) fraction 250–150 μm, (*b*) fraction 100–70 μm. Fractions have been separated from weathered granite

The interlayer space of the vermiculite structure is occupied by water molecules. Part of them form a hydration shell around exchangeable Mg^{2+} cations. The rest of water is bound less tightly and is known to vary in amount according to the external humidity. During heating this water is first to be removed. It migrates relatively easily along the interlayer space. This stage of dehydration follows first order kinetics. Its activation energy is low (51.48 kJ/mol) and is close to the latent heat of evaporation of water [10].

Loss of unbound water leads to the collapse of the interlayer space. It makes the hydration envelope of Mg^{2+} ions to be flat, each Mg^{2+} being surrounded by only four water molecules.

It was found that the increase of the external water vapour pressure prevents the collapse of structure and therefore accelerates the loss of the unbound water [10].

Water trapped in the collapsed structure needs larger activation energy and higher temperature to escape. Its removal is accompanied by intensive exfoliation and bloating of the mineral plates.

Sealed box model of the internal decomposition

The widely accepted model of a topochemical decomposition reaction is the model of a contraction disc or sphere. However, this model does not explain the phenomenon of internal decomposition, in particular when it proceeds in an explosive way with disintegration or formation of bloated porous solid product.

The course of the internal decomposition process may be described by the model of sealed box. In this model, the walls of the box are almost impermeable to the gaseous products of the process. Some of them may allow molecules to pass through at a small but measurable rate–directional permeability. Inside the box there exists a definite pressure of the gaseous decomposition products–internal or intraframework pressure.

Hypothetical walls of the box represent the forces which resist diffusion.They may be so high that the duration of the internal decomposition reaction is not long enough for a detectable part of the gaseous product to leave the box - unpermeable walls.

The gas molecules may escape outwards at low, although measurable rate - partly permeable walls.

The pressure inside the box (internal pressure) is the pressure of the free gas molecules occupiyng voids of the framework (intraframework pressure) and accumulated in gas bubbles.

The closed box volume corresponds to the mean volume of thermal domains of the decomposing solid. A thermal domain represents a uniform part of the structure of the solid, free of any discontinuities, bordered by boundaries of mosaic blocks, dislocations and other imperfections, along which gaseous products of reaction can escape [1]. An ideal crystal represents one domain, real crystals are a set of domains.

The internal pressure affects the equilibrium state of the decomposition reaction, specially the free molecule formation stage i. e. its temperature and rate relation. On the other hand this influence depends on the kinetic reversibility of the reaction. As a consequence of the very high pressure exhibited by water vapour and other gases at elevated temperatures, internal decomposition reactions are little sensitive to changes in the pressure of the gaseous decomposition products applied in the normal thermal analysis procedure. It is one of the specific features distinguishing the reactions of the internal mechanism.

Thermal decomposition begins with a dissociation reaction within the domains and the formation of free molecules of water or other gaseous components. This process is reversible and may be regarded as proceeding in a homogeneous way, the inside the structure of the decomposing solid being a chemical reaction medium. If the domains are big enough to behave as sealed box, the gas molecules become trapped in the framework voids. Part of them form and fill the bubbles and pores. When the internal pressure of the trapped gases exceeds the tensile strength of the box walls, being the function of the strength of the weakest bonds of the crystal structure, disruption of the box and release of the gas occur. It may be accompanied by exfoliation or disintegration of the grains by the ejected gas. This stage of decomposition is obviously an irrevesible process.

The rest of OH groups, water and other gaseous products remain within the framework of the solid decomposition products, independently of the fact whether it has retained its crystalline character or is X-ray amorphous. These intraframework gas molecules are subsequently released slowly with the lapse of time or temperature increase, in accordance with the model of the partly permeable box. This process is controlled by the rate of molecular diffusion through the framework.

Internal structure rearrangement and recrystallization causes the formation of new interface boundaries and facilitate the escape of gases, which brings the slow dehydration stage to an end (Fig. 1 point *d*).

The stage of formation of the gaseous products may be accompanied by a little loss of the sample mass, which increases slowly with temperature. The gas molecules escape from the surface layers and through cracks or other discontinuities being in direct contact with surrounding, so that their loss cannot be stopped by the diffusion resistance.

There are cases in which the decomposition process is at first localized on the surface and next it changes into an internal process. The change of localization appears when the physico-chemical conditions of decomposition change.

Constant-rate thermal analysis is helpful in determining stages of internal decomposition, mentioned above. In this method the parameters controlling the decomposition and maintaining its constant rate are the pressure of the evolved gas or the loss of the sample mass as it is in the Q-Derivatograph [11].

From the Q-DTG, Q-DTA and Q-T curves (Fig. 1) it is possible to determine the following steps of the process:

1. formation of intraframework water molecules and escape of the molecules from the surface layers of the crystal (section *a-b*)

2. rapid ejection of gas, destruction of solid (section *b-c*, and plateau or kick of the Q-T curve)

3. slow release of molecules enclosed in the solid product of decomposition (section *c-d*).

In the case when grains of the decomposing substance are very small, usually smaller than 1 μm, or are strongly defect so that the thermal domains are of minute volume, no diffusion barrier which will keep the gas inside exists. The *a-b* and *c-d* stages proceed then simultaneously and the process is limited only by the rate of dissociation and on the DTA and DTG curves a single peak appears. This decomposition proceeds analogously to the reactions in homogeneous liquid or gaseous systems and it may be described by the kinetic equations of such reactions. Dehydroxylation of fine, defective kaolinite of poor crystallinity, may be an example here [1].

The explosive dehydration, at normal heating rate, occurs only when the substance is sufficiently coarse-grained. The explosion of fine crystals can be induced by very rapid heating (flash heating [12, 13]) so that the decomposition rate exceeds that of water volatilization.

The kinetics of the above distinguished decomposition stages can be formally described by the well known equations for the processes of diffusion, nucleation and others. This refers in particular to the first and the last stage of decomposition. They proceed through molecular processes in homogeneous medium inside the structure of a solid body and within the given thermal domain, similar to that of homogenous processes in liquids and gases. This accounts for the fact that the functions derived from the theory of kinetics of homogenous reactions may be in some cases successfully applied for the quantitative description of reactions in the solid phase or its selected stages. However, the nature of these processes and their physical meaning are different from those commonly accepted.

Application of explosive dehydration in the industrial practice

As it has been already mentioned, internal dehydration and dehydroxylation make possible the production of porous vermiculite. By rapid heating of the volcanic glass containing water in its structure (perlite) an expanded porous material of multiple application is obtained.

Due to the specific mechanism of internal decomposition it is possible by appriopriate rapid heating of various substances to reach the state in which the water vapour or other gases inside the grains of the decomposing substance are generated faster than they are able to escape, which leads to disintegration of the material or a deep change in its consistence (exfoliation).

This phenomenon has found practical application and a suitable technique of rapid heating and cooling of materials, called flash calcination, has been developed by Davis and others [12, 13]. It allows to obtain calcined kaolin of new functional qualities [12]. Fine powdered colemanite, dispersed by flash calcination allows to leach boric acid from it by water saturated with CO_2, instead of using strong acid solution [13].

The above data and the concept of internal decomposition may become a theoretical basis for the development of modern technologies creating possibilities for its new practical applications.

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References

1 L. Stoch, J. Thermal Anal., 29 (1984) 919.
2 L. Stoch, Thermochim. Acta, 110 (1987) 359.
3 E. A. Prodan, Reactivity of Solids, 4 (1988) 363.
4 E. A. Prodan, Topokhimiya Kristallov (Topochemistry of Crystals), Nauka i Tekhnika, Minsk 1990.
5 E. Thilo and M. Wallis, Chem. Ber., 86 (1953) 1213.
6 H. Worzala and K. H. Jost, Advanced Solid State Chemistry, Proc. 2nd Int. Symposium on Solid State Chemistry, Pardubice 1989, Elsevier, Amsterdam (1989) p. 52.
7 I. Waclawska, L. Stoch, J. Paulik and F. Paulik, Thermochim. Acta, 126 (1988) 307.
8 L. Stoch and I. Waclawska, J. Thermal Anal., 20 (1981) 291.
9 J. Schomburg, 9th Conference on Clay Mineralogy and Petrology, Zvolen 1982, Univerzita Karova, Praha (1984) p. 159.
10 R. Sh. Mikhali, N. H. Guindy and S. Hanafi, J. Appl. Chem., 70 (1970) 346.
11 J. Paulik, F. Paulik and M. Arnold, J. Thermal Anal. 32 (1987) 301.
12 D. Bridson, T. W. Davies and D. P. Harrison, Clays and Clay Min., 33 (1985) 258.
13 T. W. Davies, S. Colak and R. M. Hooper, 18th Australaian Chemical Engineering conf., Auckland, New Zealand 1990, V. 2, p. 1164.

Zusammenfassung — Es werden ausgewählte Beispiele für die Dehydratation, begleitet von heftiger Zersetzung oder Aufblähen der zersetzten Feststoffe dargelegt. Diese Erscheinung wird als ein Spezialfall der internen Zersetzung von Feststoffen beschrieben. Als Modell für diesen Prozeß wird ein abgeschlossener Behälter mit unter Druck stehenden gasförmigen Produkten vorgeschlagen. Praktische Anwendungen dieser Erscheinung werden diskutiert.