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INTERNAL THERMAL REACTIONS IN MINERALS AND MATERIALS

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Rebuilding reactions of the internal structure of minerals and their artificial analogues are considered. Solid products of these reactions are formed within the structure of the parent substance. This factor determines the course of the reactions and product formation. The mechanism of internal thermal dissociation and rebuilding reactions of internal structure connected with segregation of chemical components and their redistribution (crystallization of multicomponent amorphous solids) is discussed. The internal pressure of gaseous decomposition products and rate of diffusion of chemical components are critical factors influencing kinetics of these processes. Diffusional mass transfer during internal structure rebuilding reactions is directed by acid–base interaction of the parent-structure components; this determines the stages of the reaction pathway.

Keywords: thermochemistry, topotactic reactions, phase transformations, thermal dissociation, structure rebuilding, structural mechanism

General problems and terminology

In minerals and their artificial analogues we can observe processes occurring within the bulk of the crystal grain. The solid products of these processes are formed inside the structural framework of the parent substance (precursor) by rearrangement of the elements of this structure. Some proceed without any visible change of the outer form of the parent crystal (pseudomorphism of minerals).

Such reactions belong to *mineral transformation* processes. When a close relationship between the crystal structure of precursor and product (structural inheritance) exists, the term *topotactic reaction* is used.

In solid-state physics and chemistry, the term *phase transition* is used to include structural transitions without change of chemical composition (polymorphic transformations) and formation of new phases of different chemical composition (e.g. enstatite from sepiolite). Amongst such solid-state processes, there are some which have the characteristics of chemical reactions (dissociation, synthesis of new compounds, reduction and oxidation...); these are similar to

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reactions in liquids or gases but proceed within the rigid structure of a crystalline or amorphous solid. Chemical components of the primary structure are the reaction substrates and the solid product is formed within the precursor grain.

The author has distinguished this group of reactions as *internal reactions* [1, 2].

Internal reactions take place through the 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. As a consequence of the specificity of the reaction medium, chemical processes follow particular patterns. The result is a distinctly multi-stage course of many internal reactions and step-by-step mode of establishing an equilibrium state.

The number of substances undergoing thermal reactions of internal character is considerable, particularly among those whose structure comprises polymerized coordination polyhedra with strong chemical bonds (inorganic polymers), such as silicates, borates, phosphates and glasses.

Internal reactions include:

1. Breaking of some bonds with splitting and subsequent liberation of molecules of some components (decomposition, dehydration, dehydroxylation).
2. Diffusional displacement of atoms and ions over distances greater than the crystal lattice parameters, leading to redistribution of chemical components and synthesis of new compounds (recrystallization, crystallization of amorphous solids, exsolution of solid solutions, phase segregation in multicomponent glasses).
3. Incorporation of ions and molecules in the parent structure (ion exchange causing reconstruction of the primary phase, formation of intercalation compounds of graphite, alumina etc.).
4. Change of ionic valency within the structure (oxidation and reduction reactions) sometimes manifested by change in colour.

Reactions which take place in the interlayer space of layer-silicates and in zeolite channels, often involving organic molecules, do not belong to the internal reactions considered here, as they no not change the host structure.

In internal reactions each individual solid grain can be considered as a separate thermodynamic system: closed (crystallization) or open and exchanging matter with surrounding gaseous or liquid phases (thermal dissociation, metasomatic transformation of minerals). In the latter the reaction front propagates slowly from the edges to the centre of the grain, but part of the structural framework and the outer shape of the parent substance are preserved, which is a feature that characterizes an internal reaction. The above considerations indicate that localization of reaction and the topological relationship between parent substance and solid product are the significant features distinguishing reaction in solids.

When taking the localization factor as a criterion, reactions can be divided into (i) *topochemical reactions* and (ii) internal reactions [3].

The term topochemical reactions is used with reference to processes occurring on the surface of the parent substance. The solid product of the reaction forms the outer layer, separated from the parent substance by a distinct interphase boundary. The product layer may remain in an epitaxial relationship with the parent substance. Solid products of internal reactions usually remain in a topotactic relationship with respect to the crystal structure of the parent substance.

The mode of distribution of reaction centres visible in optical or electron microscopy has been used by Prodan as a criterion for division of thermal reactions: reactions in which centres are within the bulk of crystals, are termed delocalized homogeneous reactions, but surface reactions are classed as localized heterogeneous reactions [4]. This division is based on the macroscopic distribution of reaction substrates and products. On the other hand, the specificity of a reaction in a solid medium is the fact that at least part of the atoms participating in the chemical process initially occupy strictly localized positions in the crystal lattice; this localization determines to a significant degree their reaction ability. The different participation of outer and inner OH groups of kaolinite structural layers in the dehydroxylation process is an example.

From the point of view of their atomic mechanism internal reactions are localized chemical processes depending on mobility of reactants, modified by the solid matrix with respect to rate and/or direction of the movements.

It can be assumed that at the beginning of thermal decomposition reactions, molecules of gaseous products form initially from single ions or atoms. Participating atoms are distributed more or less uniformly and deviations from uniformity only arise from anisotropy of the body structure. This very early stage of thermal decomposition is analogous to reactions in homogeneous systems, including their reversibility, and may be termed a homogeneous stage of the heterogeneous reaction of internal decomposition [5].

Solid-state chemistry concentrates mainly on interface processes. There is a lack of systematic investigation of these reactions. However, much relevant data can be found in papers on thermal reactions.

Thermal reactions proceeding within the bulk of crystal grains are well known. Some of them are accompanied by spectacular phenomena. Dehydration of certain copper compounds is accompanied by a colour change within the whole crystal. During the decomposition of hydrated phosphates, bubbles filled with the liquid and gaseous reaction products are formed within the crystal volume [4]. In the course of heating $Na_3P_3O_9{\cdot}H_2O$ intrinsic hydrolysis takes place; internal phosphate structure rebuilding is accompanied by formation of OH^- groups from H_2O molecules. No gaseous or liquid products appear in this process [6].

Structural mechanisms involved in the transformation of layer-silicates in hydrothermal conditions have been the subject of systematic study by Frank-Kamenetskij *et al.* [7]. Most of these are internal reactions with a topotactic relationship between product and parent structure. It has been proved that transformation of muscovite into kaolinite:

$$2\{KAl_2[AlSi_3O_{10}](OH)_2\} + 2H^+ + 3H_2O = 1.5\{Al_4[Si_4O_{10}](OH)_8\} + 2K^+$$

is a rebuilding reaction of the internal structure accompanied by exchange of H_2O and K_2O with the surroundings [8].

Data on internal thermal reactions are much more numerous. The mechanism of internal structure rebuilding accompanying thermal reactions of layer-silicates is well known. Crystal structure transformations have been the subject of investigations of Brindley and co-workers [9]. MacKenzie *et al.* [10, 11], studied redistribution of cations and change of their coordination numbers by NMR method.

Dehydration of phosphates (Worzala [12] and Prodan [4]) and thermal decomposition of hydrated borates (Stoch *et al.* [13–15]) have been intensively studied.

These data and related information in the literature make it possible to characterize the specificity of thermal reactions involving internal mechanisms.

Internal reactions specificity

Internal pressure of gaseous products

Dehydration and dehydroxylation of hydroxides, silicates, phosphates and borates are internal decomposition reactions with the best known structural mechanism. They comprise two processes, namely (1) formation of free H_2O molecules by the splitting off of water molecules of hydrates from their structural framework or formation of such molecules from the OH^- groups and (2) removal of the water molecules towards the outside of the framework.

These processes do not necessarily take place simultaneously. For internal decomposition 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 is an example in which these processes take place independently at different temperatures [15]. The H_2O molecules formed during the first stage remain confined within vacant sites in the framework (voids) or accumulate, forming bubbles (*internal water*). With increasing temperature, the pressure of confined gas molecules increases, resulting in disruption of the framework and liberation of molecules (*internal pressure*) [1, 3, 5]. Internal pressure determines to a considerable degree the course of the decomposition and formation of its solid products. Incomplete transformation of gibbsite $Al(OH)_3$ into boehmite, $AlO(OH)$, during its decomposition, described by Rouquerol *et al.* [16], is an example.

The process of liberation of compressed gas components occasionally induces an increase in sample volume due to exfoliation of the crystals along their cleavage planes. Sometimes the escape of vapour has a sudden, explosive character. Decomposition of such minerals as colemanite, ulexite, dickite and vermiculite are examples of explosive dehydration [17].

These phenomena can be easily explained if we assume a *sealed box* as model of this process [14]. Uniform parts of the solid grain, free of discontinuities along which the gas molecules may escape, are comparable with a box completely impermeable or only partly permeable to the gaseous decomposition products. Its permeability depends on the degree of perfection of the crystal structure, grain size and texture. This is why structural and textural factors influence kinetics of the internal decomposition much more than external pressure of gaseous products.

The box acts as micro-autoclave: splitting off of the water molecules and their release shifts to higher temperatures. Because of this, dehydration may exceed dehydroxylation temperature, if the nearest surrounding OH groups are more permeable to water molecules than those surrounding structural H_2O of hydrates. Similar behaviour is observed for some borates, for example in the chain-structure mineral colemanite. In the layered-structure mineral pandermite, spaces between boron–oxygen layers are a convenient means of escape for H_2O molecules localized there. The structure is thus permeable for them and dehydration precedes dehydroxylation. This is in accordance with the molar density value of 0.0117 mole/cm^3 for colemanite and 0.0069 mole/cm^3 for pandermite [14].

On constant rate thermal analysis or quasi-isothermal-isobaric thermal analysis (Q-derivatography) curves, the following steps of internal decomposition may be distinguished: (i) a section of constant rate of water release from the near-surface layers and macro-defects, in direct contact with the atmosphere; (ii) a step of explosive release of the internal water; (iii) a nearly rectilinear section, indicating slow removal of water molecules and remaining OH groups, confined within the framework of the solid decomposition product.

Multistage internal synthesis

The dehydration or dehydroxylation of inorganic polymers often results in loss of structure, giving rise to an X-ray amorphous state. During heating of these amorphous solids, processes tending towards their transition to a crystalline state occur. These processes proceed through metastable intermediate stages, being the result of step-by-step rearrangement of the precursor structure. High-temperature transformations of kaolinite and other dioctahedral layer-silicates are well-known examples [9–11]. Some minerals recrystallize immediately, after dehydroxylation and metastable intermediate compounds appear, which transform at higher temperatures into stable crystal phases. Trioctahedral Mg-layer-silicates are the example.

The ability of dioctahedral layer-silicates to maintain their amorphous state to relatively high temperatures may be a consequence of the easy change of Al from octahedral to tetrahedral coordination. Such flexibility of the structural components appears to be indispensable if the amorphous state is to exist.

High-temperature transformations of dehydrated amorphous borates also have a multi-stage course.

High-temperature transformations of minerals are better understood if they are compared with crystallization of glasses of a polymeric multi-component network. Crystallization of these glasses at temperatures near to the glass transition temperature is also a multistage process. The crystallization of $Li_2O–Al_2O_3–SiO_2$ glass is a typical example (Table 1).

Table 1 Stages of crystallization of multicomponents glass from the $Li_2O–Al_2O_3–SiO_2$ system

	$Li_2O·Al_2O_3·7SiO_2$ glass	+	10 wt%TiO_2 nucleator
	825°C		
Diffusional redistribution of weakly bound cations	$Al_2Ti_2O_7 + TiO_2$		
Diffusionless (anions sub-lattice) and diffusional (cations) transformation	$Li_2O·Al_2O_3·nSiO_2$ quartz solid-solution		
	950°C		
Anions and cations diffusive redistribution and reconstitution of structure	spodumene solid-solution $Li_2O·Al_2O_3·7SiO_2$ spodumene		

During the first stage of the bulk glass crystallization, a substance of complex composition is formed, having the character of a solid-solution close to the mean chemical composition and structure of the glass. In this case (Table 1) it is a solid-solution of quartz-like structure. At higher temperatures diffusional mobility of atoms or ions increases. Ordering of the structure of this solid solution then follows, this being connected with segregation and redistribution of chemical components, and their composition is gradually transformed into the composition of the crystal phase proper for the chemical composition of the glass.

Quartz solid-solution transforms to spodumene solid-solution and then into spodumene proper.

Structures of minerals amorphized by internal thermal decomposition differ from structure of glass by their heterogeneity. Large fragments of the primary structure are preserved. They may be tetrahedral sheets and elements of octahedral sheets in layer-silicate structures, and rings built of boron–oxygen tetrahedra in borates. During their crystallization, intermediate crystal phases close to preserved elements of the precursor structure appear. These can be pairs of Al-rich mullite and (Al, Si)-spinel formed in the amorphous SiO_2 matrix [11]. In amorphous (Na, Ca)-borate (ulexite), Ca-borates in the amorphous Na-borate and OH^--containing matrix crystallize first. At higher temperature OH^- groups are removed and NaB_3O_5 crystallizes. Next, new-formed compounds exchange their chemical components and $NaCaBO_3$ compounds corresponding to the equilibrium state of the system crystallize [13, 14].

Some heterogeneous transformations in solids proceed in a *diffusionless* way, by correlated displacements of whole blocks of atoms or ions. This mechanism is typical for rapidly progressing polymorphic transformations like the ZrO_2 tetragonal – monoclinic transition.

This mechanism may not occur in its pure form. In oxide systems the sub-lattice formed by the less mobile oxygen anions undergoes little correlated translations, whereas the mobile cations become displaced at greater distances. The diffusionless mechanism, with coherent substrate and product structure interface, removes the thermodynamic barrier to formation of nuclei of new phases. As a consequence metastable compounds can be formed at relatively low temperatures.

Even so, the following stages of internal synthesis may be distinguished:

1. *diffusionless displacement* of anion sub-lattice and diffusional replacement of mobile cations: formation of intermediate compounds built of preserved elements of the primary structure. The strength and/or flexibility of the primary structure and rate of diffusion of the chemical components are decisive factors.
2. *diffusive reconstitution*: recrystallization of metastable compounds formed earlier and crystallization of compounds in keeping with the equilibrium state of the system. Concentration, chemical affinity and diffusional mobility of components are decisive factors here.

These stages may overlap, or one may be omitted depending on the external parameters of the thermal process.

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Zusammenfassung — Es wurden Umbaureaktionen der inneren Struktur von Mineralen und deren künstlichen Analogen betrachtet. Feststoffprodukte dieser Reaktionen werden innerhalb der Struktur der Mutterverbindungen gebildet. Dieser Faktor bestimmt den Reaktionsweg und die Produktbildung. Es wird der Mechanismus von interner Thermodissoziation und von Umbaureaktionen der inneren Struktur in Verbindung mit der Segregation der chemischen Komponenten und deren Umverteilung (Kristallisation von Mehrkomponenten-Amorphsalzen) besprochen. Der innere Druck der gasförmigen Zersetzungsprodukte und die Diffusionsgeschwindigkeit der chemischen Komponenten sind bestimmende Faktoren, die die Kinetik dieser Prozesse beeinflussen. Der diffusive Massetransport während der Umbaureaktionen der inneren Struktur wird durch eine Säure-Base-Wechselwirkung der Komponenten der Mutterstruktur gesteuert; hierdurch werden die Schritte des Reaktionsweges bestimmt.