Journal of Thermal Analysis, Vol. 32 (1987) 1651–1658

INTRAFRAMEWORK THERMAL REACTIONS OF SOLIDS

L. Stoch

INSTITUTE OF BUILDING MATERIALS AND REFRACTORIES,
ACADEMY OF MINING AND METALLURGY, AL. MICKIEWICZA 30,
30–059 CRACOW, POLAND

Temperature-activated reactions of decomposition, the synthesis of new compounds, and reduction and oxidation, termed here intraframework reactions, take place within the structural framework of solids. They are distinguished in that they occur within the bulk volume of the substance, in the area of the influence of crystal fields. The atoms and ions participating in these reactions are displaced by diffusion, which is usually directional diffusion. The regularities governing some of these reactions are presented in the paper.

Definition

Displacements of the molecules, atoms, ions and electrons, as well as interactions between them, may take place in the structural framework of crystalline and amorphous solid bodies (glasses, gels). Hence, within this framework there occur chemical reactions similar to those observed in liquids and gases, in particular dissociation, the synthesis of new compounds, and reduction and oxidation, i.e. intraframework reactions. These reactions have a special character, which distinguishes them from reactions of the same type occurring in homogeneous gaseous or liquid systems.

Intraframework reactions proceed within the area of the influence of the crystal field. The displacement of the atoms, ions and molecules participating in the reaction is usually slow. It proceeds by way of diffusion, which in crystalline solid bodies is directional diffusion. Its directions are determined by the anisotropy of the crystal structure of the solid. Many of these reactions are temperature-activated processes.

The factor determining their kinetics is usually the rate of transport of substrates or product molecules through the framework, or the breaking of the chemical bonds. These reactions take place in the bulk of the volume of a crystal grain, often without producing any visible change in its external shape.

The special character of these reactions is distinct enough to call for their separate

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

treatment. A special term "intracrystalline reactions" has been proposed for them [1–3] and in a wider sense, including amorphous solids, the term "intraframework reactions" is proposed.

The intraframework processes include:

1. Thermal dissociation proceeding while the essential framework elements of the primary substance are retained.
2. The processes of internal structure rebuilding:
   a) synthesis of new phases and segregation of the components,
   b) transformation of the glassy state,
   c) polymorphic transformations, particularly of reconstructive type,
   d) crystallization of amorphous solids (glasses, gels, metamictic minerals, etc.).
3. Oxidation and reduction, usually manifested by a change in colour (photochromic effects in glasses, oxidation of iron in silicates, etc.).
4. Intercalation and interlayer reactions in substances with a layered structure, and interchannel reactions in bodies with a skeleton structure.

The first two reactions, which belong among the typical thermally activated reactions, will be sidussed in greater detail below.

Intraframework thermal dissociation

The processes of thermal dissociation differ from each other in the way the decomposition products are obtained, and also in the interrelations between the parent substance and the solid product. Accordingly, we can distinguish topochemical dissociation, occurring on the interphase boundary, and intraframework dissociation, which takes place in the bulk volume of the grain.

Intraframework thermal dissociation is characteristic of substances the structural framework of which remains preserved after the process is completed, or is only partly rebuilt or damaged.

The intracrystalline dehydroxylation of layer silicates has been investigated in some detail [1, 4].

Dehydroxylation consists of two partial processes:

1. the breaking-away of OH groups and the formation of water molecules;
2. The removal of the water molecules from the anhydrous phase.

These processes may proceed in succession, one after the other at different temperatures (colemanite) [5], or overlap to a smaller or greater extent (layer silicates).

The first of them is limited by the disruption of hydrogen-bonds and occurs at the temperature required for the energy of the OH group vibrations to attain the appropriate value.

The other process is initiated when the partial pressure of the water molecules formed in a definite volume of the crystal lattice (intracrystalline pressure) [1–3] exceeds the value required to disrupt the weakest bonds of the framework. This is occasionally accompanied by a rapid increase in the sample volume (dickite, colemanite).

The number of substances undergoing thermal decomposition of intracrystalline character appears to be considerable, particularly among those whose structure contains elements formed of polymerized coordination polyhedra with strong bonds (layers, chains), such as silicates, borates, phosphates and others.

The decomposition of syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$, described by Wieczorek Ciurowa [6], shows the features of an intracrystalline process. The structural mechanism of the decomposition of $Ni(SCN)_2(C_5H_5N)_2$ points in the author's opinion to its intracrystalline character. It consists in the removal of the pyridine ligand and the formation of $Ni(SCN)_2$, which retains the elements of the framework of the primary compound [7].

Reaction of framework rebuilding

The heating of solid bodies occasionally involves the synthesis of new crystal phases with compositions different from those of the parent substances. The new compound is sometimes formed within the framework of the parent substance. It is preceded by displacement and sometimes even by segregation of its components.

One of the better recognized processes of this type is the formation of mullite from kaolinite (Table 1). Above 925°, the decomposition and rebuilding of the framework of metakaolinite occur, marked by a weak endothermic peak. It is accompanied by a step-like decrease in the volume, which can be seen in the TD curve (Fig. 1). Immediately afterwards, the Si, Al-spinel crystals are formed, the needles of which grow within the lamellae of metakaolinite. This is accompanied by a sharp exothermic peak. The formation of Si, Al-spinel consists in rearrangements of the coordination polyhedra in the metakaolinite framework and is a very fast process. The Si, Al-spinel is subsequently transformed into mullite, gradually changing its chemical composition [8].

Another example is the high-temperature rebuilding of the structure of montmorillonite of the Cheto type, as studied by Krauz and Čičel [9].

Montmorillonite undergoes dehydroxylation at about 700°, passing into the anhydrous form with a largely retained primary structure. At a temperature of about 850–900° it becomes amorphous (endothermic DTA peak). The solid solution with quartz structure which crystallizes from it (exothermic peak at about 950°) undergoes gradual transformation, connected with a change in the chemical

Table 1 Processes of the framework reconstruction

	A) Kaolinite, according G. W. Brindley and M. Nakahira [8]	
	kaolinite $Al_4[Si_4O_{10}](OH)_8$	
equilibration ↓ recrystallization, components segregation	metakaolinite $2Al_2O_3\cdot 4SiO_2$	+ water vapour $4H_2O$
	Si, Al-spinel $2Al_2O_3\cdot 3SiO_2$	+ cristobalite SiO_2
	mullite "intermediate" $2Al_2O_3\cdot 2SiO_2$	+ cristobalite SiO_2
	mullite 3 : 2 $2Al_2O_3\cdot 1\frac{1}{3}SiO_2$	+ cristobalite SiO_2
	B) Montmorillonite of Cheto type, according G. Kranz and B. Čičel [9]	
	montmorillonite $Me_{0.4}(Al_{1.6}Mg_{0.4})[Si_4O_{10}](OH)_2$	
equilibration ↓ recrystallization, components segregation	anhydrous form $Me_{0.4}(Al_{1.6}Mg_{0.4})[Si_4O_{11}]$	+ water vapour H_2O
	quartz like solid solution I $MgO\cdot Al_2O_3\cdot 6SiO_2$	
	quartz like solid solution II $MgO\cdot Al_2O_3\cdot 26SiO_2$	+ Mg-spinel (poorly crystallized)
	mullite $3Al_2O_3\cdot 2SiO_2$	+ Mg-spinel
	+	+
	cristobalite SiO_2	cordierite $Mg_2Al_3[AlSi_5O_{18}]$

composition (Table 1). It resembles the phase which is formed during the crystallization of glasses from the system $SiO_2-MgAlO_4$ [9].

In the octahedral sheet of the montmorillonite structure, the distribution of the Mg^{2+} and Al^{3+} cations has an ordered character. At higher temperatures they form $MgAl_2Si_2$ units locally, which create a solid solution having the structure of high-temperature quartz [9].

In the course of heating, vitreous solids show an endothermic DTA peak, the beginning of which corresponds to the temperature of the vitreous state

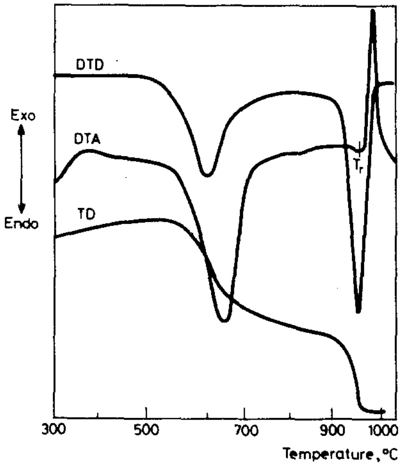

Fig. 1 DTA, TD and DTD curves of well crystallized kaolinite, T_r—temperature of rearrangement of metakaolinite framework

transformation, T_g. The nature of the endothermic peak itself is not clear. In the case of vitrified polymers at a temperature T_g, a number of weaker bonds between the chains are broken, while the chains themselves are retained. It can be assumed that a similar phenomenon takes place in the case of inorganic glasses. During melting of the crystal SiO_2, only 15% of the bonds are broken [10]. At the transformation temperatures of glasses, the number of broken bonds should thus be smaller than or similar to this. This provides an explanation for the small value of the heat of the process and the small DTA peak in the DTA curves of glasses.

In the DTA curves of easily crystallizing glasses, an exothermic crystallization peak appears behind the endothermic peak described above. It is now known that the temperature of the maximum nucleation rate of glasses occurs at temperature T_g or slightly higher, practically coinciding with the endothermic DTA peak.

Vitrified basalts and glassy blast furnace slags are characterized by a distinct endothermic peak preceding the exothermic peak of the crystallization of pyroxenes (Fig. 2). Examination of these glasses [11] has also confirmed the occurrence of nucleation within the area of the endothermic DTA peak. The endothermic peak is accompanied by a rapid, step-like decrease in the volume, visible in the TD curve (Fig. 2). Crystallization is usually associated with a decrease in the volume of the substance. In the case under consideration, it takes place before the exothermic peak of crystallization, which is not accompanied by a change in volume.

The above observation lead the author to assume that within the endothermic peak a rearrangement of the atoms in the glass structure occurs. This consists in the formation of domains whose chemical composition and ordering in the arrange-

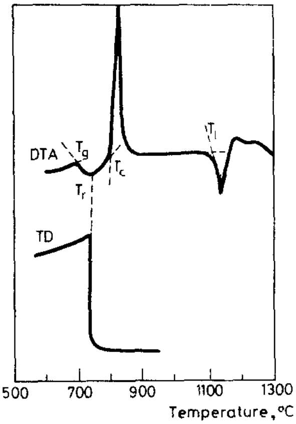

Fig. 2 DTA and TD curves of vitreous basalt. Temperature of glass transformation—T_a, rearrangement of glass framework—T_r, crystallization of glass—T_c and melting of crystals—T_l

ment of atoms are close to those of a substance crystallizing without the appearance of crystals. Within the exothermic peak the growth of crystals takes place by the reorientation and topological adjustment of these domains.

When glasses from the system $SiO_2-Al_2O_3-MgO$ are crystallized, a solid solution having the structure of high-temperature quartz is formed first [12], which is similar to that resulting from the rearrangement of the structure of montmorillonite. At higher temperatures, its chemical composition is changed and it passes into corderite, $Mg_2Al_3[AlSi_5O_{18}]$, an equilibrium crystal phase in this system.

It can be seen that the mechanisms of intraframework reactions of new crystal phase formation from X-ray amorphous products of dehydroxylation of layer silicates and glasses reveal great similarities, in spite of the quite different parent substances. The investigations of the crystallization of gels ([13] and others) indicate that it also has a similar mechanism. It is accompanied by the endothermic effect of disrupting part of the bonds of the old framework and the rearrangement of the atoms, followed by the exothermic process of the growth of crystals of a new phase. Its chemical composition may undergo change with increasing temperature, until the equilibrium state is reached.

This makes us assume a modified approach to the problem of the crystallization of a new phase in this process.

According to the classical theory of crystallization, the formation of a nucleus of a new phase has a negative value of the thermodynamic potential ΔG. It is compensated by the positive value of the increase in the surface energy of the nucleus being formed. At the phase transformation temperature, when $\Delta G = 0$, the thermodynamic potential of the nucleus with critical radius is infinitely great and its formation is not possible in thermodynamic terms [14]. This barrier is overcome, among other things, due to heterogeneous nucleation.

The intracrystalline reactions descried present yet another way of avoiding the thermodynamic barrier in the new phase nucleus formation. The new phase develops by small rearrangements of the framework of the parent phase and through the formation of the metastable phases from it. Subsequently, the metastable phase is gradually rebuilt into the stable equilibrium phase.

One can point here to the general regularities governing the formation of new phases in intraframework processes:

Principle of local similarity: The first product of the synthesis or crystallization process proceeding inside the framework of the parent substance is the phase the chemical composition and structure of which are close to the chemical composition and structure of the submicroregions (domains) of this framework. The chemical composition of the newly formed phase may thus be different from the average chemical composition of the parent substance.

Principle of equilibration: The newly formed phases have a tendency to reach an equilibrium chemical composition, corresponding to the average chemical composition of the parent substance, by means of the gradual rearrangement of their structure, the segregation of the chemical components and recrystallization.

Principle of energy economy: The growth of crystals of the new phase in the intraframework processes proceeds by way of the gradual ordering of the earlier-formed structure elements (domains). This permits minimalization of the energy required to produce the interphase surface, necessary for the appearance of the nuclei of a new phase. The endothermic process of the rearrangement of the framework of the primary substance, and the ordering of the structure and chemical composition of the domains, precede the growth of the crystals of the new phases, which is an exothermic process. In vitreous solids it starts with the temperature of transformation.

References

1 L. Stoch, J. Thermal Anal., 29 (1984) 919.
2 L. Stoch, Proc. of 8th ICTA '85 Bratislava—Thermochim. Acta 92 (1985) 97.
3 L. Stoch, Thermal Analysis Highlights 1985—Thermochim. Acta 110 (1987) (in press).
4 L. Stoch and I. Wacławska, J. Thermal Anal., 20 (1981) 291, 305.
5 F. Paulik, J. Paulik, I. Wacławska and L. Stoch, J. Thermal Anal., 32 (1987) (in press).
6 K. Wieczorek-Ciurowa, Proc. of 8th ICTA '85 Bratislava—Thermochim. Acta 92 (1985) 485.
7 A. Reller and H. R. Oswald, J. Solid State Chem., 62 (1986) 306.
8 G. W. Brindley and M. Nakahira, J. Amer. Ceramic Soc., 42 (1959) 311.
9 G. Kranz and B. Čičel, Slikattechnik, 36 (2) (1985) 38.

10 T. Sakaino, Proc. Tenth Int. Congr. Glass, Kyoto, 12 (1974) 16.

11 L. Stoch and P. Wyszomirski, Mineralogical Transactions, Polish Academy of Sciences, Cracow, 45 (1976) 75.

12 W. Schreyer and J. F. Schairer, Z. Krist., 116 (1961) 60.

13 K. Haberko, preparation and Properties of Zirconia Micropowders (thesis), Academy of Mining and Metallurgy, Cracow, 1983.

14 J. Šesták, Thermo-physical Properties of Solids. Academia, Praha, 1984.

Zusammenfassung — Im Strukturgefüge von Feststoffen treten sogenannte Intratexturreaktionen auf: durch Wärme hervorgerufene Zersetzungsreaktionen, Synthese neuer Verbindungen, Reduktion und Oxidation. Diese sind dadurch gekennzeichnet, daß sie im gesamten Volumen der Substanz, in einem vom Kraftfeld des Kristalles beeinflußten Raum ablaufen. Der Austausch der an den Reaktionen teilnehmenden Atome und Ionen wird durch eine stets gerichtete Diffusion verursacht. Es werden Gesätzmäßigkeiten beschrieben, denen einige dieser Reaktionen unterliegen.

Резюме — Происходящие внутри структурного каркаса твердых тел температурно-активированные реакции разложения, образования новых соединений, реакции окисления и восстановления, определены как внутрикаркасные реакции. Они отличаются от обычных тем, что происходят внутри объемной массы вещества, т. е. в зоне, затрагиваемой кристаллическими полями. Атомы и ионы, участвующие в таких реакциях, смещаются вследствии диффузии, которая обычно однонаправленная. Представлены закономерности регулирования некоторых из этих реакций.