Thermochimica Acta, 148 (1989) 149-164
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

STRUCTURAL THERMOCHEMISTRY OF SOLIDS

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ABSTRACT

Advanced techniques for crystal structure investigations permit the study of the actual mechanism of thermal reactions on an atomic scale. The results of these techniques modify our knowledge of thermal reactions of solids based on traditional kinetics. Internal structure dependent phenomena accompanying the thermal reactions of solids are discussed. Localization of reactions as well as topological relations between precursors and products, interactions between solids and newly evolved gaseous products, topotaxy, multistep modes of equilibrium establishment and other internal structure dependent phenomena, accompanying thermal reactions of solids are considered. General principles governing them are discussed.

INTRODUCTION

Present day methods of thermal analysis, supplemented by the results of investigations using high resolution electron microscopy, X-ray diffraction, NMR, IR and other spectroscopic methods, provide data which considerably extend our knowledge of the thermal reactions of solids. They permit the study of the actual mechanism of these reactions on an atomic scale.

The concept of the mechanism of thermal reactions of solids, known so far, was based on the measurement of the kinetics of these reactions and on relating the experimental curves of the relationship between rate and extent of reactions $dx\backslash dt=f(x)$ to

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Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21-25 August 1988.

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functions derived from theoretical models of these processes.

The generalized rate equation is used to compute kinetic parameters for many kinds of processes. It can be expressed as

$$\mathbf{dx/dt = A \exp (E/RT) f(x)} \tag{I}$$

where t - time, x - fraction reacted, T - temperature, A - preexponential constant, E - activation energy and R - universal gas constant. This procedure derives from the rules of kinetics of homogeneous systems. These kinetics have been developed for reactions in the gaseous phase and subsequently extrapolated to reactions in liquids. The liquids also represent continuous isotropic media, and the degree of their homogeneity is incomparably greater than that of solid bodies.

Most papers currently published in journals of thermal analysis and thermochemistry deal with the kinetics of different thermal reactions determined in this manner. However, with increasing amount of kinetic data for these reactions, the value of many of them seems to be doubtful. The question arises of to what extent can the kinetics of homogeneous reactions be applied to heterogeneous systems. The values of the obtained parameters E, A and the functions $f(x)$ and especially their physical meaning, are questionable.

A critical analysis of the data obtained so far leads one to the conclusion that homogeneous kinetics may find application only in certain types of reactions [1,2]. In the case of reactions to which it can be applied, it is possible to select one of the theoretical equations and to determine reaction rates as a function of time and temperature. The pattern of the reaction mechanism derived on the basis of these dependences is of a very general nature. The information on hypothetical rate limiting factor and rate equation is not sufficient to control the given process nor is it satisfactory from the scientific point of view, considering the high level of modern solid state chemistry.

Traditional kinetics has played a positive role at the beginning of the study of thermochemistry of solids, but its possibilities have been virtually exhausted and any further marked progress is not to be attained in that direction. Recently published works suggested essential improvements of the methods of examining the kinetics of thermal decomposition and deriving the function $f(x)$ [3,4]. Their application should help to minimize differences in the obtained values of the kinetic parameters and to improve their accuracy. Nevertheless, they cannot change the nature of the problem.

The doubts presented above are more and more frequently raised in publications, presented inter alia at the 8th ICTA in Bratislava, 4th ESTAC in Jena and, in particular at the 9th ICTA in Jerusalem and in discussions at these congresses. Also knowledge of the thermodynamic aspects of the investigated thermal reactions, which is undoubtedly necessary, seems now to be insufficient for the study of these processes. The kinetic and thermodynamic data must be supplemented with a detailed description of the changes in the internal structures and textures of the reactants undergoing the solid state thermal reactions. They must also be supplemented by a description of the mechanism of atomic movements and how atoms are displaced in the course of the reaction. The required information is obtained by modern methods which were previously mentioned. On the basis of a complete set of such data with reference to various processes it will become possible to define trends, and even general rules, which are characteristic for solid state thermal reactions and to formulate modern structural thermochemistry for solids. This should be one of the more important tasks for future international congresses on thermal analysis.

The aim of the present paper is to discuss some selected phenomena characteristic of the thermochemistry of solid bodies and their structural aspects. The starting points of the discussion are the differences between heterogeneous and homogeneous systems, resulting from the internal structure of the solids. This approach seems more promising than searching for similarities between entirely different processes.

SPECIFIC FEATURES OF THE THERMAL REACTIONS OF SOLIDS

Solids differ from gases and liquids in that they have a relatively rigid network. The geometry of the crystal lattice, the nature and directions of the chemical bonds and the anisotropy of the crystal structure and properties are the main factors governing the thermal reactions of solids and determining their kinetics. The atoms and ions which form the structure of solids in principle occupy fixed positions which may change to a limited extent. The displacement of atoms and ions taking part in thermal reactions usually proceeds by way of differential transport which is slow, and which is directional in crystal solids. The directions depend on the anisotropy of the internal structure. The defects of the structure are responsible for the fact that the medium in which this transport is taking place often has a discontinuous nature.

When the temperature is close to the reaction temperature the atoms and ions in the structure become mobile. As has been demonstrated by Maciejewski and Oswald [5], near the decomposition temperature of calcite the edges and corners of its crystals become rounded. Bridges and neckings are formed between them through which the crystals are linked together similarly as in the sintering process. On the other hand, dehydroxylation of the layer silicate kaolinite, is preceded by increased mobility and displacements of only part of the OH groups, while the structural framework remains essentially unchanged [6].

The mobility of the atoms and the degree of freedom of their displacements vary. However, even when the freedom is considerable, as in the case of calcite, the influence of the crystal is still evident. This comprises the essential difference between the thermal reactions of solids which are localized and those in gases which are delocalized. It is due to these factors that often no direct relation can be found between the reaction rate of solids and their concentration. The kinetics of these reactions is also influenced by specific surface area, the morphology of the crystal grains, macro- and micro- defects and others. Long lists of these factors can be found in the literature. In this way the reaction kinetics of solid bodies at constant pressure and temperature is determined, in addition to the concentration, by the intrinsic factors connected with the structure and particularly with the degree and type of its defects, f_{intr} and in case of some reactions (decomposition) by morphology and grain size, f_{morph}.

The significance of the structure and mode of transport which is dependent on it and which was discussed above, are evidenced by special features of the thermal reactions of solids. These features have already been described elsewhere [7]. They are:

1. localization of reactions and topological relations: parent substances - solid products of the reaction,
2. interactions between solids and gases which are evolved during the reaction, and
3. multi stage step by step mode of equilibrium establishment.

One of the specific features of the thermal reactions of solids is the localization of the reaction centers visualized in the mutual relation: parent substance - solid product. When taking this factor as a criterion the reactions can be divided into: (1) topochemical reactions and (2) intraframework reactions [7]. The consequence of this relation is the structural and textural dependence of the product on the precursor which is occasionally defined as topotaxy and which has recently become an object of special attention and interest.

The interaction of the gaseous and the solid products of reaction is characteristic of certain reactions of thermal decomposition. Most probably it also plays some role in other reactions occurring in solid bodies with the participation of the gaseous phase.

The reaction rate V is influenced by the above mentioned intrinsic and morphological factors, as well as by the gaseous products of decomposition with a pressure P_{gp}, and by the concentration x. It can be formulated as follows:

$$V = dx/dt = f(x, f_{intr}, f_{morph}, P_{gp}) \quad P,T - \text{constant} \qquad (II)$$

Consequently the parameter E in the Arrhenius equation will also be a function of these factors. If the assumption is made that the kinetics of the given reaction depends only on concentration and that it is described by the equation $V = kf(x)$, the influence of these factors becomes part of the value of the constant k. Consequently, the constant E also becomes dependent on them.

The kinetics parameters of a reaction in the solid state are structurally sensitive. Comparative studies of their values determined by the methods of thermal analysis, under identical experimental conditions, may supply information about structural differences and grain shape and size of crystals in different samples of the particular substance.

The activation energy E of the dehydroxylation reaction of the layer silicate kaolinite, as determined from the TG and DTG curves using the Freeman-Craoll method, decreases with increasing grain size. There is a significant linear correlation between the specific surface area and activation energy of a given kaolinite. The angular coefficient of the regression line varies with the degree of structural disorder [8].

The prevailing common opinion at present is that there exist many systems, including most inorganic compounds, for which the general kinetic equation is totally without merit, and many others - most polymer and other glassy systems - for which this system is fairly well established [1]. To this category belongs among others, the crystallization of inorganic glasses. Its kinetics is usually well described by the Avrami-Erofeev equation. This equation is also valid for solid-melt reactions such as in the halogenoxy salts and MoO_3 system [9]. The reason for this should be sought in the influence of the above mentioned factors. The exponential equations of the Arrhenius type equations also well describe the temperature dependence of many properties of solids. To this category belong the ionic electric conductivity of glasses and other inorganic substances, diffusion and viscosity of melts. Their general similarities, as in the case of glass crystallization, are the elementary processes which consist in the displacement of ions, atoms or groups containing them.

For thermal reactions with such a mechanism the Arrhenius equation may be successfully used. This is due, inter alia, to the fact that the rate of these reactions is determined mainly by the concentration and by the structural factors proper for the given substance, while the influence of the experimental conditions is less. Thus we can state:

$$V \approx k\, f(x, f_{int}) \qquad P,T - \text{constant} \qquad \text{(III)}$$

The progress of glass crystallization corresponds to the model of the process: nucleation - growth. This model assumes that the process begins at random points on the surface of each particle and grows uniformly in two or three dimensions at rates still describable by the function f(x).

A new approach to the kinetic study of the nucleation and growth process by means of thermal analysis has been proposed by Ozawa [10]. The Arrhenius type of temperature dependence of both elementary processes is assumed, and to estimate the dimensions of the growth and the overall activation energy a method is derived from the fundamental non-isothermal kinetic equation.

A variety of data is provided by different authors on the kinetics of decomposition reactions. The values for the activation energy of calcite decomposition, which is the model reaction for thermal decomposition, given by different authors, range from 142 to 3,828 kJ/mol [11]. This fact is explained as being due to different experimental conditions, especially different partial pressures of the gaseous products of decomposition [2,7]. The CO_2 partial pressure affects the value of E and the morphology of the decomposition products of calcite [4,12].

The divergence of the investigation results of the kinetics of the decomposition reactions of solids is explained by some authors as being due to imperfection of the experimental methods and to difficulties in the identification of the function f(x), while accepting the applicability of the Arrhenius equation. For this reason Reading [3] claimed that Constant Rate Thermal Analysis has a number of advantages in comparison with the conventional methods. In this method instead of regulating and programming temperature, which is changing according to an adopted program, a quantity is programmed which is directly related to the reaction rate and kept constant during the measurement. In the known Quasi Isothermal Quasi Isobaric Thermal Analysis developed by J. Paulik and F. Paulik this quantity is the change in the sample mass [13]. Here the controlled reaction parameter is the pressure of the gas evolved within a continuously evacuated reaction chamber [14]. In this way the control over the reaction environment and thereby over the sources of experimental error is greater.

To determine the activation energy Reading prefers the method of "jump mode" in which the controlled quantity, usually temperature, is changed in an abrupt discontinuous manner. He has also introduced the method of the rate of reaction jump by an appropriate change in the pressure of the gaseous decomposition products. To determine the function f(x) and to adjust it to the proper kinetic equation it is recommended to make use of the reduced time plot, taking as the basis the time for $x = 0.9$. It is also expected that these modifications will help to obtain kinetic data as reliable as that obtained for reactions in gases and fluids [3].

The specific property of the exponential function from the Arrhenius equation is the interrelation of the values of the parameters A and E. Such a relation is encountered in the thermal decomposition reaction and is known as the compensation effect expressed by the equation:

$$\log A = a + bE \qquad \text{(IV)}$$

where a and b are constants. Attempts are being made to find the cause and the physical meaning of this dependence.

From results of the investigations of the decomposition of carbonates and hydrates the compensation effect is explained as the consequence of the effect of the pressure of the evolved gases on the value of k and consequently on A and E [15].

A very good correlation in the log A - plot was obtained for the non-isothermal dehydration of $CaC_2O_4.H_2O$ at various heating rates using the function $f(\alpha)$ estimated from isothermal analysis. The compensation effect may be of use in the selection of the most suitable kinetic equation to describe the given reaction [16]. This is an indication that the compensation effect is also a consequence of the dependence of the A and E values on experimental conditions, external and morphological factors, as well as the methods of determining the kinetic equations from experimental data and their mathematical interpretation.In the case of the decomposition reaction the measurement conditions, and particularly the pressure of the gaseous decomposition products, has the greatest influence on these values. For other reactions the influence of intrinsic factors will be the main determinant.

The great number of factors determining the rate of the decomposition reaction, which can be seen from the above shown dependence, as well as the usually complex nature of the decomposition process, running through many stages, are the cause of the difficulty in describing it by means of simple functional dependence as derived for homogeneous systems.

TOPOCHEMICAL AND INTRINSIC PROCESSES

As has been demonstrated [6, 7, 17] for heterogeneous reactions the location of the reaction centers and the interrelation parent substance - solid product are of the greatest importance. Until now thermochemistry has been chiefly concerned with topochemical reactions which include thermal decomposition and oxidation - reduction processes.

As a topochemical process we shall consider the reaction which occurs 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 can remain in an epitaxial relation with respect to the parent substance. Topochemical reactions belong to the class of contracting volume processes. Decomposition of carbonates, sulphates, complex compounds of metals and some hydrates may serve here as examples. These usually consist in breaking one type of metal-ligand chemical bond.

Thermal dissociation may be a multi-step process accompanied by recombination of gaseous products and synthesis of new intermediate compounds (e.g. decomposition of $PbCO_3$ to PbO via $nPbO.mPbCO_3$ compounds). The topochemical thermal dissociation is sensitive to the partial pressure of the gaseous decomposition products. This partial pressure which prevails at the phase boundary and/or at the layer of the solid product, is the leading factor determining reaction rate.

The propagation rate of the decomposition front in crystals has an anisotropic character and is related to its internal structure. This is clearly visible, e.g. in dehydration of single crystals $CuSO_4.5H_2O$ [18].

Attention has recently been called to the less known, although frequently occurring reactions localized in the bulk of a crystal grain [6, 17, 19]. The reaction starts at the active centers in the bulk of a crystal grain and spreads around them. The solid product of the reaction is formed inside the parent substance and its structure usually remains in a topotactic relation with respect to the structure of the parent substance. It is often unaccompanied by a change in the external shape of the crystal. The specific character of these reactions is distinct enough to use a special term "intracrystal reactions" for them [6, 7] and in a wider sense, including amorphous solids, the term "intraframework" reactions [17, 19]. The factor determining their kinetics is usually the rate of transport of the atoms, ions and molecules through the framework of the parent solid, which in crystalline bodies goes in certain directions. Dehydration of $Na_3P_3O_9.6H_2O$ is an example [20].

The rate of these reactions can be described by equations of diffusion or volume contraction. The substances undergoing intraframework thermal reactions are usually those whose structure contains elements formed of polymerized coordination polyhedra with strong bonds (layers or chains) such as silicates, borates, phosphates, organic polymers, etc. The intraframework thermal reactions include thermal dissociation and processes of internal structure rebuilding.

The characteristic feature of the intraframework thermal dissociation is that the structural framework of the parent substance remains preserved after the completion of the process or is only partly damaged. In some cases the decomposition front propagates from the edge to the crystal centers (dehydration of some phosphates and layer silicates) but the outer shape and structural framework of the parent substance is preserved.

The intraframework decomposition process consists of two partial processes: (1) breaking off of atoms or ions and molecules (such as OH, H, H_2O, CO_2) and formation of free molecules of gaseous decomposition products; (2) removal of gas molecules from the framework of solid products. The temperature of both processes may be considerably shifted with respect to each other (e.g. some borates [19]). The actual mechanism of these processes differs from the models considered so far, although from among the known kinetic equations we may find some which apparently can describe it correctly.

TOPOTAXY

A frequently observed phenomenon is the inheritance of certain structural and morphological features of the precursor by the solid products of reaction. This inheritance may be dependent to some extent on the experimental conditions, including the partial pressure of the evolved gases. The actual mechanism of formation of the solid products consists often in slight non-diffusive shifting of anions, to which the more mobile cations adjust themselves by means of diffusion. This is made possible when the structures of the precursor and of the product show great similarity. An example of this is the formation of MgO from $Mg(OH)_2$ [21] or hematite (α-Fe_2O_3) from goethite (α-FeOOH) [22].

Within the plates of the layer silicate, kaolinite, at about 1,000°C, mullite of defective structure becomes crystallized in the shape of lathes oriented appropriately with respect to the geometry of the network of the precursor. Above 1,200°C it recrystallizes and acquires the habit and structure typical for well crystallized mullite.

The features of the precursor structure may also be inherited by the product, when its layer grows in an epitaxial mode and there is a compatibility between both the contacting structures at the interphase boundary. This phenomenon makes it possible to some extent to control the substance´s properties through deliberate choice of the precursors and of the reactions. The phenomenon of topotaxy has been utilized to obtain particularly active catalysts [23, 24].

From mixed Mn and Cu carbonates, depending on the atmosphere and on heating temperature, oxides of rock-salt or spinel structure of various concentration and vacancies distribution are obtained [25]. Using as a precursor a specially prepared vitreous carbon it is possible to obtain diamonds at a pressure much lower than that currently applied for their synthesis [26]. By means of an appropriate choice of the CO_2 partial pressure near the decomposition temperature of calcite, Maciejewski succeeded in transforming it into amorphous $CaCO_3$ of high chemical activity [4].

GASEOUS AND SOLID PRODUCTS INTERACTIONS

The interaction of the gaseous and solid decomposition products in the course of this process influences the decomposition kinetics and the intermediate and final products. In topochemical reactions the partial pressure of the gaseous products prevailing at the phase boundary is almost the same as the decomposition pressure at the given temperature. Its value is affected by the total pressure operating on the surroundings. The relation between these quantities depends on the rate of transport of the evolved gas mulecules from the interphase through the layer of the solid product. For this reason the relation between the product gas pressure, measured in the surroundings of the sample and the decomposition rate is often complex and depends on the experimental conditions.

The effect of the gaseous products on the decomposition kinetics is mainly due to the reverse reaction. Carbon dioxide is adsorbed on the surface of the decomposing calcite, forming carbonate particles which effectively block this surface. This results, inter alia, in the increase of the value of E [12]. The easier the reversibility of the decomposition reaction, the higher its sensitivity to the pressure of the gas product, what can also be observed on the curves of thermal analysis, as a shifting of the peak [27].

A concentration gradient of the gaseous product is obtained near the interphase boundary. This makes possible the formation there of the intermediate compounds containing smaller and smaller molar fractions of the volatile component, decomposing at higher temperatures. The decomposition of cerussite ($PbCO_3$) may serve as an example of this phenomenon.

The formation of compounds representing the intermediate decomposition stages is strongly dependent on the experimental conditions which affect the concentration of the gaseous products near the interphase. The interrelation between the solid and the gas products as well as atmospheric oxygen, is also responsible for oxidation or reduction of solids (e.g. the decomposition of $MnCO_3$). As a result the chemical composition of the boundary layers and the bulk phases of the solid products is often complex. An example of this is the thermal decomposition of Cr_3S_4 [28].

Dehydration and dehydroxylation often proceed in a complex and multi-step manner. An example is the decomposition of $MgBr_2.6HOH$ examined in detail by Shoval, Yariv and Kirsh [29]. Its dehydration is connected with the melting of the hydrate, and at higher temperatures dehydroxylation takes place through the removal of HBr.

The intraframework dehydroxylation takes a special path which is influenced by small structural changes. An example of this is the layer silicate kaolinite [6]. The dehydroxylation therein comprises two processes, (1) formation of the H_2O molecules within the alumino-silicate framework and (2) removal of water molecules with partial destruction of the framework. These processes may occur at various temperatures giving distinct DTA peaks [30] as in the case of the chain borate of calcium colemanite. The intraframework dehydroxylation often proceeds in a few stages. The layer calcium borate pandermite undergoes dehydroxylation in two stages, separated by the recrystallization of the framework already deformed by the removal of part of the OH groups.

The final effect of the release of OH groups in the intraframework processes is to render the structure amorphous in most cases. The amorphous product recrystallizes at higher temperatures and the type of new phases formed is then determined by the preserved elements of the framework of the primary phase (inheritance of the structure). The dehydroxylation of $CuSO_4.3Cu(OH)_2$ has a two-stage character. Its completion is followed by recrystallization [31]. In view of the above it also seems to have an intraframework character.

MODES AND STEPS OF ESTABLISHING EQUILIBRIUM

The final stage of thermal reactions in solids, which usually corresponds to the establishment of an equilibrium state, is often attained in a few stages through the formation of intermediate compounds. This is consistent with the known empirical rule of stages formulated by Ostwald. The thermal topochemical reactions with the participation of the gaseous phase often proceed according to the principle of gradual change of composition.

The decomposition of solid substances, especially those of complex chemical composition, occurs through the formation of substances of still simpler composition which contain less and less of the evolving components, as seen from the diminishing concentration of this component near the interphase boundary.

In the case of synthesis of new compounds through reaction with the surrounding gaseous atmosphere as, for example, during oxidation this principle is realized in the reverse direction. An example of a process proceeding according to such a path is the decomposition of some carbonates (e.g. $PbCO_3$) and basic carbonates (e.g. hydromagnesite, huntite) through oxy-carbonates containing smaller proportions of carbonate to oxide molecule, or decomposition of hydrates with lower proportions of water in their formula.

The formation of intermediate compounds requires appropriate chemical affinity of the solid and gaseous reactants and structural similarity of the parent and neoformed solid substances. Among the intraframework reactions special attention should be given to the processes of framework rebuilding.

The heating of solids occasionally results in the synthesis of new crystal phases. The new compound is formed within the framework of the parent substance. It is preceded by displacement and even by segregation or rearrangement of its components [17, 19]. Typical processes of this kind are the crystallization of glasses and amorphous solids which have evolved through the thermal decomposition of crystalline substances of stable framework (silicates, borates, phosphates). An example of this is the formation of (Al,Si)-spinel within the layers of metakaolinite, which subsequently converts into the stable phase mullite $3Al_2O_3.2SiO_2$. After dehydroxylation montmorillonite becomes amorphous. When the heating continues the amorphous phase is the first to be recrystallized into a quartz-like solid solution and defective spinel, from which the stable phases, (Mg-spinel, cordierite) are formed at a later stage.

The amorphous products of the dehydroxylation of colemanite and pandermite recrystallize, giving calcium borates. In the framework of glasses there occur regions with chemical composition and ordering of structure close to the corresponding crystal substance.

The first product of the crystallization with regard to its chemical composition and structure is close to the submicro regions in the framework of glass [19].

Comparative studies of the neoformed crystal phases and their relation to the structure of the precursor allow the proposal of empirical principles indicating the directions and mechanism of these processes [17]. They are given below in detailed form:

Principle of structural similarity: The first product of the synthesis or crystallization process, proceeding inside the framework of the parent substance is the phase whose chemical composition and structure is close to the chemical composition and structure of the microregions (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 synchronized rearrangements: The formation of a new compound within the framework of the precursor occurs through the displacement of cations and mutual adjustment of their positions together with the framework elements corresponding to the anion sublattice of the new compound.

Principle of local saturation: The formation of crystallites of a new compound is possible at the point when the concentration of the chemical components constituting the new phase attains a locally appropriate value in a volume exceeding the critical size of its nucleus, in spite of the low average content of any one of these components in the whole volume of the solids.

Principle of equilibration: The newly formed phases have a tendency to reach an equilibrium chemical composition and crystal lattice state by means of the gradual rearrangements of their structure, and segregation of the chemical components.

Principle of succession: Simple compounds, made up of chemical elements which are less strongly bound in the structure of the precursor, and are more mobile, tend to be the first to crystallize. The formation of simple compounds is succeeded by formation of compounds with more and more complex anions.

Like all general "rules" these contain many oversimplifications. There probably also occur exceptions to these rules. They appear, however, to be useful as they lead to a correct orientation and facilitate the interpretation of the results of thermal analysis.

They may also help to predict the course of these processes and ways of controlling them.

CONCLUSIONS

Kinetic investigations of thermal reactions of solids, supplemented with data on the structural transformation and rearrangement of chemical components of solids accompanying these reactions, modify our understanding of their mechanism. The actual mechanism of many of them differs from the traditional models.

The experimental data obtained so far make possible formulation of some rules which govern thermal reactions. These rules help in understanding the phenomena recorded by the thermal analysis plots. They can also facilitate prediction of the course of technological processes and their control.

The development of a modern unified concept of the thermal reactions of solids, taking into account structural factors, is an important goal for future thermal investigation.

REFERENCES

1 P.D. Garn, Thermochim. Acta, 135 (1988) 71.
2 M. Maceijewski and A. Reller, Thermochim. Acta, 110 (1987) 145.
3 J.H. Flynn, J. Thermal Anal., 34 (1988) 367.
4 M. Reading, Thermochim. Acta, 135 (1988) 37.
5 M. Maceijewski and H.R. Oswald, Thermochim. Acta, 85 (1985) 39.
6 L. Stoch, J. Thermal Anal., 29 (1984) 919.
7 L. Stoch, Thermochim. Acta, 110 (1987) 359.
8 L. Stoch and I. Waclawska, J. Thermal Anal., 20 (1981) 291.
9 K. Suba and M.R. Udupa, Thermochim. Acta, 135 (1988) 191.
10 T. Ozawa, Thermochim. Acta, 135 (1988) 85.
11 M. Reading, D. Dollimore, J. Rouquerol and F. Rouquerol, J. Thermal Anal., 29 (1984) 775.
12 M. Maceijewski and J. Baldyga, Thermochim. Acta, 92 (1985) 105.
13 J. Paulik, F. Paulik and M. Arnold, J. Thermal Anal., 32 (1987) 301.
14 J. Rouquerol, Thermal Analysis (R.C. Mackenzie, Ed.), Vol. 1, Academic Press, Inc., New York, 1969.
15 J. Pysiak and B. Sabalski, J. Thermal Anal., 17 (1979) 287.
16 N. Koga and H. Tanaka, Thermochim. Acta, 135 (1988) 79.

17 L. Stoch, J. Thermal Anal., 32 (1987) 1651.

18 H. Tanaka and N. Koga, Thermochim. Acta, 133 (1988) 227.

19 L. Stoch, Thermochim. Acta, 133 (1988) 197.

20 E.A. Prodan and S.I. Pytlev, J. Thermal Anal., 32 (1987) 1697.

21 R. Pampuch and Z. Librant, Ceramicka. Polish Acad. Sci. Cracow Div., 5 (1968) 11

22 S. Yariv and E. Mendelovici, Appl. Spect., 33 (1979) 410.

23 H.R. Oswald, Thermochim. Acta, 135 (1988) 3.

24 H.R. Oswald and A. Reller, J. Thermal Anal., 33 (1988) 67.

25 J.M. Jimenez Mateos, J. Morales and J.L. Tirado, Thermochim. Acta, 133 (1988) 257.

26 A. Niedbalska, A. Szymański and S.A. Zalewski, Int. Con. New Diamond Sci. Technol. Proc., Tokyo, 1988.

27 L. Stoch, Archiv. Mineral. (in Polish), 21 (1957) 185.

28 Y. Shigegaki, S.K. Basu and M. Taniguchi, Thermochim. Acta, 133 (1988) 215.

29 S. Shoval, S. Yariv and Y. Kirsh, Thermochim. Acta, 133 (1988) 263.

30 I. Wacławska, L. Stoch, J. Paulik and F. Paulik, Thermochim. Acta, 126 (1988) 307.

31 H. Tanaka and N. Koga, Thermochim. Acta, 133 (1988) 221.