Journal of Thermal Analysis, Vol. 32 (1987) 1635–1644

SOME KINETIC PROBLEMS OF INORGANIC TOPOCHEMISTRY

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Some problems of the kinetics and mechanisms of reactions of inorganic solids have been considered: the subject of inorganic topochemistry and its interrelation with adjacent disciplines; localization forms and typical forms of kinetic curves of topochemical reactions; the choice of single-meaning characteristics of the stability of solid compounds; and the employment of rational methods of investigation of decomposition kinetics.

There are some problems which are important from the point of view of the kinetics and mechanisms of solid-state reactions, but which are not covered in complete detail in the known monographs and reviews. A scrutiny of these allows the distinction of essential signs, the totality of which characterizes a comparatively new scientific discipline—inorganic topochemistry—and determines its place among adjacent chemical and physical disciplines, such as crystal chemistry, physical chemistry, colloid chemistry, inorganic chemistry, solid-state physics and chemical physics.

The kinetics and mechanisms reflect the temporal and spatial ways of any chemical reaction proceeding homogeneously or heterogeneously, with or without the participation of a solid. However, whereas in homogeneous systems they reflect primarily the number and sequence of elementary acts and intermediate stages through which the reaction proceeds, in systems containing reacting solids they additionally reflect the spatio-temporal effects of localization. The latter represent the fundamental specificity of solid-state reactions.

The fact that a reaction is localized does not itself mean that it should be classified as a topochemical (solid-state) one. In particular, reactions localized on liquid-liquid and liquid-gas interfaces do not belong in this class. Localized reactions in which the solid substance is not consumed and accumulated, but appears to be an invariable support, carrier or catalyst, do not belong in this class either. Such chemical reactions are localized on stationary surfaces, whereas topochemical reactions are localized on constantly renewed surfaces. In topochemical reactions, the solid phase appears either as the initial substance which undergoes chemical transformation, or as a reaction product resulting from chemical transformation of

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the initial solid, liquid or gaseous substance. Many cases of crystal growth from solution, the melt or the gaseous phase, accompanied by simultaneous chemical processes (chemical crystallization) are preferably classified by specialists as topochemical reactions [1]. The above also relates to reverse processes of dissolution, melting and vaporization of crystals.

Care should be taken over the sign of stationarity or non-stationarity of the surface on which a reaction is localized, e.g. when considering heterogeneous reactions on solid catalysts. The point is that the properties and chemical composition of the catalyst surface change as a rule in the course of the reaction, i.e. the condition of solid-surface stationarity is not obeyed, so that there may be doubt as whether to classify such a reaction as a heterogeneous catalytic or topochemical ones. Most frequently, two reactions of both types proceed simultaneously: the main heterogeneous catalytic reaction and the collateral topochemical one, responsible for the change in the catalyst properties and its ageing.

There may be an analogous situation in electrochemistry, when in some cases the solid electrode surface is stationary and serves as the site of liquid(gas)-phase process localization; in other cases it is non-stationary, and the electrochemical reaction proceeds on a constantly renewed electrode surface. The processes of the latter type constitute one of the Kohlschütter classes of topochemical reactions.

Besides the sign of the surface non-stationarity, the sign of the reaction localization form is essential. The Kohlschütter class of reactions which are localized in living organisms and are the subject of histological topochemistry is not considered here. The reactions of polymers (organic, inorganic and biopolymers) and localization forms which are characteristic of them, such as the localization of reactions on the active links of macromolecules, or on macromolecule branching points, the localization of reacting particles at certain sites of biopolymers, etc., are not considered either. These forms are analysed in organic, bioorganic, bioinorganic and biological topochemistry.

In inorganic topochemistry it is convenient to consider the forms of localization on a model single-crystal, e.g. a triclinic one, bearing in mind that the obtained results may be used with certain modifications when considering polycrystalline, massive, layered, fibrous specimens, etc.

It is convenient to arrange the typical forms of localization in a sequence according to their increasing complexity [2, 3] (Fig. 1).

1. Uniform localization on all crystal faces. This is the simplest form of localization, when the entire surface of all faces reacts instantly, and the process then goes on according to the model of a homothetically or unhomothetically contracting geometrical figure, depending on the relationship between the linear velocities, v_a, v_b and v_c of the flat reaction front advance in directions a, b and c, respectively. For this case, comparatively simple kinetic equations have been obtained [4, 5].

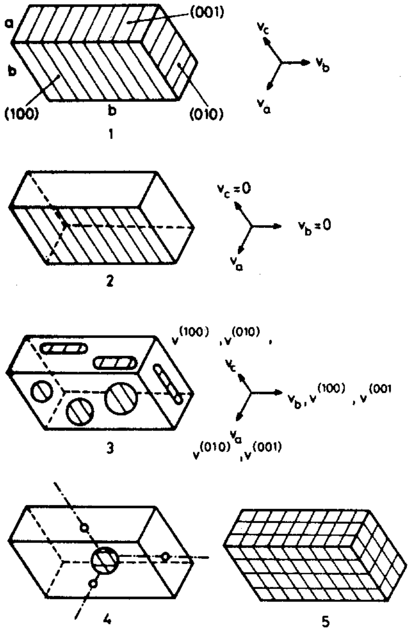

Fig. 1 Typical localization forms of topochemical reactions

2. Uniform localization on active crystal faces. The inactive faces either do not react (their induction periods exceed the time of reaction $\tau_{\text{ind}} > \tau_{1.0}$) or they react in certain temporal periods—$\tau_{\text{ind}}^{(100)}$, $\tau_{\text{ind}}^{(010)}$, $\tau_{\text{ind}}^{(001)}$. On the introduction of induction periods into the known equations [4] and after transformation, the described formula [2, 3] for the degree of conversion of a triclinic single-crystal can be obtained:

$$\alpha = 1 - \frac{[a_0 - v_a(\tau - \tau_{\text{ind}}^{(100)})][b_0 - v_b(\tau - \tau_{\text{ind}}^{(010)})][c_0 - v_c(\tau - \tau_{\text{ind}}^{(001)})]}{a_0 b_0 c_0} \tag{1}$$

where a_0, b_0 and c_0 are the halves of the lateral lengths of the initial crystal in directions a, b and c, respectively; and τ is time. If all induction periods are equal to zero, as in case 1, and if for an equidimensional crystal ($a_0 = b_0 = c_0$) all linear velocities are equal to one another ($v_a = v_b = v_c$), we obtain the known formulae for a homothetically contracting cube:

$$\alpha = 1 - \left(1 - \frac{v_a \tau}{a_0}\right)^3 \tag{2}$$

or

$$\alpha = 1 - \left(1 - k' \frac{\tau}{\tau_{0.5}}\right)^3 \tag{3}$$

where $\tau_{0.5}$ is the half-conversion period, and $k' = 0.2063$. Depending on the induction periods and the relationship between v_a, v_b and v_c, the reaction may proceed without self-acceleration, or with one-fold or multi-fold self-acceleration [6, 7]. For crystals with a large number of sequentially reacting faces, it is possible for the process to proceed according to auto-oscillatory or periodical types of reactions.

3. Spot surface localization on active sites. The crystal faces react simultaneously, as in case 1 ($\tau_{\text{ind}} = 0$ for all faces), or in turn, as in case 2 with different induction periods ($\tau_{\text{ind}}^{(100)} \neq \tau_{\text{ind}}^{(010)} \neq \tau_{\text{ind}}^{(001)}$). Besides the mentioned velocities v_a, v_b and v_c, the velocities of reaction front propagation from active centres in other directions, including those in the plane of the crystal faces ($v^{(100)}$, $v^{(010)}$ and $v^{(001)}$ are also taken into account. If the surface velocities $v^{(100)}$, $v^{(010)}$ and $v^{(001)}$ considerably exceed the volumetric ones v_a, v_b and v_c case 3 in essence reduces to case 1 or 2 and the process can be described by Eqs (1), (2) and (3). The number of active centres, their distribution on the surface of the crystal faces, and the velocity of their entering into the reaction are also taken into account. Active centres may react instantly, with constant rate, or according to the law of exponential function or other functions. In the present case there are more possibilities for the reaction to proceed with one-fold or multifold self-acceleration than in the previous case.

4. Spot localization in the crystal volume. The process is initiated on active centres inside a crystal (active centres may react according to one of the given laws) and further develops, in particular, through the growth of gaseous-liquid inclusions. The disproportionation localized in the volume of $MnHPO_4 \cdot 3H_2O$ crystals proceeds according to such a scheme [8]. This form of localization has been investigated comparatively poorly.

5. Uniform localization in the crystal volume. The process is practically delocalized; it proceeds uniformly in the crystal volume according to the homogeneous type of reactions. Homogeneous reactions of crystals have been still less well investigated as compared with reactions of the previous type. This is not so rare a phenomenon as might appear at first sight. As an example, we may take the solid-state decyclization which takes place on the heating of $Na_3P_3O_9 \cdot H_2O$ crystals [9, 10]. At any site inside the crystal there is one molecule of H_2O per anionic cycle, and cycle opening according to the mechanism of intrinsic hydrolysis may occur with approximately equal probability at any point of the crystal volume.

In the above cases, with the exception of the last one, the reaction may propagate in various directions isotropically or anisotropically, in the form of a flat or wavy front, in a fibrous or layered manner, on the grain boundaries, etc. There are combined cases, when uniform localization prevails on some crystal faces, spot localization prevails on others, a flat reaction front propagates from some faces, while a wavy or layered reaction front spreads from others. Investigations of the influence of temperature and the pressure of water vapour on the disproportionation velocity have revealed that the reaction is localized in a spot-like manner on the surface of $MnHPO_4 \cdot 3H_2O$ crystals or in the crystal volume; the active centres are situated at various depths in the volume, depending on the duration of storage of the crystals.

Various combinations of localization forms are observed when going from single-crystal to polycrystal and massive specimens. In the case of polycrystal substances, not only the sequence of separate crystal faces entering into the reaction, but also that of separate crystals should be taken into account. For some properties of these substances, such as lump formaton, loose fluidity, and the ability to become caked when stored, surface reactions and surface forms of localization are essential.

In contrast, for massive specimens the volume processes and volume forms of localization are more essential than the surface ones. Let us imagine a material utilized in a corrosion-active medium affecting its strength. Under uniform corrosive etching of the surface, the loss of strength approximately correlates to the quantity of lost material, whereas under selective penetration of the reaction into the material according to an intergrain corrosion scheme, there is no such correlation. In the latter case, a sharp change in strength may occur at low degrees of interaction of the material with the corrosion-active medium, including degrees which are not registered by the existing control methods. Changes of this kind take place during the induction period preceding the beginning of material destruction.

As concerns the induction period of this and similar processes, and the methods of its determination, the following should be noted. In the present paper, cases with an induction period unconditioned by temperature lag or instrumental lag are considered. This means that, with the existing methods of investigation of isothermal decomposition kinetics of polycrystalline substances, values of the order $\tau_{\text{ind}} \geqslant 30$ minutes are considered. One such period is shown in Fig. 2, where experimental data for the thermal decomposition of powder-like cadmium carbonate in an oxygen atmosphere at 260° are given. The analytically pure grade reagent contains a small quantity of residual water; therefore, the initial part of the curve does not merge into the time axis, but is somewhat higher. The induction period at 260° continues for 100 hours, the maximum reaction rate is obtained in 350 hours, and it takes more than 100 hours to complete the reaction. In the literature, there are some other cases where the induction period lasts for many days, and the period for the maximum reaction rate to be reached continues for many months.

The results of induction period determination depend on the sensitivity of the device which records the starting-point of the reaction. Because of this fact and also because of the high structural sensitivity of the obtained value, it has been proposed

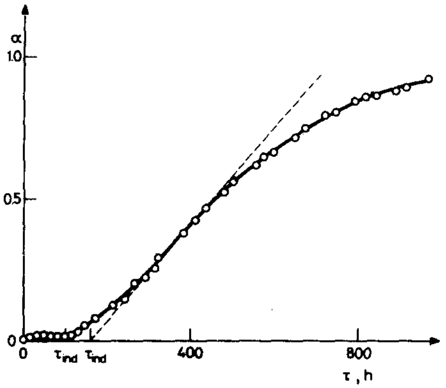

Fig. 2 Kinetic curve of thermal decomposition of powder-like cadmium carbonate in oxygen atmosphere at 260 °C

to determine a conventional induction period τ'_{ind} along with τ_{ind}. To determine τ'_{ind}, it is necessary to draw an inflectional tangent to a sigmoid curve and find the point of its crossing the time axis. The two values complement each other well, for the τ_{ind} value characterizes the part of the curve up to its separation from the time axis, while the τ'_{ind} value characterizes the initial part up to the point of inflection of the curve.

Depending on whether the process proceeds with an induction period or without one, and on the character and nature of the induction period, basic types of kinetic curves of topochemical reactions, and in particular reactions of thermal decomposition of solid substances are distinguished (Fig. 3).

Curve 1 corresponds to decomposition without self-acceleration. The curves of this type formally correspond to the kinetic laws of reactions of first, second or fractional order, including 2/3, when the process proceeds according to the model of a uniformly contracting geometrical figure, which reproduces the spatial picture of decomposition of a crystal or of a whole specimen. Logistical curve 2 characterizes a decomposition with self-acceleration, preceded by an induction period of various durations, including zero duration. In differential form, the curve may be either symmetric or asymmetric. If partial decomposition of the substance takes place before the induction period, e.g. the loss of 2/6 of the crystal water, as observed in the dehydration of $Na_5P_3O_{10}\cdot 6H_2O$, we obtain a curve of type 3, with an intermediate horizontal part. If the process has an auto-oscillatory character, the repetition of this part is possible. Curve 4 corresponds to a very slow initial decomposition, which then spontaneously accelerates and further proceeds as in the cases of curves 2 and 3. In the study of the thermal decomposition of comparatively large crystals of sodium hydrocarbonate in a nitrogen atmosphere at 110°, a period

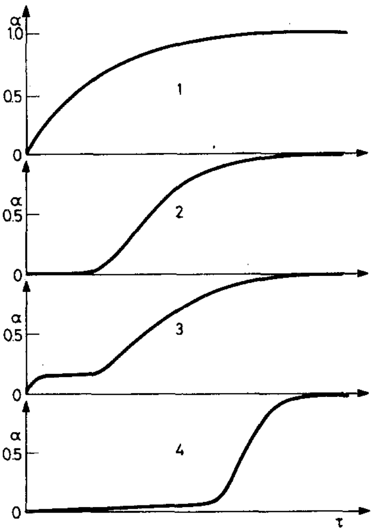

Fig. 3 Typical forms of kinetic curves of thermal decomposition of solids

of slow decomposition with $\tau = 10$ days has been recorded, during which the degree of decomposition reaches $\alpha = 0.1$, the reaction then sharply accelerates, and it is completed within the following 2 or 3 days.

Kinetic curves with another combination of the various parts are known. A slow decomposition is usually preceded by an induction period. This may be represented by curve 2 complemented with a period of slow decomposition, or by curve 4 complemented with an induction period. With a full set of non-recurrent curve parts the process goes on sequentially through the phases of induction period (lag phase), slow reaction, self-acceleration (log phase) and deceleration.

The study of induction periods and periods of slow reaction is necessary in order to forecast the durability of materials and substances, to evaluate their thermal stability, and to search for a low-temperature limit of reaction. Attempts to use the "temperature of decomposition beginning" show that this value is not always a single-meaning characteristic of the thermal stability of substance.

Firstly, it depends upon a large number of factors (the chemical purity of the substance, the method of its production, its state and granulometry, the gaseous phase composition and pressure, and the type of equipment used), and in some cases it characterizes the state of the substance and the conditions of the reaction rather than the substance itself. A consideration of all the factors affecting the thermal stability of substances shows that "temperatures of decomposition beginning" differing from each other by hundreds of degrees may be obtained for one and the same compound.

Secondly, the "temperature of decomposition beginning" depends on a temporal factor. If we return to Fig. 2 and try to determine the "temperature of decomposition beginning" by varying the temperature, we shall face the following circumstance. After having waited for 100 hours at 260° and having observed no signs of decomposition, we may consider that there is no reaction at this temperature. We shall come to an analogous conclusion after having waited for 30 minutes at 280° and also at other temperatures, though in all cases the reaction is actually proceeding. To judge unambigously, we should know the low-temperature reaction limit, without which we may speak only about a relative characteristic of thermal stability, bound to a fixed period of time.

Here we face the problem of the characterization of the substance and the standardization of the experimental conditions, on which the Standardization Committee of the International Confederation for Thermal Analysis is working. However, the problem is wider and is not limited only to thermal analysis. In particular, to describe the properties of solids, and primarily their reactivity, and to obtain the kinetic characteristics of a reaction, it is desirable to have information about how these properties and characteristics change depending on the substance state gradiation. If it is possible to produce the same compound in the form of a perfect single-crystal, an ultrafine powder and a substance in an intermediate state, the gradiation range may be sufficiently wide.

There is an urgent problem concerning the choice of rational kinetic methods for studying the thermal decomposition of solids and other classes of topochemical reactions. Traditional methods do not always allow us to obtain an adequate picture of the reaction, and in some cases they appear to be of low efficiency. Thus, popular gravimetric, manometric, volumetric and other isothermal and non-isothermal methods, based on measurement of the quantity of gas evolved, are of little use in studies of reactions with gas evolution which are localized inside a crystal. Due to the effect of gas encapsulation, the value of α does not correspond to the true value of the degree of transformation of the substance.

For this reason, curve 2 (Fig. 4), presented in Δm vs. τ coordinates and conforming to the course of the process in the crystal volume [8], can not be converted into a curve in α vs. τ coordinates, for it actually represents not the course of a chemical reaction (disproportionation with water vapour evolution), but the release of water vapour from gaseous-liquid inclusions enclosed in crystals. The given limitation does not extend to curve 1, which represents the course of a process on the surface of crystals. In complex cases, methods of microscopy, decrepitation or acoustic emission are expedient.

Direct-optical and electron-microscopic methods, and also indirect methods, designed for measuring the velocity of reaction front advance in various directions, provide valuable information concerning a spatial picture of the reaction

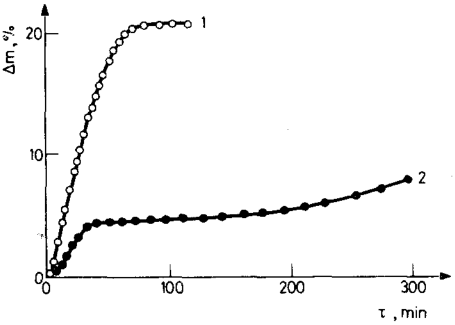

Fig. 4 Kinetic curves of mass loss of $MnHPO_4 \cdot 3H_2O$ crystals in vacuum and in atmosphere of water vapour: 1 – dehydration at $t = 90$ °C and $p = 10^{-3}$ hPa ($MnHPO_4 \cdot 3H_2O$ (cryst.) $\rightarrow MnHPO_4 \cdot 0.5H_2O$ (amorphous) $+ 2.5H_2O\uparrow$); 2 – disproportionation at $t = 80$ °C and $p = 20.4$ hPa ($5MnHPO_4 \cdot 3H_2O$ (cryst.) $\rightarrow Mn_5H_2(PO_4)_4 \cdot 4H_2O$ (cryst.) $+ H_3PO_4$(liquid) $+ 11H_2O$)

propagation in a crystal, but they demand preliminary specification of the nature of the moving interface. For this purpose, independent and mutually complementary methods of investigation may be used. The fruitfulness of such an approach is shown on the example of the dehydration of crystals of sodium cyclotriphosphate hexahydrate, $Na_3P_3O_9 \cdot 6H_2O$.

The presented list does not include all the problems which are important from the point of view inorganic topochemistry and which at the same time are not presented completely enough in the special literature. However, this was not the purpose of the present paper; a wider list is given in the monograph [11]. The author sees his task in drawing researchers' attention to some questions, the solution of which allows an understanding of the nature of topochemical processes in more detail, and which can be useful in throwing light on all the particulars of their mechanisms.

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Zusammenfassung — Es werden einige Probleme hinsichtlich der Kinetik und des Mechanismus der Reaktionen von Feststoffen betrachtet: Gegenstand der anorganischen Topochemie und dessen Beziehung zu angrenzenden Wissenschaftszweigen; Lokalisations- und typische Formen der kinetischen Kurven topochemischer Reaktionen; Auswahl eindeutiger Charakteristika für die Stabilität feststoffiger Verbindungen und Entwicklung zweckmäßiger Methoden zur Untersuchung der Kinetik von Zersetzungsvorgängen.

Резюме — Рассмотрены некоторые проблемы кинетики и механизма реакций неорганических твердых тел, а именно: предмет неорганической топохимии и ее взаимосвязь со смежными дисциплинами, частные и типичные формы кинетических кривых топохимических реакций, выбор однозначных характеристик устойчивости твердых соединений и использование рациональных методов исследования кинетики реакций разложения.