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...
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].

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