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THE PROBLEM OF FEED-BACK IN SOLID-STATE CHEMISTRY

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The paper deals with some of the assumtions and limitations of 'classical' models used in thermal analysis kinetic studies of solid-state rections.

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Introduction

Solid-state chemistry is an interdisciplinary area of research. Many groups study reactions of solids: thermodynamics, kinetics, spatial picture, properties of the products formed. The approaches to the solution of the problems arising during such studies are quite different in different 'clubs'. It would be hardly an exaggeration to say, that there exist as many 'theories of solid-state reactivity' and 'solid-state kinetics' as the research groups. As an illustration materials of numerous discussions during the last Thermal Analysis Meetings can be used [1–6].

Jaroslav Šesták has mentioned once: 'Substances are not aware of any theories and react according to their make-up (i.e. certain internal dispositions) under the experimental conditions applied' [7]. Still, whenever a scientist tries to describe a solid-state reaction he uses unavoidably a model, a 'theory'. When a model is suggested for the first time, the limitations of its applications are normally discussed in details. The more time has passed since the model has first been proposed, the more are all these limitations forgotten. The model becomes 'classical' and is applied to all the processes without an adequate analysis.

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In my present paper I would like to attract attention to some of the assumptions and limitations of 'classical' models traditionally used in thermal analysis kinetic studies of solid state reactions.

Theoretical considerations

A usual kinetic study by TA involves the measurement of some characteristic of a solid versus temperature, the temperature being changed with time: $X = X(T, t)$ [1, 7]. These primary experimental data are treated then in this or that way to calculate either $f(\alpha)$ (differential analysis), or $g(\alpha)$ (integral analysis), or $p(x)$, i.e. exponential-integral function [1, 5, 7]. The next step is to make a conclusion, concerning the 'mechanism' of the reaction. Numerous tables, correlating $f(\alpha)$, $g(\alpha)$, $p(x)$ with 'the reaction mechanism', are to be found in literature [7, 8]. It is worth mentioning, however, that there exist as many points of view what the mechanism of a solid-state reaction is, as the scientists, studying solid state reactivity. In his plenary lecture at ICTA-7 in 1982 Galwey has pointed cut two aspects of studying a mechanism of a solid-state reaction, namely studying 1) interface geometry and 2) interface chemistry [9]. If we look at the tables of type '$f(\alpha)$ - mechanism' published in literature, we can see, that the term 'mechanism' in these tables has almost nothing to do with interface chemistry, but concerns mainly the interface geometry.

The problem of correlating 'interface geometry', i.e. spatial picture of the reaction, with the changes of degree of transformation versus time (either under isothermal or under nonisothermal conditions) is really one of the central in the solid-state kinetics [10, 11]. Many efforts were made to solve it at least at some approximations. As a result some topokinetic 'nucleation - growth' models were proposed, giving e.g. 'classical' Johnson–Mehl–Avrami–Kolmogorov–Yerofeev equation. Since that time this equation is widely used. However, hardly one half of those, who apply the famous equation in their everyday practice, are aware of the main assumptions of the model, used to derive the equation, and even less people try to test, whether these assumptions are true in the particular case under study.

The main assumptions of 'classical' topokinetic 'nucleation-growth' models are the following:

1. Reaction starts at 'potential centers' and proceeds via formation and growth of product nuclei.
2. 'Potential centers' are present in the crystal from the very beginning of the reaction. Their number is constant.

3. The nuclei formed are assumed to have a regular shape and to grow homothetically.
4. The rate of the interface advance is assumed to be constant.
5. The reaction interface is assumed to be a thin layer, each site of which has similar properties. The characteristics of the interface are assumed not to be changed in the reaction course.

Although these assumptions might seem obvious, they turn out to be not always true:

1. We can imagine a situation, when a crystal has initially no 'potential centers', i.e. all the sites are equivalent in respect to the reaction under study. Still, reaction proceeds neither homogeneously, nor via 'classical' nucleation - growth process [12].
2. The initially equivalent sites of a crystal can become not equivalent in their reactivity during the reaction course. The distribution of 'local reactivity' in the crystal can be different at every time moment [13].
3. If reaction does proceed via the formation and growth of nuclei, the rate of the interface advance can be not constant [14–16].
4. The rate of the interface advance can be different for different nuclei [16].
5. Interface turns out to be not a thin homogeneous layer. The characteristics of the interface are different at its different sites [17–19].

All these examples used to illustrate the fact, that the main assumptions of 'classical topokinetics' may be not true, have something common. During all these processes both the characteristics of the reacting solid and the 'external parameters' such as temperature, pressure, environment were observed to be changed. It is rather a general feature of any solid state reaction, than an exception. Using the terms of J. Šesták, already cited in this paper [7], we can say, that both 'internal disposition' and 'the experimental conditions' are changed as the reaction proceeds. The changes are usually not homogeneous within the bulk of the reacting crystal. Different sites in the crystal become not equivalent.

To understand these phenomena, closely related to the problems of solid-state kinetics, we have to go out the limits of 'interface geometry treatment' and to deal with 'interface chemistry', 'interface physics', 'interface mechanics'.

Various terms are used in literature to characterize the effect of changes, produced in the system by a solid-state reaction, on the further course of this reaction (Table 1 [20]). Since 'feed-back' seems to be the most general of them, we shall use this very term in our discussion.

Table 1

Term	What result(s) of the reaction affect(s) its further course	Result affects:	
		Kinetics	Spatial progress
Auto - catalysis (inhibition)	A product is formed, that is not consumed or modified in the course of further reaction	+	
Impedance	A layer of solid product poorly permeable to gaseous product(s) is formed	+	
Self-acceleration (retardation)	any	+	
Autolocalization	any		+
Positive (negative) feed-back	any	+	+

Feed-back arises in case, that any change in the system, induced by the reaction itself, affects further course of the reaction. The changes in the system can be quite various: formation of new chemical substances in gaseous, liquid, solid-state; temperature changes; mechanical stress generation; crystal structure distortion; changes in the concentration and spatial distribution of various defects (point defects, dislocations, etc.); changes in the size and morphology of reacting particles. Many of these changes are summarized in the review [21], concerning the problems of spatial development of solid-state reactions, i.e. the problem of 'autolocalization'. In the same review various reactions are cited as examples of 'autolocalization due to some definite factor' – mechanical stress generation ($KBr + Cl_2$), contact potential difference (thermal decomposition of $KMnO_4$), generation of protons (thermal decomposition of NH_4ClO_4), etc. Such an approach, when some 'change' in the system is considered as 'the main one', is really rather typical. In many cases it was successfully used to control the reactivity of solids [22, 23]. However, if we are interested in the details of a mechanism of a solid state reaction (not in the sense of 'interface geometry' but in the sense of 'interface chemistry'), it seems to be not adequate to consider only one possible change in the system and its affect on further reaction course. As a matter of fact, many various changes in the system are to be expected as a solid state reaction proceeds. Thus e.g. when a nucleus of product phase is formed at the surface or within the bulk of the parent solid reagent, at least four main 'types of changes' in the system are to be expected:

1. Temperature changes, since a reaction is characterized by some value of the reaction enthalpy;

2. Electrical potential difference arises, since a new interface between the parent and the product phases is formed;
3. Mechanical stresses arise, since molecular volumes and crystal structures of the parent and product phases are different;
4. Concentration of ions, vacancies, radicals and other 'chemically active' particles in the vicinity of the nucleus may be changed.

All these changes in the state of the parent crystal can take place simultaneously, as a result of one and the same solid state reaction. All (or at least several of) the changes observed may be expected to affect further reaction course.

Since a) a solid-state reaction can be affected by many factors, b) various characteristics of the solid can be changed simultaneously due to the reaction and c) different processes in solids are closely interrelated, complicated feed-back loops rather than simple ones are to be expected to operate in solid- state reactions [20]. Examples of such complicated loops can be found in [20].

A complicated structure of feed-back loops, operating in solid-state reactions, is to be taken into account both when the feed-back phenomenon is studied and when kinetics and/or spatial picture of the process are considered.

Three main types of investigation of the feed-back phenomenon in the solid state reactions are to be suggested:

– Direct experimental studies of each link in the loop;

– Computer simulation of the changes in the crystal induced by the reaction;

– Computer simulation of the kinetics and spatial picture of the process on the basis of a detailed study of feed-back loop.

Direct experimental study of individual links in the loop

This would require *a*) direct experimental study of all the changes, produced in the system by the reaction (if possible, at a quantitative level) and *b*) the study of the effect of each of these changes on the reaction course.

I am not aware of any example of such an exhaustive study of a solid-state reaction. However, examples of successful studies of separate links can be cited.

Let us first consider 'reaction –result studies'.

Generation of mechanical stress and its distribution in the parent crystal was studied qualitatively in a number of papers by observing growing product nuclei in polarized light (see e.g. [16, 21]). Attempts to estimate the value of generated stress were also made. Thus in [24] the stress generated in the crystals of $[(Co(NH_3)_5NO_2]Cl \cdot NO_3$ during linkage photoisomerization was estimated on the basis of measuring the curvature of irradiated crystals. The value was shown to be equal approximately to 1 kbar. McBride *et al.* [25, 26] have estimated the stress arising in the crystals of some organic peroxides during their photolytic decomposition to be ~20–30 kbar. The researchers followed the position of the asymmetric stretching vibration band of CO_2, evolved during the decomposition, in FTIR spectra. The fact, that mechanical stresses do arise during solid-state reactions is supported also by observations of plastic deformation and/or self-fragmentation of solids, although such observations do not provide quantitative information [27].

One of the 'results' best of all studied experimentally at a quantitative level with good spatial resolution is the change in concentration of various particles in the vicinity of the reaction interface. As examples, studies of Schmalzried's research group (see e.g. [28]) and those of Boldyrev's research group (see e.g. [29]) may be cited. Electrophysical measurements, local diffraction techniques, microprobe techniques, optical microscopy observations can be used for these studies.

Strange as it is, local temperature changes seem to be the worst studied. The early publications on studying self-cooling of the parent crystals near the interface during the dehydration of crystal hydrates appeared in 1940 [30] and in 1951 [31]. A number of thermocouples was used for these measurements. Since that time not many attempts were made to carry out local temperature measurements during solid-state reactions. Bertrand *et al.* [32] tried to use IR-microthermography to scan a crystal of $CuSO_4 \cdot 5H_2O$ during its dehydration. They have reported only qualitative observations of anisotropic temperature changes in the vicinity of growing nucleus. Unfortunately, no quantitative measurements were carried out.

The 'result – reaction studies' are even less numerous, than the 'reaction - result' ones, briefly discussed in the previous section. I would like to cite three examples from the experience of Novosibirsk solid state chemistry research group.

Boldyreva and Sidel'nikov have studied the effect of elastic stress on the linkage photoisomerization in the crystals of $[(Co(NH_3)_5NO_2]Cl \cdot NO_3$ [24]. The quantum yield of the process was shown to decrease as the crystals were elastically compressed.

Zaikova and Lomovsky managed to control the rate of the interface advance during thermal decomposition of NH_4ClO_4 and $Cu(H_2PO_2)_2$ [33, 34]. For this purpose they changed the concentration of protons in the vicinity of the interface.

Sidel'nikov and Chupakhin have shown mechanical stress generation to be 'the main result', affecting the kinetics and spatial picture of β-NH_4Cl–α-NH_4Cl polymorphous transformation [16, 27]. To prove this idea they have controlled the course of the transformation by changing mechanical properties of the crystals.

Computer simulation studies

Computer simulation could be successfully used to study various aspects of the feed-back problem.

The changes in the crystal, induced by the reaction, could be simulated. Thus e.g. computer optimization of the interaction of product particles with their surrounding in the organic solids helps to predict possible distortions of crystal structure, induced by the reaction [35].

It is also possible to use computer simulation to look for correlations between the changes of molecular structure in the ground state and the kinetic parameters of the reaction under study [36]. If the distortion of molecular structure is induced by a corresponding change in the crystal structure due to a reaction, already started in the neighbourhood in the crystal, then such a study could contribute to elucidating the problem of feed-back in organic solid state chemistry.

Finally, computer simulation can be used to predict kinetics and spatial picture of the reactions with various types and quantitative characteristics of feed-back loops.

As an example of such studies for the reactions with simple feed-back loops publications [12, 13, 37] can be cited. The dependencies 'degree of transformation versus time' and 'the effective rate constant versus the degree of transformation' were studied in details as a function of the parameters of feed-back loops. The rate of the interface advance (for the reactions with positive feed-back) was studied. The distribution of the reacting sites by their reactivity was followed. The spatial picture of the processes was carefully analyzed.

Another example of a theoretical prediction of the reaction course on the basis of careful analysis of the feed-back loop provide the studies of Bertrand *et al.* [38]. In these studies the morphology of the oxides formed during oxidation of a number of metals and alloys is predicted. Local heat evolution and mechanical stress generation during the reaction are taken into account.

To conclude my present paper I would like to remind an old indian fairytale. Four blind men have met an elephant and tried to understand, what it was. Each of the four examined carefully a part of the elephant. The conclusions were very contradictory: 'a leaf', 'a fortress wall', 'a rope', 'a broom'. The four blind men argued with each other and could not come to any accord.

The situation seems to be very similar to what happens when a solid state reaction is studied. Some research groups concentrate on the role of dislocations in the reaction, other measure the heat evolved, the third observe the growth of nuclei or measure some electrophysical parameters of the samples. Everybody 'a son siège fait', i.e. does not even try to combine all these observations together and to get a general view of what the complicated process under study really is. Construction of most detailed feed-back loops for solid state reactions is the way, how we can 'see an elephant as an elephant, and not as a set of a broom, a rope, a leaf and a wall'. Thermal analysis could contribute much to the direct studies of individual links in feed-back loops. In turn, the interpretation of TA measurements could benefit from better understanding of solid state reactivity on the basis of studying the feed-back phenomenon. Such a cooperation between 'reactivity of solids' and 'thermal analysis' clubs seems to be much more fruitful, than constant confrontation.

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Zusammenfassung — Vorliegende Arbeit beschäftigt sich mit einigen Annahmen und Grenzen von "klassischen" Modellen, die in thermoanalytischen kinetischen Studien von Feststoffreaktionen verwendet werden.