

Inorganic Compounds

REACTIVITY OF SOLIDS*

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A review of studies of reactivities of solids is presented, concentrating on localization and autolocalization phenomena. Some examples of feed-back and structure of the reaction zone are given.

Keywords: feed-back, localization and autolocalization, solid-state reactions, reactivity of solids, solid-state reaction mechanism

Introduction

Modern thermal analysis is largely based on advances in solid-state chemistry and I believe that it would be useful to acquaint the experts in the area of thermal analysis with those problems we have to encounter in modern solid-state chemistry. One of these problems is the reactivity of solids.

In classical chemistry, reactivity means the characteristics of the chemical activity of substances which takes into account, first, the variety of chemical reactions in which a given substance takes part and, second, the rate of the chemical reactions occurring with the participation of this substance.

The main factor determining reactivity in classical chemistry is the composition and structure of molecules and, as a measure of reactivity, the rate constant of a reaction is used. When passing from classical chemistry of liquids and gases to solid-state substances, the established understanding of reactivity has to be substantially revised, because from the chemistry of individual molecules we transfer to the chemistry of crystals, being an association of molecules interacting

* Plenary lecture.

with each other. Since the relative arrangement of atoms, ions or molecules and the ensuing character of interaction determine the physical and chemical properties of substances, every disturbance of this order occurring during formation of the crystal, storage and various kinds of treatment will influence the reactivity of the substance. This explains the known relationship between the reactivity of solids and their 'biography', i.e. the method of preparation, subsequent treatment, etc. These facts, well-known since investigations in solid-state chemistry began, have served as a basis for fundamental investigations of Hedvall in Sweden [1], Frike [2] in Germany, Hüttig [3] in Austria and Roginsky [4] in the Soviet Union. These authors tried to relate the real crystal structure to the reactivity of solids. Central to their approach is the thesis that the larger the number of defects in the crystal, the greater its reactivity, other conditions being equal. The excess energy associated with disordering has been commonly measured by the calorimetric method and this ordering itself by change in shape of lines on X-ray diffraction patterns.

However, despite the attractiveness and simplicity of this idea, this is not always supported by experiments. This may be illustrated by two examples. In the mid-1950s, when we began our investigations in Tomsk University we sought to elucidate the influence of various ions introduced into crystals as impurities during preparation on the rate of thermal decomposition of silver salts. Cadmium ions, which are known to easily form isomorphous mixtures with silver during coprecipitation from solutions, were used as the dopant impurities, and the salts of silver decomposing in the solid state such as oxalate, sulphite and silver carbonate, were used as the subjects of investigation. Comparison of the heats of dissolution (formation) in a nitric acid solution showed that, in all cases, doping with cadmium led to a 10–15% increase in the heat of dissolution. After doping, lines in the X-ray diffraction patterns broadened, indicating that doping produced damage in the crystal.

One would assume that the rate of thermal decomposition would be higher following doping. However, this turned out not necessarily to be so. For silver carbonate, after doping the rate of thermal decomposition actually increased. For the oxalate and sulphite, the rate decreased.

Another example is quite recent. The Japanese scientists Isobe and Senna [5] investigated the effect of Pb^{2+} and Sr^{2+} doping on the rate of aragonite calcite phase transformation. Their experiments proved that, despite doping leading to an accumulation of energy in aragonite, which manifests itself in an excess heat of phase transformation, the rate of transition did not increase, but on the contrary, decreased.

These contradictions can be eliminated if one assumes that for every given chemical reaction, depending on its mechanism, not all the defects are required, but only a definite kind of defect. Then it becomes clear that employment of integral methods such as line broadening in X-ray diffraction patterns or excess heats are not sufficient for understanding the influence of defects on the rate of solid-state chemical reaction.

Table 1 Types of defects in solid-state chemistry

Reaction	Defects of crystal			Defects of lattice		
	surface change	habitus	heterophase impurities	dislocations	point defects	impurities incorporated in lattice
I {	xx	xx	-	-	-	-
	xx	xx	x	-	-	-
	x	x	x	xx	-	x
II {	x	-	xx			xx
	x	x	xx	xx	xxx	xxx
	x	-	x	x	xxx	xxx
		-	-	x	xxx	xxx
		-	-	x	xxx	xxx

It becomes evident that, in studies of the influence of defects on the reactivity of solids, features of the mechanism of chemical reaction should be also taken into account. In this paper I should consider some results of this study.

The influence of defects on the initial period of reactions. Classification of thermal decomposition reactions. Classification of defects

All thermal decomposition reactions may be conventionally placed in two groups [6]. The first includes chemical reactions in which rupture and formation of new chemical bonds occur locally. The second group covers reactions in which charges are transferred within a path length much longer than interatomic distances. The charge can be carried by electrons or by ions.

It is easy to see that chemical reactions which belong to the first group usually start at the surface. The start of the reactions which belong to the second group also involves the volume of the crystal. It follows from many of our results that the effect of different defects on the reactivity of solids depends on which of these two groups the reaction belongs to (Table 1)[7, 8].

Classification of defects

There is a variety of classifications of defects. In our work, we conventionally divide defects into crystal defects and lattice defects. The first of these leads to a change in the relationship between surface and volume of a crystal, whereas the second leads to a change in mobility of lattice elements, especially those through which charge transfer can occur.

How defects affect reactivity

Bearing in mind the above we can divide all cases of action of defects on reaction into direct and indirect ones. Direct action defects participate in the reaction itself. In indirect action, as a result of defects the change of the condition for chemical reaction in solids takes place. Some examples are shown in Table 2.

From experimental results obtained on the relationship between mechanism of reaction and the effect on it of serious defects, two important conclusions follow.

First, we can use the data obtained to control solid-state chemical reactions. Many examples can be cited to illustrate this [7, 8]. Here I shall consider only one example. It is known that the problem of thermal stability of ammonium perchlorate, which is one of the components of solid rocket propellants, is one of the most important in the manufacture of perchlorate, its storage and use. When we started to study this, there were no data on the mechanism of the thermal decomposition of ammonium perchlorate. Results of our work and these of P. Jacobs [11], published a year before our own, have shown that the initial stage of the thermal decomposition of perchlorate is the transfer of a proton from the am-

Table 2 Examples of the effect of defects on solid-state reactions

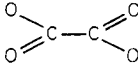
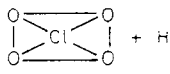
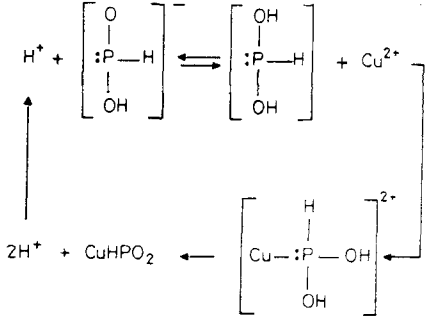
Defects	Reaction	Mechanism of influence
1. Direct participation of the defects in breaking and formation of chemical bonds		
a) breaking of chemical bonds		
[Ag ⁺]	$\text{Ag}_2\text{C}_2\text{O}_4 \xrightarrow{t} 2\text{Ag} + 2\text{CO}_2$	 <p>Distance from C-C bond to Ag_i⁺ = 2.05 Å, to Ag⁺ = 2.55 Å, as a result probability of charge transfer channeling from C-C to silver ion increased</p>
[H ⁺]	$\text{NH}_4\text{ClO}_4 \rightleftharpoons \text{NH}_3 + \text{HClO}_4$ \searrow $1/2\text{H}_2\text{O} + \text{ClO}_2 + 1/2\text{O}_2$	 + H <p>Decrease of stability of ClO₄⁻ as a result of protonization</p>
[H ⁺]	$\text{Cu}(\text{H}_2\text{PO}_2)_2 \longrightarrow \text{Cu} + 1/2\text{P}_2\text{O}_3 + \text{H}_3\text{PO}_2 + 1/2\text{H}_2\text{O}$	 <p>Decrease of stability of anion as a result of protonization</p>
[ClO ₃]	$\text{NH}_4\text{ClO}_4 \rightleftharpoons \text{NH}_3 + \text{HClO}_4$	$\text{ClO}_3^- + \text{H}^+ \rightarrow \text{HClO}_3,$ $\text{HClO}_3 \rightarrow \text{ClO}_2 + \text{H}_2\text{O} + \text{O}_2$ $\text{ClO}_2 + \text{ClO}_4^- \rightarrow \text{ClO}_3^- + \text{Cl}_2 + \text{O}_2$ Regeneration of the proton acceptor

Table 2 Continued

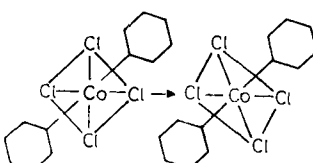
Defects	Reaction	Mechanism of influence
b) formation of new bonds		
$[V_a^+]$	$AlH_3 \xrightarrow{h\nu} Al + 3/2H_2$	$e^- + V_H^o \rightarrow F$ [16] Trap of electron from conductivity band – first step of metallic nuclei formation. Doping by Zn^{2+} , Mg^{2+} accelerated decomposition
Clusters of defects	$2Cu + 1/2O_2 \rightarrow Cu_2O$ $2AlH_3 \rightarrow 2Al + 3H_2$ $MgH_2 \rightarrow Mg + H_2$	$(^{100})Cu \parallel (^{111})Cu_2O$ [17–18] $(^{001})AlH_3 \parallel (^{111})Al$ $(^{001})Mg \parallel (^{110})MgH_2$ Product \parallel parent crystal; topotaxy
c) transport phenomena		
$[Ag_i^+]$	$Ag_2C_2O_4 \rightarrow 2Ag + 2CO_2$	Formation of silver nuclei as a result of migration Ag_i^+ as more mobile compared with Ag^+ [10]
$[V_{H_2O}]$	$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot (5-x)H_2O + xH_2O$	Water molecule migration through vacancy in product lattice [19]
2. Indirect effects of defects on the reaction		
Defects	Reaction	Mechanism of influence
$[\perp]$	$\alpha-CoPy_2Cl_2 \rightarrow \beta-CoPy_2Cl_2$	Local increase of free volume in lattice in vicinity of dislocation [20]
		
$[\perp]$	$MoO_3 + H_2 \rightarrow MoO_2 + H_2O$ $2KBr + Cl_2 \rightarrow 2KCl + Br_2$	Increase of residence time of molecule adsorbed at the surface of solids [21–22]

Table 2 Continued

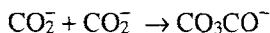
Defects	Reaction	Mechanism of influence	
[\perp]	$\text{NH}_4\text{ClO}_4 \rightleftharpoons \text{NH}_3 + \text{HClO}_4$ $1/2\text{H}_2\text{O} + \text{ClO}_2 + 1/2\text{O}_2$ $\text{ClO}_2 + \text{NH}_4\text{ClO}_4 \rightarrow$ $\rightarrow \text{NH}_4\text{ClO}_3 + \dots$	Separation of NH_3 and HClO_4 in pores formed by dislocation at the surface	[23]
[e/p]	$\text{MnO}_4^- + \text{MnO}_4^- \rightarrow$ $\rightarrow \text{MnO}_4^{\circ} + \text{MnO}_4^{2+}$ \downarrow $\text{MnO}_2 + \text{O}_2$	Change of e/p equilibria at the contacts with heterophaseous additives	[24]
[V_{Ag}^{\cdot}]	$\text{Ag}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Ag} + 2\text{CO}_2$	Interaction: $\text{Ag}_i^+ + V_{\text{Ag}} = \text{Ag}^+$ Doping by Cu^{2+} , Pb^{2+} or Cd^{2+} . As a result the velocity of nucleation decreases	[9]
[V_{H}°]	$\text{AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$	Doping by Hg^{2+} , Zn^{2+} . Velocity of nucleation increases	[16]
[\perp]	$\beta\text{-NH}_4\text{Cl} \rightleftharpoons \alpha\text{-NH}_4\text{Cl}$	Doping by Cu^{2+} ions leads to formation of Cottrell cloud around dislocation and as a result the velocity of reaction increases	[25]
habitus	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow$ $\rightarrow \text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$	Change of the ratio between {111} and {110} face	[26]

monium cation to the anion [12]. Simultaneously it has been established that ammonium perchlorate is a proton conductor and this type of disordering is common, as seen by the data of coulometry and dielectrometry and the composition of the gas evolved during electrolysis. Besides, it has been established that the thermal decomposition of ammonium perchlorate is extremely sensitive to the presence in the crystal of linear defects (dislocations). All of these allowed recommendations to be developed for control of the thermal stability of perchlorate. It turned out that it is possible to control the thermal stability of ammonium perchlorate by carrying out doping of crystals with ions which were proton donors or acceptors. Doping of the perchlorate with proton donors such as HSO_4^- led to an increase in rate of thermal decomposition and hence to a decrease in thermal stability of the perchlorate. Conversely, introduction into the lattice of stable proton acceptors such as the PO_4^{3-} ion decreased thermal stability [15].

Since the rate-determining stage of the decomposition of the perchlorate involves not only formation and migration of protons in the perchlorate lattice, but also that fate of the ClO_4^- ion after its protonation, it turned out that its thermal stability could be controlled by varying the amount of ClO_3^- ions in the perchlorate lattice which are not proton acceptors but in contrast to, for example, the phosphate ion form unstable HClO_3 on the capture of a proton. As is known, during decomposition of HClO_3 , one of the possible products is ClO_2 [27]. Interaction of ClO_2 with ClO_4^- leads to formation of new ClO_3^- ions, thus initiating a chain mechanism in the solid state [15]. Therefore, in order to obtain stable perchlorate it should be carefully purified from traces of chlorate ions which are a common technological impurity. Finally, the high sensitivity of ammonium perchlorate to the presence in the crystals of dislocations which may be potential reaction centres allowed a recommendation to be made to monitor the plastic deformation of the crystal during its preparation, storage and formation of the propellant composite.

A second conclusion from the data obtained, not less important than the possibility of controlling the reactivity, is the possibility of determining the mechanism of reactions in terms of which groups of defect influence the rate. Silver oxalate has been found to be an ion conductor disordered after Frenkel. Thus, the main defect participating in the transfer process is due to interstitial silver ions. By doping silver oxalate with bivalent copper and using the Koch-Wagner procedure [28], it has been possible to determine the concentration of interstitial silver ions for specimens doped with different concentrations of copper ions and for an undoped specimen. This allowed change in reaction rate at the initial period of the thermal decomposition to be plotted against concentration of interstitial silver ions [29]. Such a large influence of the concentration of interstitial silver ions for initiation of thermal decomposition of the complex has helped to elucidate features of the mechanism of the thermal decomposition of oxalates. Analysis of the literature and our data on thermal decomposition reactions of oxalates showed that these may be divided into three groups: i) decomposition of alkaline oxalates, the products of which are the carbonate and carbonmonoxide, ii) decomposition reactions which yield the metal oxide and a mixture of oxide and carbon dioxide, and iii) decomposition reactions of the oxalates of metals having a high ionization potential and decomposing to the metal and carbon dioxide [30].

In 1970 we proposed [31] a mechanism for the decomposition of oxalates according to which the C-C bond initially broke to yield CO_2^- radicals which then interacted to form the carbonyl carbonate ion:



In turn this ion then decomposed to the carbonate ion and carbon monoxide, which exactly corresponded to the compositions of the products belonging to the first group of our classification.

If the forming carbonate is less stable than the starting oxalate, as is the case with the oxalates of transition metals, it immediately decomposes to the metal oxide and carbon dioxide. In this case, the composition of the products corresponds to that of the second group of our classification. In the case of heavy metal oxalates, simultaneously with the rupture of the bond, the transition of electrons from oxalate to metal ions takes place. The mechanism proposed in [31] remained a hypothesis until recently. Angelov and co-workers in Sophia have obtained direct evidence of the formation of CO_2^- radicals during thermal decomposition of strontium oxalate crystals [32]. After this, only one not quite clear aspect remained in the mechanism of the thermal decomposition of oxalates, i.e. which way the electron transition from the oxalate ion to the metal proceeded. The assumption that this proceeded as in the case of, for instance, silver azide by transition of an electron from the valent zone to the conduction zone had to be rejected because of the considerable (of the order of 3 eV) width of the forbidden zone of silver oxalate and the small kT value for the temperatures at which the thermal decomposition of oxalate occurred. The suggestion made in our early works [9] about the excitation state of the electrons could not explain the problem. It has been the recognition of the exceptional sensitivity of the thermal decomposition of oxalates to interstitial silver ions which has offered explanations of these observations. It is evident that in one and the same crystal, the silver ions in the lattice sites and the interstitial silver ions differ in ionization potential value and the distance from the breaking C–C bond. As regards the ionization potential value, then taking into account that the silver ion in the lattice site occupies a more stable position than the interstitial one, it is difficult to suggest that the ionization potential of the interstitial ion might be larger than that of the silver ion in the normal lattice site. Most probably this would be quite the reverse. As to the distance, the interstitial silver ion is much closer to the breaking C–C bond ($d = 2.05 \text{ \AA}$) compared with the distance between a normal site in the lattice and the C–C bond ($d = 2.55 \text{ \AA}$). The latter factor appears to be of prime importance and suggests that the charge transfer from the oxalate ion to the silver cation proceeds by tunnel electron transition, the possibility of which is greater the smaller the distance between the centres of the transition.

In an analogous way, the character of the defects has been used in the development of a model of the mechanism of the thermal decomposition of permanganates [24] and copper hypophosphites [24].

Further course of a reaction. Changes in the crystal induced by a reaction. Autocalization of the process

Our approach to the study of reactivity of solids proved to be successful for control of the initial period of solid-state reactions. However it turned out to be much more difficult to control the course of further reaction. As a solid-state reaction proceeds, the reactivity of the reacting crystal can change due to the feed-

back phenomenon. Concentration of the defects induced in the crystal by the reaction itself may be substantially greater than the initial concentration before the reaction. Other types of defects compared with those characteristic for the initial state of the solid may appear during the course of the reaction. The rate-limiting step of the reaction may be changed.

For example I return to the thermal decomposition of oxalates. As seen above, the initial rate of thermal decomposition of silver oxalate correlates with concentration of interstitial silver ions in the lattice. It was important to test if this correlation exists also in the later stages of thermal decomposition. For this purpose we measured the conductivity of $\text{Ag}_2\text{C}_2\text{O}_4$ during its thermal decomposition, since the conductivity of $\text{Ag}_2\text{C}_2\text{O}_4$ has been shown to be a function of the concentration of Ag_i^* [9, 10]. When pressed pellets of a compound are used for conductivity measurements, phenomena related to the existence of intercrystalline boundaries and contacts between the pellet and electrodes make interpretation of the results complicated and often ambiguous. To avoid these problems we applied a method of contactless measurement of conductivity in single crystals of $\text{Ag}_2\text{C}_2\text{O}_4$ [33, 34]. A needle-shaped crystal of $\text{Ag}_2\text{C}_2\text{O}_4$ (4–5 mm long) was hung on a silk thread between the orthogonal pairs, of electrodes (Fig. 1). Thus a circular electric field was created in the space between the electrodes, where the crystal was placed. Interaction of this field with the charge carriers (interstitial silver ions) in the $\text{Ag}_2\text{C}_2\text{O}_4$ crystal resulted in the ponderomotive effect. The sample declined from its initial position and this declination was measured by a light indicator. A heating device introduced between the electrodes allowed measurement of conductivity changes during thermal decomposition 'in situ'. Results of the measurements are also shown in Fig. 1. During thermal decomposition the conductivity decreased, whereas the reaction rate increased. These data were in good agreement with results obtained by another experimental technique based on creating thermoelectric states in the sample and measuring the thermopolarizing current during thermal decomposition [35].

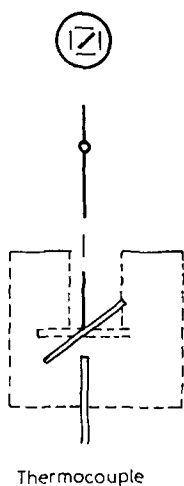
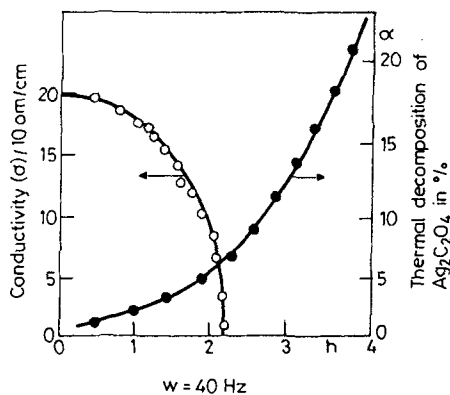
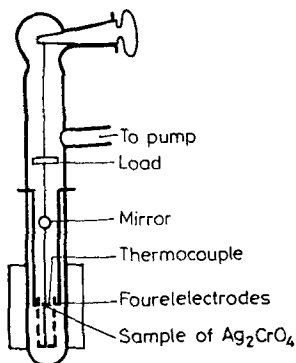
Results of electro-physical measurements are in good agreement with data on the influence of impurities on the thermal decomposition. Cu^{2+} or Cd^{2+} ions introduced in crystals of $\text{Ag}_2\text{C}_2\text{O}_4$ cause a decrease in concentration of interstitial silver ions. Doping the crystals of oxalate with these impurities results in a change in induction period of thermal decomposition. Subsequent reaction stages were not affected by these impurities.

Thus, a very important result was obtained: a solid-state reaction may be sensitive to some definite type of defect in the initial stages, but may become insensitive to the same defects as the reaction proceeds. The reason is that, as the reaction proceeds, changes are induced in the system which influence the reaction rate and even result in a change of the rate-limiting step.

We suppose that at the very beginning of the reaction thermal decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$ is limited by a rupture of the C–C bond in an oxalate ion. Interstitial silver cations facilitate the C–C bond rupture, since mutual orientation of the C–C bond and interstitial silver ions are more favourable for the reaction than that of

C-C bond and silver ions at regular lattice sites. As thermal decomposition proceeds further, structural reconstruction at the interface silver-silver oxalate becomes a rate-limiting step and it is no longer sensitive to subtle concentrations of the impurities.

Set up for measuring conductivity without contacts



Thermocouple

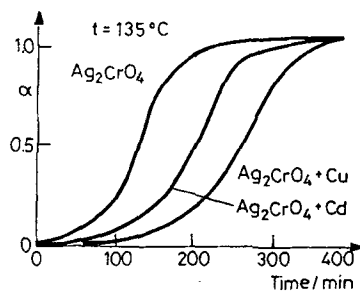
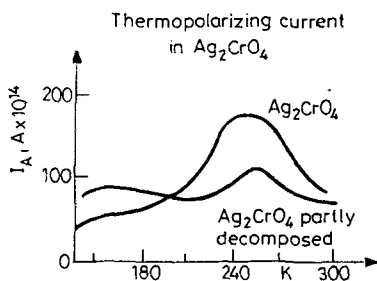


Fig. 1 Measurement of conductivity of silver oxalate in the course of its thermal decomposition at 135°C, [33]

Formation and growth of nuclei during thermal decomposition reactions seems to resemble nucleation and nuclei growth in the course of crystallization. Therefore a traditional approach to a description of nucleation and nuclei growth during thermal decomposition is that borrowed from the theory of crystallization of melts. Although the model (often referred to as a 'topochemical model') was

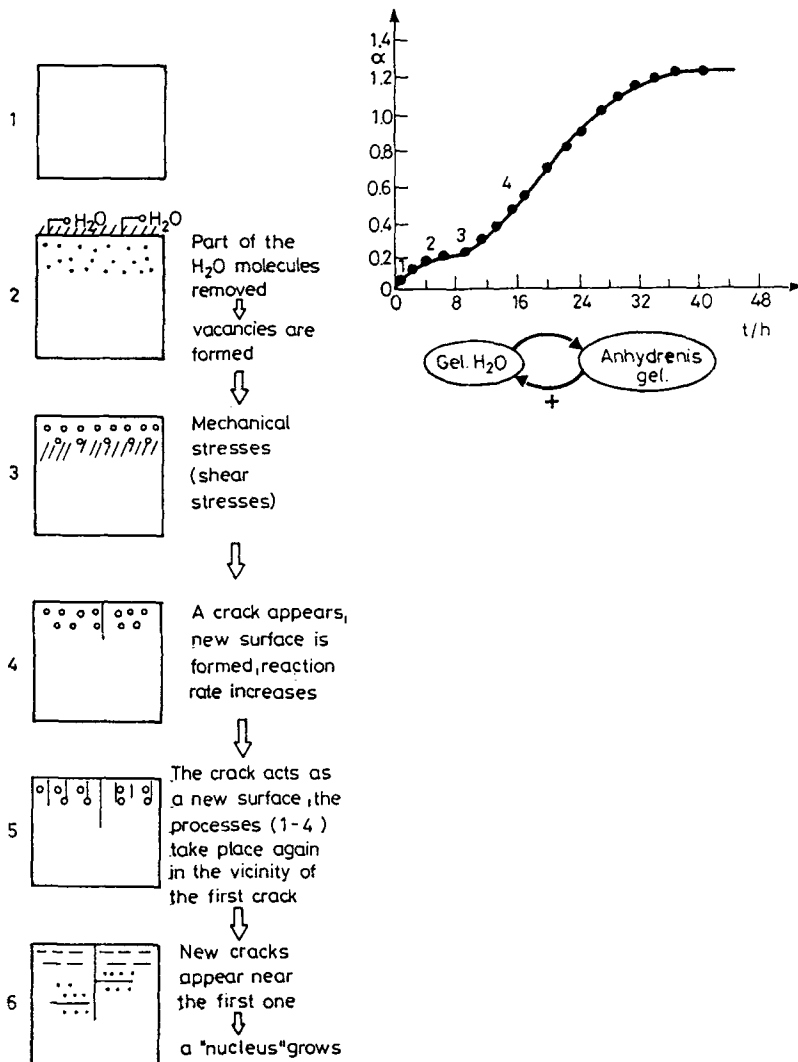


Fig. 2 Dehydration of silica glue

suggested long ago, it is still widely used despite numerous criticisms in the literature. I do not want to go into detail of formal topokinetic models and the contradictions of recent experimental data as this topic has been discussed in a number of my publications [36, 37] as well as those of the younger generation, e.g. Maciewskii [38] and Boldyreva [39, 40]. One of the main conclusions of reference [40], was that in order to adequately describe solid-state reactions it is necessary to study the phenomenon of feed-back in detail. Such studies are carried out at our Institute and we try to move in the following directions.

Computer simulation of feed-back in solid-state reactions

Computer simulation of solid-state reactions with positive and negative feed-back allow study at a molecular level of the main forms of feed-back. The influence of quantitative parameters characterizing feed-back both on the kinetics and the spatial propagation of the reaction have been analysed [41, 42]. One of the more interesting results was that the spatial picture of the reaction is sensitive both to positive and to negative feed-back, deviating from random product distribution. Positive feed-back was responsible for classical autolocalization, i.e. formation and growth of nuclei, whereas negative feed-back resulted in ordering of the product, i.e. formation of superstructures, which could be also qualified as a type of autolocalization in a broad sense.

It is also worth noting that introducing feed-back in the model of a solid-state reaction allows kinetic results to be obtained which are very similar to those given by formal topokinetics, but based on quite different assumptions. Thus a model with feed-back loops may serve as an alternative to a classical nucleation model when interpreting experimental data.

Constructing of detailed feed-back loops. Study of elementary physical and chemical processes responsible for feed-back phenomena

This problem has been discussed in a number of publications [e.g. 7, 37]. The main idea of this type of investigation is that a number of factors may be responsible for feed-back phenomena in solid-state reactions. At the same time we can choose the systems in such a way to accentuate a particular factor. To illustrate this I would like to show you several examples:

The most common factor responsible for autolocalization of a solid-state reaction is generation of mechanical stress at the reagent product interface.

A model study illustrating the role of this factor has been carried out recently by Sidel'nikov (unpublished data; Fig. 2). He studied dehydration of silica glue, i.e. dehydration of a dried water solution of sodium silicate. The system is of special interest since the dehydrating system is solid but not crystalline. In the course of dehydration mechanical stresses arise due to the formation of water vacancies in the surface layer. As a result of stress relaxation a crack is formed, and this crack now plays the role of a new surface. New cracks are formed in the vicinity of the first one and as a result a nucleus can be observed under the microscope.

Another model system also chosen to demonstrate the role of mechanical stress in solid-state transformations was studied by Sidel'nikov and Chupakhin in 1986 [25]. This was a phase transition in NH_4Cl (Fig. 3). In contrast to the dried silica glue, ammonium chloride is crystalline both in the starting α -phase and in the product β -phase. Due to the difference in molar volumes of α - and β -polymorphs, mechanical stress arises as a result of formation of the first nucleus. According to the phase diagram this stress must inhibit further transformation. However stress can relax via punching of dislocation semi-loops slipping from the interface into the volume of the parent crystal. As pile-ups of dislocation loops are formed, the back-stress from a pile-up on the nucleus prevents formation of new semi-loops. As a result relaxation of stress is hindered and the growth of the nucleus stops. It is also interesting to note that formation and growth of each new nucleus is hindered compared with the previous one (Fig. 3). The reason is that stress relaxation becomes more and more difficult as new nuclei are formed since the number of dislocation pile-ups increases.

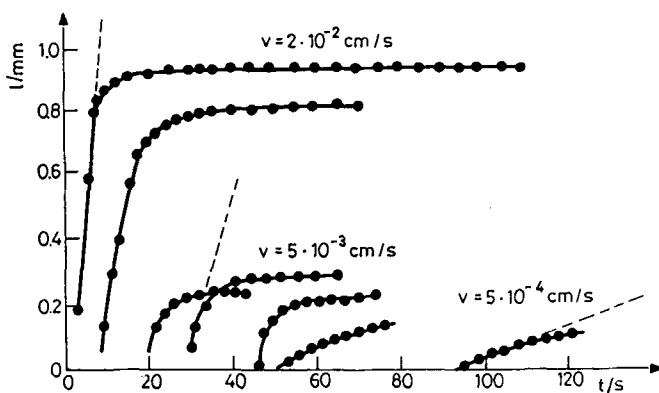


Fig. 3 Inhibition of nuclei growth rate initiated by performed nuclei

Even more complicated is a feed-back loop describing thermal decomposition of NH_4ClO_4 . Not only mechanical stress at the interface becomes an important factor affecting autolocalization of the reaction, but also changes in concentrations of chemically active particles. At least three possible processes responsible for autolocalization may be considered. First, thermal decomposition starts at a dislocation, so the first molecules of NH_3 and HClO_4 are formed not at the surface but in the subsurface layer. A gaseous bulb is formed inside the parent crystal and as a result mechanical stress arises. Relaxation of mechanical stress produces new dislocations which are as new centres where further chemical reaction is initiated [43].

Second, we have shown HClO_4 to be accumulated in a micro-pore since smaller and lighter NH_3 molecules leave this micropore more easily. As concentrations of protons in a pore increases, their migration to dislocations in the

vicinity of the pore becomes effective and thus dislocations newly infected by protons become new reaction centres, form new pores, and so on [23].

Finally, at least one more process is important when considering the feed-back loop in this reaction. ClO_2^* -radicals are known to be among the products of thermal decomposition of NH_4ClO_4 [13]. ClO_2^* is also known to react with solid NH_4ClO_4 giving ClO_3^- ions, which are stronger proton-acceptors than ClO_4^- ions of the parent NH_4ClO_4 crystals. At the same time HClO_3 formed when a ClO_3^- ion accepts a proton is less stable than HClO_4 . When HClO_3 decomposes, new ClO_2^* radicals are formed and thus a chain process starts. Thus formation of ClO_3^- ion acting as a proton acceptor and being regenerated in the course of the decomposition is also a factor which contributes to the autolocalization of the reaction [15].

Even more complicated feed-back loops may be used to demonstrate the approach to the problem of autolocalization developed at our Institute, e.g. that for thermal decomposition of copper hypophosphite. One more factor has to be taken into account: the electronhole equilibria at the interface copper-copper hypophosphite. Similar problems have to be solved when considering thermal decomposition of KMnO_4 , where both the parent and the product solids are semiconductors.

I think I have given enough examples to prove that a study of feed-back in solid-state reactions requires detailed experimental work based on application of various techniques. Interpretation of a kinetic curve alone can hardly be compared with this careful procedure.

Reaction interface

The term reaction interface is used to determine the zone separating the parent crystal and the product. It is the reaction interface where a solid-state reaction proceeds.

In the very first publications on solid state reactivity, starting from the classical paper of Langmuir [44], the reaction interface was considered to be a flat thin layer. Such an assumption was the simplest possible one and most convenient for the needs of formal topokinetics, which was in fashion in the 1960s. However as early as the 1930s, Slonim in Poland [45] and Garner in Great Britain [46] supposed the reaction interface to be a diffuse layer. Similar ideas were developed later [47, 48]. In the region of the interface, changes in chemical composition and structural reconstruction may be separated. Introduction into solid-state chemistry of such concepts as topotaxy made it unrealistic to consider flat thin interfaces in topochemically reacting systems.

The aim of many studies in solid-state chemistry is to obtain a desired product, i.e. a solid with predicted morphology. Therefore the problem of the structure of the interface was treated mainly from the point of view of product properties. The part of the interface adjacent to the product was studied in more detail than that of the parent phase.

Experimental study of the reaction interface requires development of local techniques with high spatial resolution. The very first studies of the interface formed during solid-state reactions were based on optical microscopy observations. The nuclei seen under the microscope were photographed at regular time intervals. The boundary seen in the microscope, i.e. the region where the refractive index is changed, was considered to coincide with the reaction interface. Recent experimental data have shown this hypothesis is not always true. I shall briefly discuss two examples.

Direct measurement of proton concentration at the reaction interface during thermal decomposition of NH_4ClO_4 [49]

As already mentioned, migration of protons from sites where HClO_4 is accumulated is one of the factors responsible for autolocalization during thermal decomposition of NH_4ClO_4 . To demonstrate this we designed an experimental device, schematically shown in Fig. 4. A partly decomposed crystal of NH_4ClO_4 was placed in a sample holder of an optical microscope. The surface of the crystal was treated by an indicator (iodide-iodate solution + starch) which changed colour in the presence of excess protons. The crystal was illuminated from above and a light conductor, placed under the crystal, could be moved with respect to the crystal with a micrometer screw. Moving the light conductor along the crystal from the nucleus to the parent crystal, and measuring light absorption, we could follow the distribution of the protons as a function of the distance from the nucleus, since the intensity of blue colour of the indicator was proportional to proton concentration.

Similar experiments were carried out on the thermal decomposition of copper hypophosphite [50].

Study of structural changes at the reaction interface by synchrotron diffraction [51, 52]

Synchrotron X-ray radiation is 10^6 times more intensive than commonly used X-ray radiation. Therefore the time of the diffraction experiment and the size of the sample area under investigation can be reduced to 10^{-3} – 10^{-4} seconds and $1\ \mu\text{m}$ correspondingly. The higher spatial resolution of the technique compared with common X-ray experiments enables study of the structure of the reaction interface. Two types of experiments have been carried out [51, 52].

In the first a position-sensitive one-coordinate X-ray detector was used. The experimental device is presented schematically in Fig. 5a. A partly dehydrated single crystal of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was studied. Usually, the border between blue parent crystal and white dehydrated product phase is considered as the reaction interface in this system. A special device allowed the crystal to be scanned, starting from the parent phase into the product nucleus. The half-width, intensity, shape and position of a pre-chosen diffraction maximum, characterizing structural changes, were measured as a function of spatial coordinate (Fig. 6). The ex-

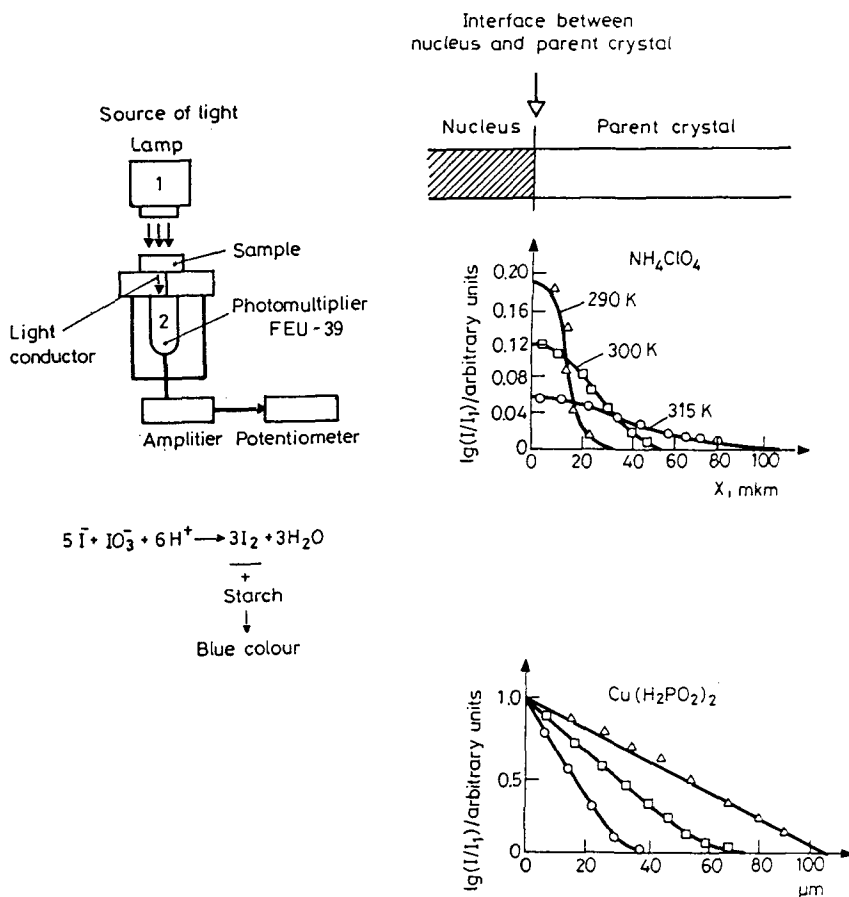


Fig. 4 Injection of protons in parent crystal from nuclei

periments showed structural distortions to be present in the parent phase far from the visible boundary. The width of the interface was estimated to be 150–200 μm , depending on the experimental conditions of dehydration.

The second variant of diffractometry was also developed, based on the use of a two-coordinate detector and polychromatic synchrotron X-ray radiation (Laué method).

The experimental device is illustrated in Fig. 5b. As a result of the experiments not only a new information concerning the width of the reaction interface was obtained, but also the textural details and morphological characteristics of the interface region were studied. Some results are shown in Fig. 7.

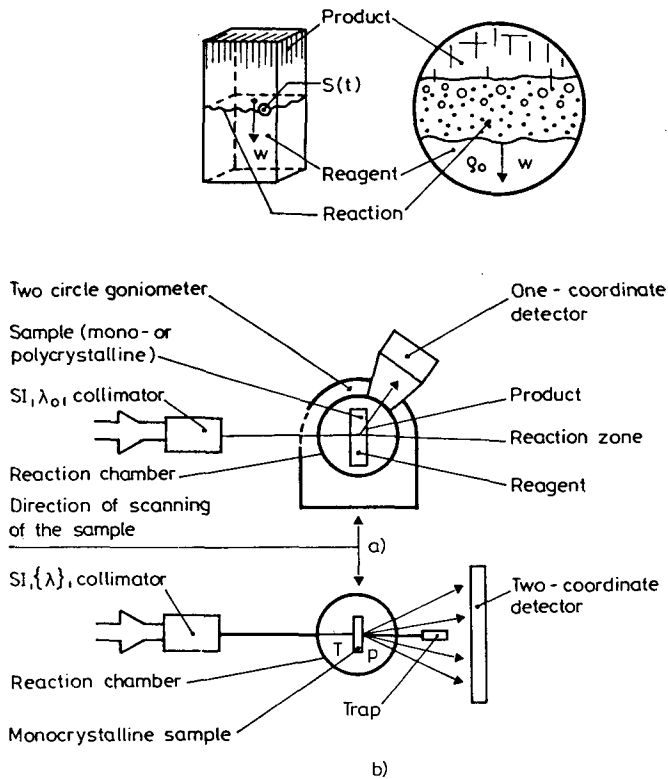


Fig. 5 Setup for study of structure of reaction zone by irradiation [51]

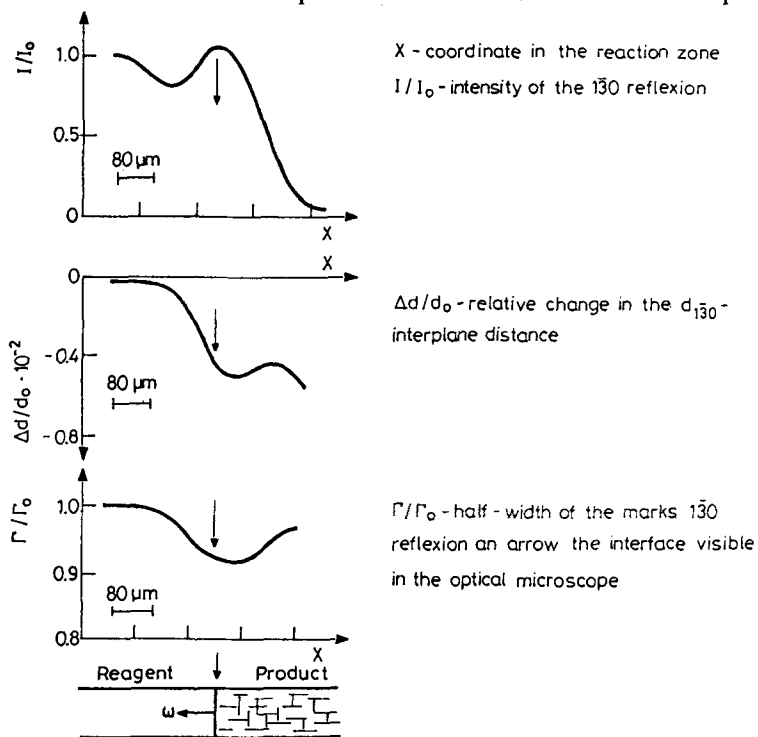
Conclusions

Studying reactivity of solids resembles in some respect a long trek across a desert in search of a source of water. Sometimes it seems to us that at the horizon there is an oasis with water, trees and flowers. Many people rush in the direction of the oasis, leaving a wide road behind them. Those who follow the running crowd look at the road and think that the fact that the road is well-trampled is the best proof that it leads to a real oasis. And only those who were the first to start moving in the direction realize that the oasis is only an optical illusion. It is sad to say so, but the confidence that it is possible to gain all necessary information concerning solid-state reaction mechanisms and solid-state reaction kinetics on the basis only of analysis of a kinetic curve seems to have turned out also to be an illusion. No computer program and no computer can turn this illusion into reality until physics and chemistry of the transformation are studied properly using a variety of experimental techniques and theoretical approaches. And this of course

requires development of new instrumentation, including thermoanalytical equipment, specially aimed at the detailed study of reaction mechanisms rather than on the routine measurements usually required by industry or analytical chemistry.

To make the last statement clear, I shall give you such an example.

X-ray diffraction is also an experimental technique widely used for routine analysis. However, a higher level of investigations also exists and it is based not only on the application of more and more modern computers and computer programs to the treatment of experimental data obtained with the help of the dif-



Change in Γ/Γ_0 and $\Delta d/d_0$ with time after the partial pressure of water vapour was increased (an arrow indicates the time of $P_{\text{H}_2\text{O}}$ increase)

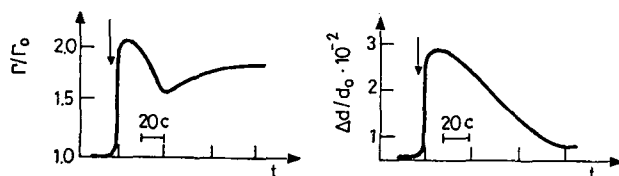


Fig. 6 Study of the interface in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during the course of dehydration

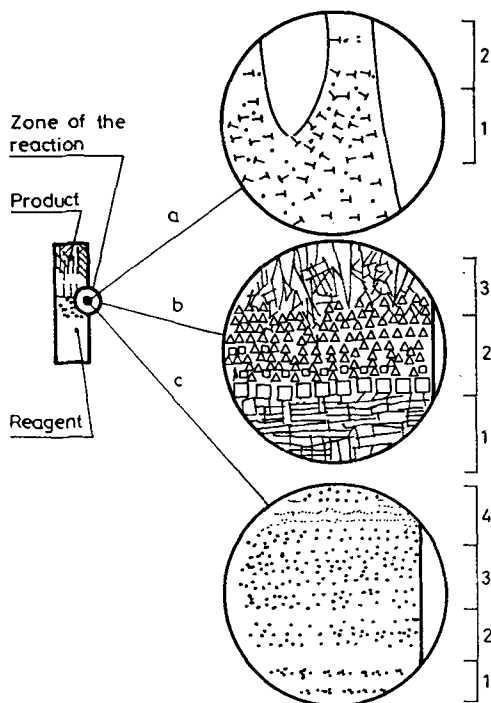


Fig. 7 Schematic of composition of reaction zone in the course of dehydration of some crystalline hydrates: a – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; b – $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; c – $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot 5\text{H}_2\text{O}$. 1. Vacancy-enriched zone; 2. Shear stress; 3. Crack formation

fractometers designed for routine analysis. Special equipment of a new generation is being developed, making it possible to study microsamples, with high spatial and time resolution, allowing an approach to the reaction interface and study of fast reactions.

It is a pity to say this, but I do not think that manufacturers of thermoanalytical equipment are committed to develop this 'higher-level' generation of thermoanalytical instruments. We do know examples of pioneering research studies of Wiedemann, Bertrand, Lallemand, Rouquerol and others, who try to increase space and time resolution of standard techniques or to modify these so as to satisfy the needs of fundamental studies.

Although the road followed by these researchers seems to be not so well-trampled as that of formal kinetic studies, it does lead to a real source of water and not to an optical illusion. And if other researcher as well as companies producing research equipment followed these pioneers, probably we could hope to reach water sooner.

* * *

I express my gratitude to E. Boldyreva, I. Konstanchuk and A. Polyakova for help in preparation of this paper.

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Zusammenfassung — Dies ist ein Überblick über Untersuchungen zur Reaktivität von Feststoffen unter besonderer Hinsicht auf Lokalisation und Autolokalisation. Einige Beispiele für Feed-back's und für den Aufbau von Reaktionszonen sind gegeben.