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Topochemistry of the Thermal Decomposition of Solid Substances

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Factors which determine localisation and autolocalisation in topochemical processes are considered systematically in this review. The specific features of the formation and growth of nuclei in topochemical reactions, the role of the anisotropy of the properties of the initial crystal, and various versions of the catalysis of solid and gaseous products during the thermal decomposition of solid inorganic substances are given. Promising investigations in this region are noted. Bibliography of 83 references.

CONTENTS

I. Localisation and autolocalisation of topochemical processes 515
II. Causes of the autolocalisation process in the thermal decomposition of solid substances 516

I. LOCALISATION AND AUTOLOCALISATION OF TOPOCHEMICAL PROCESSES

A characteristic feature of many solid-state chemical reactions is their localisation in definite parts of the crystal. This distinguishes solid-state reactions from those in liquids and gases, the reaction zone in which is uniformly distributed throughout the entire volume.

The localisation of chemical reactions in the solid state, owing to which these reactions have been termed topochemical (from the Greek word "topos", meaning place) is apparent both in the reaction starting at individual points of the solid body which are characterised by increased reactivity and are usually found at the surface, and in that having started at a definite site of the crystal the reaction proceeds by advancement of the reaction zone from the centre at which the reaction started into the neighbouring regions of the crystal. Such a unique nature of the development of topochemical reactions leads in their kinetic analysis to the necessity of considering the process not only in time coordinates (as is done in ordinary chemical kinetics) but also in spatial coordinates. Although this feature of topochemical reactions is well known and one of the main problems of the kinetic analysis of solid-state chemical reactions is the finding of the relation between the rate of formation of the nuclei of the new phase and their growth rate, the physicochemical causes which lead to the localisation of the process have in many instances not yet been studied. In the investigation of specific topochemical reactions it is usually difficult to state beforehand how the initial centres in a solid will be distributed and which factors will be responsible for the occurrence of a process in which the reaction, having started in some part of the crystal, continues to develop in the same place or its immediate surroundings. Moreover, the development of investigations in this direction is important, since it allows both the planning of new methods of directed regulation of the rate of reaction in a solid phase and also the obtaining of a solid decomposition product with previously specified morphological properties.

To the first approximation two groups of factors can be distinguished on which the degree and nature of the localisation process in topochemical reactions can depend. The first group includes those which depend on the potential conditions which exist in the solid until the start of the reaction. These factors are determined by the difference between the reactivities of the various parts of the initial solid substance. They include primarily the difference between the properties of the surface of the solid and

those of its bulk, the non-equivalence of the reactivity of different points of the surface and the bulk of the crystal, associated with the presence of defects of the crystal and defects of the crystal lattice, which determine the mobility of the lattice elements, etc.

The influence exerted by these factors on the reactivity of solids has been examined in detail in many papers concerned with the correlation between the real structure of a crystal and the kinetics of solid-state chemical reactions[1-4]. These questions will not therefore be discussed in the present review.

The second group comprises the factors which determine the change in the degree of localisation during the course of the process. In other words, this group of factors includes those which determine the probability that when the process has started at some point on the surface of the crystal or in its bulk it will continue to develop at the same place or close to it.

In comparison with the factors which belong to the first group, those which are due to the change in the degree of localisation during the course of the process, usually autolocalisation, have been studied much less, although the need for investigations to be made in this direction was stated long ago, starting with the earliest papers dealing with the study of topochemical reactions[5-8].

Not only have the reasons for the autolocalisation of the topochemical reactions been little studied, but in many instances the criteria which characterise the change in the degree of localisation with time remain obscure. Presumably the autolocalisation process, which leads to the formation of nuclei and their growth, is a function of the ratio of the rate constant for the formation of the nuclei to the rate constant for their growth. However, such a determination can hardly be regarded as sufficient and complete, since it is based on an extremely primitive model of topochemical reactions and does not take into account other forms of the autolocalisation process (for example, the change in the degree of "compactness" in the distribution of nuclei in the solid body).

In addition, it remains unknown whether there is a reason for the difference in the nuclei formation and growth constants, that is, that in one instance the development of a reaction proceeds by the growth of a small number of reaction nuclei and in another the reaction develops mainly by nuclei formation. There have been many hypotheses and conjectures along these lines. The most general was advanced by Sakovich[9], in which the change in the degree of localisation of the process was determined as a function of the ratio of "crystal-chemical" and "thermal" components of the activation. The "thermal" component of the activation in the thermolysis of solids is determined by the change in the energy distribution of the phonons in the lattice of the solid and should generally be assigned to the entire volume of the crystal. The "crystal-chemical" component of the activation is the consequence of the breakdown of that equilibrium which existed until the occurrence of a chemical act between the structural units (molecules, atoms, or ions) situated in the bulk of the crystal and the associated change in the reactivity of the structural units adjacent to the lattice node at which the reaction has just taken place. Hence when the thermal component of the activation predominates during the thermolysis, then according to Sakovich it should be delocalised and the reaction must be expected to proceed throughout the entire volume. When the crystal-chemical component of activation predominates an autolocalisation process and its development by the formation and growth of nuclei must be expected.

Despite the obvious merit of Sakovich's scheme, it needs further additions and development. Above all, the hypothesis about the equilibrium distribution in the crystal of the "thermal" constituent of activation is really quite approximate, and as we have already noted[10] the function which corresponds to it should be modelled with allowance for the distribution in the crystal of various types of defects. In addition the crystal-chemical component of activation can also have the most diverse nature and for each specific instance its physical significance should be defined precisely and the factors which could be the cause of autolocalisation found.

II. CAUSES OF THE AUTOLOCALISATION PROCESS IN THE THERMAL DECOMPOSITION OF SOLID SUBSTANCES

The causes of the autolocalisation process in the thermal decomposition can be most diverse. As a first approximation they can be divided into three groups: (a) autolocalisation of thermal decomposition due to crystal-chemical features of the structure of the crystals of the initial substance; (b) autolocalisation of the process due to release of a product during the course of the reaction; (c) autolocalisation of the process, the reason for which is a change in the reactivity of the initial solid substance due to the gaseous products released during the reaction.

We will examine these reasons in more detail.

1. AUTOLOCALISATION OF THE PROCESS OF THERMAL DECOMPOSITION DUE TO CRYSTAL-CHEMICAL FEATURES OF THE STRUCTURE OF THE INITIAL SOLID SUBSTANCE

One of the reasons for the autolocalisation of topochemical processes in general, and of thermal decomposition reactions in particular, can be connected with the anisotropy of the crystal. Thanks to this faces which exhibit increased reactivity can develop during the process. Buntin[7] was interested in the possibility of an autolocalisation of this type during the occurrence of topochemical reactions. This type of autolocalisation has been examined in greater detail in Pavlyuchenko's studies[11,12]. Different places on the surface of a crystal are known to be non-equivalent in reactivity. For example, if the crystal is a cube the particles situated at its vertices are more reactive in thermal decomposition than those situated on the edges. In turn, the particles situated on the edges are more active than those on the faces of the crystal, etc.

We will assume that the reaction starts at the most active sites in the crystal—its vertices. When as a result of the first reaction act a particle is removed from a vertex of the crystal, this brings about the appearance of three new particles which are equivalent in reactivity to that which has disappeared. When these three particles are also removed as a result of chemical reaction, there are then six such particles in the next layer, and so forth (Fig. 1). Since the reactivity of these particles is higher than that of the particles situated in the remaining parts of the crystal the localisation of the thermal decomposition takes place at this particular site.

Hence the mechanism of thermal decomposition is regarded as analogous to that previously developed in studies of the mechanism of dissolution of ionic crystals[13-15]. Therefore, just as in the dissolution of a crystal, as a result of the merging of reaction zones, which

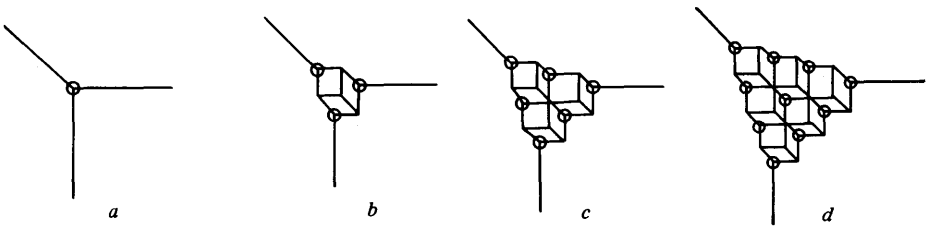


Figure 1. Autolocalisation of the thermal decomposition due to crystal-chemical features of the structure of the initial substance. *a*) Start of the reaction; *b*), *c*), and *d*) separate stages in its development.

are sometimes characterised as a form of negative crystals[16], the crystal ultimately acquires a spheroidal form and the further development of the process is described by the law of contracting spheres.

Thermal decomposition with such a process of autolocalisation is usually characterised by the absence of catalysts among the solid and gaseous products which are formed in the thermal decomposition.

The thermolysis of mercury(II) oxide crystals[16] can serve as an example of this type of process. The decomposition of mercury(II) oxide crystals was found to start at the defect sites on the surface of the crystal and to develop with different rates in different crystallographic directions with the formation of decomposition figures analogous to etch figures and negative crystals. In later studies[17] it was shown that when the temperature was raised the decomposition proceeded over the entire surface. An analogous picture is observed in the thermal decomposition of silver cyanamide[18,19] and in the sublimation of certain ammonium salts, for example, ammonium perchlorate[20]. For the latter it has been shown that when the decomposition (sublimation) takes place at low temperatures the reaction is localised in the zone of dislocations.

2. AUTOLOCALISATION OF THERMAL DECOMPOSITION DUE TO THE FORMATION OF A SOLID PRODUCT DURING THE COURSE OF THE REACTION (AUTOCATALYSIS BY A SOLID PRODUCT OF THE REACTION)

a. General Positions of the Theory of Phase Transformations

The possibility of the autolocalisation of the process of thermal decomposition due to the formation of a solid product during the reaction has been discussed repeatedly[5,8,21,22]. This has been thought[6] to follow from the analogy between the occurrence of topochemical processes and other types of phase transformation (for example, crystallisation from aqueous solutions or from melts, polymorphic transformations, etc.). And although later investigations have shown that this analogy is by no means always complete we will employ it in the present review, mentioning as we go those factors specific for solid-state chemical reactions, which must be taken into account in studying this type of phase transformation.

As follows from the general theory of phase transformations[23-25], the formation of nuclei of a new phase can be regarded as the result of local fluctuations in temperature or concentration in the system, due to which nuclei of a new phase are formed. The change in free energy (the magnitude of which ultimately determines the formation of a new phase) can be written as a sum:

$$\Delta g = \Delta g_v + \Delta g_s,$$

where Δg_v is the change in free energy due to the chemical reaction pertaining to the entire volume, and Δg_S the change in free energy due to the formation of the surface of the new phase.

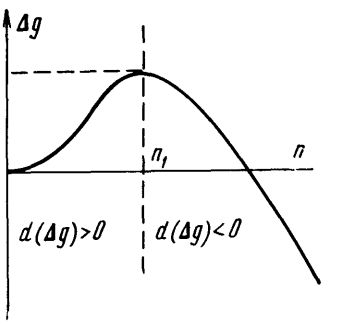


Figure 2. Change in free energy in the formation of nuclei of a new phase during the course of a phase transformation.

The change in free energy for the processes of condensation of vapour and crystallisation from a liquid medium can be written:

$$\Delta g = n(\mu_1 - \mu_2) + \alpha\gamma n^{2/3},$$

where n is the number of moles of reaction product, μ_1 and μ_2 are the chemical potentials of the initial substance and reaction product, α is a coefficient which depends upon the form of the nuclei, and γ the surface energy.

When the solution is supersaturated, $\mu_2 > \mu_1$, the first term in the right-hand part of the equation has a minus sign, and therefore Δg in the change of dimensions of the nuclei is characterised by some extremal value, after reaching which the nuclei become capable of stable growth (Fig. 2).

For the nuclei to reach a dimension greater than the critical one it is necessary to expend energy not only in its formation (Δg) but also the additional amount of energy necessary for the transfer of the particles of the new

phase from the solution or melt through the phase separation boundary. Therefore the rate of formation of the nuclei can be described by the equation:

$$w = c \cdot e^{-\frac{(\Delta g + u)}{kT}}$$

For certain types of phase transformation, for example, in crystallisation from a melt or in the polymorphic change from a high-temperature form into a low-temperature one, the changes $-\Delta u/kT$ and $-\Delta g/kT$ proceed differently (the change in Δg proceeds antibathically to the change in Δu) and as a result a maximum appears on the rate curves—supersaturation. For certain other phase transformations, in particular, in thermal decomposition, this antibathic relation and consequently the maximum may not exist[26].

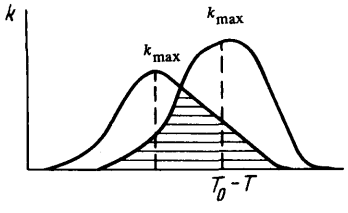


Figure 3. Temperature dependence of the constants for the formation of nuclei and for their growth.

The growth of a nucleus after it has been formed and reached critical dimensions can be regarded as the result of the formation of two-dimensional nuclei on the crystal surface. The change in free energy for the formation of two-dimensional nuclei can be written as

$$\Delta g_2 = n(\mu_1 - \mu_2) + \gamma n^{1/2}$$

and the rate:

$$w = c_2 \cdot e^{-\frac{(u_2 + \Delta g_2)}{kT}},$$

passes through a maximum, just as does the rate for three-dimensional nuclei. Since the dependence of Δg_1 and Δg_2 on supersaturation is different, u_1 and u_2 are different, and so are c_1 and c_2; in general, the positions of these maxima do not coincide (Fig. 3) and therefore either the formation or the growth of nuclei, or both processes together, can take place, depending upon the supersaturation in the system (shown on the Figure by the departure of the temperature from the equilibrium value in crystallisation, induced by cooling of the system).

b. Phase Transformations in the Thermal Decomposition of Solid Substances

When this theory is used for other types of phase transformation, and, in particular, for thermal decomposition, allowance must be made for those specific factors which can significantly alter the general picture of the transformation.

Formation of clusters. Topotaxy. An important factor, which determines both the relation of the chemical and phase stages and also the general nature of the influence exerted by the nuclei of the reaction product on the properties of the initial crystal is the presence of a coherent bond between the lattices of the initial substance and the reaction product.

The possibility of the appearance of this factor depends, firstly, upon some specific features of the formation of nuclei of a new phase in the occurrence of solid-phase processes, and secondly, upon the possibility of effecting an approximate correspondence between the lattice of the initial substance and the lattice of the product.

By analogy with the processes which take place in crystallisation from a melt or a solution when the heterophase fluctuations are the result of the motions of individual atoms or molecules, nuclei are also formed when processes occur in the solid phase. However, the results of more detailed investigations showed that in fact the formation of nuclei in solid-phase reactions is a more complex process, which includes the stage of aggregation in clusters of point defects or dissolved atoms, which become especially significant at the moment of the transformation preceding the formation of a nucleus of the new phase. The interaction can be different in nature but also appears for monotypical defects and for defects of different types.

For identical defects (or atoms) in a polar crystal it comprises the forces of repulsion due to the interaction of the coulombic field and the field of the elastic stresses which surround the defects in the crystal and the attractive forces due to the quantum-chemical interaction. When the attractive forces are greater than the repulsive forces the curves of the potential energy of interaction will be characterised by a minimum. When the depth of this minimum is greater than the mean energy of the phonons in the lattice (κT) the defects can be expected to form clusters[27,28].

For defects of different signs the possibilities of interaction are increased to an even greater degree, for both elastic and coulombic interaction in this instance can lead to attraction and the probability of the formation of clusters is increased accordingly.

In this sense the dependence of cluster formation and in particular of the structure of the clusters in the very first stages on the conditions under which separation of the new phase takes place is extremely important, although there is almost no information about this. Among the few papers in this direction is that of Johanneson and Person[29], who used an electronic computer to model the growth of atomic clusters in the deposition of thin films of silver on the surface of alkali halide crystals. For the modelling they took a relatively simple model, in which the interaction between the adsorbed silver atoms was given by the Morse function

$$\Phi(r) = D[\exp -2\alpha(r - r_0) - 2\ \exp -\alpha(r - r_0)],$$

the calculated values of which for silver are known, the interaction between the adsorbed atoms and the surface is given by the potential function:

$$V(x, y, z) = -\left[Q_d/4\left(\sin\frac{2\pi x}{x_0} + n\frac{2\pi y}{y_0}\right) + Q_{ads} - Q_{dif}/2\right]\exp(-z/z_0)$$

where x_0, y_0, and z_0 are the lattice constants in the direction of the three geometric axes, and Q_{dif} and Q_{ads} are the activation energies of the diffusion and adsorption of the atoms on the surface.

The variation, as parameters of the system in the determination of the energy minimum, of Q_{ads}, Q_{diff}, and d (periodicity of the lattice) showed that not only two-dimensional but also three-dimensional, nuclei can be stable, and that of the three parameters being varied the most important is the interatomic distance of the lattice (d), on which the adsorption takes place. It has been shown[29] that as a result of the change in d the form of the primary cluster consisting of six atoms changes from rectangular to orthorhombic. The form of the cluster is also extremely sensitive to the number of atoms forming the cluster and its dimensionality. What is significant in this is that the three-dimensional nuclei-clusters can be just as stable as the two-dimensional and the addition of each new atom, at least in the initial stage, significantly affects the form of the cluster.

It is quite natural that a similar type of estimation can also be made when we are considering not the deposition of metal atoms from the gas phase on the surface of a crystal, but a solid-phase reaction in which clusters are formed from the defects, for example, from internodal ions, ionic vacancies, and not in a vacuum, but within the crystal lattice. The number of parameters being varied in this instance should be changed and the value of the Morse function should be found for the interaction of the internodal ions, vacancies, etc. Evidently, in principle the approach used for calculating the form of the clusters in the epitaxial growth of thin films is applicable also for topochemical reactions.

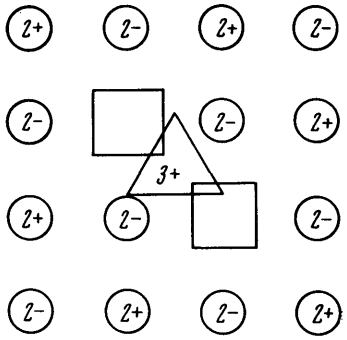


Figure 4. Elementary stages of the formation of Fe_3O_4 in the decomposition of FeO.[28]

As an example, now classical, there is the formation of nuclei of a magnetite phase in the decomposition of wüstite[30]. In the decomposition, which proceeds by the overall scheme:

$$4FeO \rightarrow Fe + Fe_3O_4,$$

the composition of the wüstite phase becomes $Fe_{1-x}O$, where x denotes a position in the lattice occupied by Fe^{3+} ions and cationic vacancies, the formation of which is necessary for the compensation of the charge. Being found at the normal node of the lattice and having smaller dimensions than Fe^{2+}, the Fe^{3+} ion tends to go to an internodal position with the formation of a complex from the Fe^{3+} ion and two cationic vacancies situated symmetrically relative to it. The Fe^{3+} ion occupies the positions which are typical for the tetrahedral node of the spinel formed (Fig. 4). Similar examples are also known for other solid-phase reactions[31].

In addition to the crystal-chemical aspect of the significance of clusters it is also important to bear in mind the thermodynamic aspects[31], which lead to an increase in the probability of the surmounting of the energetic barrier for attaining nuclei of critical dimensions.

An orientation correspondence of the crystal-chemical parameters of the old and new phases is extremely important not only for the formation of these phases but also to an even greater extent for their growth in ensuring that the lattices of the new and old phases are coherent.

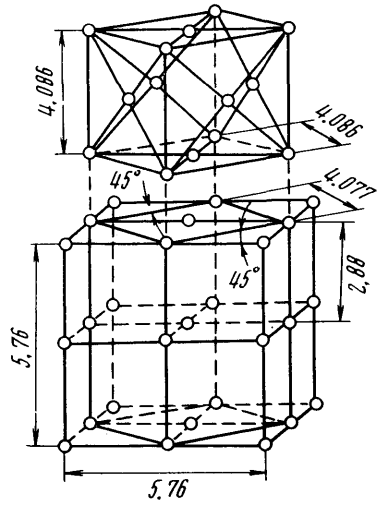


Figure 5. Orientation correspondence between the lattices of silver bromide and silver.

The condition under which there is an orientation correspondence which ensures the uninterrupted change from a phase of the initial substance to a phase of the reaction product was formulated by Dankov[32,33]. According to Dankov, chemical changes on the surface of a solid body develop in such a manner that the configuration of the atoms of the initial phase is retained (or more precisely, almost retained) in the new solid phase. The crystal lattice of the new phase formed in this process is joined with that of the initial phase by similar crystal planes, the parameters of which remain minimal. As an example of the orientation correspondence in decomposition reactions, there is the orientation growth of silver on the surface of silver bromide (Fig. 5). Whether two-dimensional nuclei of a new phase will be orientated according to the lattice of the initial substance or whether independent nuclei will be formed depends on the deformation energy of the two-dimensional lattice of the new phase E and the work of formation of the independent three-dimensional nucleus A. If $E < A$ there will be an orientation correspondence and the epitaxial and topotaxial growth of the nuclei of the new phase will be possible; if $E > A$ then the formation of the nuclei of the new phase will proceed independently of the lattice of the initial substance.

This principle was developed further[34,35], and it was found that when the orientation correspondence is observed the lattice of the product can correspond with the lattice of the initial substance in two (epitaxy) or three (topotaxy) measurements. Many examples of topotaxial transformations in solid-state chemical reactions (including those of thermal decomposition) are now well known and have been reviewed[36,37].

Owing to the topotaxial change from one crystal lattice to another there is always a decrease in the activation energy of transformation, which for non-topotaxial transformations should be equal to or greater than the heat of the phase transformation[38,39].

It is often possible for there to be produced a fine structure of the lattice of the reaction product under the lattice of the initial substance and for topotaxy to be guaranteed not only in the initial part of the process but also in its subsequent stages. This occurs when there is disparity between the lattice parameters of the initial substance and the transformation product, which can increase with growth of the product lattice along the phase separation boundaries, will be removed by the formation of dislocations at the separation boundary of the lattices[40], and especially will ensure retention of continuous contact between the lattice of the initial substance and the reaction product.

Thickness and structure of the interfacial zone. For many processes which take place in the solid phase, including thermal decompositions, the rate of the chemical reaction can be much greater than the rate of the phase stage and therefore the stages will not agree in either time or space. The possibility of the occurrence of topochemical decomposition reactions in this manner was noted by Roginskii[41].

Such processes were studied in detail later by Frost and coworkers[42-44]. Owing to the separation of the chemical and phase stages of the process it appears that an intermediate layer is formed instead of an interfacial surface which separates the lattice of the solid reaction product and the initial substance. Sometimes, when the chemical and phase stages are separate and the localisation of the process at the phase separation boundary is not connected with the catalytic action of the solid product there is almost complete agreement of the activation energy of thermal decomposition with the change in enthalpy during the process. As examples of this type of thermal decomposition, there are the decompositions of silver carbonate[44] ($\Delta H = \Delta E = 20$ kcal mole^{-1}), calcium carbonate ($\Delta H = \Delta E = 50$ kcal mole^{-1}),[45] ($\Delta H = \Delta E = 42.5$ kcal mole^{-1}) and cobalt[46] and zinc sulphates ($\Delta H = \Delta E =$ 54 kcal mole^{-1}).

A similar agreement of the activation energy with the change in enthalpy is also observed for other phase transformations in the solid phase (for example, the polymorphic transformations of sulphur, 2-nitroaniline into 3-nitroaniline, etc.[39]), when the possibility of a topotaxial transformation from the initial substance to the reaction product is absent and the formation of the lattice of the new phase precedes the complete breakdown of the initial lattice.

The reasons for the formation of a layer instead of a surface of separation of an initial crystalline phase and a reaction product can be various. On the one hand, as Cahn and Hillard[49] have shown, thermodynamic causes linked with the need for minimising the free energy at the phase separation boundary can lead to the appearance of a layer between the initial substance and the reaction product. According to this condition the minimum free energy at the separation boundary occurs at a strictly definite thickness and composition of the separation boundary, and these ultimately are functions of the temperature and the heat of mixing of the initial substance and reaction product.

On the other hand, after the appearance of the transitional layer which separates the phase of the initial substance and the phase of the product, kinetic factors can also be responsible. Their effect will appear when, for example, the change of the product phase from metastable amorphous or cryptocrystalline into the thermodynamically stable crystalline state is hindered for some reason.

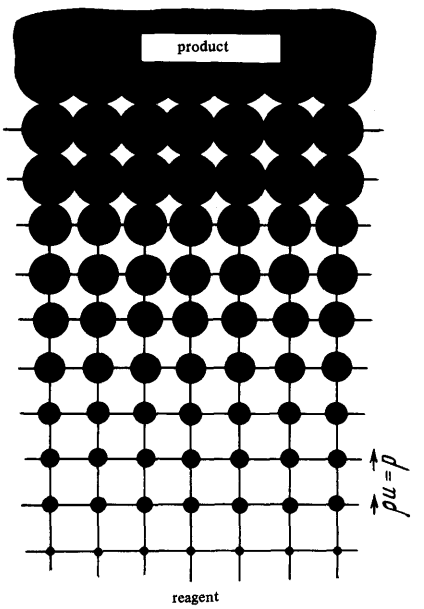


Figure 6. Diffuseness of the reactivity zone at the separation boundary between the initial substance and the reaction product[53].

The possibility of allowing for this factor can be shown by the example of the dehydration of a crystalline hydrates[50,51]. In this thermal decomposition the probability of the separation of chemical and phase stages ultimately is greater the stronger the bonding with one another of the atoms in the dehydration products formed. When this bond is strong enough, as is observed for the products obtained in dehydrating zeolites, the phase stage generally cannot start until after the complete removal of the water. On taking a crystal hydrate in which the structural components in the anhydrous residue are still bonded but much more weakly than in the zeolites (for example, magnesium sulphate heptahydrate) the phase stage will be observed but with some lagging behind the chemical one, and between the lattices of the initial crystal hydrate and of the dehydration product an intermediate amorphous layer is formed.

If we take such a crystal hydrate, in which the energy of the bond between the elements of the lattice is low (for example, copper chloride dihydrate) the chemical and

phase stages can proceed at similar rates and therefore in this instance the thickness of the intermediate layer between the initial substance and the reaction product can be extremely low.

The separation of the chemical and phase stages and the associated conversion of the interfacial surface into a layer can affect the kinetics of the thermal decomposition in various ways. Firstly, the separation of the crystalline phase of the reaction product from the initial substance also reduces the probability of the catalytic action of the reaction product on the initial substance (this will appear particularly when the mechanism of catalysis is connected with the orientation-deformation interaction of the lattices of the initial substance and reaction product). Secondly, the conversion of the planar reaction zone into a layer implies the existence of significant changes in the models which are now used for the kinetic analysis of topochemical reactions (in most of these it is assumed that the interfacial surface is planar).

de Boer[52] was interested in such special instances of the occurrence of topochemical changes. Hill[53,54] showed that the diffusion of the reaction zone (see Fig. 6) and the change from a planar reaction zone to a layer can occur when there is a drift of atoms or ions from the layer of the product into the layer of the initial substance, as a result of which there is continuous formation of nuclei of the new phase around the main reaction front. At a certain ratio of the rates of nuclei formation, the rate of diffusion of ions which "contaminate" the initial substance, and the rate of motion of the interphase surface, a diffusion layer is formed between the initial substance and reaction product; this layer consists of a mixture of the initial substance and nuclei (of various sizes) of the reaction product. The result of this can be many kinetic anomalies, for example, the anomalously high values of the pre-exponential factor in the dehydration of chromium alum, observed by Anous and coworkers[54].

When the decomposition can proceed not only on the surface of the solid body but also within its bulk and the diffusion coefficient of the volatile product which is formed is sufficiently great the situation can arise in which a diffusion layer is also formed instead of a smooth separation surface. It is easy to understand that the profile of the gradient of the concentration of the reaction product removable from the system will be the reverse of that examined by Hill. A diffusion-kinetic model of such reactions was recently given by Mandelis and Strunin[55].

Deformation of the lattice close to a growing nucleus. In the formation of crystals of a new phase from a gas, solution, or melt, the volume changes are readily compensated as a result of flow of the liquid or gas. When the initial substance is a crystal then the relaxation of the deformations which occurs during the course of the transformation can be effected either by elastic deformation or plastic flow, or alternatively by diffusion processes[56]. Therefore the equation for the free energy of nuclei formation for solid-phase processes contains yet another term Δg_e connected with the deformation of the surrounding medium by the growing nucleus:

$$\Delta g = \Delta g_v + \Delta g_s + \Delta g_e$$

The second term Δg_S for solid-phase processes also has a somewhat different physical significance, since instead of the surface energy it includes the energy of the surface of separation between the two crystalline phases.

Usually this energy is represented as the sum of chemical and structural constituents[57]. The chemical constituent can be found when the crystal structures of the initial phase (α) and the reaction product (β) have the same symmetry and lattice parameters. In this instance the surface energy at the $\alpha-\beta$ phase separation boundary can be evaluated simply to the first approximation as the energy of interaction of nearest neighbours:

$$\sigma_{\alpha\beta} = n_s z_s [\varepsilon_{\alpha\beta} - {}^1/_2 (\varepsilon_{\alpha\alpha} + \varepsilon_{\beta\beta})],$$

where n_S is the number of atoms per unit area of the interfacial surface, z_S the number of $\alpha-\beta$ bonds per α or β atom in the plane of the $\alpha-\beta$ phase boundary; and $\alpha\beta$, $\alpha\alpha$, and $\beta\beta$ are the energies of the bonds between the different types of atoms in the system at 0°K. Since these energies are difficult to determine directly, the formula for calculating the energy of dissolution ΔE per g-mole or g-phase of β in an infinitely dilute solution of α and β can be used for the experimental determination of $\sigma_{\alpha\beta}$:

$$\Delta E = N Z_1 [\varepsilon_{\alpha\beta} - {}^1/_2 (\varepsilon_{\alpha\alpha} + \varepsilon_{\beta\beta})],$$

where N is Avogadro's number and Z_1 the coordination number. On combining these equations, we have:

$$\sigma_{\alpha\beta} = \frac{n_z \cdot Z}{N Z_1} \Delta E$$

To calculate the structural constituent, we assume that the lattice parameters of phases α and β at the phase separation surface are different although the arrangement of the atoms in the two lattices are similar. Then the parameter of non-correspondence of the lattices (maladjustment) is determined as:

$$\Delta = (a_\alpha - a_\beta)/a_\alpha,$$

where a_α and a_β are the atomic distances in the regions in contact. Since the density of dislocation is proportional to $1/\Delta$, then knowing the energy necessary for the formation of a single dislocation the structural constituent can also be calculated. $\sigma_{\alpha\beta}$ can also be approximately represented as the difference in energy of the lattices of the phases in contact per unit interfacial surface[58].

The deformation of the lattice both owing to the energy at the phase boundary and owing to the difference in molecular volumes of the initial substance and reaction product can be calculated when the volume change, the form of the region in which the change took place, and the form of the crystal of the new phase are known (the possibility of such a calculation has been shown for certain examples of phase changes in metals and alloys[56]).

According to Nabarro's work[59], the form of the nuclei which are formed should depend mainly upon the two main components bringing about the deformation of the lattice which surrounds the growing nucleus: the components of the deformation K_S, associated with the interfacial energy, and the components of dilatation K_V due to the change in volume during the transformation. When K_S is large, the nuclei will tend to adopt the form with the minimal ratio between the surface and the volume, that is, when the medium in which its growth takes place is isotropic, the form of a sphere. When K_V is large, the tendency to the minimisation of the energy of deformation will result in the nuclei formed being planar and extended along the surface. The combination of these factors with the anisotropy of the deformability of the initial substance will lead to various forms of nuclei, which are observed in experimental investigations.

The deformation of the lattice of the initial crystal as the nuclei of a new phase grow in it has been observed

experimentally in certain instances, for example, by Morrison and Nakayama[60], who studied the topochemical interaction of gaseous chlorine with a potassium bromide crystal and used birefringence for observing the deformation of the bromide crystal around the growing nucleus. As Fig. 7 shows, there is especially pronounced deformation in the region of the crystal adjacent to the corners of the growing nucleus.



Figure 7. Formation of a deformation zone around the growing nucleus.

The deformation of the lattice around a nucleus can lead to a change in the reactivity of the crystal in this region. The low-temperature transformation of austenite into martensite is the classical example of how significant is the elastic deformation of the lattice close to the growing nucleus for the development of solid-state processes[61]. The peculiarity of this process is that the transformation of the initial substance (austenite) into martensite proceeds without diffusion and for it to occur only requires some movement of the iron atoms in the lattice by a distance less than the parameters of the lattice (Fig. 8). The elastic stresses which arise in austenite as a result of the appearance of the nuclei of a new phase and which are situated in advance of the phase transformation front help the transformation to become collective and the rate of transformation to become very large, approaching the rate of propagation of sound in austenite.

Dislocations evidently may occur as a result of the relaxation of lattice deformations in the region around growing nuclei. This is confirmed by the experimental results on the increase in the density of dislocations close to the growing nucleus, which have been obtained for several systems[62-64].

The formation of dislocations in a crystal close to a growing nucleus can significantly alter the reactivity in this place, particularly when the decomposition takes place at low temperatures. In a thermal decomposition the formation of dislocations simultaneously alters both the conditions of transport of the reagents and reaction products in the mass of the crystal and also has an action on the decomposition of the solid solution and reconstruction of the lattice of the initial substance, which usually accompanies the thermal decomposition.

Possible paths for the influence of dislocations on the thermal decomposition have been examined frequently. It has been thought that in the thermolysis of certain ionic crystals, for example, lead azide and sodium bromate at very low temperatures, the dislocations will be the only places in the crystal where it is possible to expect development of a reaction[65]. The dislocations can be channels through which rapid migration of the product ions can occur, from the "contaminated" non-reacted region of the initial crystal, according to Hill's hypothesis, which we have already mentioned. The appearance of channels by which ions can move at rates many times greater (this difference can reach several orders of magnitude) than in the bulk of the crystal enables dislocations to play a significant part in the supply of material needed for the construction of the lattice of the reaction product. This is necessary to ensure the normal growth of the nuclei for the thermal decompositions in which the stoichiometry of the nuclei growth process proceeds owing to one of the elements of the lattice and the aggregation of these atoms or ions is a necessary stage. For example, such happens in the thermal decomposition of metal salts to the metal (for example, in the thermolysis of silver oxalate).

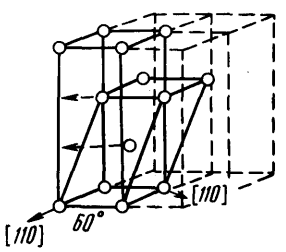


Figure 8. Scheme of the martensitic transformation.

In addition to the influence on the transfer process of dislocations which arise as a result of the relaxation of elastic strains in the lattice of the initial substance around the growing nucleus, the thermal decomposition can be accelerated by impurities and dissolved atoms and ions from the lattice accumulating in the zone of extension of the dislocations. Since in this part the most favourable conditions for the breakdown of the solid solutions and reconstruction of the lattice are set up, the place where the dislocations emerge at the surface are often potential centres at which formation of the nuclei of a new phase occurs during thermal decomposition. The change in the topography of the position and density of the dislocations in the crystal (for example, owing to polygonisation in annealing and the physical ageing of the crystals) is reflected in the kinetics of the thermal decomposition.

An illustration of what has been said is given by the results of our experiments, which showed a connection between the change in the density of the dislocations in crystals of lead oxalate and the kinetic parameters of the thermal decomposition of this salt (cf. Ref. 66 and pp. 124–157 of Ref. 1) and also the work of Thomas which was specially concerned with the appearance of dislocations in various topochemical reactions[67-71].

c. Other Forms of Autolocalisation Process Connected with the Influence of a Solid Reaction Product

In addition to the deformation action associated with the orientation interaction at the separation boundary of two phases and the volume changes throughout the process in certain types of topochemical transformations of a solid reaction product there are other specific influences on the reaction rate. When the thermal decomposition is a redox reaction the solid product which is formed can alter the conditions under which an electronic transition takes place and thereby accelerate or inhibit the thermal decomposition.

As an example of such an effect, which arises in the formation of a solid product, we can examine the development of the thermal decomposition of barium azides. According to the ideas of Torkar and his coworkers[72,73] the formation of nuclei in the thermolysis of barium azide takes place as a result of the capture of the excited state of the azide ion on a defect, which can, for example, be an anionic vacancy. Owing to this, as a result of the transfer of an electron trap

$$N_3 + \text{phonon} \rightleftarrows N_3^{-*} + \square \rightleftarrows [\square N_3^{-*}],$$
$$[\square N_3^{-*}] \rightarrow [\square e]\, N_3^0,$$

and then its localisation on a neighbour with a cation trap, formation of a Ba^+ ion takes place:

$$[\square e]\, N_3^0 + Ba^{2+} \rightarrow [\square Ba^+]\, N_3,$$
$$2N_3^0 \rightarrow 3N_2,$$

and the azide radical is converted into nitrogen. It is assumed that the complexes

$$[\square e\, Ba^{2+}] \rightleftarrows [\square Ba^+]$$

are nuclei of the last thermal decomposition. Since the Ba^+ level should represent an acceptor level in the lattice lying at the limits of the forbidden band, its presence will facilitate the last transfer of an electron from a neighbouring azide ion at this level:

$$\square_a Ba^+ + N_3^- \rightarrow \square_a\, BaN_3^0 \rightarrow \square_a Ba\square_a + {}^3/_2\, N_2,$$

as a result of which a complex is formed from a metal atom and two anionic vacancies:

$$\square_a Ba\square_a + Ba^{2+} \rightarrow [\square_a BaBa\square_a]^{2+} \rightarrow \square_a Ba^+ Ba^+ \square_a$$

As a result of the process, stabilisation of the complex and regeneration of its acceptor properties takes place (Fig. 9). This ensures maintenance of the conditions for the autolocalisation of the process at the place where the nucleus arises and determines its growth. Since the conversion of barium azide into the metal proceeds topotaxially and diffusion processes do not play a significant part, the limiting rate of growth of the stages is the redox process at the metallic barium—azide boundary. The nature of the development of the process described above corresponds to activation energies of formation (63 ± 5 kcal mole^{-1}) and growth (26 ± 1 kcal mole^{-1}) of nuclei of metallic barium in the thermolysis of the azide.

If the solid substance which undergoes thermal decomposition is an electron or hole semiconductor and the reaction for the decomposition is a redox reaction then the solid product which is formed in the decomposition can alter the reactivity of the substance in the region adjacent to the place where formation of the reaction product occurred, owing to the changes in the concentrations of electrons and holes close to the phase boundary. An example of this process is the thermolysis of potassium permanganate, the mechanism of the decomposition of which was studied in detail in our laboratories[74]. According to the scheme proposed, the thermal decomposition of potassium permanganate, which is an n-type semiconductor[75,76] takes place owing to the transfer of an electron from one permanganate ion to another:

$$MnO_4^- + MnO_4^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} MnO_4^0 + MnO_4^{2-}$$
$$\downarrow$$
$$MnO_3 + O_3$$

As a result of the transfer the unstable MnO_4^0 is formed, which immediately decomposes into MnO_4 and O_2. On making the natural assumption that the electronic decomposition is rapid and the rate-limiting stage is the decomposition of the MnO_4^0 radicals then a stationary state is established in the system.

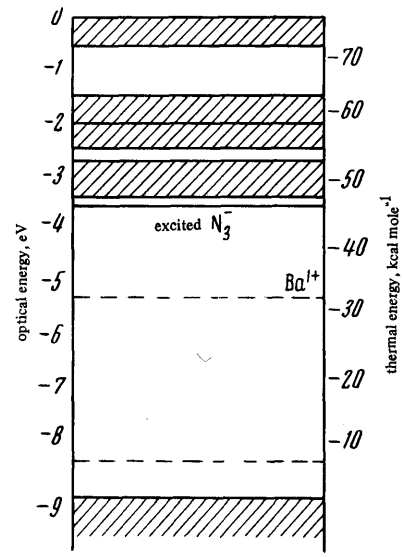


Figure 9. Scheme of the energy levels in barium azide.

It is easy to see that the overall rate of the process will be increased by the shift of the electron—hole equilibrium k_1/k_2 to the right and decreased when it is shifted to the left. The condition for such a shift in the equilibrium can arise, for example, owing to the contact potential difference at the separation boundary between the initial permanganate—and the solid reaction products, which are MnO_2 and the double salt $K_3(MnO_4)_2$, which is an ion associated with the MnO_4^{2-} ion.

Measurement of the electron work functions of potassium permanganate, manganate (as the double salt), and manganese dioxide showed (Fig. 10) that under conditions close to those for thermal decomposition the electron work function of manganese dioxide is greater than that for permanganate, but that from manganate, on the other hand, is less. In accordance with this and our scheme of thermolysis of permanganate, MnO_2 should be an acceptor of electrons and therefore should catalyse the thermal decomposition of permanganate, whereas manganate should be a donor of electrons and inhibit thermolysis. Actually, as is clear from the results (Fig. 11) on the thermolysis of potassium permanganate with additions, the addition of

MnO_2 accelerates the thermal decomposition of permanganate, but additions of manganate, on the other hand, retard it. Therefore the well-known phenomenon of autocatalysis in the thermal decomposition of permanganate is itself the superimposition of the catalytic action of one of the reaction products and the inhibiting action of the other.

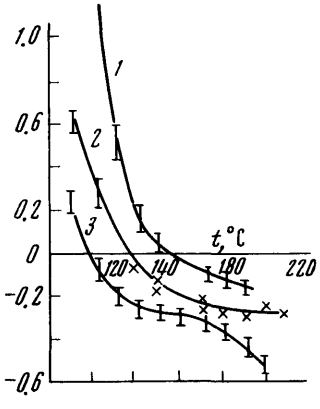


Figure 10. Work function from permanganate and its decomposition products: *1*) $K_3(MnO_4)_2$; *2*) $KMnO_4$; *3*) MnO_2.

A peculiarity of the autolocalisation in this instance is that the influence of the solid product of the reaction is not limited to the surface layer of the initial substance adjacent to the product but extends into the depth of the initial solid phase according to the length of the screening charge and therefore the formation of MnO_4^0 radicals can take place in the bulk of the crystal at some distance from its surface. Since the decomposition into MnO_2 and O_2 is almost irreversible, the liberation of gas in the bulk of the crystal ultimately leads to the dispersion of the crystal during its thermal decomposition. This and not the difference in the lattice parameters of the product and the initial substance, which, judging from our results, will hardly be significant, is the true reason for the self-shattering of permanganate.

In addition to what has been described, there can be other forms of autolocalisation of a process, for example, those linked with special conditions for proton transfer, which exist at the phase separation boundary in the dehydration of crystal hydrates and oxide hydrates, the presence in this place of anomalous valence states of the elements, etc.[77,78] However, these factors have been insufficiently studied.

The following conclusions can be drawn on the basis of the above considerations: the influence of the reaction product depends very strongly on the degree of its contact with the initial substance. Therefore to the first approximation all the thermal decompositions can be divided into two classes, depending upon whether the coherency of the lattices of the product and initial substance during the course of the process are maintained or not. It is quite natural that the coherency, and consequently the contact, will be ensured to the greatest extent when the formation of a product from the initial substance takes place topotaxially. However, here only some of the properties will be altered by the discontinuity at the separation boundary. For example, in the thermal decomposition of barium azide, the lattice parameter changes smoothly at the separation boundary but the electrical properties change suddenly. With growth in the layer of reaction product the necessary orientation correspondence can be ensured by the substructure of the lattice of the product under the lattice of the initial substance (or the reverse), for example, owing to the formation of dislocations at the phase separation boundary.

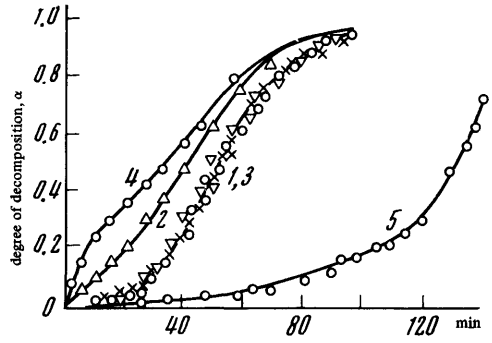
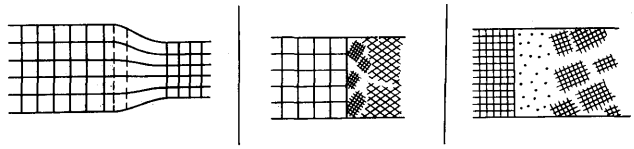


Figure 11. Kinetic curves of the influence of MnO_2 and K_2MnO_4 on the decomposition of $KMnO_4$. *1*) Decomposition of permanganate at 220°C; with addition of MnO_2 (reagent); *2*) the same with addition of MnO_2, obtained in the thermal decomposition of $KMnO_4$; *3*) with addition of MnO_2 obtained by heating $Mn(NO_3)_2$ at 170°C; *4*) with addition of MnO_2 made by oxidation of 5% $MnSO_4$ heated to 60°C; *5*) with addition of K_2MnO_4 (cocrystallised); *6*) decomposition of permanganate without any additions (below *1*, *3*).

Table 1.

Nature of the formation of a solid reaction product

coherent (topotaxy)		incoherent	
total	partial	$V_{phase} \sim V_{chem}$	$V_{phase} \ll V_{chem}$



Factors leading to a change in the reactivity of a solid substance close to incipient nuclei of the product

(a) deformation connected with energy of interfacial orientation interaction of the two lattices; (b) deformation connected with change in volume; (c) change in the conditions for the occurrence of electronic and ionic processes in the near-contact region at the phase separation boundary.	(a) deformation connected with the change in volume; (b) change in the conditions for the occurrence of electronic and ionic processes in the near-contact region.	(a) change in the conditions for the occurrence of electronic and ionic processes in the near-contact region.

Another extreme instance is the complete destruction of the lattice of the initial substance as a result of the thermal decomposition and absence of coherency between the lattices of the initial substance and the reaction product. In this instance, depending upon the ratio of the

rates of the chemical and phase stages observable as a result of the reaction of the amorphised layer, the product can either be found in contact with the initial substance or will be separated from it by a layer of the amorphous material: depending upon which of these two distinct possibilities arises so will the influence of the solid product of the reaction on its rate be determined (Table 1).

If there is a coherency between the lattice of the product and the lattice of the initial substance it is to be expected that the energy of interfacial interaction will greatly affect the properties of the initial substance. When as a result of the reaction there is a considerable increase in the specific volume of the reaction product in comparison with the volume of the initial substance, there can prove to be a significant associated deformation of the lattice of the initial substance, which will happen even in the absence of coherency.

Finally, the change in the nature of the occurrence of electronic and ionic processes in the region near the contact can appear when the phase and chemical stages do not coincide.

3. AUTOLOCALISATION OF THE THERMAL DECOMPOSITION DUE TO THE RELEASE OF GASEOUS PRODUCTS DURING THE COURSE OF THE REACTION (AUTOCATALYSIS BY GASEOUS PRODUCTS)

When the gaseous products formed during the thermal decomposition undergo further chemical change and the resulting products interact with the substance that has not yet reacted, this can also be a reason for the autolocalisation of the thermal decomposition.

An example of this type of autolocalisation is the formation of nuclei in the low-temperature thermal decomposition of ammonium perchlorate. Bircomshaw[79] showed that the low-temperature decomposition of ammonium perchlorate is accompanied by the formation of cigar-shaped nuclei. More detailed microscopical observations showed that each such nucleus is itself an aggregate consisting of finer nuclei and the growth of a nucleus takes place by the appearance of new nuclei around the edges of the aggregate[20]. Since ammonium perchlorate decomposes without the formation of a solid reaction product, the formation of nuclei in the low-temperature thermal decomposition could not be connected with the catalytic influence of the solid reaction product, the nature of the development of the nucleus does not provide the possibility of relating the localisation of the low temperature thermal decomposition with the anisotropy of the properties of the initial crystal. It was therefore postulated that the reason for the autolocalisation process in the low-temperature decomposition of an ammonium perchlorate could be the action, during the course of the process, of gaseous products formed during the course of the reaction (for example, the oxidation of ammonia by the products of the thermal decomposition of perchloric acid from the ammonium perchlorate that has not yet reacted, Fig. 12).

In the investigation of low-temperature thermal decomposition[80] it was shown that in this instance, when the dissociation of ammonium perchlorate takes place on the inner, not the outer, surface of the crystal (for example, at the boundaries of blocks, dislocation nuclei, etc.), since the molecular weights of ammonia and perchloric acid are different, it could be expected that during the course of the process in these parts there will initially be

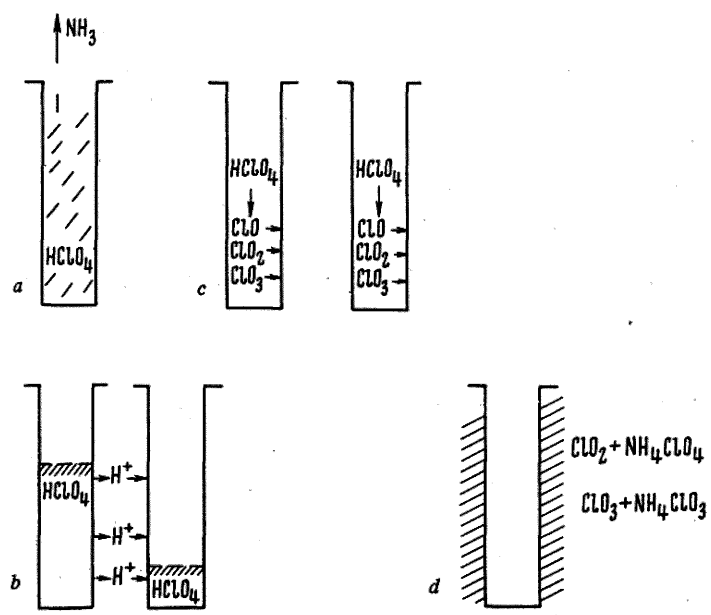
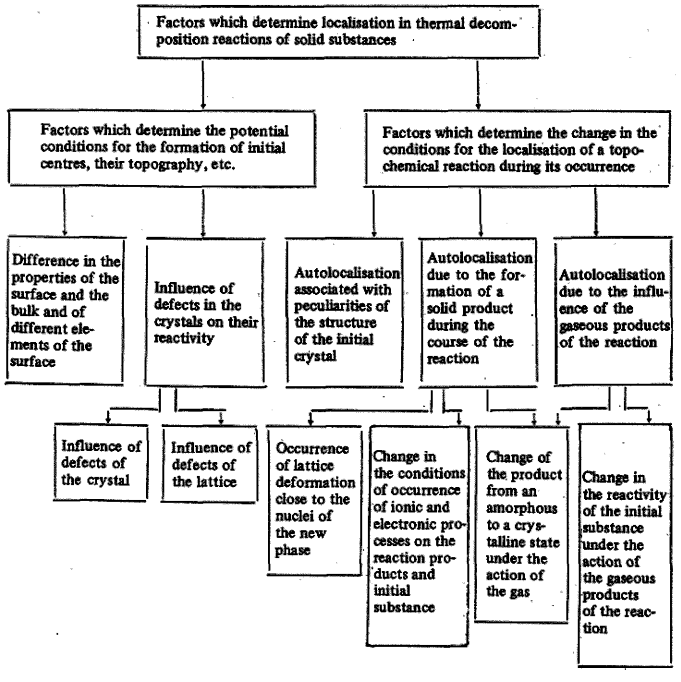


Figure 12. Scheme of low-temperature decomposition of ammonium perchlorate: *a*) separation of ammonia and perchloric acid in a pore due to the difference in the diffusion rates; *b*) migration of perchloric acid into a neighbouring pore; *c*) decomposition of perchloric acid; *d*) interaction of the decomposition products of perchloric acid with unreacted ammonium perchlorate.

an accumulation of perchloric acid and then its decomposition. Simultaneously with the decomposition owing to the proton conductivity[81,83] which is specific for ammonium perchlorate migration of the acid to the neighbouring potential centre (for example, a dislocation nucleus) and the initiation of the reaction in it can occur. The decomposition products of perchloric acid (for example, ClO, ClO_2, and ClO_3) react with ammonium perchlorate on the walls of dislocations of the boundaries of blocks, and subsequently thermal decomposition takes place owing to this reaction. It is extremely significant that during the course of the reaction there can be regeneration of the molecules of perchloric acid or chlorine oxide (for example, according to the scheme of Koroban and Svetlov[83]), which ensures decomposition of the chain, thanks to which the growth of a nucleus, as distinct from its formation, is much less dependent upon the equilibrium pressure of perchloric acid.

Table 2.



Hence whereas the formation of a reaction nucleus is connected with the dislocation processes of ammonium perchlorate and the subsequent decomposition of perchloric acid, the growth of nuclei proceeds due to the interaction of the products of perchloric acid with ammonium perchlorate.

The difference in the chemistry of these processes corresponds to different activation energies—50 ± 5 kcal $mole^{-1}$ for the formation of reaction nuclei and 30 ± 2 kcal $mole^{-1}$ for their growth process. This also is responsible for the experimentally observable autolocalisation process, which continues to develop preferentially at the place where the reaction started.

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Table 2, which we give at the end of the review, shows the mutual relation between the various factors which determine the localisation in the thermal decomposition of solid substances.

The study of the physicochemical reasons responsible for the localisation and autolocalisation of the thermal decomposition is an extremely important task. Its solution allows us to understand more thoroughly the peculiarities of the development of topochemical reactions and to note the path of their directed regulation. Should this problem be solved, then (a) conditions will be created for the quantitative study of the rates of topochemical reactions; (b) new possibilities of regulating the rates of topochemical reactions during their occurrence will be discovered. Until then in most instances the directed regulation is limited by the initial stage of the process and is carried out at the qualitative level.

The experimentally observable autolocalisation process considered above which is recorded by investigators as the ratio between the formation rates and growth rates or as the "compactness" (that is, the formation of new nuclei around the old ones), can be the result of superimposition of several factors which alter the reactivity of the initial substance.

Depending upon the nature of the long-range action of various factors due to autolocalisation, in some instances there will be growth of the nuclei which are formed, and in others there will be a change in the compactness. Therefore in any investigation in the field of topography of solid-state chemical reactions and in particular of thermal decompositions, it is important to investigate the contribution being made by each factor to the change in reactivity around the growing nucleus. The directed regulation of the development of topochemical processes not only in time but also in space is a possibility. This would permit the regulation of the morphological properties of the solid product formed, which is important in the use of thermal decomposition in the preparation of catalysts for obtaining highly active oxide masses in the metallurgy of rare metals, in the preparation of ceramic materials of the ferrite type, etc. Finally, the development of these studies can even lead to the creation of technological processes new in principle, in which the stages of the production of a substance and the formation of articles from it will be combined.

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