

LOCALIZATION PHENOMENA OF TOPOCHEMICAL REACTIONS

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Typical localization forms of topochemical reactions taking place on the surface and inside a crystal have been compared. A kinetic model of triclinic crystal decomposition, which in contrast to known models takes into account that crystal faces react non-simultaneously, has been studied. It has been shown that depending on the value of the induction period that precedes entry of the crystal face into the reaction, and on the ratio of the linear velocities of interface advance in different directions, the decomposition may proceed without self-acceleration, or with one-fold or multi-fold self-acceleration.

Topochemical or solid-state reactions are as a rule localized to certain sites in reacting solids. There are also delocalized reactions in solids, e.g. when under the action of freely-penetrating radiation the process of radiation-induced decomposition occurs with the same probability on the surface and at any point inside the crystal. This is visualized in the following way: in the course of radiation-induced decomposition the whole volume of the crystal gradually becomes non-transparent. These and similar cases constitute a separate subject for analysis and are not considered here.

In contrast to delocalized decomposition, localized decomposition does not usually produce a uniform loss of the transparency of the crystal. The illusion of uniform transparency loss may arise due to the fact that the whole surface of the crystal undergoes uniform decomposition. However, should such a crystal be broken up, an intact transparent nucleus will be seen.

Simultaneous reaction of the whole solid surface constitutes one of the simplest localization forms. For this form, proceeding from the assumption of the isotropic properties of the solids, the kinetic equations for the reaction of a grain with different relations of its dimensions, for assemblages of grains of the same size, and for assemblages of grains of various granulometric compositions have been obtained [1]. The equations can describe not only decomposition, but also other solid-state processes: the reduction of metal oxides, the dissolution of solid substances, the oxidation of metals, etc.

Uniform localization on the whole surface results in the formation of an interface, the linear velocity of advance of which into the grain may be equal or differ in dif-

ferent directions. In this case the kinetic curves α vs. $\tau/\tau_{0.5}$ (α is the conversion degree, and $\tau/\tau_{0.5}$ is the relative time) lie above the straight line which connects the origin with the point of intersection of the curves. The integral kinetic curves have no reaction self-acceleration part, and the differential curves do not pass through a maximum.

Uniform surface localization is characteristic for a process which takes place under severe conditions. In this case active and non-active sites of the grain surface react at practically the same time. Under mild conditions they react at different times, and various spot localization forms are observed instead of uniform surface localization forms.

The spot surface localization forms are usually observed for crystals the faces of which differ in their reactivity. On such crystals it is possible to observe various localization forms, including possible intermediate cases between uniform and spot forms. Among such cases of interest is that when the localization on the crystal faces is uniform, but the faces react non-simultaneously. This case is unusual in the respect that the corresponding differential kinetic curves, in contrast to above-mentioned ones, do pass through a maximum.

Let us consider a trielinic crystal with developed (100), (010) and (001) faces as an embodiment of this case. Such a choice is determined by the fact that it is possible with such a crystal to compare a calculated kinetic curve with the experimental one. Such a comparison is known [2] to be connected with some reservations with respect to the extent of coincidence or correlation between the visually observed interface and the true reaction interface. If there is no correlation, it may appear that the experimental kinetic model virtually reflects the spatio-temporal course not of a chemical reaction, but of an accompanying process, that determines the change in optical properties of the crystal and the appearance of a visually observed interface.

In order to consider the lag-times of different crystal faces, it is enough to introduce the values of the induction period into known formulae [1]:

$$a = a_0 - v_a (\tau - \tau_{\text{ind}}^{(100)}) \quad (1)$$

$$b = b_0 - v_b (\tau - \tau_{\text{ind}}^{(010)}) \quad (2)$$

$$c = c_0 - v_c (\tau - \tau_{\text{ind}}^{(001)}) \quad (3)$$

a , b and c being characteristic dimensions of the unreacted crystal nucleus at the moment of time τ ; v_a , v_b and v_c are the linear velocities of interface advance along the (100), (010) and (001) directions, respectively; a_0 , b_0 and c_0 are the half lateral lengths of the initial crystal along the same directions; and $\tau_{\text{ind}}^{(100)}$, $\tau_{\text{ind}}^{(010)}$ and $\tau_{\text{ind}}^{(001)}$ are the induction periods of reaction at the corresponding crystal face (τ_{ind} for two opposite faces is assumed to be the same, i.e. $\tau_{\text{ind}}^{(100)} = \tau_{\text{ind}}^{(\bar{1}00)}$).

The percentage of the unreacted part of the crystal is equal to its mass divided by the mass of the initial crystal. As their densities are equal, we will use volume instead of mass for conversion degree calculation:

$$1 - \alpha = \frac{V}{V_0} \tag{4}$$

V and V_0 are the volumes of the unreacted nucleus and the initial crystal, respectively. The following relationships are valid for the volumes:

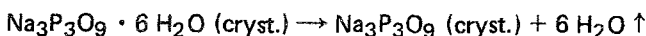
$$V = \varphi_f abc \tag{5}$$

$$V_0 = (\varphi_f)_0 a_0 b_0 c_0 \tag{6}$$

where φ_f and $(\varphi_f)_0$ are the form factors, equal to 8 for a rectangular parallelepiped, and to 4/3 for an ellipsoid [1]. For a triclinic crystal, such factors are determined by the α , β and γ values. If it is assumed that the interface orientation in relation to the initial crystal face from which the interface advances does not change in the course of reaction, and that the interface itself remains flat, then we have $\varphi_f = (\varphi_f)_0$. Hence, after substitution of (5) and (6) into (4), replacement of a , b , and c by their values from (1), (2) and (3), we have

$$\alpha = 1 - \frac{[a_0 - v_a(\tau - \tau_{ind}^{(100)})][b_0 - v_b(\tau - \tau_{ind}^{(010)})][c_0 - v_c(\tau - \tau_{ind}^{(001)})]}{a_0 b_0 c_0} \tag{7}$$

For further analysis of Eq. (7) it is advisable to correlate the equation parameters with specific values of some real process. As a model reaction, let us use the dehydration of the known triclinic crystals of sodium cyclotriphosphate hexahydrate, $\text{Na}_3\text{P}_3\text{O}_9 \cdot 6 \text{H}_2\text{O}$, with developed (100), (010) and (001) faces [3, 4]. The process



which has been thoroughly investigated in our Institute by S. I. Pytlev by means of experimental kinetic and computer techniques, is useful in the respect that, as a function of the temperature and partial water vapour pressure, the process takes place according to a model of uniform or spot surface localization and the (100), (010) and (001) faces react simultaneously or non-simultaneously. Chromatographically pure, flawless crystals (size ranges: from 1–3 mm to 10–15 mm) were chosen for the experiments. If orientated as in [3], the crystals are elongated to various extents along the [010] direction. The experimental methods used have been described earlier [5, 6]. The results indicate that the visually observed interface correlates with the reaction interface.

In vacuum and air at low relative humidity (r), the unreacted transparent nucleus acquires the form of a parallelepiped which, depending on the temperature, contracts homothetically or unhomothetically. At about 30°, homothetic contraction prevails. At about 10°, the contraction becomes unhomothetic and the contracting nucleus gradually elongates along the (010) direction. This is shown in Fig. 1 for $\tau = 80\text{--}100$ min and $t = 10^\circ$, when the hexahydrate crystal loses 4–5 mol H_2O .

If dehydration is carried out in humid air at $r \leq 25\text{--}30\%$ ($t = 20\text{--}50^\circ$), then the (100), (010) and (001) faces react in the sequence of the decrease of their activity:

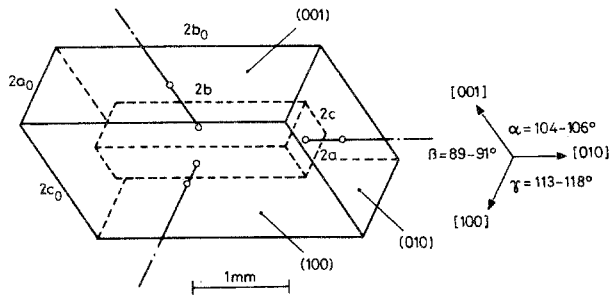


Fig. 1 Model of unhomothetically contracting nucleus of triclinic crystal

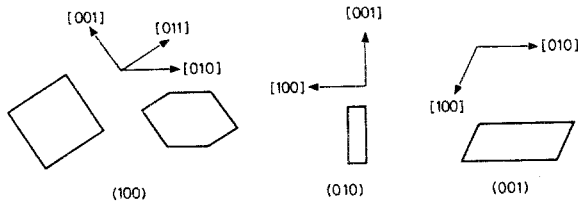


Fig. 2 Surface spot localization forms characteristic for dehydration of $\text{Na}_3\text{P}_3\text{O}_9 \cdot 6 \text{H}_2\text{O}$ single-crystal in humid air

first (100), then (001) and (010). On the increase of r , the uniform surface localization gradually changes into one of spot type, which prevails at $30\% < r < 50\%$. Characteristic well-defined dehydration figures are shown in Fig. 2. From the (100) plane there is practically no dehydration growth into the crystal. From (010) and (001) growth occurs in the (100) plane, which coincides with the plane of crystal cracking.

Let us return to the analysis of Eq. (7), taking into account the experimental data for the dehydration of single-crystals of $\text{Na}_3\text{P}_3\text{O}_9 \cdot 6 \text{H}_2\text{O}$.

First we choose values corresponding to the conditions of the known model [1]: $a_0 = b_0 = c_0$, $v_a = v_b = v_c$, and for all cases $\tau_{ind} = 0$. These conditions are easy to realize experimentally by choosing hexahydrate crystals of equal size, with their subsequent dehydration in vacuum or dry air.

In this case Eq. (7) assumes the following form:

$$\alpha = 1 - \left(1 - \frac{v_a \tau}{a_0}\right)^3 \tag{8}$$

or, after substitution of a_0/v_a by $\tau_{0.5}$:

$$\alpha = 1 - \left(1 - \frac{\tau}{\tau_{0.5}}\right)^3 \tag{9}$$

The experimental kinetic curve obtained under the above-mentioned conditions coincides with the theoretical one calculated according to Eq. (9) with an ES-1036

computer, the α -scale being divided into 15–30 parts. It also coincides with the curve calculated according to Eq. (7) with $a_0 = b_0 = c_0 = 1$ mm, $v_a = 10^{-2}$ mm/min, $v_b = 1.7 v_a$, $v_c = 2.3 v_a$ and $\tau_{ind} = 0$. Both with the above values and with other values of v_a , v_b and v_c , the curves have no self-acceleration section. This appears only when the (100), (010) and (001) faces react non-simultaneously and only with certain relations between v_a , v_b and v_c .

Let us assume $a_0 = b_0 = c_0$, $v_a \neq v_b \neq v_c$, $\tau_{ind}^{(100)} = 0$, and $\tau_{ind}^{(010)} = \tau_{ind}^{(001)} = \tau_{0.1}$. Equation (7) then has the following form:

$$\alpha = 1 - \frac{[a_0 - v_a \tau][a_0 - v_b(\tau - \tau_{0.1})][a_0 - v_c(\tau - \tau_{0.1})]}{a_0^3} \tag{10}$$

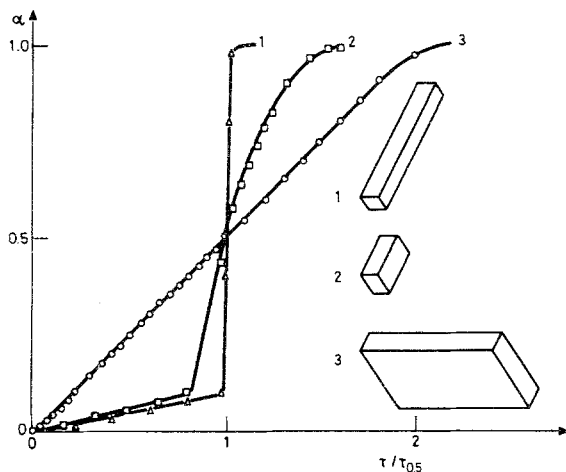


Fig. 3 Decomposition of triclinic crystal according to Eq. (10): 1. $v_b = v_c = 100 v_a$; 2. $v_b = v_c = 10 v_a$; 3. $v_b = v_c = 0.01 v_a$

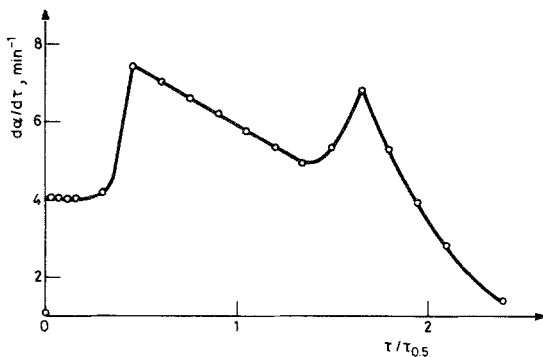


Fig. 4 Decomposition of triclinic crystal according to Eq. (7), with $a_0 = c_0 = 1$ mm, $b_0 = 3$ mm, $v_a = 10^{-4}$ mm/min, $v_b = v_c = 3 v_a$

$\tau_{0.1}$ is the time of achievement of $\alpha = 0.1$. For calculation we use $a_0 = 1$ mm and $v_a = 10^{-2}$ mm/min. If, from opposite (100) and $(\bar{1}00)$ faces with a zero induction period, the interfaces advance towards each other with a velocity considerably exceeding other velocities, then a self-acceleration section is not observable (Fig. 3). If $v_b = v_c = 0.01 v_a$, curve 3 in the range from $\alpha = 0$ to $\alpha = 0.9$ is practically a straight line. Self-acceleration becomes noticeable when velocities v_b and v_c are comparable with or exceed v_a .

A two-fold self-acceleration of the reaction of a single-crystal is also possible.

For example, let us assume that $\tau_{\text{ind}}^{(100)} = 0$, $\tau_{\text{ind}}^{(010)} = \tau_{0.1}$, and $\tau_{\text{ind}}^{(001)} = \tau_{0.7}$. With the above parameters of Eq. (7) the differential kinetic curve passes through two maxima (Fig. 4). The asymmetric form of the maxima is connected with the assumption that at the end of the induction period the crystal face reacts momentarily. In reality it enters into reaction in the course of a certain time different from zero.

The number of maxima may exceed two if, for instance, the induction periods of opposite crystal faces do not coincide, or if dehydration of hexahydrate crystals with substantially developed $(\bar{1}10)$ and $(1\bar{1}0)$ faces is taken into account.

The analysed kinetic model based on equations of type (7) is not limited only to reactions of triclinic crystals. It also includes the reactions of crystals of other symmetry systems. In this case the equation of type (7) must be enlarged by new factors taking into consideration all reacting crystal faces and all directions of interface advance. Such a model, which in contrast to known models takes into account the fact that crystal faces react non-simultaneously with different lag-times, may be used for the development of mathematical apparatus for reactions of a single-crystal and a multitude of crystals.

Thus, within the framework of a comparatively simple localization phenomenon (uniform localization on the solid surface), as a function of the lag-time that precedes entry of a crystal face into the reaction and as a function of the relation between linear velocities of interface advance in different directions the topochemical process involving a single-crystal takes place without self-acceleration, or with one-fold or with multi-fold self-acceleration. This conclusion is of interest due to the fact that the self-acceleration effect is usually assumed to be connected with spot surface localization phenomena, when the reaction starts on active centres and is localized around them, with subsequent broadening of the reaction zone. In the present case, broadening of the reaction zone takes place due to new crystal faces undergoing a reaction; in the general case it is due to entering into reaction of new surfaces, formed as a result of cracking of the crystal in the process of its reaction.

The spot surface localization makes the kinetic model more complicated. Besides taking into account the fact that crystal faces react non-simultaneously, it is also necessary to consider the law of nucleation, the nature of the active centres, their number and distribution on the crystal faces, the form of the reaction figures and the relative velocities of their growth in different directions. The data that we obtained on the dehydration of $\text{Na}_3\text{P}_3\text{O}_9 \cdot 6 \text{H}_2\text{O}$ crystals show that the active centres in most

cases (about 60%) have a dislocation nature and that the nucleation on the (010) and (001) faces proceeds with constant velocity.

The regular contours of the dehydration spots in Fig. 2 reflect the crystallographic specificity of the crystal, but do not mean that the same picture will be obtained for other processes taking place on the same crystal face. This is proved by comparison of dehydration figures and etching pits on the (001) face of the hexahydrate crystal.

In this respect it is of interest to consider the studies by V. V. Samuskevich of crystals of manganese hydrophosphate trihydrate, $MnHPO_4 \cdot 3H_2O$, that allow comparison of the localization phenomena of different processes taking place on the (111) face. Figure 5 shows typical localization forms of three processes (methodological features are given in [6, 7]) disproportionation of the trihydrate to a less protonated salt and H_3PO_4 ; dehydration of the trihydrate to a less hydrated amorphous salt; and its ammoniation by gaseous NH_3 to crystalline ammonium manganese orthophosphate. These processes differ in localization forms, the phase composition of the reaction products and the distribution of respective reaction active centres.

Depending on the temperature and partial water vapour pressure, disproportionation is localized on the surface or inside the crystal. In the latter case a complex gaseous-liquid-solid inclusion (within which grow prismatic crystals of the new phase) grows from the centre, which is apparently a visually not observable defect in the volume of the transparent crystal. Inside the inclusion an elevated pressure is created, which facilitates the crystallization of the new phase. The growth of prismatic crystals abruptly decelerates at the moment when the inclusion opens due to its approach to the surface during growth. Prismatic crystals in the inclusions which have not yet reached the surface continue to grow with the former velocity.

The consideration of possible localization phenomena and of corresponding kinetic models presents a stage for development of the theory of solid-state reactions at an atomic-molecular level.

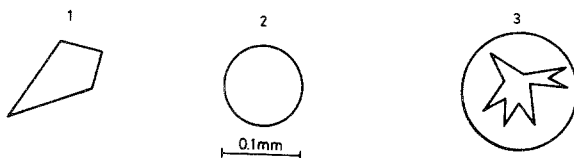


Fig. 5 Surface spot localization forms of different types of reactions taking place on the (111) face of a $MnHPO_4 \cdot 3H_2O$ single-crystal: 1 — disproportionation, 2 — dehydration in water vapour atmosphere, 3 — ammoniation in NH_3 atmosphere

References

- 1 B. Delmon, Introduction à la cinétique hétérogène, Paris, 1969.
- 2 E. A. Prodan, *Obschie Zakonomernosti Termicheskoho Razlozhenija Kristallohydratov Neorganicheskich Soedinenij (General Regularities of Thermal Decomposition of Inorganic Compound Crystal Hydrates)*, Publ. Inst. Chemii, Płock, Poland, 1979 (in Russian).
- 3 H. M. Ondik and J. W. Gryder, *J. Inorg. Nucl. Chem.*, 14 (1960) 240.
- 4 J. Tordjman and J. C. Guitel, *Acta crystallogr. (B)*, 32 (1976) 1871.
- 5 E. A. Prodan and S. I. Pytlev, *Neorgan. Materialy*, 19 (1983) 639.
- 6 E. A. Prodan, V. V. Samuskevich, T. N. Galkova and S. I. Pytlev, *Neorgan. Materialy*, 18 (1982) 1329.
- 7 *Geterogennye Khimicheskije Reaktsii (Heterogeneous Chemical Reactions)*, Publ. "Nauka i Technika", Minsk, BSSR, 1979 (in Russian).

Zusammenfassung — Typische Lokalisationsformen topochemischer, auf der Oberfläche und im Kristallinneren verlaufender Reaktionen werden zusammenfassend dargestellt. Das kinetische Modell der Zersetzung von triklinen Kristallen, das im Gegensatz zu bekannten Modellen die nicht gleichzeitig verlaufenden Reaktionen der einzelnen Kristallflächen berücksichtigt, wird untersucht. Es wird gezeigt, daß abhängig von der Länge der dem Start der Reaktion an den einzelnen Kristallflächen vorausgehenden Induktionsperiode und von der linearen Geschwindigkeit des Fortschreitens der Grenzfläche in verschiedene Richtungen die Zersetzung ohne oder mit einfacher oder vielfacher Selbstbeschleunigung verlaufen kann.

Резюме — Сопоставлены типичные формы локализации топохимических реакций, протекающих на поверхности и в объеме кристалла. Исследована кинетическая модель разложения триклинного кристалла, которая в отличие от известных моделей учитывает неодновременное вступление его граней в реакцию. Показано, что в зависимости от величины индукционного периода, предшествующего вступлению грани в реакцию, и соотношения линейных скоростей продвижения поверхности раздела в разных направлениях разложение возможно без самоускорения, с однократным или многократным самоускорением.