REACTIONS IN SOLID STATE: LOCALIZED AND DELOCALIZED

E. A. Prodan

INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY OF THE BELORUSSIAN ACADEMY OF SCIENCES, 220606 MINSK, U.S.S.R.

It is not necessary to classify homogeneous (delocalized) solid state reactions as rare or unusual. Their specificity lies in the fact that in contrast to gas-phase and liquid-phase reactions they may be interpreted as homogeneous processes at different dimensional levels in the range between atomic-molecular size scale and the size scale of crystals. Some oscillating reactions accompanied by superposition of high-frequency reaction rate oscillations (connected with consecutive entering into reaction of crystal faces) on low-frequency reaction rate oscillations, which are attributed to consecutive entering into reaction of crystals (particles) and fractions of polycrystalline and powder-like substances, were discussed.

Delocalized reactions proceeding homogeneously in the bulk of a solid or uniformly in the volume of a crystal seems to be rare and unusual, e.g. some radiation-induced processes caused by radioactive decay of uniformly distributed radio-nucleids or connected with uniform ionization when external radiation passes through matter. Usually solid state reactions are believed to proceed in a localized manner, i.e. through formation of continuous or discontinuous reaction front which moves in different directions with equal or unequal linear rate. The cases of chemical transformation of solids without formation of moving reaction front are seldom analyzed, the reports on their kinetic models are extremely rare.

The history of solid state chemistry shows that delocalized reactions are poorly studied not for the reason that they have become known only in recent years. The first reports on these reactions appeared nearly at the same time with those on the localized ones. But nowadays it must be stated that the kinetics and mechanisms of delocalized reactions represent one of the less studied fields in the chemistry of real crystals.

It is possible to list a number of circumstances which have led to the present situation. let us point out a few of them.

The difficulties of the mathematical analysis and kinetic modelling, which, applying to the process under discussion, is restricted by a comparatively simple case, when active centres are distributed uniformly within the volume of the solid and nucleation proceeds according to some simple laws, have been already discussed [1-3]. The known diffusion kinetic model of irreversible solid state decomposition with gas evolution is based on the assumption, that the reaction goes on homogeneously within a spherical solid, the diffusion belongs to the intralattice type, the flow of evolved gas diffusing through the bulk of the solid behaves as ideal heat flow, the diffusion coefficient remains constant during the reaction [4]. Not all the listed conditions take place in real processes.

Difficulties concerning experimental methods are also obvious, as traditional methods worked out for the study of localized reactions only seldom can be used for the investigation of intrinsic solid state reactions such as intracrystalline decomposition, intracrystalline disproportionation (decyclization) etc. [5].

Last time intracrystalline (intraframework, intrastructural) reactions in minerals containing layers and chains of water molecules or molecules of other volatile compounds as well as in minerals which have channels serving as ways for escaping the evolving gaseous product are of particular interest [6-10]. Attempts to systematize these and other described [11-13] types of intrinsic reactions in solids and to clarify their place in the classification systems of reactions show that the division of chemical transformations of solids into homogeneous (delocalized) and non-homogeneous (localized) is conventional and have to be defined more exactly [5, 14, 15].

In case of reactions in solid state, in contrast to homogeneous gas-phase and liquid-phase reactions, it is necessary to elucidate at which size scale the process can be regarded as homogeneous (delocalized): at atomic-molecular size scale, as in case of reactions in gaseous and liquid state, at the size scale of the described [16] elementary reacting blocks, crystallytes and microblocks, crystal grains, structural layers, powder particles, large crystals. Depending on the choice of dimensional level one and the same intrinsic solid state reaction can be interpreted as localized or delocalized.

The uniform colour change of a reacting crystal (or if the crystal becomes cloudy through the whole bulk) is an optical indication of delocalyzed-type process. However, there are some localization forms of swarm-like type which manifest themselves in the same manner: the reaction proceeds owing to the formation of a large quantity of small optically indistinguishable seeds, which increase in number but do not grow, and as a result the chemical transformation of the crystal seems to be homogeneous.

If the solid state reaction proceeds homogeneously even at atomic-molecular dimensional level it does not mean that the traditional mathematical expressions which are valid for homogeneous gas-phase and liquid-phase reactions can be applied without any revision and that it is possible to interpret the corresponding reaction rate constants in the same manner, in particular the rate constants k and k' in differential

$$d\alpha/d\tau = k \, (\, 1 - \alpha \,) \qquad (1)$$

and integral

$$\alpha = 1 - \exp \, (\, - k'\tau \,) \qquad (2)$$

forms of the first order reaction equation (α – the transformation degree, τ – time). It is necessary to introduce some corrections which reflect the alteration during the reaction of the physical properties of the solid matrix, of the conditions of gaseous product removal / supply, and the change of the activity of reactants.

It should be pointed out that nominally equations (1) and (2) have been used for a long time at mathematical analysis of decomposition kinetics of powder-like substances (in this case the homogeneous kinetics representations are suitable at the size scale of powder particles) and crystals, when the structure due to the high density of crystal lattice defects or because of the existence of extended inner surface is distorted to such extent that large crystals can react practically homogeneously. For powder-like solids consisting of spherical particles of equal size the equation of (1) and (2) type were obtained by Mampel [17].

The same concerns other types of reactions is solid state. The reversible interaction of porous solids with gaseous reactants in also interpreted in such a way as if the reaction proceeds homogeneously through the whole bulk of the solid phase according to the first order reaction law [18, 19].

The reaction mechanism and the corresponding kinetic equation may change depending on the conditions in which the reaction is carried out. As it is known [20], irreversible thermal decomposition of silver azide takes place as the first order reaction in respect to the consumption of initial substance if annihilation of the holes proceeds through their coupling. If the majority of the holes is not coupled, but interacts with electrons, the number of electron traps being constant, other equations are realized instead of (1) and (2).

The alteration of kinetic law with the change of outer conditions is typical of thermal transformations of sodium cyclotriphosphate monohydrate crystals, $Na_3P_3O_9 \cdot H_2O$. As far as at any point inside the crystal there is one molecule of crystallization water per each anion cycle which can be consumed for ring opening according to the mechanism of intrinsic hydrolysis without formation of gaseous and liquid products, it is logical to expect, that irreversible decyclization will represent a homogeneous solid state process going on according to equations (1) and (2). The experimental results obtained show that decyclization really proceeds as the first order reaction, but under the conditions that the process is carried out in gaseous ammonia atmosphere at sufficiently high pressure close to $p_{NH_3} = 930$ hPa [21]. When adding water vapour to gaseous ammonia, the former strengthening the decyclization action of the latter, the kinetic curve form changes (Fig. 1), the ring opening going on faster than it should be expected according to equations (1) and (2). In vacuum and at small ammonia pressures (not higher than 130-140 hPa) the reaction is arrested at $\alpha \leq 0.5$ and the kinetic curve aquires that form which is typical of diffusion-limited processes.

A probable explanation of such effect lies in the fact that the homogeneous decyclization according to the mechanism of intrinsic hydrolysis prevails only inside the crystals. On the surface of crystals and in the subsurface layers, from where part of the water of crystallization may escape into the gas phase, the ring opening under the action of gaseous decyclizing agent prevails. The relation between delocalized inside and localized outside processes changes depending on the crystal size and density of crystal lattice defects. Applying to the sample studied with average crystal size 0.01-0.1 mm the qualitative estimation of such relation shows, that according to the mechanism of delocalized processes reacts no more than a half of the initial substance.

The already analyzed problem of granulometry in solid state chemistry [1, 22, 23] is not touched upon here, we will discuss only the problems concerning interpretation of some regularities under question. In many cases it is desirable to know not only the distribution function of the sizes of powder particles or of the sizes of the crystals of polycrystalline substances, but also the distribution function of their reactivity, distribution function of activity of crystal faces of single crystals, as well as the sequence of entering into the reaction of crystal faces, individual crystals and powder particles. Taking into account these factors it is possible to interpret reactions in solid state with unusual form of kinetic curves, including the case of oscillating reactions of solids.
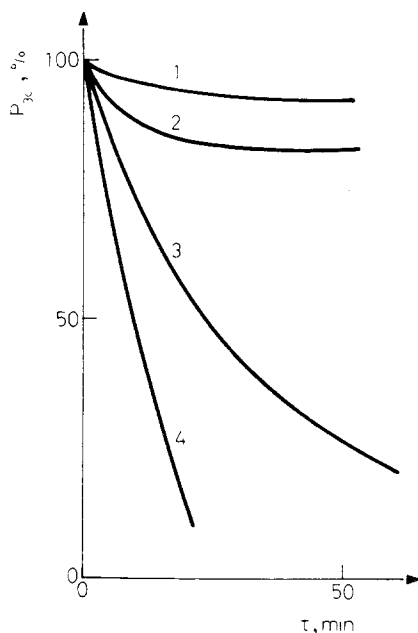
Fig. 1 The change of phosphorus content in the form of cyclotriphosphate (P_{3c}) during isothermal treatment of polycrystalline $Na_3P_3O_9 \cdot H_2O$ in controlled atmosphere ($t = 172.5°C$, crystal size $D = 0.01-0.1$ mm, sample mass $m = 10 \pm 2$ mg): 1 - vacuum, $p = 10^{-2}$ hPa: 2 - gaseous ammonia, $p_{NH_3} = 113$ hPa; 3 - gaseous ammonia, $p_{NH_3} = 930$ hPa: 4 - mixture of $NH_3 + H_2O$, $p_{NH_3} = 906$ hPa, $p_{H_2O} = 24$ hPa

The oscillations of reaction rate of powder-like or polycrystalline substances (in most cases two-fold oscillations were noted) usually are considered to be conditioned by the fact that the samples used are twofractional and in the beginning reacts the fine dust-like fraction, then the mean-size and large-size fraction. When studying monofractional substances the non-desirable contamination of dust-like fraction, which appears as a result of self-rubbing of particles at mechanical treatment, is often separated before the kinetic experiment by sieving, blowing, decantation, elutriation or other procedures.

For two fractonal substances the reaction rate passing through two maxima depending on time or transformation degree was shown theoretically [24]. The experiment confirms the results of theoretical calculation. At the same time it points out the possibility of reaction rate oscillations at chemical transformation not only of polyfractional substances, but also of monofractional ones as well as of single crystals. This may be discovered ex-

perimentally when the chemical transformation is carried out under suffi-
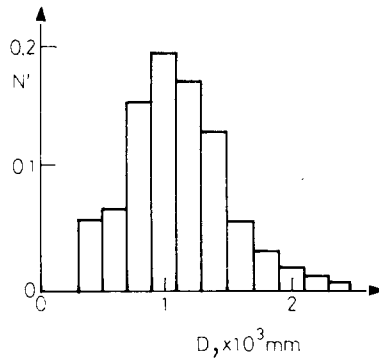ciently soft conditions or at fairly low reaction rates.

Fig. 2 The distribution of particle sizes for microcrystalline CdCO3 (N' – the number of
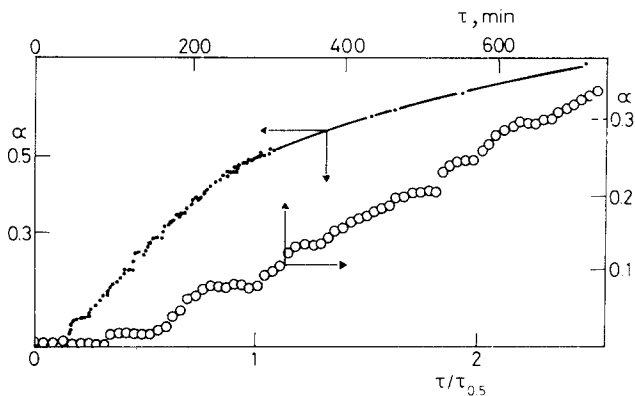particles in portions of their total quantity)

Fig. 3 Integral kinetic curves for thermal decomposition of CdCO3 in CO2 atmosphere ($t = 385°$,
$p = 800$ hPa)

Let us consider the results of the investigation of slow thermal decom-
position of cadmium carbonate in the atmosphere of carbon dioxide [25] and
other gases [26]. The microcrystalline substance used, containing no volatile
or dust-like contaminations, represents a comparatively uniform fraction
(Fig. 2), its major part of particles (at $N' = 0.92$) being of $D = 0.0006$-
0.021 mm average size. At sufficiently low thermal decomposition rate on

the initial part of the integral kinetic curves α–τ and α – $\tau/\tau_{0.5}$ ($\tau_{0.5}$ – half-life period) some irregular repeating horizontal or close-to-horizontal steps were observed (Fig. 3). They are connected, according to the microscopic data, with consecutive entering into reaction of groups or conglomerates of particles and with self-desintegration of conglomerates.

The corresponding differential kinetic curve $d\alpha/d\tau$ – τ or $d\alpha/d\tau$ – $\tau/\tau_{0.5}$, the wave-like form of which is characteristic for stepwise decomposition kinetics, goes through a total large maximum at the maximum value of the overall reaction front. In some cases the wave-like differential curve passes through two or three large maxima (Fig. 4, Table 1). In the last case the first sharp maximum is ascribed to the fast decomposition of the dust-like contamination present in the sample used (D = 0.0004-0.0026 mm, N' = 0.85-0.90). Not touching upon the nature of these and other effects (alternative explanations are as well possible) we shall point out only the fact itself of repeatedly observed under various conditions of the oscillatory phenomena connected with superposition of high-frequency (short amplitude) reaction rate oscillations on low-frequency (large amplitude) reaction rate oscillations.
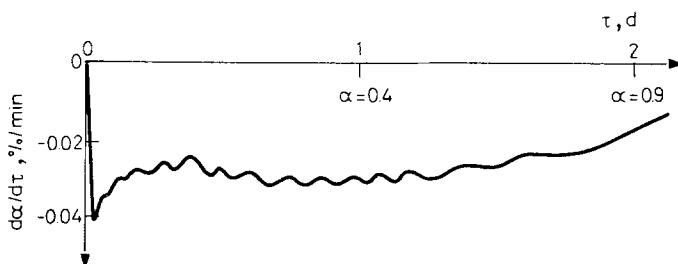

Fig. 4 Differential kinetic curves for thermal decomposition of CdCO3 in He atmosphere (t = 280°, p = 1100 hPa)

Table 1 Co-ordinates of maxima for low-frequency rate oscillations of CdCO3 thermal decomposition (D = 0.0004-0.0026 mm, N' = 0.85-0.90)

t, °C	p, hPa	First maximum τ, min	First maximum α	Second maximum τ, min	Second maximum α	Third maximum τ, min	Third maximum α
280 [26]	p_{N_2} = 1010	5.0	0.001	110	0.03	1060	0.25
325 [25]	p_{CO_2} = 13.3	1.5	0.002	130	0.02	1150	0.13

Similar superposition for the reaction of one or two cubic single crystals will be obtained using the previously considered ideas [5, 16]. Schematically it is demonstrated in Fig. 5 for two synchronically reacting cubic crystals (I) and (II). It is supposed that crystal faces enter into reaction consequently in equal intervals of transformation degree, namely in $\alpha = 0.15$ intervals: for crystal faces (100) and ($\bar{1}$00) of crystal (I) the induction period is equal to zero ($\tau_{ind(I)}^{(100)} = \tau_{ind(I)}^{(\bar{1}00)} = 0$), for (100) and ($\bar{1}$00) of crystal (II) its value is equal to the time at $\alpha = 0.15$ ($\tau_{ind(II)}^{(100)} = \tau_{ind(II)}^{(\bar{1}00)} = \tau_{0.15}$), for (010) and ($0\bar{1}0$) of crystal (I) it is equal to $\tau_{0.30}$ ($\tau_{ind(I)}^{(010)} = \tau_{ind(I)}^{(0\bar{1}0)} = \tau_{0.30}$) and so on (Table 2). The reaction starts instantly on the whole area of the crystal face and the formed plane reaction front moves in directions a, b, c with constant linear rate $v_a = v_b = v_c$.
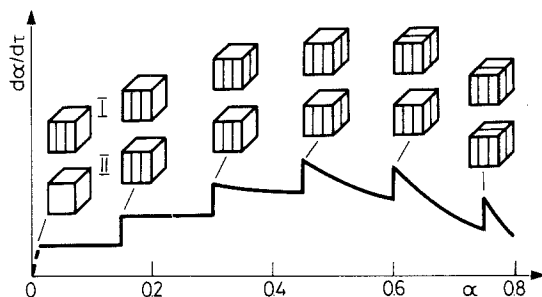

Fig. 5 The scheme of reaction rate oscillations for two synchronically reacting cubic crystals (the induction periods for corresponding crystal faces are listed in Table 2)

Table 2 Induction periods of crystal face entering into reaction for two synchronically reacting cubic crystals

Induction period	Crystal face	Crystal No.
0	(100), ($\bar{1}$00)	(I)
$\tau_{0.15}$	(100), ($\bar{1}$00)	(II)
$\tau_{0.30}$	(010), ($0\bar{1}0$)	(I)
$\tau_{0.45}$	(010), ($0\bar{1}0$)	(II)
$\tau_{0.60}$	(001), ($00\bar{1}$)	(I)
$\tau_{0.75}$	(001), ($00\bar{1}$)	(II)

At the moments when the next crystal face enters into reaction there is a sudden rise of reaction rate, the latter being represented in abstract units. The quantity of reaction rate oscillations is equal to the number of consecutive reacting crystal faces. The overall reaction front area and the overall

reaction rate passes through a total large maximum and as a result the superposition of short amplitude reaction rate oscillations (saw-tooth waves) on the large amplitude oscillation of the overall reaction rate may be observed.

Analogous results were obtained for a reacting cubic single crystal the opposite crystal faces of which do not enter into reaction simultaneously. If $\tau_{ind}^{(100)} = 0$, $\tau_{ind}^{(\overline{1}00)} = \tau_{0.15}$, $\tau_{ind}^{(010)} = \tau_{0.30}$, $\tau_{ind}^{(0\overline{1}0)} = \tau_{0.45}$, $\tau_{ind}^{(001)} = \tau_{0.60}$ and $\tau_{ind}^{(00\overline{1})} = \tau_{0.75}$ the dependence $d\alpha/d\tau$ vs. α for such a crystal is the same as shown in Fig. 5. In real processes the crystals do not react synchronically and various kinds of irregular reaction rate oscillations instead of regular ones may be noted.

The oscillatory effects under discussion are not identical with the traditional oscillatory effects of liquid-state and solid state reactions [27-29]. They are connected with unequal chemical activity of crystal faces for a single crystal, unequal reactivity of crystals or groups of crystals for polycrystalline substances as well as of particles and groups of particles for powder-like materials.

On the basis of the results discussed it should be noted that homogeneous or delocalized solid state reactions do not represent a rare or unusual class of chemical transformation of solids. They differ from the well investigated homogeneous gas-phase and liquid-phase reactions by a specificity which lies in the fact that the model of localized or delocalized processes may be realized at different dimensional levels in the range from atomic-molecular size scale to the size scale of microblocks, powder particles and large crystals. For instance, a reaction localized on the surface of microblocks may proceed homogeneously through the volume of single crystals if the induction periods for microblocks are close to each other.

For localized reactions it is important to know the reactivity distribution of crystal faces for a single crystal, of individual crystals (particles) and groups of crystals (particles) for polycrystalline and powder-like substances. Depending on distribution function shape it is possible to observe an oscillatory phenomena accompanied by superposition of high-frequency reaction rate oscillations connected with consecutive entering into reaction of crystal faces on low-frequency reaction rate oscillations attributed to consecutive entering into reaction of individual crystals and particles, groups of crystals and particles. If spot-like localization and consecutive entering into reaction of active centres may be taken into account also, besides the fine structure of $\alpha - \tau$ and $d\alpha/d\tau - \tau$ curves a hyperfine structure of the kinetic curves is expected to be observed.

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Zusammenfassung — Homogene (delokalisierte) Festphasenreaktionen brauchen nicht als selten oder unüblich betrachtet zu werden. Ihre Besonderheit liegt darin, daß sie im Gegensatz zu Reaktionen in Gas- oder Flüssigphasen als homogene Prozesse interpretiert werden können, die in verschiedenen Größenordnungsniveaus im Bereich zwischen der Größe von Atomen/Molekülen und der Größe von Kristallen ablaufen. Es wurden einige oszillierende Reaktionen besprochen, die von der Überlagerung von Oszillationen mit hochfrequenten Reaktionsgeschwindigkeiten (verbunden mit einer konsekutiven Teilnahme an Reaktionen von Kristallebenen) und niederfrequenten Reaktionsgeschwindigkeiten begleitet werden, wobei letztere einer konsekutiven Teilnahme an Reaktionen von Kristallen (Partikeln) sowie polykristallinen und pulverartigen Fraktionen zugeschrieben werden.