

The zonary model of thermal transformations of alkali metal triphosphates

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Abstract

From a generalization of the results of a study of the isothermal and non-isothermal transformations of pentasodium triphosphate (PSTP), pentapotassium triphosphate (PPTP), and their crystallohydrates $\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$ and $\text{K}_5\text{P}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$, in different gaseous media, the specific features of the zonary model of propagation of a topochemical process in a single crystal, a granule and a polycrystalline sample are considered. Taking into account the concept of the rate-limiting step, the feasibility of using the zonary model in the analysis of the kinetics of multi-stage reactions of solids is evaluated.

INTRODUCTION

Thermal transformations of solids are, as a rule, multi-stage topochemical processes consisting of a number of successive and parallel steps, such as physical transformations involving a change in state of the aggregation and phase composition, the degree of dispersion, the density, porosity, bulk mass and geometry of a substance and chemical transformations involving a change in the chemical composition with formation of intermediate stable and unstable compounds, and intermediate active states. For analysis of the kinetics of such processes proceeding under isothermal and non-isothermal conditions, the concept of a rate-limiting step sensitive to the effects of temperature, gas composition and pressure, heating rate, and other factors is important [1,2]. The rate-limiting step may change in the course of a reaction, accompanied by a change in activation energy, pre-exponential factor and other characteristics; this is illustrated on the basis of the known zonary model of topochemical processes and exemplified by localized and delocalized transformations of crystals [3,4] and

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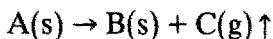
Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

polycrystalline substances [5,6]. This is interesting for the elaboration of phenomenological kinetic models which consider a combination of all the simultaneous processes [7].

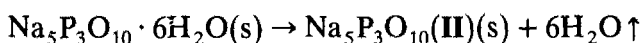
When applied to the thermal transformations of alkali metal triphosphates and their crystallohydrates, the zonary model has a certain specificity which is related both to properties associated with the triphosphate, whose chain is capable of anion reorganization, and to features deriving from different processes, occurring with its participation. Let us consider some typical cases and illustrate them with examples relating to isothermal and non-isothermal transformations of polycrystalline and granulated samples of pentasodium triphosphate (PSTP) (low-temperature $\text{Na}_5\text{P}_3\text{O}_{10}$ (II) and high-temperature $\text{Na}_5\text{P}_3\text{O}_{10}$ (I) crystalline forms), pentapotassium triphosphate (PPTP) and their crystallohydrates, $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ and $\text{K}_5\text{P}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$. Particular emphasis is given to the cases allowing a comparison of the zonary development of the same reaction in a powder-like (polycrystalline) sample, a granule and a single crystal.

THE ZONARY MODEL OF DEHYDRATION OF CRYSTAL HYDRATES

The most comprehensive information is available for the isothermal and non-isothermal transformations of the hexahydrate $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ according to the scheme



i.e.



The zonary model of reaction propagation in a monocrystal, a granule or a powder-like (polycrystalline) sample, to which a certain geometric form is imparted, is shown in Fig. 1 as a section normal to the geometric surface of the sample. If a powder or polycrystalline sample is in the form of a thin layer, then the zonary model may be applied not to the whole sample (as in the case when it is given the form of a cone, a cut cone or another configuration) but to separate particles or crystals forming the sample. A similar situation is met in thermal transformations of monocrystals, as was found in the investigation of KH_2PO_4 [8], when a reaction first propagates quickly along grain boundaries, and then each separate grain reacts according to the zonary model.

The intermediate zones (a), (b), (c) and (d) (see Fig. 1), located between zones of the initial substance A(s) and reaction product B(s) are designated by convention [9]. The evolving gaseous product C(g) diffuses successively from a surface of the hexahydrate core of A(s) through the layers (a), (b), (c) and (d), then through the layer B(s), and propagates from an external geometric surface of the sample into the gaseous phase.

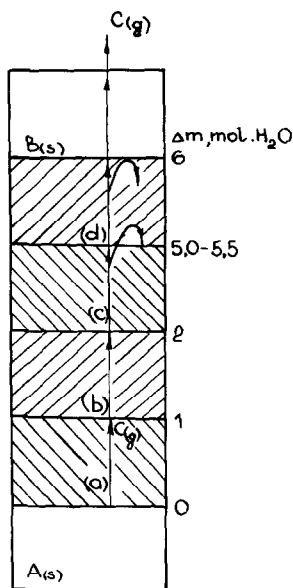
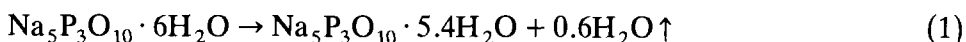


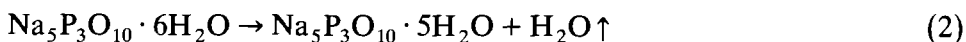
Fig. 1. The zony model of thermal transformations of a monocrystal, a granule, or a polycrystalline $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ sample according to the reaction scheme $\text{A(s)} \rightarrow \text{B(s)} + \text{C(g)} \uparrow$ (shown normal to the geometric surface of the sample).

Each of the intermediate stages (a), (b), (c) and (d) includes a number of reactions discussed earlier [10–12], among which the basic ones will be considered below.

Stage (a). With respect to kinetic characteristics and mass loss, $\Delta m = 0.6 \text{ mol H}_2\text{O}$ or $\Delta m = 1.0 \text{ mol H}_2\text{O}$, two non-degradation reactions can be distinguished

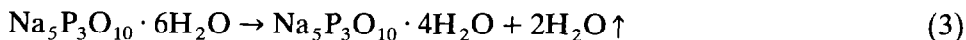


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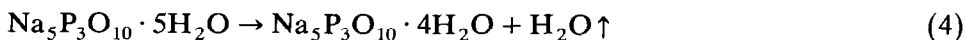


which in a vacuum or in an inert gas flow proceed reversibly in kinetic or diffusional-kinetic regions. The contribution of reactions (1) and (2) to the total process depends on the size of the hexahydrate crystals.

Stage (b). Stage (b) may be represented either by the reaction

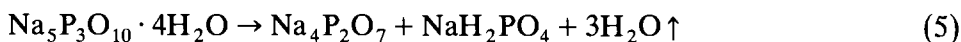


which includes reactions (1) and (2) or by the reaction

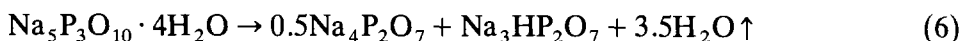


proceeding after completion of reaction (2). Both reactions are diffusion limited. Under certain conditions, for instance with a rapid rise in temperature, they take place in a reversible manner without deep degradation of triphosphate.

Stage (c). At this stage there is complete decomposition of the triphosphate chain, according to the Thilo scheme

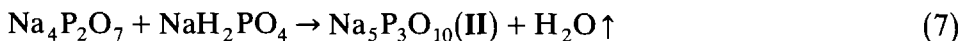


or the Quimby scheme

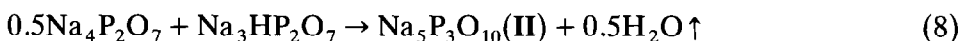


or simultaneously according to both reactions.

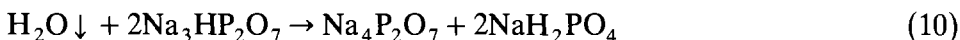
Stage (d). Chemical transformations are completed at this stage by recondensation of products formed in reaction (5)



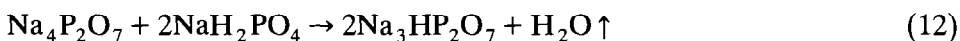
or in reaction (6):



From stage (c), the evolving water vapour is capable of interacting with some products in the zones through which it diffuses, and is transformed into a chemically bound state

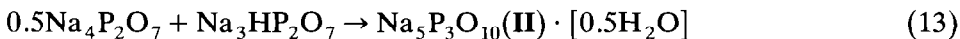


The water is then released with formation of the same or other products

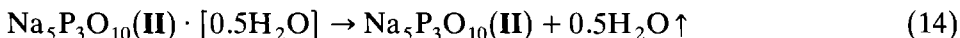


The absorption of some of the diffusing water vapour is indicated by round arrows in Fig. 1. Here, multiple repetition of the cycle of absorption and release of water vapour is possible [9].

It is assumed [9] that during diffusion through zone B(s), some portion of the water vapour forms the hypothetical complex $\text{Na}_5\text{P}_3\text{O}_{10}(\text{II}) \cdot [0.5\text{H}_2\text{O}]$. The formation of this complex implies that the water released in reaction (8) does not immediately evolve into the gaseous phase but first remains in the solid phase



and is later liberated as a result of the decomposition of the hypothetical complex



The above assumption is dictated by different circumstances including those pertinent to the repeatedly discussed problem concerning the equilibrium pressure of water vapour above crystalline PSTP forms [5,12,13]. It is known that crystalline $\text{Na}_5\text{P}_3\text{O}_{10}(\text{I})$ and $\text{Na}_5\text{P}_3\text{O}_{10}(\text{II})$ are capable of absorbing and reversibly releasing a small amount of water, provided a

hexahydrate phase is not formed. Because it is not physically adsorbed water, we may logically assume that it is bound in the form of the complexes $\text{Na}_5\text{P}_3\text{O}_{10}(\text{I}) \cdot [0.5\text{H}_2\text{O}]$ and $\text{Na}_5\text{P}_3\text{O}_{10}(\text{II}) \cdot [0.5\text{H}_2\text{O}]$.

However, the hexahydrate may reversibly release water of crystallization and reversibly absorb water vapour only in the region of composition $\text{Na}_5\text{P}_3\text{O}_{10} \cdot x\text{H}_2\text{O}$ (cryst.), where $4 < x < 10$, i.e. predominantly at stage (a) and partially at stage (b). At these stages, we can consider the equilibrium pressure of water vapour above the crystalhydrate $\text{Na}_5\text{P}_3\text{O}_{10} \cdot x\text{H}_2\text{O}$ ($4 < x < 10$), bearing in mind the possibility of multiple repetition of the hydration–dehydration cycle without triphosphate chain destruction. This is also the case for stage (d), i.e. an equilibrium pressure of water vapour above the mentioned complexes of PSTP(I) and PSTP(II) capable of releasing and absorbing water many times without anion rearrangement.

A similar situation occurs for crystalline PPTP, as well as for solid solutions of PPTP and PSTP: an equilibrium pressure above the crystalhydrate $\text{K}_5\text{P}_3\text{O}_{10} \cdot x\text{H}_2\text{O}$ is established with multiple repetition of non-degradation hydration–dehydration cycles within the range $2 < x < 6$. As for PSTP, anhydrous PPTP can reversibly absorb a small amount of water without crystallization of a tetrahydrate phase, which suggests the existence of a similar complex and an equilibrium pressure of water vapour above it.

THE ROLE OF PHYSICAL FACTORS

The reaction stages discussed above proceed at an optimal rate within definite temperature regions, the position of which may change with the composition of the gaseous phase and partial pressure of its components, the size of the crystals (powder particles) and granules, the mass and geometry of the sample, and the thermal treatment conditions. For isothermal treatment of finely crystalline $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ (mean size of crystals, $D = 0.001\text{--}0.046$ mm; specimen mass, $m = 20$ mg) in a vacuum at a residual pressure $p = 10^{-4}$ hPa and dry air atmosphere (relative humidity (RH), 0%), the optimal temperature ranges 0–40, 50–90, 100–160 and 190–250°C are appropriate for stages (a), (b), (c) and (d) respectively. On heating a $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ sample ($D = 0.02\text{--}0.2$ mm, $m = 4.83$ mg) by the DSC method in a dry nitrogen flow with a heating rate (HR) of 20 K min^{-1} , endoeffects are registered at 139, 147 and 183°C, for which the endoeffect at 139°C corresponds to stages (a) and (b) proceeding simultaneously [9,14].

An increase in the mass of a sample which results in the formation of a pile of powder instead of a thin layer in experiments with low sample weights, gives rise to one endoeffect on the DTA curve corresponding to total release of water of crystallization. Figure 2 shows the DTA, TG and T curves obtained on heating a comparatively large sample of chromatographically pure $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ in an open ceramic sample-pan at a non-controllable pressure of water vapour (a standard derivatograph OD-

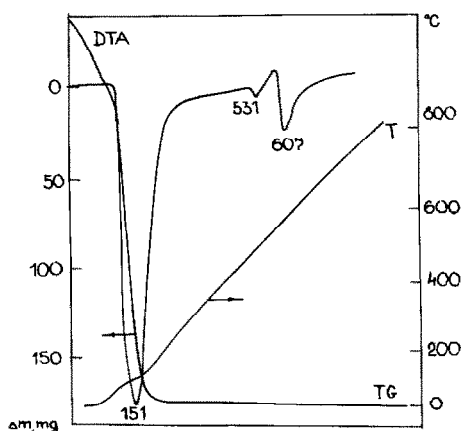


Fig. 2. The derivatogram of a polycrystalline $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ sample, $D = 0.01\text{--}1.0$ mm, $m = 800$ mg, $\text{HR} = 10 \text{ K min}^{-1}$; sample holder is thermo-ceramic, open.

103 MOM was used [15]). The unsplit endoeffect at 151°C corresponds to total removal of 6 mol H_2O ; the endoeffects at 531°C and 607°C correspond respectively to the transition $\text{Na}_5\text{P}_3\text{O}_{10}(\text{II}) \rightarrow \text{Na}_5\text{P}_3\text{O}_{10}(\text{I})$ and the melting of $\text{Na}_5\text{P}_3\text{O}_{10}(\text{I})$.

A similar regularity is typical of the crystallohydrate $\text{K}_5\text{P}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$, the intermediate dehydration stages and the composition of the corresponding zones of which have been less extensively studied than those described above. The use of small sample weights allows the fine details of the constituent stages to be revealed; for thermal analysis of large sample weights, these merge with each other, e.g. the endoeffects are at 120 and 150°C (Fig. 3). A DSC curve (Fig. 4) typical of samples with $m = 7\text{--}10$ mg has been obtained by Lesnikovich et al. [50] using a Mettler TA 300

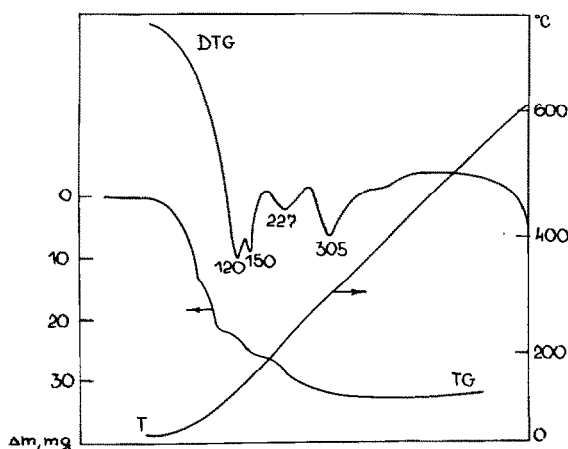


Fig. 3. The derivatogram of polycrystalline $\text{K}_5\text{P}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$, $D = 0.1\text{--}0.5$ mm, $m = 200$ mg, $\text{HR} = 10 \text{ K min}^{-1}$; sample holder is thermo-ceramic, open.

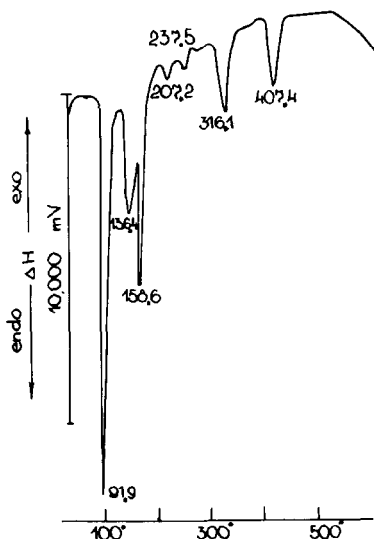
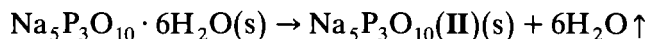


Fig. 4. The DSC curve for polycrystalline $K_5P_3O_{10} \cdot 4H_2O$, $D = 0.1\text{--}0.5$ mm, $m = 10.12$ mg, $HR = 10$ K min^{-1} ; sample holder is aluminium, open.

thermoanalyser with a DSC 20 cell by heating chromatographically pure $K_5P_3O_{10} \cdot 4H_2O$ in an open aluminium sample pan. In accordance with the results of quantitative thin-layer chromatography and the TG data, the first three endoeffects at 91.9, 136.4 and 158.6°C correspond to the intermediate stages of non-degradation dehydration ($\Delta m = 2.0\text{--}2.5$ mol H_2O); the other effects correspond to the stages of removal of the remaining water with simultaneous anion degradation and subsequent anion condensation, which is complete at temperatures higher than 400°C.

Depending on the factors mentioned above, the boundaries between zones shown in Fig. 1 may be distinct or smeared, and the zones may be overlapping and have different thicknesses. Under non-isothermal conditions the thickness of the zones of the intermediate products decreases with increasing heating rate (HR) which tends to suggest the direct transformation of $Na_5P_3O_{10} \cdot 6H_2O$ into $Na_5P_3O_{10}(\text{II})$, as described in the literature, at high HR when the process proceeds in a self-generating atmosphere without accumulating significant amounts of intermediate products [12,16–18]. Although these facts do not support the degradation-less mechanism of hexahydrate dehydration, they are of interest because they confirm that the transition



takes place with minimum loss of the basic substance.

The same result may be attained at low HR or under isothermal conditions if the process takes place in an atmosphere of water vapour. Figure 5 shows the change in the content of phosphorus in triphosphate

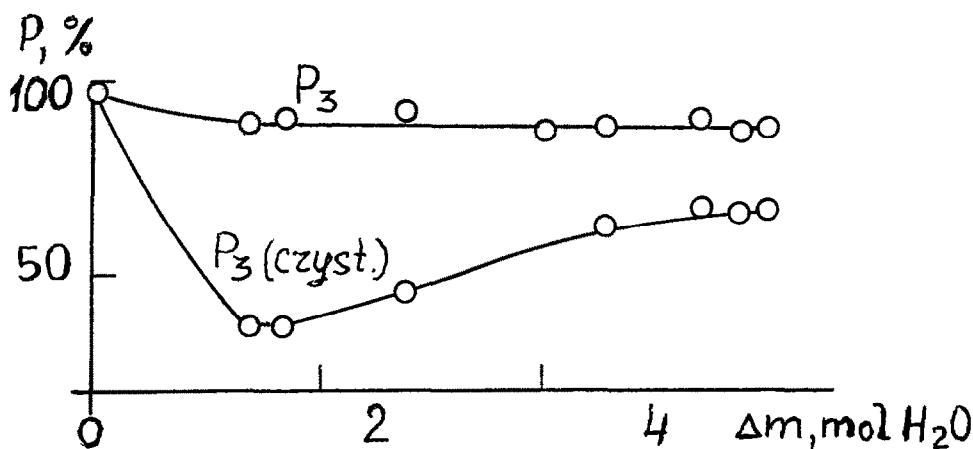


Fig. 5. Variation of P_3 and $P_3(\text{cryst.})$ content in a $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ sample under isothermal treatment in a steam flow at $p_{\text{H}_2\text{O}} = 986 \text{ hPa}$, $D = 0.01\text{--}1.0 \text{ mm}$, $m = 30 \text{ mg}$, $T = 200^\circ\text{C}$, $\tau = 0\text{--}1.0 \text{ h}$.

form (P_3) and the sum of crystalline triphosphates $P_3(\text{cryst.})$ on isothermal treatment of polycrystalline $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ in a water vapour flow at $T = 200^\circ\text{C}$ in a time interval from $\tau = 0$ to $\tau = 1 \text{ h}$. Values of P_3 were determined by quantitative paper chromatography, while $P_3(\text{cryst.})$ values were determined by quantitative X-ray diffraction analysis using the normal procedure with an internal MgO standard [19], slightly modified to apply to the determination of the sum of the crystalline phases, $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O} + \text{Na}_5\text{P}_3\text{O}_{10}(\text{II})$. For further details, the reader is referred to ref. 20.

As can be seen, the P_3 content is not lower than 86–91%, i.e. zones (c) and (d) are compressed so that no more than 9–14% of the total phosphorus is present in the products forming these zones. At the same time the $P_3(\text{cryst.})$ content passes through a minimum; in the region of the minimum the samples contain more than half the total phosphorus content in the form of amorphous triphosphate.

Unfortunately, the nature of amorphous triphosphate is not established unambiguously. Taking into consideration the earlier assumption [21] concerning mass losses corresponding to the descending branch of the curve in Fig. 5 within the limits of zones (a) and (b), it is reasonable to interpret amorphous triphosphate as being a pseudomorph of the hexahydrate phase (a strong distortion of the crystalline lattice of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ is sufficient to transform it into an X-ray-amorphous state), while within the limits of the narrowed zones (c) and (d), it is logical to interpret it as being cryptocrystalline II, the particles of which have not reached sizes that can be resolved by X-rays. Therefore in the region of the minimum, amorphous triphosphate represents a mixture of hexahydrate pseudomorphs and cryptocrystalline $\text{Na}_5\text{P}_3\text{O}_{10}(\text{II})$.

KINETIC CHARACTERISTICS OF DEHYDRATION OF CRYSTAL HYDRATES

A change in the thickness of the zones, in their gas permeability and other properties, is related to a change in the rate-limiting step and kinetic characteristics in the course of the dehydration of the crystallohydrates. This is manifested, in particular, in the fact that the effective activation energy E_v (calculated from the temperature dependence of the dehydration rate of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ in a vacuum at different Δm values) in the limits of zones (a) and (b), increases from 42–50 to 96–105 kJ mol^{-1} with an increase in Δm ; it remains constant at 160–180 kJ mol^{-1} in zone (c) and again increases in zone (d) from 125–140 to 250–270 kJ mol^{-1} [14].

A series of changes in the kinetic parameter n in the following equation is characteristic

$$\alpha = 1 - \exp(-k'\tau^n) \quad (15)$$

where α is the degree of transformation, τ is the time and k' is the constant related to the reaction rate constant k by the equality $k = n(k')^{1/n}$. Equation (15) is known as the Kolmogorov–Erofeev–Kazeev–Avrami–Mampel (KEKAM) equation, the Johnson–Mehl–Mirkin–Sirota (JMMS) equation etc., and represents a particular case of the general Volterra–Kolmogorov equation for evolution processes (the bibliography of this problem is given in ref. 5). Stage (a) corresponds to the diffusional-kinetic region ($n_{(a)} = 0.6\text{--}0.7$), stage (b) to the diffusional region ($n_{(b)} = 0.3\text{--}0.4$); stage (c) to the kinetic region at $\Delta m = 2\text{--}4$ mol H_2O ($n_{(c)} = 0.8\text{--}1.2$) and to the diffusional-kinetic region at $\Delta m = 4\text{--}5$ mol H_2O ($n_{(c')} = 0.4\text{--}0.8$), and at stage (d) to the diffusional region ($n_{(d)} = 0.2\text{--}0.5$).

The specific features of the dehydration of the crystallohydrates mentioned influence the kinetic analysis of the results of non-isothermal studies. This refers to triphosphates not only of alkali metals but also of other metals. Attempts to calculate activation energy E , pre-exponential factor A , reaction order n' and enthalpy ΔH from non-isothermal data do not produce positive results in all cases or for all reaction stages. Thus, in spite of the use of small sample weights, the results of computer-aided calculations of A , n' and ΔH for the dehydration of finely crystalline $\text{KCa}_2\text{P}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ ($D = 0.004\text{--}0.009$ mm) using the programs KINETIC and INTEG (a Mettler TA 3000 thermoanalyser and TG 50 module; $m = 20\text{--}30$ mg; DSC 20 cell, $m = 7\text{--}10$ mg) have failed to be satisfactory; only for E have data been obtained that are consistent with the results of an isothermal experiment [22]. This may be explained by the low sensitivity of numerical E values to the form of the kinetic equation used.

In addition to using eqn. (15) with $0.2 \leq n \leq 4$, the program KINETIC also includes the equations

$$\frac{d\alpha}{d\tau} = k\alpha^a \quad (0 \leq a \leq 1) \quad (16)$$

$$\frac{d\alpha}{d\tau} = k(1 - \alpha)^{n'} \quad (0.5 \leq n' \leq 1.5) \quad (17)$$

$$\alpha = k'\tau^b \quad (0.5 \leq b \leq 6) \quad (18)$$

together with the Jander, anti-Jander, Mampel etc. equations, 17 simple equations in all [5].

Similar results using the programs KINETIC and INTEG are derived for polycrystalline $K_5P_3O_{10} \cdot 4H_2O$ dehydration at the stage of degradationless removal of 2 mol H_2O in a kinetic region. Only in the interval between the endoeffects at 91.9 and 158.6°C (Fig. 4) are the E values calculated at certain heating rates (between 45–55 and 110–150 kJ mol^{-1}) close to isothermal E values (70–80 in vacuum and 110–130 kJ mol^{-1} at $p_{H_2O} = 3.7$ hPa [23]); in the remaining regions they are overestimated 2–5 times.

In order to calculate the kinetic characteristics of half-dehydration of $K_5P_3O_{10} \cdot 4H_2O$ on the basis of the derivatographic data, programs DISCR and INVAR (calculated on an Elektronika D3-28 computer) were also employed [24]. The program DISCR allows computation of kinetic characteristics using the known method [25] of statistical discrimination of the same 17 simple equations by the residual sums-of-squares. The program INVAR employs the determination of invariant kinetic parameters [26], according to which calculation is performed without a choice of the formal reaction model, using the point of intersection of the apparent compensation relations corresponding to different heating rates. Computation by the program INVAR, unlike DISCR and in spite of using a comparatively large weight ($m = 200$ mg), gives $E = 54.6 \text{ kJ mol}^{-1}$ close to the E value of 72.0 kJ mol^{-1} calculated by eqn. (15) on the basis of the results of an isothermal experiment (Table 1).

TABLE 1

E and $\log A$ calculated from data on isothermal and non-isothermal dehydration of polycrystalline $K_5P_3O_{10} \cdot 4H_2O$ ($D = 0.1\text{--}0.5$ mm, $\Delta m = 2$ mol H_2O)

HR (K min^{-1})	E (kJ mol^{-1})	$\log A$ (min^{-1})
DISCR, derivatography		
1.25	5.8 ± 0.5	-4.4 ± 0.2
2.5	8.9 ± 2.7	-3.6 ± 0.7
5.0	1.5 ± 1.8	-4.1 ± 0.6
10.0	6.5 ± 1.8	-3.8 ± 0.5
20.0	2.8 ± 1.8	-4.2 ± 0.4
INVAR, derivatography		
1.25–20.0	54.6 ± 10.0	4.2 ± 3.4
Eqn. (15), isothermal conditions [23]		
$T = \text{constant}$	72.0 ± 12.6	9.3 ± 2.6

Analysis of the presented data reveals that in some cases when reactions of the type $A(s) \rightarrow B(s) + C(g) \uparrow$ proceed according to the zony model, a rate-limiting step localized within the limits of one of the zones may be separated, and the results of isothermal and non-isothermal studies allow calculation of some of its kinetic characteristics. In the case of the reversible degradationless dehydration of $Na_5P_3O_{10} \cdot 6H_2O$ in a vacuum, in an inert gas and in air, these are stages (a) and (b) proceeding in the diffusional or diffusional-kinetic regions; in the case of the similar $K_5P_3O_{10} \cdot 4H_2O$ dehydration, it is the half-dehydration stage proceeding in a kinetic region. The dehydration of complexes $M_5P_3O_{10} \cdot [0.5H_2O]$ ($M = Na$ or K), the kinetics of which are insufficiently studied, also involves reversible degradationless stages.

SOME APPLICATIONS

Another order of mutual location of zones shown in Fig. 1 is typical of granulated PSTP and PPTP, whose advantage over powder-like PSTP and PPTP in preparing synthetic detergents lies in the fact that they represent a non-dusting material convenient for transportation with a controllable dissolution rate and controllable strength of granules. Such modified material is obtained by granulation of powder-like PSTP and PPTP with partial or complete moistening to the water content of the corresponding crystallohydrate (with subsequent drying or calcination) or by granulation combined with production of triphosphates [27].

If a PSTP granule is moistened up to a hexahydrate composition, then at drying its zony structure in section corresponds to the location of zones shown in Fig. 1. If a hexahydrate zone is located on the granule surface, the core of which consists of powder-like $Na_5P_3O_{10}$ (II), then a zony structure of the granule is distinguished from a powder-like carrier zone positioned below zone A(s). On drying and calcination, such a granule consists of a core of $Na_5P_3O_{10}$ (II) encapsulated in a hexahydrate shell whose surface is coated with a layer of efflorescence product which corresponds to zones (a) and (b) or with a layer of degradation and recondensation products which corresponds to zones (c) and (d).

A peculiar feature of granules obtained by hydration of a PSTP powder, in particular by soft granulation of PSTP [28,29], is a specific strengthening network of acicular $Na_5P_3O_{10} \cdot 6H_2O$ crystals covering a surface (Fig. 6). In the microscopic studies, a scanning electron microscope (SEM) JSM-35C was employed (deposition of a thin gold layer). Scanning electron micrographs of granules obtained by a non-hydration technique, including PSTP granules of pilot samples (Knapsack, Germany and Mario Balestr, Italy) do not exhibit this network of crystals.

Investigations of the surface of granules, prepared by nodulizing and moistening a PSTP powder in high-speed granulators of different types

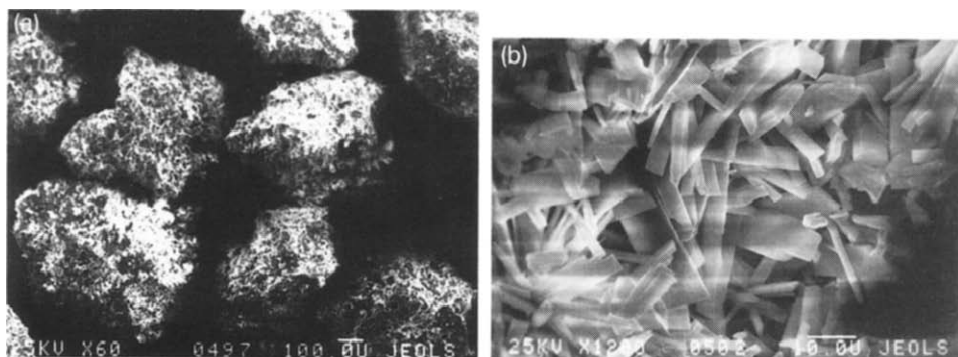


Fig. 6. Scanning electron micrograph of granules obtained by soft granulation of PSTP powder (water content is 2.3% H_2O : original magnification $\times 60$ (left) and $\times 1200$ (right)).

under eddy flow conditions, show that the form of the crystals formed and their morphology change with the quantity of water absorbed by the powder. At a moderate content of water in the granules, which does not exceed 22.71% H_2O calculated for $Na_5P_3O_{10} \cdot 6H_2O$, e.g. 17.2% (Fig. 7) or 13.9% (Fig. 8), the surface of the granules is coated with a network of acicular, pillar-shaped or elongated laminar crystals of hexahydrate. The observed crystals resemble, in a somewhat modified form, those shown in Fig. 6. If granules containing 13.9% H_2O are subjected to calcination in air at $400^\circ C$ for 2 h until their transformation into anhydrous PSTP granules, smeared contours of the network of pseudomorphs of the initial crystals may still be distinguished on the SEM micrographs (Fig. 9).

When an excess amount of water, compared with 22.71% H_2O , is absorbed by a PSTP powder, when the main component of the granules is a crystalline phase $Na_5P_3O_{10} \cdot xH_2O$ ($6 < x < 10$) (a zone of which is below zone A(s)), the surface of the granules exhibits druses of crystals of the

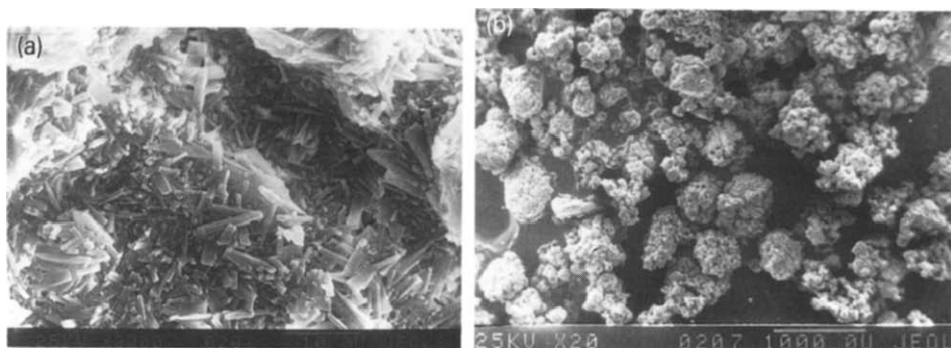


Fig. 7. Scanning electron micrograph of granules obtained by water spraying on a PSTP powder in a vertical high-speed granulator (17.2% H_2O : original magnification $\times 20$ (right) and $\times 2000$ (left)).

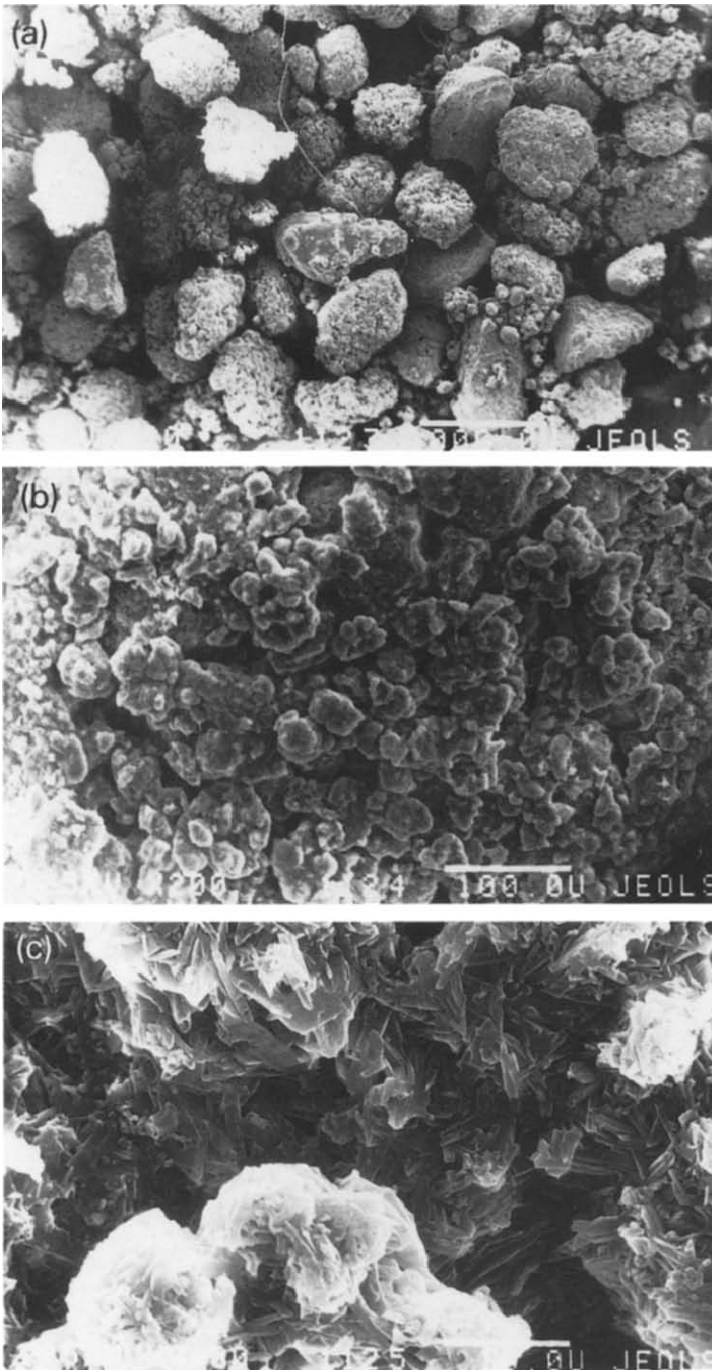


Fig. 8. Scanning electron micrograph of granules prepared by moistening PSTP powder in a TL-07 granulator until reaching a liquid: powder ratio of 3:2 (13.9% H₂O: original magnification ×20 (top), ×200 (middle), ×2000 (bottom)).

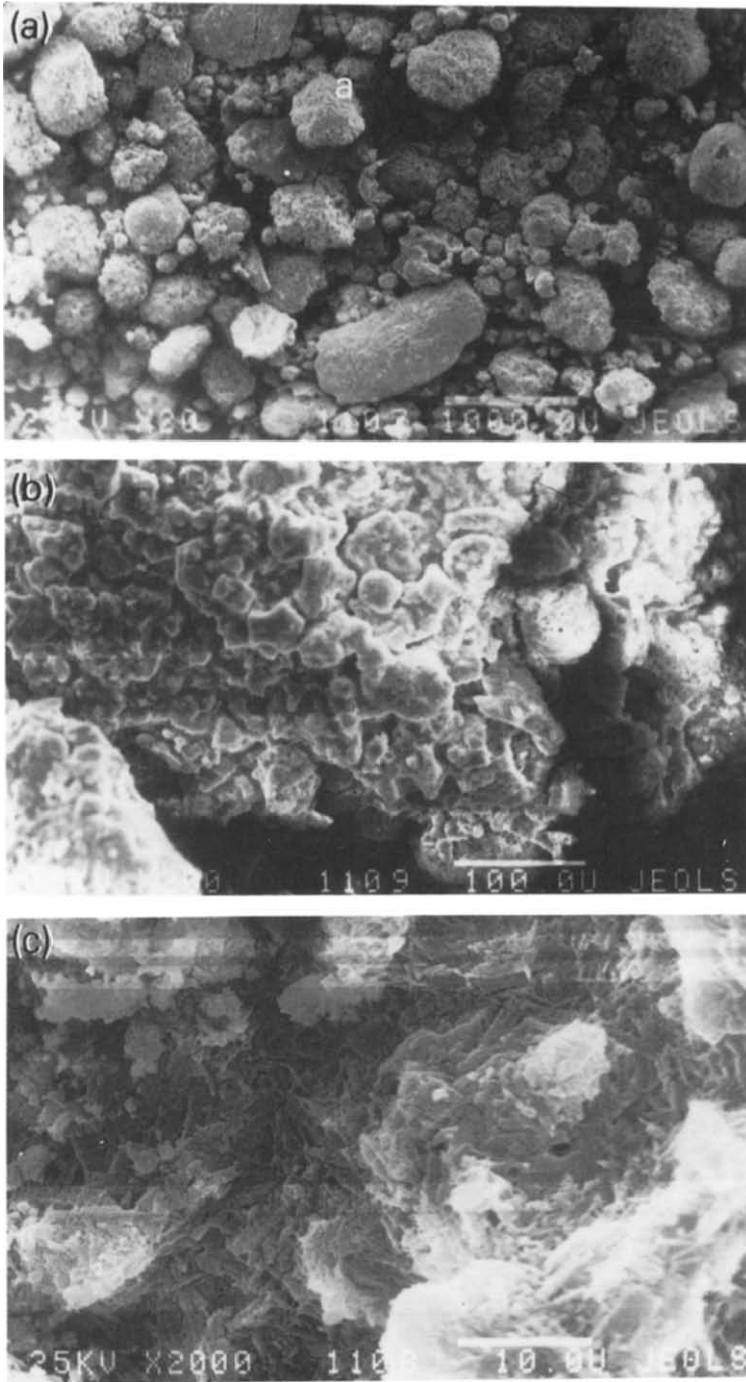


Fig. 9. Scanning electron micrograph of granules containing 13.9% H_2O after calcination at 400°C in air for 2 h (original magnification $\times 20$ (top), $\times 200$ (middle), $\times 2000$ (bottom)).

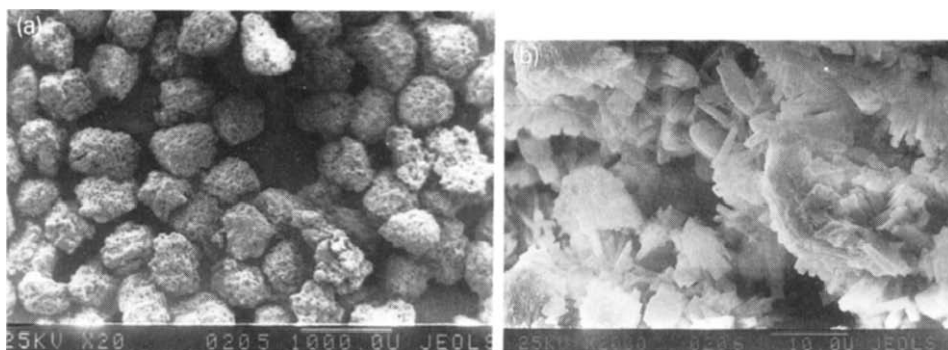


Fig. 10. Scanning electron micrograph of granules prepared by water spraying onto PSTP powder in a tray granulator (29.0% H₂O: original magnification $\times 20$ (left), $\times 2000$ (right)).

phase Na₅P₃O₁₀ · xH₂O (29.0% H₂O, Fig. 10) or very shortened pillar-shaped crystals of the same phase (31.5% H₂O, Fig. 11). On the surface of granules containing 31.5% H₂O after 2 h extra calcination in air at 400°C, there appears a network of pillar-shaped crystals which probably form at the stage of water removal to give a hexahydrate composition, and are then preserved in the form of pseudomorphs (Fig. 12).

SEM data show that on forming the granules, in addition to the chosen physical method of nodulizing and moistening the PSTP powder, the phase composition of the granules, the sequence of phase distribution, including the zone distribution, and the character of the crystallization of the hexahydrate phase, are all important. The granule properties are listed in Table 2: bulk mass ($d = 0.51\text{--}0.89$ g cm⁻³; crushing strength which was determined for a fraction of the granules with a mean diameter $D' = 1.0$ mm ($M = 2.2\text{--}17.6$ MPa); the yield of granules with $D' = 0.2\text{--}1.0$ mm (13.4–90.0%) and $D' = 1.6$ mm (1.8–86.6%); dissolution rate at $T = 25^\circ\text{C}$ ($\tau_d = 2.4\text{--}11.8$ min) where τ_d is the time required for dissolving 5 g of a sample in 100 ml of water at 60–70 rev min⁻¹ of a magnetic stirrer. The P₃ content in the granules varies between 92.6 and 97.4%.

The regulation of the zone structure of the granules, the density of the separate zones and their gas permeability, which control the rate of the limiting step of dehydration, are associated with the specific design features of the apparatus intended for PSTP granulation. Thus, when an installation for PSTP soft granulation is used, the total granulation time is subdivided into two main parts [29]

$$\tau = \tau_1 + \tau_2 \quad (19)$$

where τ_1 is the time consumed for fast processes, the duration of which is measured in seconds and fractions of seconds (condensation and sorption of water vapour, dissolution of the surface layer, evaporation of excess moisture, agglomeration, the onset of Na₅P₃O₁₀ · 6H₂O crystallization),

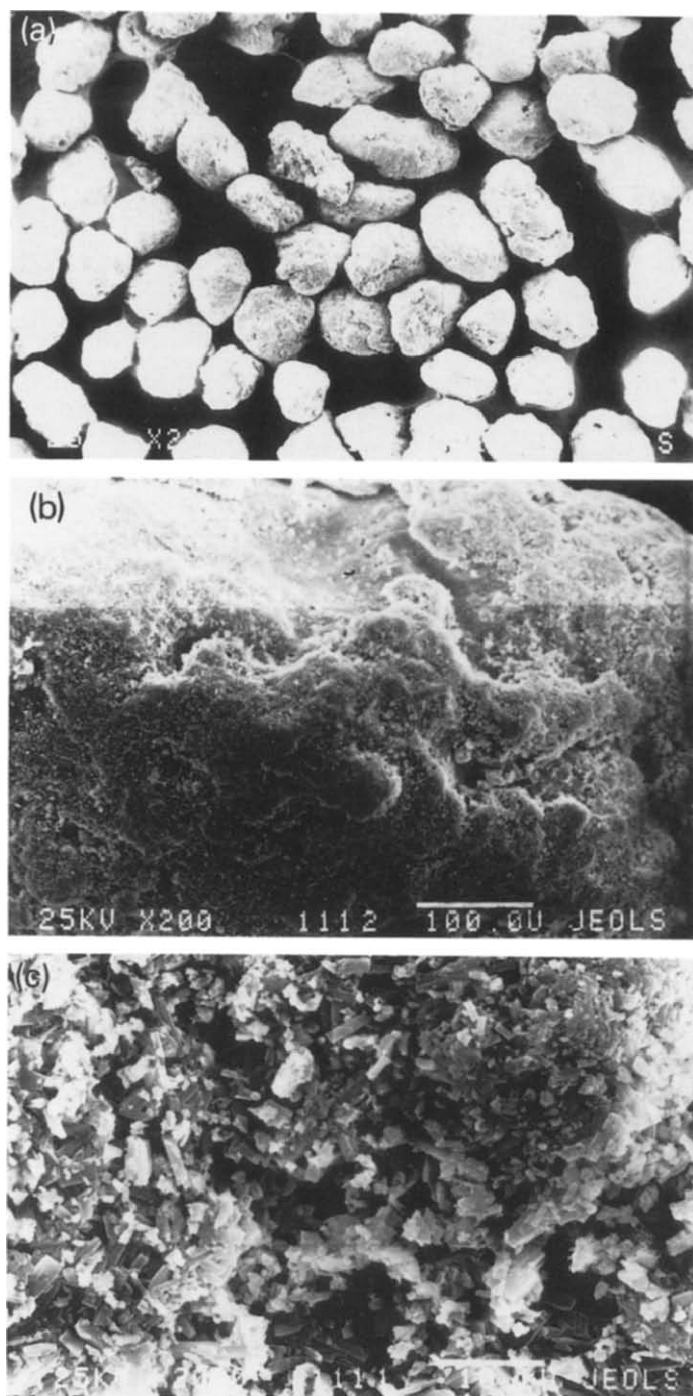


Fig. 11. Scanning electron micrograph of granules obtained by spraying 10% $\text{Na}_5\text{P}_3\text{O}_{10}$ solution onto PSTP powder in a horizontal high-speed granulator (31.5% H_2O : original magnification $\times 20$ (top), $\times 200$ (middle), $\times 2000$ (bottom)).

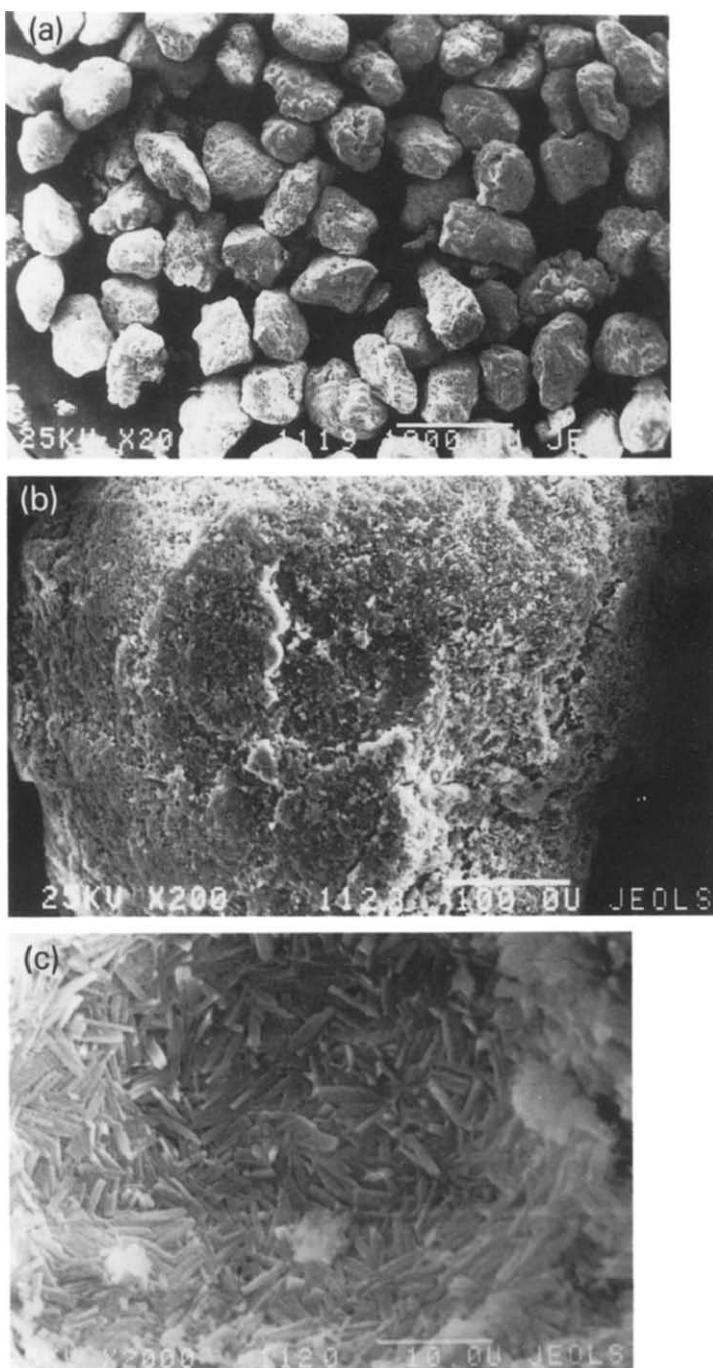


Fig. 12. Scanning electron micrograph of granules containing 31.5% H_2O after calcination at 400°C in air for 2 h (original magnification $\times 20$ (top), $\times 200$ (middle), $\times 2000$ (bottom)).

TABLE 2

Composition and properties of granules obtained by PSTP nodulizing and moistening in high-speed granulators

Content (wt.%)		d (g cm^{-3})	M (MPa) ($D' = 1.0 \text{ mm}$)	Granule yield (wt.%)		τ_d (min) ($T = 25^\circ\text{C}$)
H_2O	P_3			$D' = 0.2\text{--}1.0 \text{ mm}$	$D' = 1.6 \text{ mm}$	
13.9	92.6	0.51	4.8	90.0	1.8	3.0
17.2	97.4	0.57	5.1	84.4	15.3	3.0
29.0	96.5	0.59	2.2	63.3	36.3	2.4
31.5	94.4	0.89	17.6	13.4	86.6	11.8

and τ_2 is the time for slow processes, the duration of which is measured in minutes and hours (diffusional moisture evaporation limited by the rate of water vapour diffusion from a granule bulk to its geometric surface, and the formation of a strengthening network of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ crystals). In order to calculate the dimensions of a chamber granulator, it is important to know the constituents of τ_1 , because τ_2 corresponds to processes which may occur outside the limits of a chamber granulator and do not affect the quality of the end product.

The discussion above refers to thermal transformations of crystalline forms of not only PSTP but also PPTP, which are used in the formulation of synthetic detergents for increasing the effectiveness of their action [30,31], and also to the thermal transformations of triphosphates of other metals [12,32]. As applied to the preparation of alkali metal triphosphates, their use and transformations under the effect of different factors, the zony model undergoes various changes. In particular, it manifests itself in a decrease in the rate of removal of iron salts in suspension from orthophosphate solutions in PSTP production, a decrease in the rate of oxygen loss by peroxyphosphate granules at the expense of forming a dense layer of decomposition products on the surface of the granules, etc. [3].

A peculiar manifestation of the zony model is revealed in the region of $\text{Na}_5\text{P}_3\text{O}_{10}(\text{I})$ pre-melting [14]. Because of bad adhesion with the material of the sample holder, $\text{Na}_5\text{P}_3\text{O}_{10}(\text{I})$ powder, present as a thin layer in the holder, undergoes a transformation into a clotted spherical conglomerate consisting of three zones: an external zone of a melt which on cooling turns into a glass-like mass; an internal zone or a powder-like $\text{Na}_5\text{P}_3\text{O}_{10}(\text{I})$ core; and an intermediate zone of compressed, partially sintered powder containing the products of triphosphate anion rearrangement. With increasing the number of heating-cooling cycles confined by a pre-melting region, the size of the powder-like core decreases, while the thickness of the external zone increases until conglomerate transformation into a glass sphere takes place after the 18th cycle.

The zonary development of the phase transformation and anion rearrangement processes is displayed typically on DSC curves as an evolution of the split exoeffect of vitrification [14]. This phenomenon may be of certain interest from the viewpoint of the kinetics of non-equilibrium phase transitions [33].

In a general case, the zonary model considered for the above examples may be useful for analysis of various problems of isothermal and non-isothermal kinetics of multistage solid state reactions, including the problems of theory and methodology of thermal analysis [34,35]. They also include such aspects as the role of structural factors [36–38] and interphase boundaries [39,40] in thermal transformations of solids taking place as localized [41] or homogeneous processes [3,42], kinetic analysis of complex reactions [43,44] with an account of the effect of temperature, pressure and other factors on their rate [45–47], and other general problems of non-isothermal kinetics [48,49].

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