Thermal transformations of $Mg(H_2PO_4)_2 \cdot 4H_2O$

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Abstract

Isothermal and non-isothermal transformations of $Mg(H_2PO_4)_2 \cdot 4H_2O$ in vacuum, water vapour, dry and humid air atmosphere at 20–900°C were studied by the methods of DTA, XRD, paper chromatographic analyses, gravimetry and optical microscopy. It has been shown that the size of initial tetrahydrate crystals and the composition of gaseous phase affect not only the dehydration rate but the chemical and phase composition of the resulting intermediates as well. At the same time, the crystalline polyphosphate $[Mg(PO_3)_2]_n$ is the end product, irrespective of the heat-treatment conditions. © 1998 Elsevier Science B.V.

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1. Introduction

Magnesium dihydrogenphosphate may be isolated from acidic phosphate solutions in the form of di- or tetrahydrate [1,2]. The dihydrate belongs to the well-known series of isostructural crystallohydrates $M^{II}(H_2PO_4)_2 \cdot 2H_2O$ (M – Mg, Mn, Co, Ni, Fe, Zn) and it has been rather fully investigated. In particular, the sequence of $Mg(H_2PO_4)_2 \cdot 2H_2O$ chemical and phase transformations has been revealed during its non-isothermal heating [3,4]. Information on the tetrahydrate is not so extensive. This substance was synthesized for the first time by Belopolsky et al. [5]. Subsequently, identified by X-ray analysis, $Mg(H_2PO_4)_2 \cdot 4H_2O$ [6] was found in the product of phosphorite processing [7] and during solidification of Mg-phosphate binders [8].

The available literature data on thermal transformations of tetrahydrate are limited to the two works. On the basis of derivatographic investigations, authors [9] assumed that not only the water of crystallization, but the constituent water also, is eliminated at 200°C. The acidic phosphates formed subsequently transform into $Mg_2P_2O_7$, and tetracyclophosphate $Mg_4P_4O_{12}$ crystallizes at $t>850$°C. According to [6], non-isothermal heating of $Mg(H_2PO_4)_2 \cdot 4H_2O$ is accompanied with the evolution of the water of crystallization in two steps (with the formation of the dihydrate (150°C) and anhydrous dihydrogenphosphate (250°C)) followed by the release of constituent water with magnesium metaphosphate $[Mg(PO_3)_2]_n$ formation (400°C).

The discrepancy from the published data is due to a variety of reasons. The point is that many factors which have influence on the process being investigated were not controlled in the cited works. In particular, the mass and geometry of the samples, the degree of their dispersion and the composition

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of gaseous phase were not quantified. In the present work, it has been shown that these factors may affect not only the dehydration rate but the composition of the resulting products as well.

The investigation of chemical and phase transformations of magnesium dihydrogenphosphate tetrahydrate during its iso- and non-isothermal heating were conducted in vacuum, in water-vapour atmosphere (when the p_{H_2O} values were fixed) and in air (at a controlled relative humidity RH) using samples with different degrees of dispersion.

2. Experimental

A couple of $Mg(H_2PO_4)_2 \cdot 4H_2O$ samples with identified compositions but different crystal size were used in the work. Small crystals of tetrahydrate ($D=0.05$–0.1 mm) were precipitated from the supersaturated solution of MgO (chemical grade reagent) in 62% H_3PO_4 (12 g of oxide per 100 ml of acid) with vigorous stirring at room temperature. The large crystals ($D=2$–3 mm) were isolated from the same solution on standing without stirring during 10 days. The precipitate was separated from the mother liquor on a glass filter and washed sequentially with acetone and ether. X-ray patterns of the small and large crystals were identical to one another and with literature data [6] for $Mg(H_2PO_4)_2 \cdot 4H_2O$. The composition of tetrahydrate was also confirmed by chemical analysis.

In non-isothermal experiments, we used a derivatograph OD-103 MOM (plate platinum sample holder or platinum crucible, sample weight 400 mg, heating rate 5–10°C min^{-1}). In isothermal experiments, a high-vacuum setup equipped with a quartz microbalance (spiral sensitivity 1 mg/mm, sample mass ca. 50 mg, flat-bottomed Pt sample holder in which the sample was spread as a thin layer) was used to investigate the dehydration kinetics in vacuum (residual pressure $<1 \times 10^{-4}$ hPa), in a water-vapour atmosphere ($p_{H_2O} = 1$–20 hPa) and in air (with relative humidity RH=0–100%). The products, which formed at different steps of iso- and non-isothermal transformations, were characterized by X-ray diffraction analysis (DRF diffractometer −2.0; CuK_α radiation). In a separate series of isothermal experiments, a thermostated vacuum cell with optical quartz windows was used to observe microscopically changes in the crystal. The

anionic composition of heat-treated samples was determined by quantitative ascending chromatography using FN12 chromatographic paper; EDTA was added to transfer the less-soluble products of heat treatment in solution [10].

3. Results and discussion

Dehydration begins at $t \approx 60°C$ when the large crystal samples of $Mg(H_2PO_4)_2 \cdot 4H_2O$ are heated in air (RH=60%) under conditions of the derivatographic experiment (Fig. 1(b)). The DTA response with peak temperature of 168°C corresponds to the evolution of the main part of the water of crystallization; however, it is preceded by a comparable effect at 116°C. Insofar as only 0.3 mol H_2O are liberated at this stage, it is logical to suppose that this effect is connected not with dihydrogenphosphate dehydration but with some side process; for example, with sample melting. In fact, according to microscopic observations, the crystals, if not melting completely on being heated to 110°C, will certainly lose their initial contours.

The formation of a liquid phase and its influence on the dehydration process were considered in more detail when the process was investigated under isothermal conditions. Fig. 2 shows the "mass loss Δm vs. time t" kinetic curves which were obtained when a large-crystal sample of tetrahydrate was heated in vacuum and in water-vapour atmosphere ($p_{H_2O} = 20$ hPa). Different character of the processes carrying on in two temperature regions (≤ 70 and ≥ 80 in vacuum; ≤ 75 and $\geq 80°C$ at $p_{H_2O} = 20$ hPa) may be distinguished. Over the low-temperature region, the liberation of the water of crystallization of tetrahydrate proceeds in the kinetic regime and is characterized by the presence of an induction period followed by self-acceleration of the isothermal reaction. Another picture is observed at $t \geq 80°C$, when the process becomes abruptly retarded after initial dehydration. The observations on the crystal during the course of isothermal reaction enable the identification of the reasons as being diffusion impediments to the removal of water vapour from the reaction zone. They are connected with the formation of a liquid phase on the surface of initial crystals followed by solidification in the form of a dense glassy product.
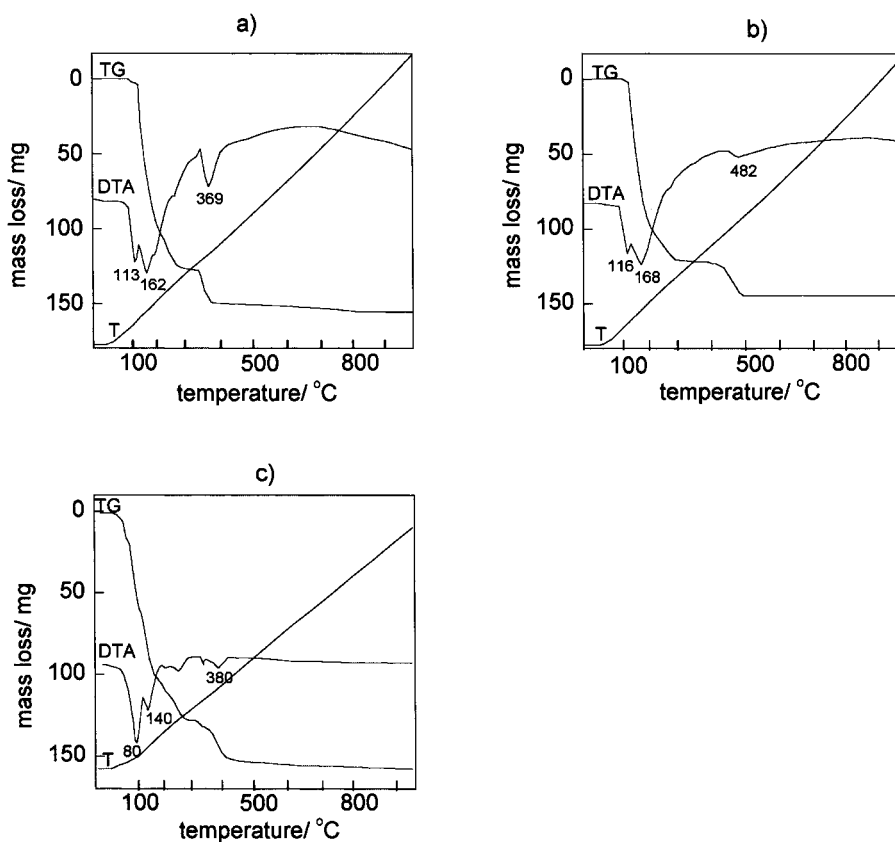
Fig. 1. The derivatograms of small (a,c) and (b) large crystals of $Mg(H_2PO_4)_2 \cdot 4H_2O$; m=400 mg; heating rate (a,b) 10°C and (c) 5°C min^{-1}; (a,b) platinum crucible or (c) plate holder.
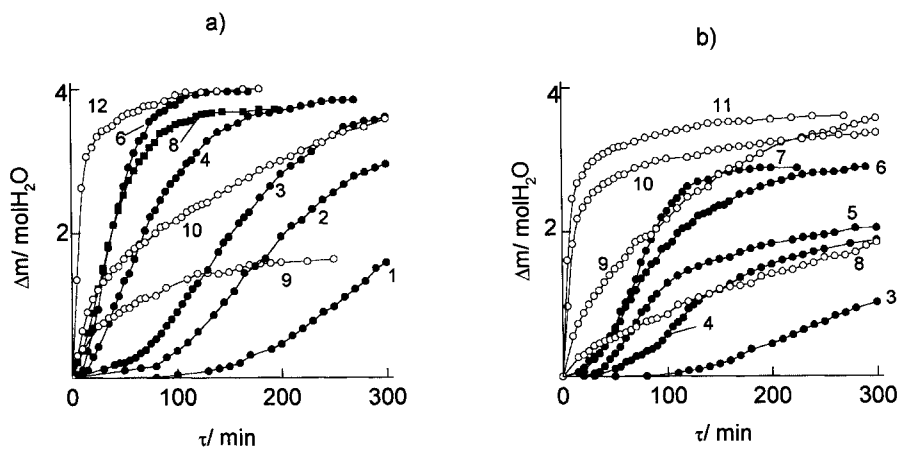

Fig. 2. The kinetic curves of $Mg(H_2PO_4)_2 \cdot 4H_2O$ large crystals dehydration (a) in vacuum or (b) in water-vapour atmosphere at $p_{H_2O} = 20$ hPa: 1 – 45°C, 2 – 50°C, 3 – 55°C, 4 – 60°C, 5 – 65°C, 6 – 70°C, 7 – 75°C, 8 – 80°C, 9 – 90°C, 10 – 100°C, 11 – 110°C, and 12 – 120°C.
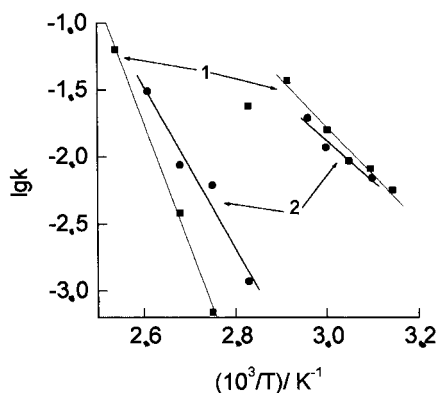
Fig. 3. Arrhenius plot of rate constant k of $Mg(H_2PO_4)_2 \cdot 4H_2O$ large crystals dehydration in (1) vacuum and (2) water-vapour atmosphere at $p_{H_2O} = 20$ hPa.

The change in the mechanism of this process leads to the observation that both, in vacuum (Fig. 2(a)) and in water-vapour atmosphere (Fig. 2(b)) the transformation degree is lower after 5 h holding at 80°C than that for the same time at 60°C. As a result, monotonous variation of the reaction rate with the temperature is disrupted and the Arrhenius plots show a discontinuity (Fig. 3). The effective values of activation energy E_k calculated from the temperature dependence of dehydration rate constant k^1 are presented in Table 1. The high values of E_k for the high-temperature dehydration corroborate the supposition made earlier that the removal of water vapour from the reaction zone is limited in this case not by the diffusion in the gaseous or liquid phases but by the diffusion through the dense layer of non-porous product.

The features described for dehydration of a large-crystal sample were found not only in vacuum or at

Table 1
The values of activation energy E_k (in kJ/mol) of dehydration of $Mg(H_2PO_4)_2 \cdot 4H_2O$ large crystals

Vacuum	68±5 (≤70°C)	179±10 (≥80°C)
$p_{H_2O}=20$ hPa	59±5 (≤75°C)	117±10 (≥80°C)

[1]The values of rate constant k were determined from the experimental data using the equations $\alpha = 1 - \exp(-k'\tau^n)$ and $k = n(k')^{1/n}$ [11], where α is the degree of transformation, τ the time, and n the kinetic parameter. Mass loss ($\Delta m = 4$ mol H_2O) was taken as $\alpha = 100\%$.

$p_{H_2O} = 20$ hPa but at other values of water vapour pressure as well; in so doing, the value of p_{H_2O} has different effect on the process rate within the low- and high-temperature regions. In the cases where solid-state dehydration is predominant (e.g. at 70°C), in line with the generalities of reversible topochemical reactions, a regular decrease of the dehydration rate is observed as the water-vapour pressure is increased (Fig. 4(a)). At higher temperatures (90°C), this regularity breaks down; sometimes the opposite effect occurs (Fig. 4(b)).

The water-vapour pressure over the sample affects not only the dehydration rate but the compositions of the resulting amorphous products as well. If under isothermal heating of tetrahydrate in vacuum the evolution of the water of crystallization always proceeds in one step with the formation of anhydrous dihydrogenphosphate $Mg(H_2PO_4)_2$ (Fig. 2(a)), the composition of the products of $Mg(H_2PO_4)_2 \cdot 4H_2O$ dehydration in a water-vapour atmosphere depends on p_{H_2O} and t values.

In spite of diffusion impediments, the process is completed by the formation of anhydrous salt at $p_{H_2O} \geq 6$ hPa and $t \geq 80°C$; however, at lower temperatures the kinetic curves (the S-type form of which points to the kinetic regime of reaction in process) flatten out when the transformation degree corresponds to the evolution of 3 mol H_2O from 4 mol H_2O (Fig. 2(b) and Fig. 4(a)). The products of such composition may present both, a monohydrate and a mixture of formed anhydrous dihydrogenphosphate with unreacted tetrahydrate. The lack of diffraction peaks for the initial phase in X-ray diffraction patterns as well as of unreacted substance nuclei in the bulk of crystals dehydrated under specified conditions ($p_{H_2O} > 6$ hPa, $t \leq 75°C$) confirms, at first glance, the formation of individual monohydrate. However, it is not ruled out that in reality, anhydrous dihydrogenphosphate, which tightly holds the residual water, corresponds to the gross monohydrate composition. Such a peculiarity is characteristic of active products of crystallohydrate dehydration; instances have been described when ca. 70% of the volatile product was retained even at very high temperatures [12].

Dehydration is also completed without reaching the anhydrous salt composition within the region of low values of water-vapour pressure ($1 \leq p_{H_2O}$ hPa); in doing so the plateau on the kinetic curves is regularly

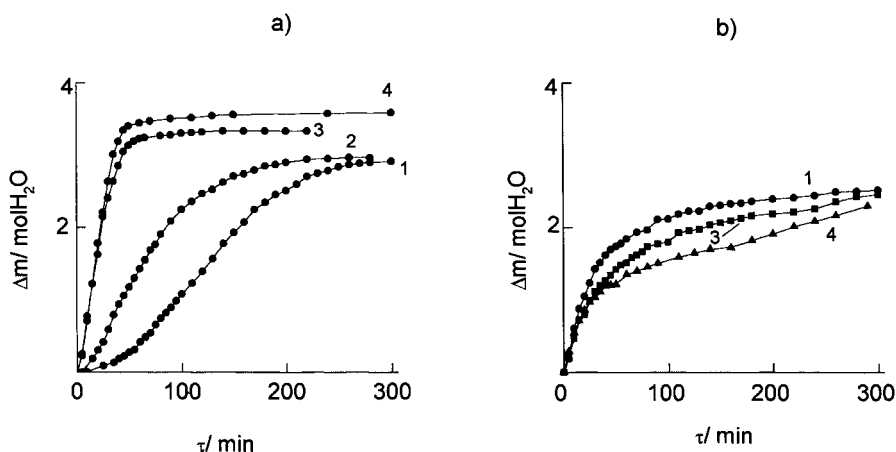Fig. 4. The kinetic curves of $Mg(H_2PO_4)_2 \cdot 4H_2O$ large-crystal dehydration in water-vapour atmosphere at (a) 70 and (b) 90°C: $1 - p_{H_2O}$ =20 hPa, 2 – 13 hPa, 3 – 5 hPa, and 4 – 1.5 hPa.

shifted in the direction of high Δm values as the water-vapour pressure is reduced.

The X-ray amorphous products formed by dehydration of the tetrahydrate in a water-vapour atmosphere are unstable and absorb moisture actively up to total dissolution on cooling to room temperature at $p_{H_2O} = 20$ hPa. The hydration rate falls off and the process proceeds in the solid state with increase in temperature and decrease in water-vapour pressure. In this case hydration is restricted to the formation of the tetrahydrate, crystallization of which lags behind the chemical reaction. This may lead to an unusual proceeding of isothermal reaction within certain p_{H_2O} and t ranges (Fig. 5). The appearance of a maximum in the kinetic curve is explained by the fact that initially formed amorphous (or poorly crystallized) product, when the hydration rate is high, has elevated reactivity and adsorbs excess quantities of water, which is released as crystallization takes place. The effect of the passage of the hydration rate through a maximum value may, or may not, show itself depending not only on the p_{H_2O} and t values but on other factors capable of changing the relationship between the reaction rate and the rate of crystallization as well. Among these factors are the mass and configuration of sample, the depth of layer, etc.

Taking into account the fact that the hydration rate of the products of tetrahydrate dehydration is sufficiently high, we carried out the investigation of reversibility of the $Mg(H_2PO_4)_2 \cdot 4H_2O$ topochemical
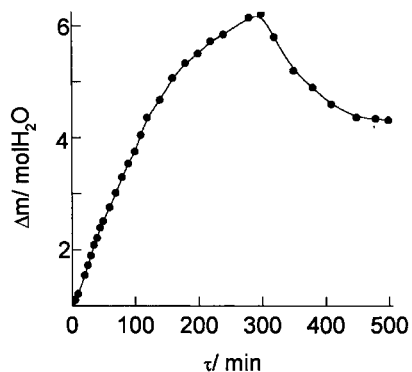

Fig. 5. The kinetic curve of rehydration of X-ray-amorphous product, having composition $Mg(H_2PO_4)_2 \cdot H_2O$, at 20°C and $p_{H_2O} = 13$ hPa.

transformations which proceed on heating. The possibility of hydration–dehydration processes to occur in cyclic regimes depends on the state of the resulting products. Where impedance occurs [11], equilibrium of the system is disturbed and the rates of hydration and dehydration vary with each cycle. In the system being considered, dehydration begins even faster than for the initial tetrahydrate after the first cycle (Fig. 6); in doing so the reaction starts at a maximum rate, but henceforth diffusion impedes the removal of water vapour from the reaction zone. These impediments are enhanced from cycle to cycle and each time the dehydration rate decreases by a factor of 1.5–2.
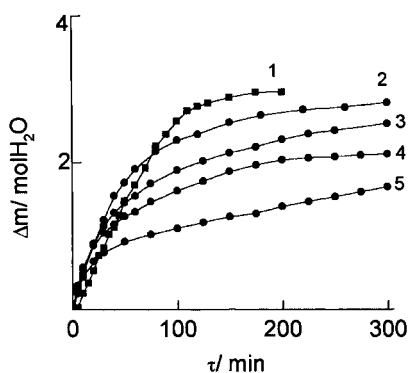
Fig. 6. The kinetic curves of $Mg(H_2PO_4)_2 \cdot 4H_2O$ large-crystal dehydration under conditions of "hydration–dehydration" cycle regime. The figures on curves correspond to the cycle number; $70°C$, $p_{H_2O} = 13$ hPa.

Fig. 7. The kinetics of $Mg(H_2PO_4)_2 \cdot 4H_2O$ small-crystal dehydration in (1) vacuum and (2) water-vapour atmosphere at $p_{H_2O} = 20$ hPa.

Some of the peculiarities noted for $Mg(H_2PO_4)_2 \cdot 4H_2O$ large-crystal isothermal transformations are characteristic of small-crystal sample too. We have already mentioned [13] the ability of products formed as a result of polycrystalline tetrahydrate dehydration to hold the residual water and about the peculiar kinetics of their rehydration. At the same time, the formation of a liquid phase in the course of dehydration and the ensuing anomalous influence of p_{H_2O} and t on the rate and other process characteristics have been observed for single crystals only. The dehydration of small crystals in vacuum, and in water-vapour atmosphere proceeds in the kinetic regime in agreement with the generalities of reversible topochemical reactions (Fig. 7). The reaction rate rises regularly with the increase in temperature and decrease in water-vapour pressure.

With the aforesaid allowed for, it may be expected that the dehydration of small crystals during non-isothermal heating under conditions of derivatographic experiment will be substantially different from that of large crystals. At the same time, our data (Fig. 1(a) and Fig. 2(b)) show that at the stage when the evolution of the water of crystallization proceeds, the trend of thermoanalytical curves is slightly different. The DTA curve obtained for the small-crystal sample of $Mg(H_2PO_4)_2.4H_2O$ also has endothermic effect with a peak temperature of $113°C$ which is connected (as follows from the microscopic observations) with the sample melting. The distinction in the nature of topochemical transformations (solid-state
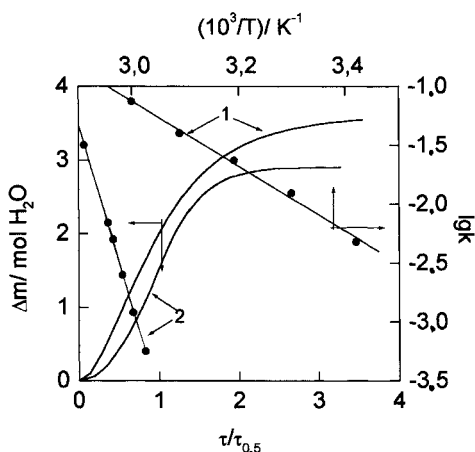
process during isothermal holding or the formation of a liquid phase under non-isothermal heating) of $Mg(H_2PO_4)_2 \cdot 4H_2O$ small crystals may be caused not only by the heating technique but by such factors as sample mass (50 and 500 mg, respectively) or gaseous phase composition (vacuum or water-vapour atmosphere in the first case and moist air in the second) as well.

The investigations carried out showed that the small-crystal sample is liable to melt during isothermal heating in air at a relatively low temperature ($60°C$) and low partial pressure of water vapour (5 hPa). The sample melting causes the abrupt deceleration of the process (Fig. 8), such effect being observed even in dry air (curve 2). Thus, the effect, known in topochemistry as a shielding gaseous jacket [12], connected with the impediments in diffusion of water vapour through air reveals itself. In this case, an uncontrolled water-vapour pressure which by far exceeds the p_{H_2O} value, corresponding to that specified in experiment in air humidity, arises in the porous solid product.

On the other hand, if the sample is distributed as a thin layer at the plate holder and the heating rate is not high, removal of the water of crystallization is not accompanied by sample melting under conditions of derivatographic experiment (Fig. 3(c)). In this case, dehydration begins at lower temperatures (as compared with heating in crucibles) and the first endo-
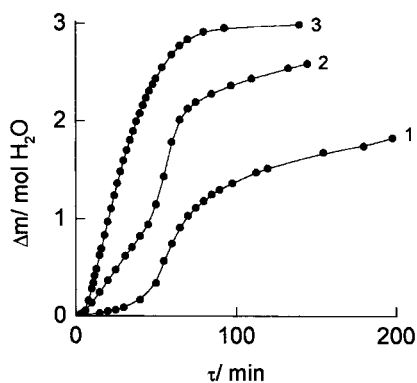
Fig. 8. The kinetic curves of $Mg(H_2PO_4)_2 \cdot 4H_2O$ small crystals dehydration in water vapour atmosphere at $p_{H_2O} = 5$ hPa (3) and in air at relative humidity RH=0% (2) or 25% (1) (partial water pressure $p_{H_2O} = 5$ hPa).

thermic effect with peak temperature of 80°C exactly corresponds to dehydration.

TG curves (Fig. 1(a–c)) have only poorly pronounced bends when the mass loss is equal to the total evolution of the water of crystallization (Δm=24.8%). This is a demonstration of the low stability of X-ray amorphous, anhydrous dihydrogenophophate $Mg(H_2PO_4)_2$ which is formed during non-isothermal heating of small and big crystals of tetrahydrate. One turns into a crystalline dihydrogenpyrophosphate as further heating takes place. Under

conditions of derivatographic experiment this substance ($MgH_2P_2O_7$) is stable across a wide temperature range irrespective of whether it was obtained during the heating of small- or big-crystal sample. Under isothermal conditions the character of $Mg(H_2PO_4)_2$ chemical and phase transformations essentially depends on the crystal size of the precursor (the initial tetrahydrate). Fig. 9 presents the kinetic curves obtained when dehydration of two samples of anhydrous dihydrogenphosphate $Mg(H_2PO_4)_2$, accompanied with anionic condensation, was conducted in vacuum. One of the samples was prepared from small crystals of tetrahydrate (isothermal heating in vacuum at 60°C), the other was prepared from large crystals (isothermal heating in vacuum at 110°C).

In the first case, the kinetic curves are regularly shifted in the direction of high Δm values with increase in temperature. Dehydration is attended by anionic condensation, in so doing the mixture of X-ray-amorphous chain phosphates is formed (Table 2). If the process proceeds at temperatures higher than 400°C, this mixture transforms into the crystalline end product $[Mg(PO_3)_2]_n$.

During the isothermal heating of anhydrous dihydrogenphosphate that was prepared from large crystals of tetrahydrate, the monotonic change in dehydration rate breaks down within the temperature range of 200–250°C (Fig. 9(b)). The results of X-ray analysis of the products formed showed that this is connected with the

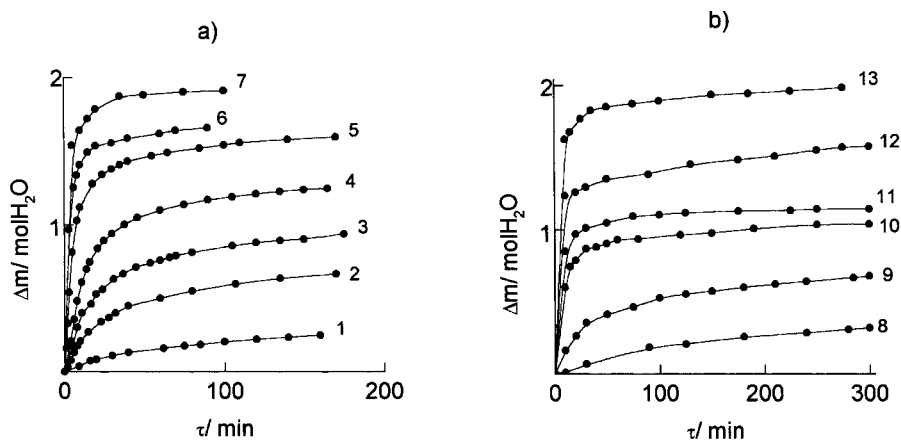Fig. 9. The kinetic curves of $Mg(H_2PO_4)_2$ dehydration in vacuum; 1 – 95°C, 2 – 125°C, 3 – 150°C, 4 – 190°C, 5 – 208°C, 6 – 230°C, 7 – 450°C, 8 – 130°C, 9–150°, 10 – 200°C, 11 – 250°C, 12 – 350°C and 13 – 450°C. The samples of $Mg(H_2PO_4)_2$ were prepared from (a) small-crystalline and (b) big-crystalline tetrahydrates.

Table 2
The anionic composition of products formed during isothermal holding of $Mg(H_2PO_4)_2$ in vacuum

$t/^\circ C$	Δm/mol H_2O	Content of phosphorus in the form of					Crystalline phases
		P_1	P_2	P_3	$P_{>4}$	On start	
Sample prepared from large crystals of tetrahydrate							
130	0.22	46	40	14	—	—	amorphous
150	0.66	35	40	25	—	—	amorphous
200	1.04	30	36	33	—	—	$MgH_2P_2O_7$
250	1.18	—	90	—	—	10	$MgH_2P_2O_7$
350	1.58	—	28	—	—	72	$MgH_2P_2O_7$ $[Mg(PO_3)_2]_n$
450	2.00	—	—	—	—	100	$[Mg(PO_3)_2]_n$
Sample prepared from small crystals of tetrahydrate							
125	0.68	45	41	14	—	—	amorphous
150	0.92	28	39	22	11	—	amorphous
190	1.20	15	30	21	34	—	amorphous
208	1.50	12	25	20	43	—	amorphous
230	1.75	10	18	20	52	—	amorphous
450	2.00	—	—	—	—	100	$[Mg(PO_3)_2]_n$

generation of well-crystallized intermediate product, namely the above-mentioned $MgH_2P_2O_7$. When the temperature is higher than $300^\circ C$, together with dihydrogenpyrophosphate the crystalline polyphosphate $[Mg(PO_3)_2]_n$ is formed; the latter becomes the only product of heat treatment at $t \geq 450^\circ C$.

During non-isothermal heating, the influence of degree of dispersion of the initial tetrahydrate manifests itself in the appreciable distinction in the temperature range in which the transformation of $MgH_2P_2O_7$ into $[Mg(PO_3)_2]_n$ occurs (Fig. 1). For large crystals, the endothermic effect corresponding to this process has a peak temperature almost 100° above that of the small-crystal sample (482° and $369^\circ C$, respectively). At the same time, if in the first case the TG-curve reaches the plateau at $500^\circ C$, in the second case a slight mass loss is observed up to $800^\circ C$.

4. Conclusions

1. The investigations conducted have shown that the characteristics of $Mg(H_2PO_4)_2 \cdot 4H_2O$ chemical and phase transformations under heating, as well as the composition of the resulting intermediates substantially depend on the conditions of heat treatment, size of initial crystals, composition of gaseous phase over the sample, etc. The discre-

pancy in the available literature data on the tetrahydrate thermal transformations is explained by the fact that many of the above-mentioned factors were not controlled during the experiment.

2. It was established that increase in heating rate, in size of the crystals and other factors hindering the removal of water vapour from the reaction zone result in melting of the sample. This causes the number of unusual kinetic effects under isothermal heating (decrease in dehydration rate with increase in temperature and decrease in water-vapour pressure, a discontinuity in Arrhenius plots) and a complication of the trend of the thermoanalytical curves.

3. From the rehydration under study, it has been shown that the rate of isothermal process may pass through a maximum, which is connected with the features of accompanying crystallochemical transformations.

4. It has been established that, in spite of the violation of reversibility, the processes of dehydration–rehydration may proceed in a cyclic regime, although the dehydration rate decreases from cycle to cycle.

5. The difference in the nature of isothermal dehydration of large- and small-crystal samples (with, or without melting) has an effect on the kinetics of subsequent anionic condensation. In the first case, the process goes through the formation of

intermediate crystalline $MgH_2P_2O_7$, and in the second case the mixture of X-ray amorphous chain phosphates is formed. Crystalline $[Mg(PO_3)_2]_n$ is the end product in both the cases.

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