

## Thermal transformations of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

O.A. Lukyanchenko\*, V.V. Samuskevich

*Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Surganov st.9, 220072, Minsk, Belarus*

Received 23 September 1998; received in revised form 29 September 1998; accepted 1 December 1998

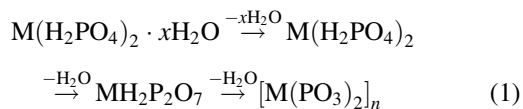
### Abstract

Thermal transformations of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  in air, vacuum, water-vapor atmosphere were studied by the methods of DTA, XRD, paper chromatographic analyses and gravimetry. It was established that the removal of the water of crystallization is accompanied by the processes of anionic condensation and disproportionation when dihydrate is heated in air. It was also shown that X-ray-amorphous anhydrous cobalt dihydrogenphosphate is formed only in vacuum under isothermal conditions. The kinetic characteristics of this reaction were obtained and the possibility of proceeding of dehydration–rehydration processes in cyclic regime was studied. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Phosphates; Thermal transformations; Kinetics and mechanism

### 1. Introduction

The classical scheme of dehydration of dihydrogenphosphates  $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  ( $\text{M} - \text{Mg, Ca, Ba, Mn, Co, Ni, Fe, Cd, Zn}; x=1, 2, 4$ ) which was used in the former works [1] assumes the successive liberation of the water of crystallization and the constituent water:



Subsequently it has been shown that the water of crystallization cannot be usually removed without the destruction of anion because the first and the second steps of the scheme given above are often overlapped. It has been also found that, as a rule, the X-ray-

amorphous mixture of chain phosphates rather than a single pyrophosphate is formed initially as a product of anionic condensation (the second step) [2]. The composition of this mixture may become simpler owing to the preferential dihydrogenpyrophosphate crystallization during the process of further heating. However, the formation of  $\text{MH}_2\text{P}_2\text{O}_7$  was not fixed in some cases; in doing so the mixture of chain phosphates transformed into the end product (polyphosphate) directly. Even for one compound the mechanism of anionic condensation is sometimes dependent on the heating conditions or as it has been established in our work for  $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  on the size of initial crystals [3].

There is also no consensus of opinion among the authors on the nature of the end dehydration product. Its structure is ascribed at times to high-polymeric chain phosphate [4] and at other times to tetracyclophosphate [5].

The process of dihydrogenphosphates dehydration is complicated not only by their anionic condensation.

\*Corresponding author. Fax: +37-5172-842703; e-mail: kulak@igic.bas-net.by

A peculiar feature of such compounds is their tendency to the disproportionation reaction which results in the formation of less-proton phosphate and free phosphoric acid [6]. When the disproportionation proceeds on the stage of the water of crystallization releasing, the resulting acid may react with the dehydration products, complicating essentially the following steps of thermal transformations [1].

The available literature data on thermal transformations of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  crystals [7–9] are few in number and discrepant. The reasons of the discrepancy are probably connected with the differences in heating conditions as well as with the influence of such a factor as the composition of gaseous phase over the sample which has not been taken into account in these works.

In the present work the thermal transformations of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  were investigated in vacuum, in water-vapor atmosphere and in air (when the values of the relative humidity RH were fixed) both in iso- and non-isothermal conditions. The processes of anionic condensation and disproportionation which attend, as a rule, cobalt dihydrogenphosphate dehydration were considered. The conditions when the removal of the water of crystallization is not complicated by any side process were revealed, the kinetic characteristics of this reaction were obtained and its reversibility as well as the possibility of proceeding of dehydration–rehydration processes in cyclic regime were studied.

## 2. Experimental

The sample of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  used in the work (crystal size  $D=0.05$  to  $0.1$  mm) was precipitated from the solution of  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  in 75%  $\text{H}_3\text{PO}_4$  (23 g of  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  per 100 ml of acid) by stirring at room temperature for 1 h. The precipitate was washed from the remains of the mother liquor on the glass filter with acetone and then with ether and dried at relative humidity of air  $\text{RH}=45\%$  until the mass stop to change. X-ray diffraction pattern of the sample prepared coincides with the literature data for  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  [10].

When dehydration of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  was studied in non-isothermal conditions, a derivatograph OD-103 MOM (platinum crucible, sample weight 100 mg, heating rate  $10^\circ\text{C min}^{-1}$ ) was used.

For studying the reaction of disproportionation in isothermal conditions, the weighted samples (100 mg) were held at  $t=35^\circ\text{C}$  to  $95^\circ\text{C}$  inside of hermetic vessels where the constant relative humidity was kept by the aqueous solutions of sulfuric acid within  $\text{RH}=0.02\%$  to 100%.

In isothermal experiments on dehydration kinetics we use a high-vacuum setup having a quartz microbalance (spiral sensitivity  $2 \text{ mg mm}^{-1}$ ) which permits to investigate the process in vacuum (residual pressure  $p=10^{-5}$  hPa) or in water-vapor atmosphere (the values of water-vapor  $p_{\text{H}_2\text{O}}$  were fixed with an accuracy of  $\pm 0.1$  hPa). The sample of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  was spread as a thin layer (mass ca. 50 mg) in a flat-bottomed platinum sample holder and thereafter immersed in the previously thermostated part of the reaction vessel. In the course of isothermal dehydration ( $t=60^\circ\text{C}$  to  $110^\circ\text{C}$ ) the mass loss  $\Delta m$  was periodically registered.

To study the rehydration process of the samples pre-dehydrated in water-vapor atmosphere, the setup was initially pumped and after cooling filled with water-vapor again. During the isothermal holding ( $t=20^\circ\text{C}$  to  $70^\circ\text{C}$ ) at fixed  $p_{\text{H}_2\text{O}} = 20$  hPa, the mass addition  $\Delta' m$  was recorded.

The products which formed at different steps of iso- and non-isothermal transformations were characterized by X-ray diffraction analysis (DRF diffractometer –2.0; Cu  $\text{K}_\alpha$  radiation).

The anionic composition of heat-treated samples was determined by quantitative ascending chromatography using FN 12 chromatographic paper; EDTA or  $\text{Na}_2\text{S}$  were added to transfer the less-soluble products of heat treatment in solution.

To determine the quantity of free phosphoric acid ( $a_{\text{H}_3\text{PO}_4}$ ) contained in the products, they were moved on the glass filter under the layer of acetone (25 ml) and washed (with acetone), keeping out of contact with air. The eluate was titrated with 0.01 N aqueous solution of NaOH in the presence of bromocresol green.

## 3. Results and discussion

### 3.1. Non-isothermal transformations

The derivatogram of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  obtained when the sample was heated in air is shown in Fig. 1.

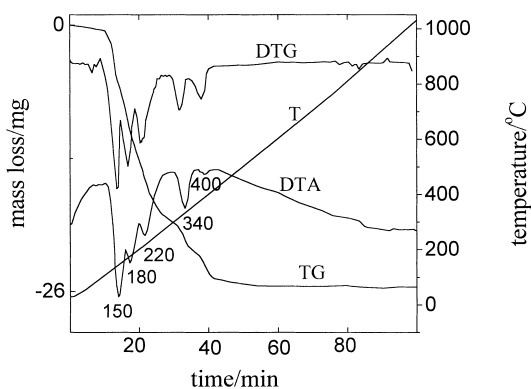


Fig. 1. Thermoanalytical curves of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ;  $m=100$  mg; heating rate  $10^\circ\text{C min}^{-1}$ .

There are five endothermic effects in the DTA curve that points to the intricate mechanism of the processes which take place. The poorly pronounced bends in the TG curve at  $\Delta m=6, 12$  and  $18$  wt% are at first glance testimony to the step-by-step liberation of 2 mol of the water of crystallization and thereafter of 1 mol of the constituent water. However, such scheme does not conform with the results of paper chromatographic analysis of products which formed at the different steps of dihydrate dehydration under the conditions of derivatographic experiment. So, when the sample was heated to  $150^\circ\text{C}$  (peak temperature of the first endothermic effect) the product has already contained about 20 wt% of pyrophosphate (see Table 1). At a temperature of  $200^\circ\text{C}$  which corresponds by the thermogravimetric data to the formation of anhydrous dihydrogenphosphate, the triphosphate was found and the total content of condensed forms reached

the value of 60 wt%. In doing so, as the diffraction peaks of the initial dihydrate in X-ray diffraction patterns are reduced up to their complete disappearance at  $\Delta m \approx 12.5$  wt%, no evidence of crystalline phases of anhydrous salt or intermediate monohydrate is observed.

The composition of the mixture of the resulting X-ray-amorphous products with the different degree of condensation is complicated during the course of non-isothermal heating, especially at  $t=350^\circ\text{C}$ . We did not fix in this temperature region the preferential formation of pyro-form which is attended with dihydrogenpyrophosphate crystallization as it was seen on heating the Mg, Zn, Ni dihydrogenphosphates [1,3,8]. The cobalt polyphosphate having formula  $[\text{Co}(\text{PO}_3)_2]_n$  is a single end product of non-isothermal heating of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The formation of  $[\text{Co}(\text{PO}_3)_2]_n$  is confirmed by the results of XRD analysis which fit well with the ASTM data for this compound [11]. This phase appears at  $t=350^\circ\text{C}$  and the following sharp acceleration of dehydration is likely caused by its crystallization that is represented by the bend in TG curve. In so doing, the exothermic effect corresponding to the crystallization process which was fixed in the paper [8] is absent. In our case it probably overlaps with the endothermic effect of dehydration with a peak temperature of  $400^\circ\text{C}$  reducing the latter practically to zero (Fig. 1).

According to the TG data the liberation of the greater part of constituent water (which is accompanied by the anionic condensation) is completed when the sample is heated to  $410^\circ\text{C}$ ; however the minor part of water (ca. 1 wt%) is removed only in the course of further heating over the wide temperature region up to

Table 1

The anionic composition of products formed at the different steps of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  dehydration under conditions of derivatographic experiments

$t$ ( $^\circ\text{C}$ )	Content of $\text{H}_3\text{PO}_4$ (wt%)	Content of phosphorous (wt%) in the form of					On start
		$\text{P}_1$	$\text{P}_2$	$\text{P}_3$	$\text{P}_4$	$\text{P}_{>4}$	
150	2.0	78	22	0	0	0	0
200	6.0	40	45	15	0	0	0
250	0.4	24	38	32	2	4	0
300	0	16	21	22	18	23	0
350	0	4	9	14	20	24	29
400	0	2	6	8	4	0	80
450	0	2	2	1	0	0	95

550°C. The results of paper chromatographic analysis show that the total transformation of X-ray-amorphous mixture of the condensed products is actually finished only at  $t=500^\circ\text{C}$ .

There is no agreement in literature regarding the structure of the end product formed on heating dihydrogenphosphates of divalent metal and having the general composition  $[\text{M}(\text{PO}_3)_2]_n$ . Paper (or thin-layer) chromatographic analysis is the most reliable method which permits to recognize the chain and cyclic phosphates. Unfortunately, it was not possible to transfer completely the products of high-temperature heat treatment in solution even when  $\text{Na}_2\text{S}$  was added. Only the ortho- and pyro-forms (which are most likely the products of sample hydrolysis during the course of analysis) were present in the soluble part. No evidence of tetracyclophosphate that was assumed to be the end product of cobalt dihydrogenphosphate anionic condensation [7,8] was found. Therefore we reason that high-polymeric chain phosphate  $[\text{Co}(\text{PO}_3)_2]_n$  is the end product of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  dehydration under conditions realized in the present work.

### 3.2. Processes of disproportionation

We have already mentioned that in parallel with dehydration and anionic condensation the processes of disproportionation giving rise to the formation of less-proton phosphate and free phosphoric acid may proceed when the acidic phosphates are heated. It has been pointed out [9] that the release of a marked quantity of acid takes place during non-isothermal heating of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (heating rate  $2.5^\circ\text{C min}^{-1}$ ) in the temperature region of 100–250°C. The content of acid in the heat-treated products increased, at first, up to 14 wt% and then decreased as a consequence of its participation in the secondary processes. Under the conditions of non-isothermal experiment realized in the present work (when the heating rate is higher) the maximum content of acid at a temperature of 200°C was 6 wt%; but the formation of acid was not fixed at all when the sample was heated to  $t \geq 250^\circ\text{C}$  (see Table 1).

We investigated the disproportionation of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  in more detail under isothermal conditions. It turned out that the rate of acid liberation is dependent essentially on temperature and relative humidity of air. Table 2 gives the data on the quantity

Table 2

The quantity of  $\text{H}_3\text{PO}_4$  (wt%) released as a result of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  isothermal holding ( $\tau=2$  h)

$t$ ( $^\circ\text{C}$ )	RH (%)			
	40	60	80	100
35	0	0	4.1	11.0
50	0	1.3	7.7	19.3
60	0.3	3.2	10.1	23.4
70	0.7	7.4	12.4	22.3
80	1.2	13.4	23.3	21.3
90	2.9	21.4	21.1	17.3
95	5.8	21.2	19.8	16.5

of acid released as a result of isothermal holding (time  $\tau=2$  h) of the dihydrate samples at different values of  $t$  and RH. As in the non-isothermal conditions, the quantity of acid liberated passes a maximum with the increase in temperature; in doing so this maximum is shifted in the direction of high temperatures when the values of RH are reduced. At RH=40% and  $t=95^\circ\text{C}$  the acid content even after 2 h is as little as 5 wt%. At first glance this result is a good evidence for the lack of substantial acid content during the derivatographic experiment under the conditions realized here, inasmuch as the temperature in this case reaches  $100^\circ\text{C}$  within 8 min.

It is necessary, however, to bear in mind that the characters of the disproportionation processes under derivatographic conditions and under conditions of isothermal experiment are radically different. In the first case the reaction is accompanied by the sample mass loss whereas in the second by its addition. Obvious correlation between the processes of water adsorption and free acid liberation engaged our attention. The data obtained during the isothermal holding of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  at RH=60% and  $t=80^\circ\text{C}$  are given in Fig. 2. These curves are chosen as an illustration because under conditions mentioned above they are practically coincident with one another if shown on the same scale. The relationship  $\Delta'm : a_{\text{H}_3\text{PO}_4}$  may be different from 1 at other  $t$  and RH values, but the fact of correlation between the processes of water adsorption and acid liberation is beyond question. This effect is attributable to one of the two reasons: either the water adsorption causes the dihydrogenphosphate to dissolve incongruently with the following crystallization of less-proton phosphate

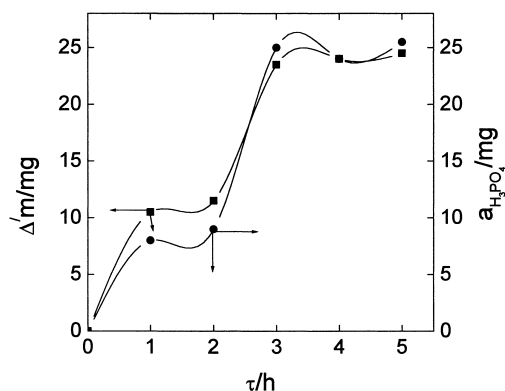


Fig. 2. Kinetics of  $\text{H}_3\text{PO}_4$  liberation ( $a_{\text{H}_3\text{PO}_4}/\text{mg}$ ) and of water adsorption ( $\Delta'm/\text{mg}$ ) during isothermal holding of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  ( $m=100$  mg) at  $\text{RH}=60\%$  and  $t=80^\circ\text{C}$ .

according to the familiar model [12], or the solid-state disproportionation, with the release of free phosphoric acid which adsorbs actively the water-vapor, takes place.

At high values of humidity and low temperatures the first variant is likely possible too, but at  $\text{RH}=40\%$  and  $t=95^\circ\text{C}$  the ordinary sorption of water is highly improbable. It is also necessary to keep in mind that the quantity of water taken up rises not only as the RH increases at fixed temperature but also as the temperature increases at fixed RH values as well (Fig. 3). If the

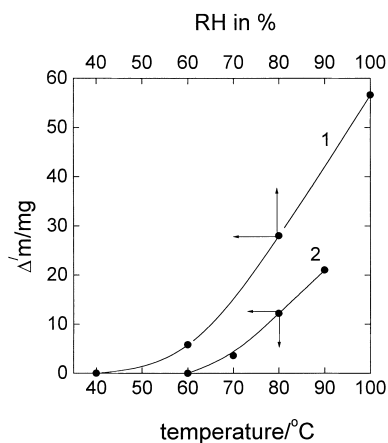
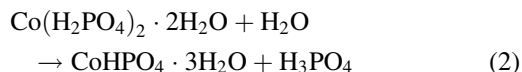


Fig. 3. The quantity of water ( $\Delta'm/\text{mg}$ ) adsorbed by the sample of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  ( $m=100$  mg) as a result of its isothermal holding ( $\tau=2$  h) at different  $t$  and RH values: (1)  $t=70^\circ\text{C}$ ; (2)  $\text{RH}=60\%$ .

regular gain of  $\Delta'm$  with the increase in air humidity is in line with the common notions of water sorption by the surface of solids, then the same effect observed as the temperature increases at fixed values of RH may be explained only by assuming that the process of water adsorption is the secondary process and the formation of free acid proceeds initially.

A topochemical character of disproportionation is confirmed by the immediate microscopic crystal observations. The water adsorption at the first stages of the reaction is not accompanied by the formation of a liquid phase. A typical solid-state process with the formation of a great quantity of small reaction nuclei which covers rapidly the crystal surface occurs at  $\text{RH}=60\%$  and  $t \leq 80^\circ\text{C}$ . The crystals lose the transparency but keep the outward form. The distinct traces of a liquid phase in the shape of drops on the surface and liquid incorporations in the bulk of crystals appear only at  $t > 80^\circ\text{C}$ . The intensive water adsorption and change in substance state and consequently the change in the mechanism of disproportionation are the chief causes of the revealed extreme temperature dependence of  $a_{\text{H}_3\text{PO}_4}$  (Table 2); it seems likely that the bends in the kinetic curves  $a_{\text{H}_3\text{PO}_4}-\tau$  (Fig. 2) are due to the substance liquefying also. Moreover, the phase transformations in the course of the disproportionation, the character of which is also dictated by the conditions of process proceeding make a contribution to the effects observed. The point is that the monohydrogenphosphate formed as a result of disproportionation is able to crystallize in the form of different hydrates. X-ray diffraction data testify that the cobalt monohydrogenphosphate trihydrate accumulates as the initial dihydrate phase runs out during the isothermal holding; this should result in the adsorption of 18 mg of  $\text{H}_2\text{O}$  per 98 mg of acid according to the equation



The  $\text{CoHPO}_4 \cdot x\text{H}_2\text{O}$  ( $x=1-2$ ) phase (that was described in studies of  $\text{CoO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  system [13]) appears along with trihydrate at the stage of acceleration of isothermal disproportionation reaction (Fig. 2). This compound is likely formed as a result of dehydration of  $\text{CoHPO}_4 \cdot 3\text{H}_2\text{O}$ ; in doing so the water released actively is redistributed inside of crystals

provoking the partial dihydrogenphosphate dissolution and thereby initiates the disproportionation processes. By this mean, disproportionation may proceed both with adsorption and with liberation of water-vapor. The function of the latter is connected to the main with their influence on the crystallization process of the solid product (monohydrogenphosphate) because the crystallization stage is really limiting in the processes of disproportionation [6].

### 3.3. Kinetics and mechanism of isothermal dehydration of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

From the above discussion it follows that when crystals of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  are heated in air at least at  $\text{RH} \geq 40\%$ , their dehydration is attended with either disproportionation or anionic condensation. Dehydration is not complicated by any side process when occurs under isothermal conditions in vacuum or in water-vapor atmosphere.

According to the results of analysis of products for the presence of phosphoric acid, the disproportionation of dihydrogenphosphate anion which has been observed during the thermal dehydration of  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  [14] in similar conditions does not happen. We did not also find the melting of the sample in the liberated water of crystallization as it took place with  $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  crystals, if heated [3]. The results of X-ray diffraction analysis show that as in the case of non-isothermal heating, the formation of new crystalline phases does not occur; the progressive reduction in the diffraction peaks of initial dihydrate up to their complete disappearance at  $\Delta m \approx 2$  mol  $\text{H}_2\text{O}$  is only observed.

The dehydration of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  in vacuum ( $p = 10^{-5}$  hPa) as well as in water-vapor atmosphere at  $p_{\text{H}_2\text{O}} = 20$  hPa proceeds in kinetic regime. It is evidenced by the values of the kinetic parameter  $n$  which are closed to 1 (Table 3). This parameter was calculated using the equation  $\alpha = 1 - \exp(-k'\tau^n)$  [15], where  $\alpha$  is the degree of transformation ( $\Delta m = 12.5$  wt% corresponding to the liberation of 2 mol  $\text{H}_2\text{O}$  was taken as  $\alpha = 100\%$ ),  $\tau$  the time and  $k'$  is a parameter which is related to the rate constant  $k$  by the equation  $k = n(k')^{1/n}$  [15]. The curves  $\Delta m$  vs.  $\tau$  (Fig. 4) are S-like in shape that is characteristic of the processes having self-acceleration and points to the spot localization of dehydration reaction.

Table 3

Kinetic characteristics of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  dehydration in vacuum and in water-vapor atmosphere

$t$ ( $^{\circ}\text{C}$ )	$n$	$k$ ( $\text{min}^{-1}$ )
$p = 10^{-5}$ hPa		
60	1.1	$8.7 \times 10^{-4}$
70	1.2	$3.5 \times 10^{-3}$
80	1.2	$7.6 \times 10^{-3}$
90	1.0	$1.3 \times 10^{-2}$
100	1.1	$2.8 \times 10^{-2}$
$p_{\text{H}_2\text{O}} = 20$ hPa		
85	1.5	$1.8 \times 10^{-3}$
87	1.2	$3.5 \times 10^{-3}$
90	1.1	$4.4 \times 10^{-3}$
93	1.3	$1.4 \times 10^{-2}$
95	1.1	$1.7 \times 10^{-2}$
98	1.2	$2.8 \times 10^{-2}$

The composition of gaseous phase over the sample affects essentially the process kinetics. If in vacuum all the water of crystallization releases in one step, the kinetic curves of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  dehydration at  $p_{\text{H}_2\text{O}} = 20$  hPa flatten out at  $\Delta m = 1.66$  mol  $\text{H}_2\text{O}$ . The rest of the water of crystallization is liberated only at  $t > 110^{\circ}\text{C}$ , when, according to the results of analysis of products for anionic composition by the method of ascending paper chromatography, the dehydration is accompanied by the anionic condensation.

The kinetic experiments conducted at different values of water-vapor show that the plateau on  $\Delta m$  vs.  $\tau$  curves is regularly shifted in the direction of high  $\Delta m$  values as the water-vapor pressure is reduced (Fig. 5). It seems likely that X-ray-amorphous products of the composition  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  ( $0 < x \leq 0.34$ ) present anhydrous dihydrogenphosphate which tightly holds the residual water. The holding of gaseous reaction product is often characteristic of crystalhydrate dehydration [16]. This effect reveals itself to a greater extent when dehydration process proceeds in air (the influence of shielding gaseous jacket). That is likely the reason for the impossibility of individual anhydrous  $\text{Co}(\text{H}_2\text{PO}_4)_2$  formation under derivatographic conditions despite the presence of corresponding bend in TG curve.

When the dihydrate dehydration is carried out in water-vapor atmosphere, the process activation energy  $E_k$  (Fig. 4) calculated from the temperature dependence of rate constant (Table 3) rises steeply. If the

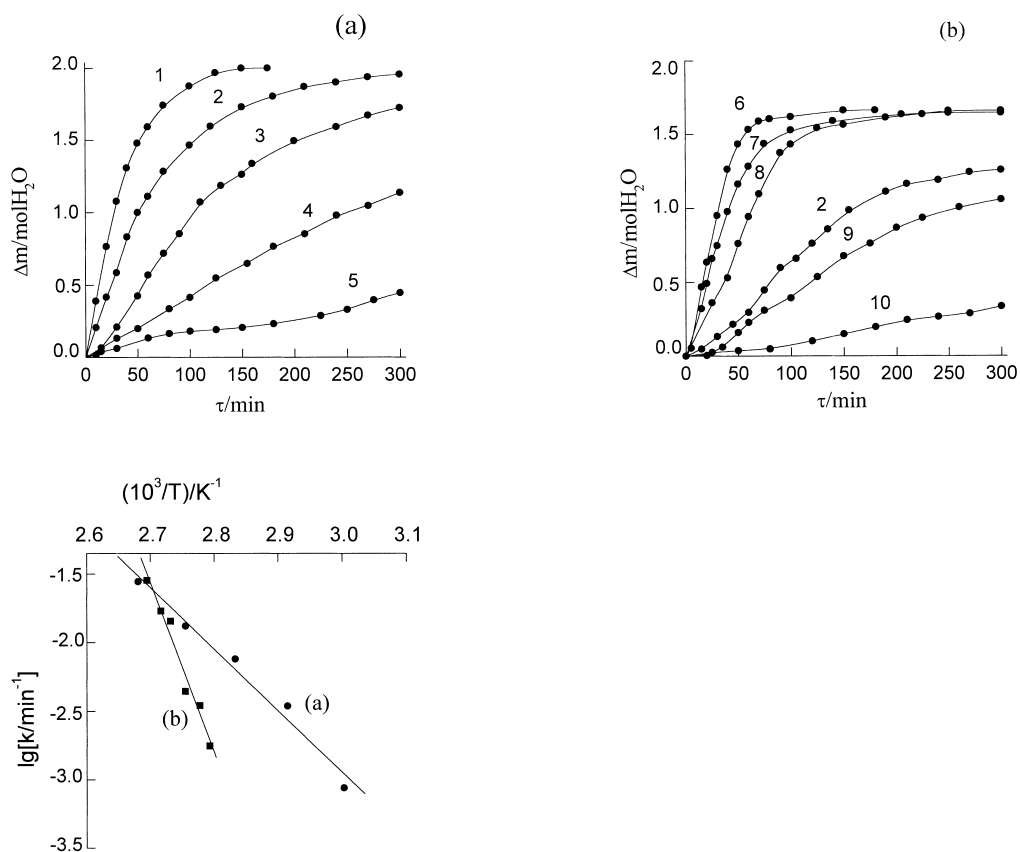


Fig. 4. Kinetics of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  dehydration in vacuum (a) and in water-vapor atmosphere at  $p_{\text{H}_2\text{O}} = 20$  hPa (b): (1) 100°C, (2) 90°C, (3) 80°C, (4) 70°C, (5) 60°C, (6) 98°C, (7) 95°C, (8) 93°C, (9) 87°C and (10) 85°C.

value of  $E_k$  in vacuum is  $202 \pm 15$  kJ mol $^{-1}$ , then at  $p_{\text{H}_2\text{O}} = 20$  hPa it is equal to  $600 \pm 45$  kJ mol $^{-1}$ . Here the regularity of Zavadzki-Bretsznaider known in topochemistry manifests itself [17]; in so doing increasing  $E$  is compensated for by changing the pre-exponential factor  $A$  ( $10^{10.5}$  min $^{-1}$  in vacuum and  $10^{31.9}$  min $^{-1}$  in water-vapor atmosphere) and by the shift of the reaction temperature region  $\Delta t$  toward the higher temperatures. Coincidentally with the shift, the region  $\Delta t$  in which the reaction proceeds with the comparable and suitable for measurements rates narrows sharply.

Such effects are typical for reversible topochemical reactions occurring in proximity to equilibrium. It is also evidenced by the results of investigation of rehydration kinetics of previously dehydrated samples.

### 3.4. Rehydration kinetics

The experiments on rehydration were carried out using the above-mentioned X-ray-amorphous product of composition  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 0.34\text{H}_2\text{O}$ . Fig. 6 gives the kinetic curves  $\Delta' m$  vs.  $\tau$  obtained when it interacted with water-vapor at  $p_{\text{H}_2\text{O}} = 20$  hPa. If the temperature is relatively small (20°C), the water adsorbs actively up to the complete sample dissolution. Hydration also begins with a marked rate at higher temperatures but thereupon the process slows down drastically turning into diffusion regime ( $n \approx 0.3$ ).

The rehydration product having the composition of dihydrate remains as X-ray-amorphous; crystalline phases, the formation of which was observed in the studies of manganese and magnesium dihydrogenphosphate rehydration [6], were not found in this case.

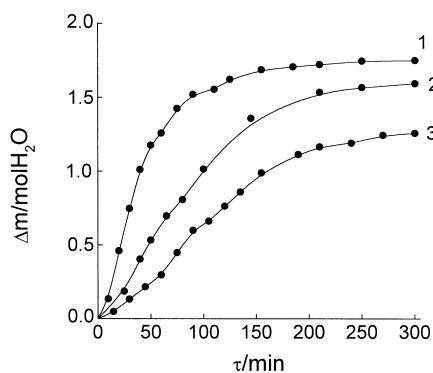


Fig. 5. The kinetic curves of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  dehydration in water-vapor atmosphere at  $90^\circ\text{C}$ : (1) 5, (2) 13, (3) 20 hPa.

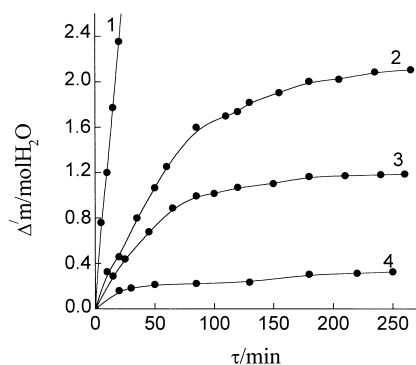


Fig. 6. The kinetic curves of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 0.34\text{H}_2\text{O}$  rehydration at  $p_{\text{H}_2\text{O}} = 20$  hPa: (1)  $20^\circ\text{C}$ , (2)  $40^\circ\text{C}$ , (3)  $50^\circ\text{C}$ , (4)  $70^\circ\text{C}$ .

This means the reversibility of transformations in the system under investigation is appreciably disturbed. However, taking into account that the hydration rate is high, we studied the possibility of process proceeding in the “dehydration–hydration” cyclic regime. For this purpose the sample of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  was initially dehydrated at  $p_{\text{H}_2\text{O}} = 20$  hPa and  $t = 100^\circ\text{C}$  and then, after cooling of setup to  $40^\circ\text{C}$ , rehydrated again.

As it is seen from Fig. 7, a second dehydration occurs markedly faster. Not only the reaction rate but the maximum quantity of water released increase in the following cycles, however, after the fourth cycle the process becomes stable. In regard to rehydration, it was established that its rate does not change practically from cycle to cycle.

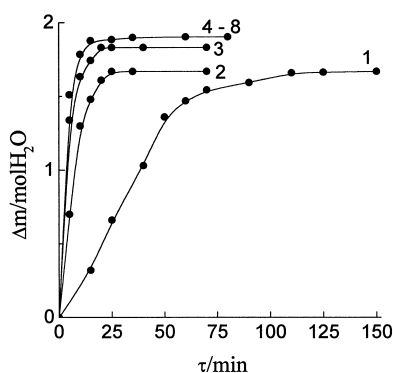


Fig. 7. The kinetic curves of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  dehydration under condition of “hydration–dehydration” cyclic regime. The figures on curves correspond to the cycle number;  $100^\circ\text{C}$ ,  $p_{\text{H}_2\text{O}} = 20$  hPa.

#### 4. Conclusions

1. The removal of the water of crystallization when  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  is heated in non-isothermal conditions is accompanied by the formation of the mixture of X-ray-amorphous phosphates with different condensation degree; this mixture transforms at  $t = 400^\circ\text{C}$  into the end product, namely, chain cobalt polyphosphate of composition  $[\text{Co}(\text{PO}_3)_2]_n$ .
2. It has been established that the anhydrous X-ray-amorphous cobalt dihydrogenphosphate may be obtained only as a result of isothermal process in vacuum. If heated in water-vapor atmosphere, the product always holds the residual quantity of water. It has been shown that in spite of some disruptions of reversibility, the processes “dehydration–hydration” may proceed in cyclic regime.
3. Solid-state disproportionation with the formation of monohydrogenphosphate and phosphoric acid takes place when  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  is heated in the moist air atmosphere. The trend has been to the transformation of this process in a liquid-state one with increasing reaction temperature and air humidity.

#### References

- [1] L.N. Schegrov, *The Phosphates of Divalent Metals*, Navukova Dumka, Kiev, 1987, in Russian.



- [2] E.D. Dzuba, V.V. Pechkovsky, G.I. Salonec, V.I. Kovalishina, N.A. Ivkovich, A.V. Chubarov, *J. Inorg. Chem. (USSR)* 27 (1982) 1939.
- [3] V.V. Samuskevich, O.A. Lukyanchenko, *Thermochim. Acta* 311 (1998) 87.
- [4] L.N. Schegrov, E.D. Dzuba, V.N. Makatun, *Proceedings of the USSR Academy of Sciences, Inorg. Mater.* 9 (1973) 2022.
- [5] D.Z. Serazetdinov, E.V. Poletaev, J.A. Kushnikov, *J. Inorg. Chem. (USSR)* 12 (1967) 3023.
- [6] E.A. Prodan, V.V. Samuskevich, *Stability and Reactivity of Phosphoric Salts*, Nauka i Tekhnika, Minsk, 1994, in Russian.
- [7] E. Thilo, H. Grunze, *Z. Anorg. Allgem. Chem.* 290 (1957) 209.
- [8] L.N. Schegrov, V.V. Pechkovsky, E.D. Dzuba, *J. Appl. Chem. (USSR)* 45 (1972) 713.
- [9] L.N. Schegrov, N.M. Antrapceva, *Ukrainian Chem. J. (USSR)* 51 (1985) 127.
- [10] Powder Diffraction Files, Card no. 28-383.
- [11] Powder Diffraction Files, Card no. 27-1120.
- [12] M. Bayramoglu, B. Keskinler, *Ind. Eng. Chem. Res.* 31 (1992) 1602.
- [13] N.A. Shkorik, V.V. Samuskevich, E.A. Prodan, *Proceedings of Belarusian Academy of Sciences, Chem. (USSR)* 2 (1991) 8.
- [14] V.V. Samuskevich, E.A. Prodan, *Proceedings of Belarusian Academy of Sciences, Chem. (USSR)* 5 (1992) 29.
- [15] E.A. Prodan, *The Regularities of Topochemical Reactions*, Nauka i Tekhnika, Minsk, 1976, p. 24, in Russian.
- [16] D. Young, *Decomposition of Solids*, Pergamon Press, Oxford, 1969, p. 12.
- [17] E.A. Prodan, *Inorganic Topochemistry*, Nauka i Tekhnika, Minsk, 1986, p. 14, in Russian.