

## STUDY OF THE THERMAL PREPARATION AND STABILITY OF TETRAMETAPHOSPHATES OF BIVALENT METALS

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### ABSTRACT

The dehydration and condensation reactions during the thermal preparation of tetrametaphosphates (cyclotetraphosphates) of bivalent metals have been followed by thermal analyses under quasi-isothermal, quasi-isobaric conditions. These analyses permitted a more detailed assessment of important factors (reaction temperatures and times, water vapour pressure) that play decisive roles from the technological point of view. A significant favourable influence of increased vapour pressure on the yields of the condensation reactions has been observed. High-temperature differential thermal analysis at various precisely defined conditions of the atmosphere was used to follow the conditions of melting of tetrametaphosphates. Conditions were established for their congruent melting and of their non-congruent melting connected with the formation of higher linear phosphates of vitreous character. Thermal analysis has also been used to evaluate the recrystallization of these polyphosphate glasses with reversible transformation into tetrametaphosphates.

### INTRODUCTION

Recently, tetrametaphosphates of some bivalent metals have proved to be important inorganic compounds. [1]. In our laboratory they have been tested as microadditives to fertilizers with long-term action [2], and some of them are special thermostable inorganic pigments, luminescent [3], anticorrosive [4] or coloured [5]. A number of papers [6–9] have dealt with the use of thermal analysis (TA) under quasi-isothermal, quasi-isobaric conditions [10] to follow the dehydration reactions of some simple phosphates. So far, however, no report has appeared on the application of this method to the investigation of the important condensation products, tetrametaphosphates. In our laboratory this method has been used to follow the condensation reactions of the formation of manganese [11], cobalt [12], copper [13], zinc [14] and cadmium [15] tetrametaphosphates which started either from the hydrogenphosphate of the respective metal or from a mixture of the respective oxide and phosphoric acid. This paper deals with a comparison of the

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conditions of preparation (on the basis of the TA method) of the first three tetrametaphosphates given above. Other workers [16–26] dealing with the problems of the thermal preparation of  $\text{Mn}_2\text{P}_4\text{O}_{12}$ ,  $\text{Co}_2\text{P}_4\text{O}_{12}$  and  $\text{Cu}_2\text{P}_4\text{O}_{12}$ , which belong to the most important tetrametaphosphates from the point of view of the application considered [2–5], did not make use of the TA method to a sufficient extent. The papers quoted do not give sufficiently precise data on the temperatures of the condensation reaction, they are not in accord when explaining the reaction mechanism and they do not report the effects of other important factors, especially the partial pressure of water vapour, the necessary calcination time, etc., on the reaction course. From the point of view of the considered application of tetrametaphosphates [2–5], which in all instances is focused, *inter alia*, on high-temperature applications, it is important to consider the thermal stability of these compounds. Available literature data on the melting of the tetrametaphosphates investigated are incomplete and non-uniform. Some workers did not consider any changes during the melting process [27,28]. Others [17] mention unequivocally only the congruency, and still others [16,29,30] in contrast, only the non-congruency. Sometimes the changes taking place during melting of these compounds were only described as modification changes [23,31]. Also, the melting temperatures given for the substances studied are non-uniform. Some workers [16] even mention possible incomplete recrystallization of the amorphous products of the non-congruent melting of the tetrametaphosphates, except for the cobalt(II) product, and without any data about the conditions of these processes.

From our previous results [32] an explanation was suggested that the melting of the tetrametaphosphates could be connected with the presence of water vapour in the atmosphere, provided that the sample carrier is absolutely inert (to the phosphate melt). Therefore, in the subsequent work [33–35] we followed the melting of Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) tetrametaphosphates by means of high-temperature differential thermal analysis. In these experiments we used special, inert crucibles made of molybdenum metal, and special atmospheric conditions. Another aim of this work is to summarize some results of the above-mentioned measurements in comparison with new results and with those obtained by high-sensitive thermogravimetry.

## EXPERIMENTAL

For the elucidation of the mass and energy transformations during the calcination of  $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  and the starting mixture of copper(II) oxide and phosphoric acid (molar ratio  $\text{CuO}/\text{P}_2\text{O}_5 = 1$ ), the three samples were first thermoanalysed by the classical dynamic method (i.e., non-isothermally) using a Derivatograph Type Q-1500 apparatus

(Hungarian Optical Works MOM, Budapest, F. Paulik, J. Paulik, F. Erdey System). The measurements were carried out in open crucible or in a six-component labyrinth arrangement [10], with a temperature increase of  $2.5^{\circ}\text{C min}^{-1}$ . (Fig. 1A and B).

In order to separate better the individual processes taking place during the calcination and to follow the effect of water vapour on their course, we submitted the starting dihydrogenphosphates and the starting mixture to TA under quasi-isothermal, quasi-isobaric conditions with the same equipment. The decomposition rate chosen was  $0.4 \text{ mg min}^{-1}$  (calculated for a 200 mg total weight change).

Various types of platinum crucibles were used for the measurements, viz., the multi-stage crucible polyplate (Fig. 2) and the six-component labyrinth set (Fig. 3). The last arrangement makes it possible to trap water vapour released during calcination of the starting sample, its partial pressure being about 100 kPa (quasi-isobaric conditions) [10]. Application of the labyrinth set, in contrast, makes the partial pressure of water vapour in the calcinated sample negligible (ca. 1 kPa). Application of the stage crucible is not suitable for determination of energy changes on the DTA curves in dynamic TA; therefore, as stated above, we used an open crucible in which the water vapour pressure corresponded to 5 kPa.

Under comparable conditions (isothermal conditions, the sample carriers corresponding to the two crucible types in TA), calcined samples were then prepared at various temperatures from the starting dihydrogenphosphates and starting mixture in an electric oven with adjustable heating. The calcinates were extracted either with acetone (the extractable phosphorus component in the form of phosphoric acid or diphosphoric acid from the dihydrogendiphosphate formed) [32], or with water (which dissolves the starting substance and the intermediate  $\text{MH}_2\text{P}_2\text{O}_7$ ) or with 0.3 M HCl (permitting the determination of the tetrametaphosphate content in the calcinate) [36]. The extracts were analysed by atomic-absorption spectrometry [37] to determine the  $\text{MO}/\text{P}_2\text{O}_5$  molar ratio. The calcinates and (for comparison) some samples obtained in TA were analysed by instrumental methods: TLC [38–40], IR spectroscopy [41,42], X-ray diffraction [43,44], NMR spectroscopy and electron and high-temperature microscopy [37].

The thermogravimetric curves from dynamic TA were also evaluated mathematically. On the basis of statistical characteristics, the validity of the individual kinetic models of the heterogeneous reactions was determined for the condensation reaction of formation of tetrametaphosphates [45]. The activation energies [46] of the individual processes taking place during calcination of the starting dihydrogenphosphate were also calculated.

We then examined the thermal stability of Mn(II), Co(II), and Cu(II) tetrametaphosphates; they were prepared in our laboratory and purified by acid extraction [36]. The DTA measurements were carried out by means of a VDTA 8 M2 high-temperature differential thermal analyser (system "Kiev",

constructed in the Institute of Metal Physics of the Academy of Sciences of the Ukrainian S.S.R.). The sample and standard carriers are placed in the apparatus in a tempered tungsten block enclosed in an evacuated chamber. The atmosphere in the chamber of the apparatus consisted of either dry or wet helium (100 kPa of He contained about 2 mg of water vapour per dm<sup>3</sup> of He). Investigation of the influence of the atmosphere (water vapour) on the melting of the tetrametaphosphates necessitated application of sample carriers made of materials completely inert to the aggressive phosphate melt. Of the materials tested, molybdenum proved to be the most suitable. Weight changes accompanying the calcination of the samples were followed by thermogravimetry using a Derivatograph Q-1500 apparatus in an atmosphere of wet argon.

The products of the thermal analyses were submitted to TLC [38–40], X-ray diffraction [43,44] and IR spectroscopy [41,42], and the processes accompanying the calcination were followed visually by means of high-temperature microscopy [37].

## RESULTS AND DISCUSSION

The TA curves recorded first under dynamic non-isothermal conditions (Fig. 1A and B) provided the first information about the dehydration and condensation reactions taking place during the calcination of  $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  and the starting Cu(II) mixture. It was already evident that the water vapour pressure above the calcinates affects the reaction course considerably: not only the temperatures and rates of the individual reactions but also the degree of conversion (see below). The DTA curves confirmed that the release of crystal and constitutional water molecules is accompanied by distinct endothermic effects. The exothermic effects of the transformation of the amorphous tetrametaphosphate into the crystalline compound were observed to be very small and occurred only with application of the labyrinth arrangement (which contradicts other data [17,19,21,24]). This result is due to the fact that the tetrametaphosphate gradually crystallizes in the calcinate, always in a form of micro-particles, as it is gradually formed. Therefore, this process as a whole (with regard to a slow temperature increase) is slow and does not make itself felt in any distinct energy change (such as was observed by other workers [17,19,21,24] using faster heating). Still another phenomenon was observed during dynamic TA, which was connected with the effects of water vapour pressure. After the reactions of formation of tetrametaphosphates were finished and the sample weight was steady at 400–500°C, the sample weight was again decreased at 700–800°C in the case of the stage crucible. For example, for the manganese product this decrease reached 2% of the original sample weight. With the copper product it reached as much as 6% in the range

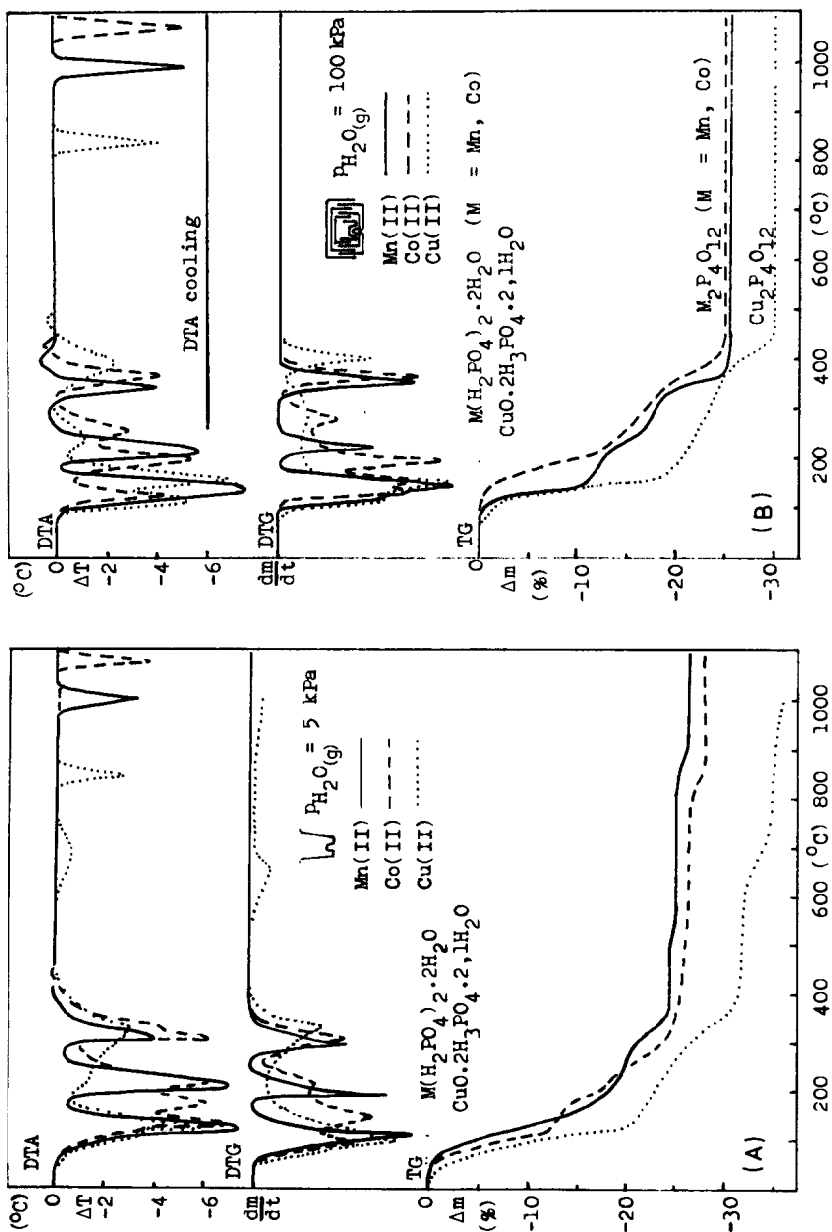


Fig. 1. Thermal curves of starting phosphates. (A) Open crucible;  $P_{\text{H}_2\text{O}(\text{g})} = 5 \text{ kPa}$ . Sample weight, 800 mg. Sample atmosphere, air. Sensitivity of the balance, TG 200 mg (500 mg, Cu), DTA, DTG 1/3; temperature increase,  $2.5^{\circ}\text{C min}^{-1}$ . (B) Labyrinth crucible;  $P_{\text{H}_2\text{O}(\text{g})} = 100 \text{ kPa}$ . Sample weight, 800 mg; atmosphere, air; sensitivity of the balance, TG 200 mg (500 mg, Cu), DTA, DTG 1/3; temperature increase,  $2.5^{\circ}\text{C, min}^{-1}$ .

600–1000°C. This result is connected with undesirable side reactions. Thilo and Grunze [16] considered that the magnitude of the divalent metal cation also influenced the ability to form tetrametaphosphate. The most advantageous cations are those whose radii are about 0.08 and 0.09 nm [Mn(II) and Co(II)], whereas with those considerably different from this value [Cu(II), 0.05] the synthesis is more problematic.

Our TA results unambiguously confirm this statement. In addition, however, they confirm that the situation is distinctly affected by the water vapour pressure in the calcination area. The decreased water vapour pressure increases the amount of undesirable side reactions, whereas the opposite is observed at increased pressure, the influence of the magnitude of the cation being suppressed in the latter instance. There even arises a problem as to the extent to which this finding can be utilized in the thermal synthesis of tetrametaphosphates with cations whose application has so far been unsuccessful.

The melting of tetrametaphosphates under non-isothermal TA conditions (accompanied by a distinct endothermic effect) was observed at 960°C [Mn(II)], 1060°C [Co(II)] and 820°C [Cu(II)]. TA under quasi-isothermal, quasi-isobaric conditions (Fig. 2) showed that the crystal (and /or non-bonded) water is released (in a medium of low water vapour pressure, polyplate crucible, 1 kPa) from  $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  in a single process beginning at 60°C, from  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  in two processes beginning at 70 and 110°C and from the Cu(II) phosphate starting mixture in a lengthy process that cannot be easily divided into individual steps in the range 40–135°C. According to expectation, in the labyrinth crucible (Fig. 3) the

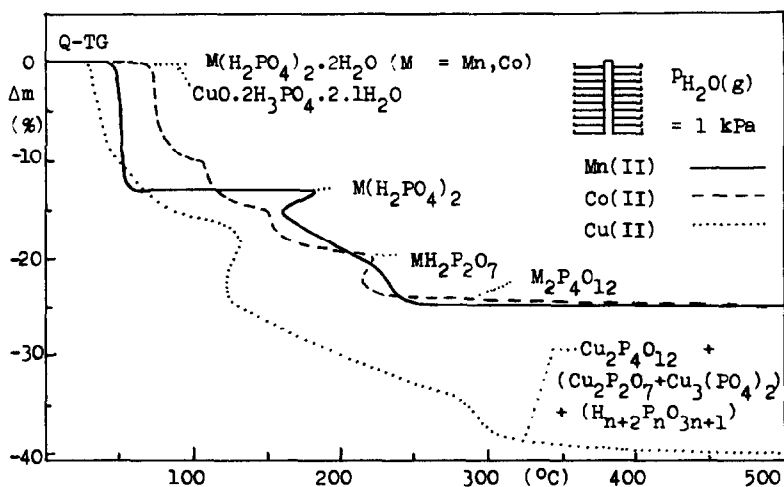


Fig. 2. TG curves of starting phosphates under quasi-isothermal, quasi-isobaric conditions. Decomposition rate,  $0.4 \text{ mg min}^{-1}$ ; polyplate crucible,  $p_{\text{H}_2\text{O}(\text{g})} = 1 \text{ kPa}$ ; atmosphere, air.

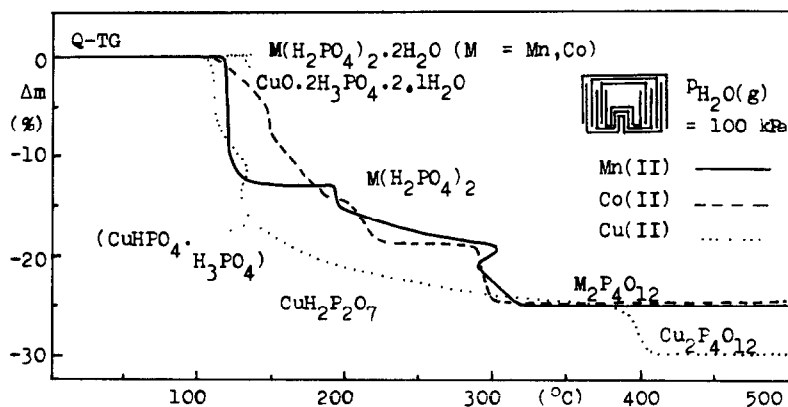


Fig. 3. TG curves of starting phosphates under quasi-isothermal, quasi-isobaric conditions. Decomposition rate,  $0.4 \text{ mg min}^{-1}$ ; labyrinth crucible,  $p_{\text{H}_2\text{O}(\text{g})} = 100 \text{ kPa}$ ; atmosphere, air.

temperatures of the dehydration processes mentioned are higher: with Mn(II) phosphate again a single process at  $120^\circ\text{C}$  and with Co(II) phosphate two processes beginning at  $105$  and  $150^\circ\text{C}$  [the existence of  $\text{Mn}(\text{H}_2\text{PO}_4)_2$  and  $\text{Co}(\text{H}_2\text{PO}_4)_2$ , respectively, was proved in the above temperature ranges and its crystalline character was confirmed]. With Cu(II) phosphate mixture at  $100 \text{ kPa}$  water vapour pressure, two processes are first observed (beginning at  $110$  and  $135^\circ\text{C}$ ), preceded by the formation of an intermediate corresponding to the formula  $3(\text{CuHPO}_4 \cdot \text{H}_2\text{O}) \cdot \text{H}_3\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$  [Cu(II) dihydrogendiphosphate cannot be formed by this procedure [47]. This intermediate then releases (at  $110^\circ\text{C}$ ) the first water of crystallization from the hydrogenphosphate section [49] and then (in the second process from  $135^\circ\text{C}$ ) further water of crystallization from the intermediate; at  $150^\circ\text{C}$  the sample can be considered to correspond to the overall formula  $\text{Cu}(\text{H}_2\text{PO}_4)_2$ , even though it rather represents a mixed product,  $\text{CuHPO}_4 \cdot \text{H}_3\text{PO}_4$ .

The first molecule of the constitutional water begins to escape from manganese(II) dihydrogenphosphate at the same temperature ( $190^\circ\text{C}$ ) in the crucibles used. Then the sample temperature spontaneously decreases to  $155^\circ\text{C}$  in the polyplate crucible, about half of the water molecules being released. This phenomenon can be explained in the following way. The formation of the nuclei that initiate the transformation begins at a higher temperature than that corresponding to the temperature of the transformation, i.e., at a higher energy content of the compound. As soon as a sufficient amount of the nuclei has been formed, the equilibrium is re-established, and the reaction proceeds at the chosen rate of  $0.4 \text{ mg min}^{-1}$  (with a total weight of  $200 \text{ mg}$ ) and at a temperature corresponding to the actual partial pressure of water vapour. In the labyrinth crucible, the first molecule of water is released at a constant temperature corresponding to the reaction course at a partial pressure of water vapour of  $100 \text{ kPa}$  and at the chosen rate at  $190^\circ\text{C}$ .

The temperature slowly increases during release of the second half of the water molecules. On the basis of earlier findings, however, it can be presumed that the porosity of the upper layer of the calcinate (which covers the nuclei of the new phase) decreases with increasing partial pressure of water vapour. Thereby the escape of water vapour from the phase boundary is made increasingly difficult as the thickness of the upper layer increases. Hence this process is finished at various temperatures (from 215 and 285°C) depending on the type of crucible used. With cobalt(II) dihydrogenphosphate this process proceeds in two phases, about one third of the water (constitutional) being released first. Then the temperature is also increased, and the second part of the water molecules is released, which is connected with the first condensation reaction giving the intermediate  $\text{CoH}_2\text{P}_2\text{O}_7$  (again at various temperatures corresponding to the actual partial pressure of water vapour within the range 125–210°C). With the Cu(II) product the course of the first condensation reaction distinctly shows the greatest dependence on the water vapour pressure in the calcination area. In the polyplate crucible there occurs an independent condensation of both the part corresponding to  $\text{H}_3\text{PO}_4$  (into diphosphoric acid and further into higher polyphosphoric acids [48]) and the  $\text{CuHPO}_4$  part (into  $\text{CuP}_2\text{O}_7$ ) [49]. However, it is only in the labyrinth crucible with a higher water vapour pressure that the  $\text{CuH}_2\text{P}_2\text{O}_7$  is formed in a sufficient amount as an important intermediate for the second condensation reaction, the formation of  $\text{Cu}_2\text{P}_4\text{O}_{12}$ .

The existence of  $\text{MH}_2\text{P}_2\text{O}_7$  (M = metal) was confirmed by instrumental methods. Electron microscopy revealed various degrees of porosity of the surface of these products depending on the water vapour pressure. Extraction experiments unambiguously defined the temperature ranges of its existence (Figs. 4 and 5): for  $\text{MnH}_2\text{P}_2\text{O}_7$  it is 190–295°C at 100 kPa and 150–240°C at negligible water vapour pressure; for  $\text{CoH}_2\text{P}_2\text{O}_7$  it is 215–290°C and 175–260°C, respectively. The temperature range of the existence of  $\text{CuH}_2\text{P}_2\text{O}_7$  (Fig. 6) at 100 kPa water vapour pressure is 200–350°C. However, in accord with the TA conclusions, the formation of Cu(II) dihydrogendiphosphate proceeds to only a limited extent in the polyplate crucible, the side products ( $\text{Cu}_2\text{P}_2\text{O}_7$  and polyphosphoric acid) not being extracted with water and acetone, so the extractable portions are markedly lower. At lower water vapour pressure the temperature of the individual processes is decreased by 30–60°C [even more for the Cu(II) product], which would be technologically advantageous, but at the same time the yields of the main products are seriously decreased. At lower water vapour pressures in the calcination area, this phase is already accompanied by an undesirable side reaction viz., splitting off of part of the phosphate component. This is split off either in the form of phosphoric acid from dihydrogendiphosphate anhydride or in the form of diphosphoric acid from dihydrogenphosphate to give the side product  $\text{M}_2\text{P}_2\text{O}_7$ , the existence of



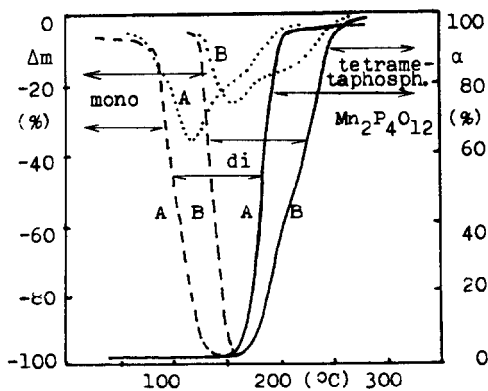


Fig. 4. Extraction experiments on Mn(II) product. Weight changes of the intermediates determined by extraction with: (-----) water; (.....) acetone; (—) 0.3 M HCl (degree of conversion,  $\alpha$ , to the tetrametaphosphate). Calcination conditions,  $p_{H_2O(g)}$ : (A) 1 kPa; (B) 100 kPa.

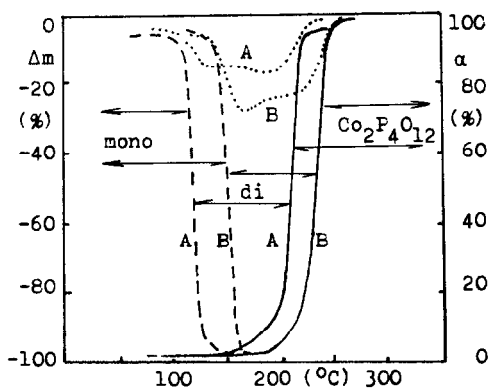


Fig. 5. Extraction experiments on Co(II) product. See Fig. 4.

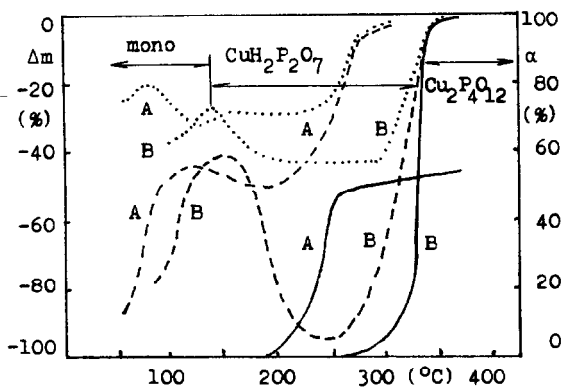


Fig. 6. Extraction experiments on Cu(II) product. See Fig. 4.

which in addition to  $MH_2P_2O_7$  was confirmed. Thereby, at the same time, the increased portion of bivalent metal in the solid residue after the above-mentioned splitting off of the part of the phosphate component is compensated. At the same time, however, the released part of the phosphorus component can be condensed independently, whereby the yield of the second condensation reaction is lowered (tetrametaphosphate formation). This condensation reaction proceeds even at the temporarily decreased temperature, higher condensates of polyphosphoric acid being formed gradually during further increases in temperature. This undesirable side process is dominant with the Cu(II) product at lower water vapour pressure.

The temperatures of liberation of the last part of water from the calcined sample correspond to the second molecule of the constitutional water of the starting dihydrogenphosphate and to the second condensation reaction, viz., the formation of  $M_2P_4O_{12}$ . They again depend on the type of crucible used, i.e., on the partial pressure of water vapour in the sample. At the same time, however, it was shown that this transformation only proceeds isothermally (280–295°C) and, hence, leads to an equilibrium with Co(II) phosphate using the labyrinth crucible. In the different types of crucible used, this process with Mn(II) phosphate proceeds in different temperature ranges, viz., polyplate 220–265°C and labyrinth 320–330°C. With Co(II) dihydrogenphosphate (polyplate crucible), the release of the second molecule of constitutional water was observed at 240°C; this process is accompanied by a distinct temperature decrease again, viz., to 225°C. This value corresponds, with the increasing amount of new nuclei, to the partial pressure at which the decomposition proceeds at the chosen rate (0.4 mg min<sup>-1</sup> for a total weight change of 200 mg). The overall weight decrease with the labyrinth crucible corresponds to the theoretical value of complete release of four water molecules from the starting Mn(II) and Co(II) phosphate.

In the other types of crucible (where, in the course of the condensation reaction giving  $MnH_2P_2O_7$ , partial release and independent condensation of phosphoric acid took place) such a weight decrease was not reached at temperatures up to the 380°C used in the measurements. This result is due to the fact that the condensation of the splitt-off phosphoric acid to higher degrees and also the partial formation of  $Mn_2P_2O_7$  are shifted to higher temperatures, i.e., above the temperature of formation of  $Mn_2P_4O_{12}$ . The final degree of transformation of the calcinate to the tetrametaphosphate is also distinctly lower in the open crucible, the maximum value reached being 80%. In contrast, in the labyrinth set the degree of conversion was above 95% at temperatures above 300°C.

With the Cu(II) product, the influence of the water vapour pressure on this second condensation reaction is still more distinct. In the labyrinth crucible a condensation reaction connected with the release of the last water molecule above 310°C occurs, this first part of the reaction taking place within a relatively narrow temperature range (395–405°C). This process is

substantially more complex and different in the polyplate crucible; the mass decrease that would correspond to the formation and existence of  $\text{CuH}_2\text{P}_2\text{O}_7$  is already attained at  $130^\circ\text{C}$  and that of  $\text{Cu}_2\text{P}_4\text{O}_{12}$  at  $200^\circ\text{C}$ . In accordance with the conclusions mentioned above and with the results of analyses of the calcinate samples by means of IMA or IAM methods and extraction experiments, however, Cu(II) tetrametaphosphate does not appear in the sample at temperatures around  $200^\circ\text{C}$ . Its formation at this low water vapour pressure is observed above about  $260^\circ\text{C}$ , a major proportion not being formed until  $290\text{--}310^\circ\text{C}$ . The  $\text{Cu}_2\text{P}_4\text{O}_{12}$  portion of the final product, however, only comprises about 50%, the rest being polyphosphoric acids,  $\text{Cu}_2\text{P}_2\text{O}_7$  and some  $\text{Cu}_3(\text{PO}_4)_2$ . Hence, the mass decrease in the polyplate crucible is substantially higher than that corresponding to 5.1 molecules of water (i.e., to quantitative formation of  $\text{Cu}_2\text{P}_4\text{O}_{12}$ ), and it is observed at lower temperatures than that of formation of tetrametaphosphate [this is a difference from the TA of Mn(II) and Co(II) phosphates]. The reason, in addition to the already mentioned ability of the small Cu(II) cation to form the tetrametaphosphate, lies especially in the fact that the experiment starts from a mixture and not from the dihydrogenphosphate, as is the case with the other two cations. Hence, part of the phosphoric acid escapes during the boiling of the phosphoric acid that can occur in this arrangement. At higher temperatures, a further part condenses independently to the final  $\text{P}_2\text{O}_5$ , which escapes at high temperatures (Fig. 1A).

The existence and the quality of the tetrametaphosphate formed were confirmed by the above-mentioned instrumental methods. The results obtained partially disagree with published findings [17–24], other workers used different temperatures and also described the formation of linear tri- and tetrapolyphosphates of Mn(II) [21–23] and even higher (up to either-membered) condensed phosphates of Co(II) [19,20,24] as the reaction intermediates.

Mathematical treatment of the TG curves (labyrinth crucible) from the dynamic thermal analyses made it possible to evaluate, on the basis of statistical characteristics [33], the scope and limitations of the kinetic models given for the heterogeneous reactions investigated. Diffusion was shown to be the limiting process of the condensation reactions. Using a geometrical model, their course can be expressed mathematically by the anti-Jander equation  $D_4 [(1 + \alpha)^{1/3} - 1]^2 = kt$ , which describes the so-called counter-current diffusion [34]. In this way it was possible to confirm the results obtained by the electron microscopy [25], which revealed a distinct porosity of the intermediate dehydrogenphosphate formed. Taking into account all the circumstances, however, we conclude that the condensation reaction for the formation of  $\text{M}_2\text{P}_4\text{O}_{12}$  (especially in the labyrinth crucible probably leads to an equilibrium, but its course is affected by the porosity of the upper layer of the calcinate which is formed on the nuclei.

The DTA of Mn(II), Co(II) and Cu(II) tetrametaphosphates measured in

vacuo (10 mPa He) showed distinct exothermic effects of their melting: 950°C for  $\text{Mn}_2\text{P}_4\text{O}_{12}$ , 1060°C for  $\text{Co}_2\text{P}_4\text{O}_{12}$  and 820°C for  $\text{Cu}_2\text{P}_4\text{O}_{12}$ . The DTA of cooling exhibited the corresponding exothermic effects of solidification of the melts of the tetrametaphosphates. Repeated DTA of heating and cooling of the same sample showed the respective effects at the same temperatures and to the same extent. The above-mentioned IMAs, or IAMs proved that the samples after repeated DTA contained the microcrystalline tetrametaphosphates only. Hence these substances only undergo congruent melting under these conditions [obviously with  $\text{Cu}_2\text{P}_4\text{O}_{12}$  the product is partially split under the high vacuum used; part of the Cu(II) is converted into Cu(I) and, therefore, the excess of phosphoric acid escapes].

The DTA curves of the tetrametaphosphates measured in a helium atmosphere (100 kPa pressure) containing small amounts of water vapour (2 mg  $\text{H}_2\text{O}$  per  $\text{dm}^3$ ) are given in Fig. 7a. Again, the melting takes place at the same temperatures as in vacuo, the exothermic effects being greater, however. The cooled samples were glassy products. The DTA curves showed no effects corresponding to solidification of the melt (which is a frequent phenomenon with glasses). The instrumental methods confirmed their composition as molecules of higher linear condensed phosphates with non-crystalline amorphous character. It is the water molecules present in the helium atmosphere that can provide end-groups for these linear chains and stabilize them. Generally the formula  $\text{M}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Cu}$ ) can be suggested for these glassy products. When the glass was cooled and ground and then heated again, a distinct exothermic effect was observed at 530°C (Mn), 580°C (Co) and 540°C (Cu). The instrumental methods showed that these effects correspond to crystallization of the glassy products with restoration of the tetrametaphosphate molecules. This process should be accompanied by release of the water molecules. Further heating of the tetrametaphosphates formed by recrystallization of the glasses results in their melting at the same temperatures as the starting phosphates. In the helium atmosphere containing water vapour this occurs again with formation of the glassy higher linear condensed phosphates. Hence, the transition of tetrametaphosphates to these glassy product represents a reversible process. The DTA curves clearly show small but perceptible endothermic effects immediately before the exothermic peaks of recrystallization of the glasses. When observed with a high-temperature microscope, these glasses showed signs of softening before the recrystallization proper. Therefore, the penetration TMA method developed in our laboratory [50] was used for the determination of the softening temperatures (Fig. 8). The onset and extrapolated onset softening temperatures for the individual glasses are 470 and 510°C (Mn), 500 and 550°C (Co), 480 and 520°C (Cu), respectively [ $T_{s(0)}$  and  $T_{se(0)}$ ].

The participation of water in the processes mentioned, which could be detected by weight changes, was followed thermogravimetrically with the use

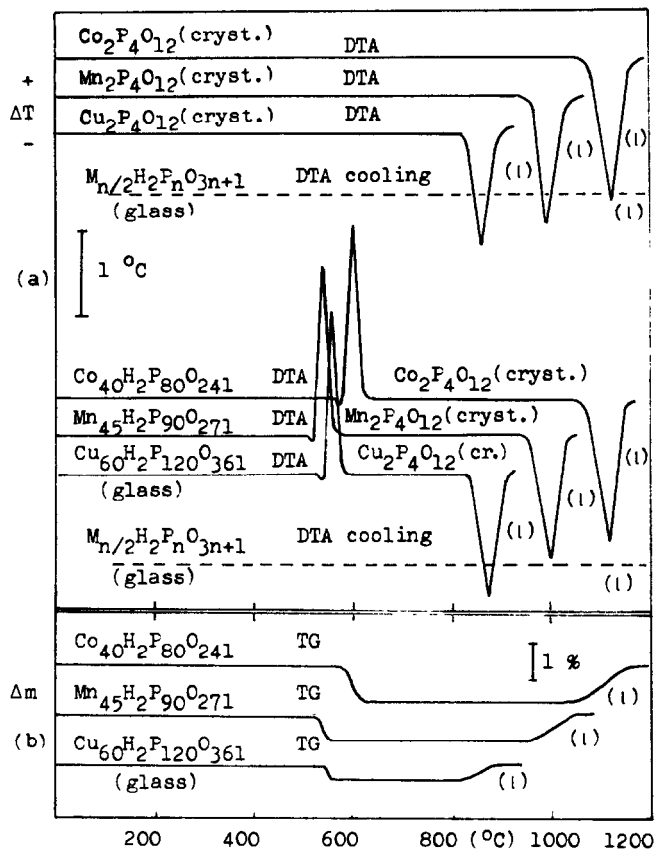


Fig. 7. (a) DTA curves of  $\text{M}_2\text{P}_4\text{O}_{12}$  and  $\text{M}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Cu}$ ) in a helium atmosphere (100 kPa) containing 2 mg  $\text{H}_2\text{O}$  per litre of He. VDTA 8 M2 apparatus ("Kiev" system); heating (cooling) rate,  $40^\circ\text{C min}^{-1}$ ; sample weight, 100 mg; standard,  $\alpha\text{-Al}_2\text{O}_3$ ; Mo crucible. (b) TG curves of  $\text{M}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$  in a wet argon atmosphere. Derivatograph, Q-1500 apparatus; heating rate,  $20^\circ\text{C min}^{-1}$ ; sample weight, 1000 mg; Pt crucible; sensitivity of the balance, 20 mg.

of a Q-1500 Derivatograph (Fig. 7b). The measurements were carried out at high sensitivity of TG in a humid argon atmosphere. It was found that the recrystallization, i.e., transformation of the glassy products into tetrametaphosphates, is accompanied by a weight decrease (0.04–0.11%). On the other hand, in the temperature ranges of melting of the tetrametaphosphates there is a comparable weight increase of the sample (a similar effect is also given by trisodium tetrametaphosphate [10]). The weight changes of the thermoanalysed samples corresponding to binding (or release) of water molecules were used for calculation of the  $n$  value in the glass formulae  $\text{M}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$ . These values varied within the limits 70–100, 80–110 and 100–140 for the Co, Mn and Cu glasses, respectively. The  $n$  values will obviously be affected by the amount of water vapour in the atmosphere

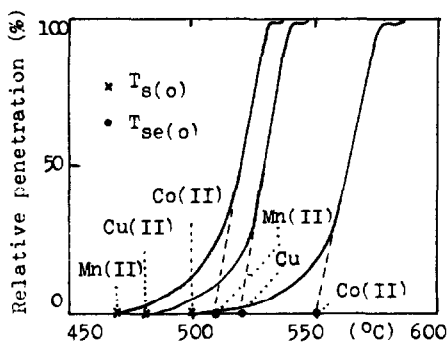
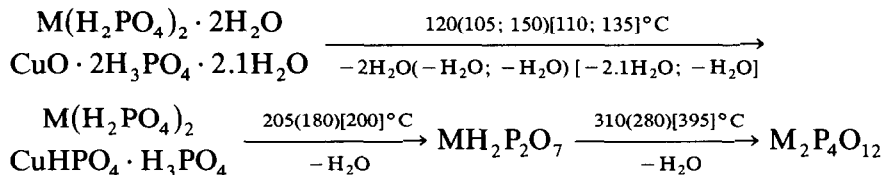


Fig. 8. TMA: penetration probe traces for  $M_{n/2}H_2P_nO_{3n+1}$  glass. Apparatus, ref. 50; low-sensitivity mode; load, 40 mg; atmosphere, air; sample (glass) thickness, 1 mm; plane,  $3 \times 3 \text{ mm}^2$ .

during the formation of these glassy products. With respect to the slight weight changes connected with the processes investigated and to the sensitivity of the apparatus used they must only be considered as "orientation" values. (For example, pressure TA has been applied to the determination of the content of bound water in phosphate glasses and also to the determination of the length of their chains [1]. No further detailed data on this method, which is patented, are available.)

## CONCLUSION

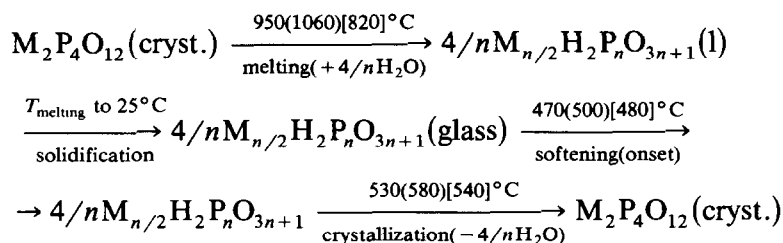
The condensation reactions proceeding during the calcination of  $Mn(H_2PO_4)_2 \cdot 2H_2O$ ,  $Co(H_2PO_4)_2 \cdot 2H_2O$  and the Cu(II) starting mixture have been followed in order to establish the effect of the water vapour present on their course. If the partial pressure of water vapour almost corresponds to atmospheric pressure (100 kPa), the individual processes can be described by the following scheme {parameters being cited for  $M = Mn$ , (Co) and [Cu]}:



At lower partial pressures of water vapour the reaction goes faster and at lower temperatures [by 30–60°C; even more with the Cu(II) product], but the yields of the final product (tetrametaphosphate) are lower. This is due to the fact that, in addition to the main intermediate  $MH_2P_2O_7$ , part of the phosphorus component is released in the form of phosphoric or diphos-

phoric acids, which are independently condensed into polyphosphoric acids. The remaining higher amount of the divalent metal component [Mn(II), Co(II), Cu(II)] results in the formation of  $M_2P_2O_7$ . The side intermediates then decrease the yield of the main final condensation product  $M_2P_4O_{12}$ .

The melting of the tetrametaphosphates examined is congruent in a dry atmosphere. In the presence of small amounts of water vapour, the tetraphosphate rings are split at the melting temperature, and the chains formed are condensed to higher linear phosphates. The chains composed of several tens of  $-PO_3-$  groups are ended with participation of water molecules. Reheating of the glassy products results in their crystallization with release of their water molecules and regeneration of tetrametaphosphate molecules. The reversible process can be represented as follows:



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