

MECHANISM OF FORMATION OF POLYMERIC PHOSPHATES AT THE HEAT TREATMENT OF CRYSTALLOHYDRATES OF DIVALENT METALS

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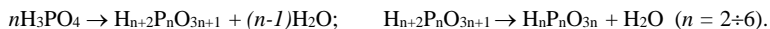
By researches of double phosphates $M^{II}_{1-x}M^{II}_x(H_2PO_4)_2 \cdot 2H_2O$ ($M^{II} = Mg, Mn, Co, Zn$), for the first time it is established, that one of peculiarities of their thermolysis is ability to the intramolecular hydrolysis. As a result of this process the dihydrophosphates thermolysis is accompanied by formation of free phosphoric acids, which expose to condensation and take part in formation of polymeric phosphates.

Such rules of solidphase transformations and the reasons of polymer formation were established by generalization of obtained experimental data:

1. The thermolysis of dihydrophosphates occurs in step-wise. The first stage characterizes removal of crystal water on two different mechanisms in an interval 80–190 °C. One of them – molecular – provides its removal as a molecular unit and realizes with formation $M^{II}_{1-x}M^{II}_x(H_2PO_4)_2$. The second mechanism – dissociation – is consequence of the protolytic dissociation of water molecules, which leads to the intramolecular hydrolysis of salt with formation in products of thermolysis of free phosphoric acids.

2. The formation of acids continues during removing of constitution water (the second stage of thermolysis, 190–270 °C). Their maximal quantity (18–22 % mass. P_2O_5 acid.) is established in products of dehydration $M^{II}_{1-x}M^{II}_x(H_2PO_4)_2 \cdot 2H_2O$ at removal of 2,2–2,5 mole H_2O and decreases at their further heating.

Characteristic peculiarity of this thermolysis stage is realization of processes of anionic condensation, both in a salt component of partial dehydration phosphates, and in an acid component. Poly- and metaphosphoric anions are formed as a result of these processes according to the following schemes:

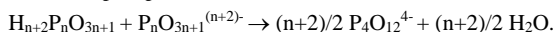


The most fullest condensation of free phosphoric acids occurs upon removal of 2,8–3,2 mole H_2O . $H_{n+2}P_nO_{3n+1}$ are formed and as a result of disproportionations of protonized condensed phosphates according to the schemes:



Anionic condensation of the salt component is realized in the greater measure ($n = 8$) and is accompanied by the complex structural reorganizations including amorphicity of intermediate products (210–260 °C) and formation of new crystal phase's structures.

3. The formation of a thermolysis finished product – solid solutions of polymeric phosphates of composition $(M^{II}_{1-x}M^{II}_x)_2P_4O_{12}$ ($M^{II} = Mg, Mn, Co, Zn$; $0 < x < 1,00$) – is realized simultaneously according to two parallel routes. One of them provides for dehydration of the acidic lowmolecular condensed phosphates according to classically known scheme. The second route, for the first time established in the present work – interaction of polyphosphoric acids with the middle condensed phosphates:



The quantitative ratios between the two thermolysis routes are determined by the nature of the cation. With increase in composition of solid solutions of manganese (II), cobalt(II) or zinc the quantity of free phosphoric acids increases. The share of their participation in formation of solid solutions of polymeric phosphates increases (up to 20–25 %).