

NEW DATA ON THE PHOSPHATES OF POLYVALENT METALS

Tananaev I.V.

Kurnakov Institute of General and Inorganic Chemistry, Academy
of Sciences of USSR, Moscow, U.S.S.R.

Abstract - In the present paper have been discussed the formation of tri- and polyphosphates in aqueous solutions, their composition and thermal properties, as well as the vibrational and luminescent properties of oxophosphates of rare-earth metals. The crystal chemistry of the phosphates of Zr, V, Nb and U formed in the $M_xO_y - P_2O_5 - (H_2O)$ systems at 100-500°C has also been discussed. The mechanism of gas transport reactions concerning the formation of metallophosphates too has been included. It contains information on the new direction in painting - the thermophosphate painting.

The chemistry of inorganic compounds of phosphorous (phosphates) has developed intensively in the last few years for the reason that, first, the phosphate compounds are most suitable for further development of the chemistry of inorganic polymers, and, second, they are finding ever increasing practical application as fertilizers, detergents and as materials used in engineering and construction.

The oxygen compounds of Si, Ge, As, Sb, S, Se and other elements may be assumed as inorganic polymers, but they are not stable in media different from those in which they are formed, for example, in aqueous solutions at different pH values. It is known that sufficient stability of polymer phosphates in this respect makes it possible to identify them by the method of paper chromatography. This fact enabled us to study the process of formation and the composition of many normal, basic and acid of both simple and mixed (double) ortho-, di-, tri- and tetraphosphates of polyvalent metals in aqueous solutions, in particular, by the residual concentration technique (1,2). This method together with the IR-spectroscopy, thermogravimetry and paper chromatography was used in the studies of tri- and polymetaphosphates of some lanthanides (G.V.Rodicheva, Zh.A.Ezhova et al).

To the constant initial amount of the solution (0.025 - 0.05 mol/l) of chlorides or nitrates of the lanthanides were added the increasing from experiment to experiment amounts of $M_5P_3O_{10}$ ($M = Li, NH_4, Cs$). In the equilibrium heterogeneous (over the precipitate) solution was determined the concentration of Ln^{3+} or $P_3O_{10}^{5-}$ ions that had not reacted. In the graphical representation of the results the values of $n = M_5P_3O_{10} / LnCl_3$ in starting mixtures are plotted on the abscissa, and the concentrations of P_3O_{10} or Ln , on the ordinate.

As is seen from Fig.1, in the $ErCl_3 - Li_5P_3O_{10} - H_2O$ system is first formed $Er_5(P_3O_{10})_3 \cdot 20H_2O$ ($n \leq 0.6$) which dissolves in excess of $Li_5P_3O_{10}$ ($n > 0.6$). Similar results are obtained with $NdCl_3$ and $GdCl_3$ (3).

In analogous systems with $(NH_4)_5P_3O_{10}$ are formed (Fig.2) one after the other the precipitates: $Ln_5(P_3O_{10})_4 \cdot 20 - 23 H_2O$ ($n = 0.6$) with an impurity of the corresponding double salt, and double salts: $(NH_4)_3Ln_3(P_3O_{10})_3 \cdot 12 H_2O$ ($n = 0.67$) and $(NH_4)_3Ln_4(P_3O_{10})_4 \cdot 14 H_2O$ ($n \geq 0.75$). In an excess amount of the reagent the precipitates dissolve. Thus the nature of the given elements appears on the right hand side of the solubility diagram. As is seen from Fig.3 which illustrates the interaction of the elements with $Cs_5P_3O_{10}$, in the case of practically identical compositions of all the three solid phases, the points of complete dissolution in $Cs_5P_3O_{10}$ are "moved apart".

It might be well to point out that in similar systems with $Na_5P_3O_{10}$ all the three elements form besides $Ln_5(P_3O_{10})_3 \cdot nH_2O$ double salts of only one composition $NaLn_3(P_3O_{10})_2 \cdot 12H_2O$.

Thus, according to the ability of forming mixed triphosphates with rare-earth elements, the univalent cations are arranged in the following manner: $Cs \geq NH_4 > Na > Li$. On the other hand, according to the ability of forming complex compounds in the system with $P_3O_{10}^{5-}$ ions the rare-earth elements are arranged as follows: $Pr > Gd > Er$, i.e., in the order of their increas-

ing atomic weights. It may thus be assumed that $(\text{NH}_4)_5\text{P}_3\text{O}_{10}$ and, in particular, $\text{Cs}_5\text{P}_3\text{O}_{10}$ can be used perhaps for separating the rare-earth elements.

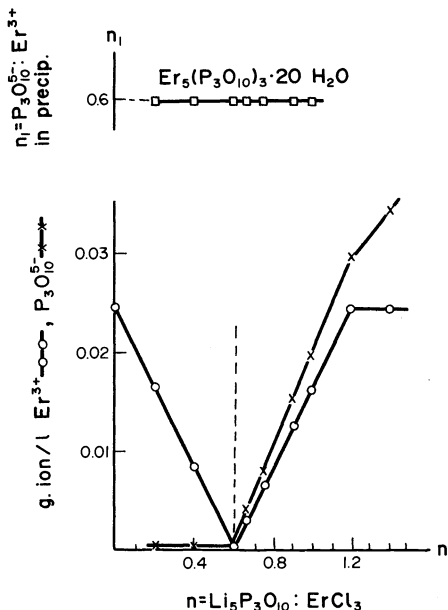


Fig. 1. The system : $\text{ErCl}_3\text{-Li}_5\text{P}_3\text{O}_{10}\text{-H}_2\text{O}$ (0°C).

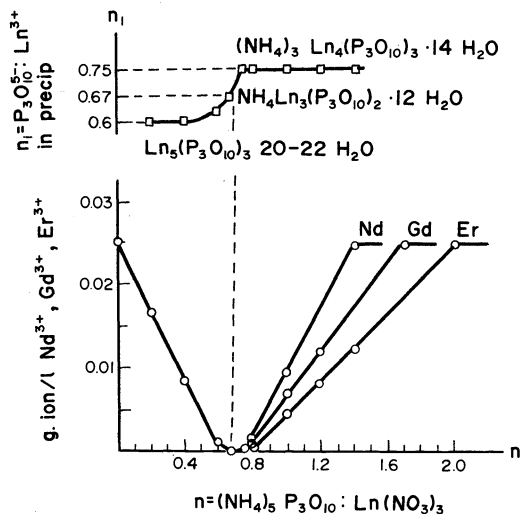


Fig. 2. The systems $\text{Ln}(\text{NO}_3)_3\text{-(NH}_4)_5\text{P}_3\text{O}_{10}\text{-H}_2\text{O}$ (0°C)
 $\text{Ln} = \text{Nd, Gd, Er}$.

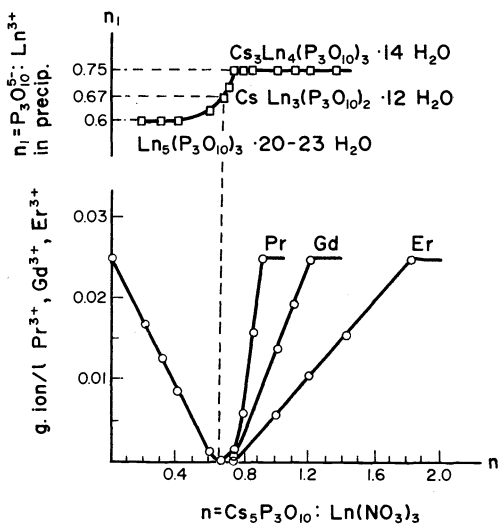


Fig. 3. The systems : $\text{Ln}(\text{NO}_3)_3\text{-Cs}_5\text{P}_3\text{O}_{10}\text{-H}_2\text{O}$ (0°C)
 $\text{Ln} = \text{Pr, Gd, Er}$.

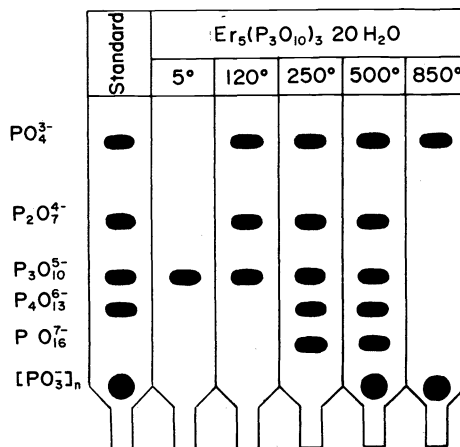
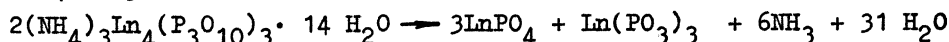
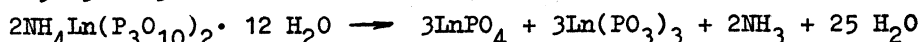
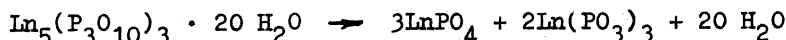


Fig. 4. Chromatograms of $\text{Er}_5(\text{P}_3\text{O}_{10})_3 \cdot 20\text{H}_2\text{O}$ and its heating products.

The thermal behaviour of simple and mixed triphosphates is characterized at the first stage of heating ($\sim 600^\circ\text{C}$) by the formation of water (or, also, NH_3), and at the second stage ($800 - 850^\circ\text{C}$) by the crystallization of amorphous mass. Completely dehydrated products heated up to 500° (Fig. 4) contain ortho-, pyro-, tri-, tetra-, penta- and more condensed phosphates. However, at 850°C only LnPO_4 and $\text{Ln}(\text{PO}_3)_3$ are formed. The corresponding chemical transformations may be represented schematically as :



Below are given the results of similar studies of the $\text{LnCl}_3 - \text{NaPO}_3 - \text{H}_2\text{O}$ systems at 0° ($\text{Ln} = \text{La, Nd, Eu, Er}$). A specially purified NaPO_3 , according to the potentiometric data, is characterized by the average degree of polymerization ~ 180 .

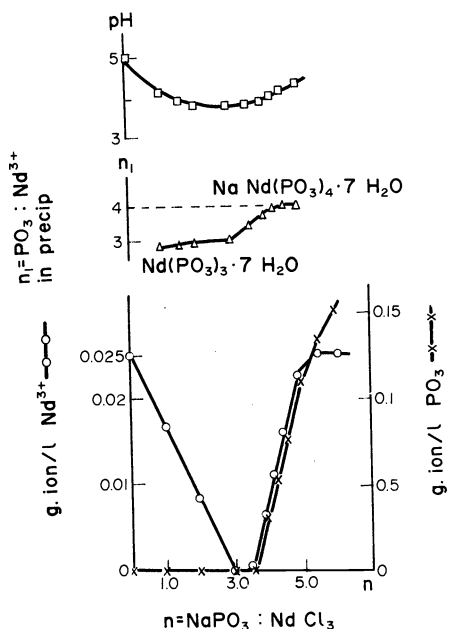


Fig.5. The system :
 $\text{NdCl}_3 - \text{NaPO}_3 - \text{H}_2\text{O}$ (0°C).

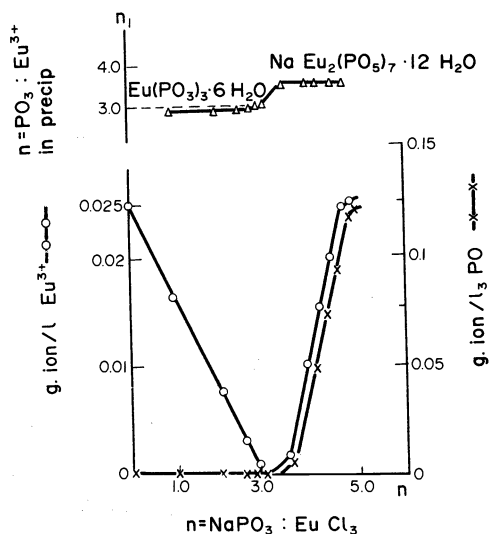


Fig.6. The system :
 $\text{EuCl}_3 - \text{NaPO}_3 - \text{H}_2\text{O}$ (0°C).

It was found that the general picture of interaction for La and Nd with NaPO_3 was practically similar (Fig.5) (4). At the first stage of interaction are formed less soluble basic metaphosphates (pH curve), in which the $\text{PO}_3:\text{Ln}$ ratio varies from 2.90 to 2.97. At $n = 2.0 - 3.0$ the amorphous $\text{La}(\text{PO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Nd}(\text{PO}_3)_3 \cdot 7\text{H}_2\text{O}$ are precipitated. At $n \geq 4.5$ $\text{NaLa}(\text{PO}_3)_4 \cdot 6\text{H}_2\text{O}$ and $\text{NaNd}(\text{PO}_3)_4 \cdot 7\text{H}_2\text{O}$ are formed. These salts dissolve at $n = 5.5$ and 5.25 , respectively. Under similar conditions europium (Fig.6) forms (5) a basic polyphosphate ($\text{PO}_3:\text{Eu} = 2.90$), $\text{Eu}(\text{PO}_3)_3 \cdot 6\text{H}_2\text{O}$ and a double salt of composition $\text{Eu}_2(\text{PO}_3)_7 \cdot 12\text{H}_2\text{O}$ ($n > 3.5$). As regards erbium (Fig.7), it forms, besides basic salts, only $\text{Er}(\text{PO}_3)_3 \cdot 5\text{H}_2\text{O}$. The third type of double phosphate was received by use of preparative methods.

As is seen from Fig.8, the points of complete dissolution are distinctly differentiated, but they are located in the reverse order in comparison to what is observed in the systems with $\text{M}_5\text{P}_3\text{O}_{10}$, this is quite unexpected. Possibly it is due to the dissimilar nature of interaction in both cases, and if the reaction of the cations of rare-earth elements with the anions of triphosphate proceeds at the molecular level, the reactions of rare-earth cations with the practically infinite long chains of polyphosphate anions proceed, perhaps, as ionic exchange in a solution.

As an example the thermogravimetric of $\text{La}(\text{PO}_3)_3 \cdot 6\text{H}_2\text{O}$ (analogous salts of Nd, Eu, Er decompose in a similar manner) is shown in Fig.9. The endoeffect at 135°C corresponds to the loss of main mass of water with the simultaneous decomposition of the polyphosphate structure of the starting compounds and the formation of a product containing (as in the case of triphosphates of rare-earth elements) phosphates, in which the phosphate anion is polymerized to different degrees. At 410° the remaining water (~ 3 moles) is removed leaving behind the anhydrous long-chain polyphosphate.

Dehydration of double polyphosphates takes place differently :

$\text{NaLa}(\text{PO}_3)_4 \cdot 6\text{H}_2\text{O}$ in two stages at 140 and 335°C;

$\text{NaNd}(\text{PO}_3)_4 \cdot 7\text{H}_2\text{O}$ in three stages at 140, 370 and 385°C;

$\text{NaEu}(\text{PO}_3)_7 \cdot 12\text{H}_2\text{O}$ in one stage at 120°C.

At the exoeffect temperature (580°C) the dehydration products crystallize forming double anhydrous polyphosphate of europium. Characteristic of all the above mentioned double salts is the incongruent melting at 800-850°C.

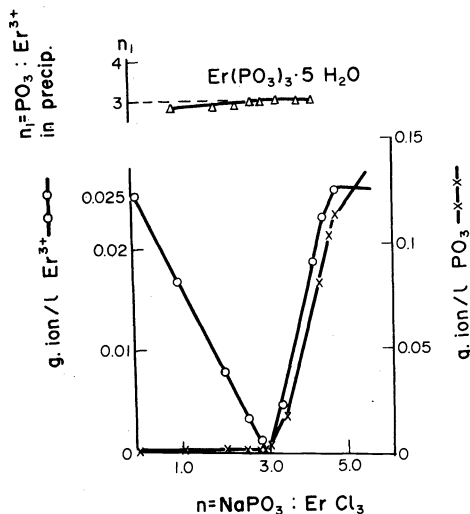


Fig. 7. The system :
 $\text{ErCl}_3 - \text{NaPO}_3 - \text{H}_2\text{O}$ (0°C).

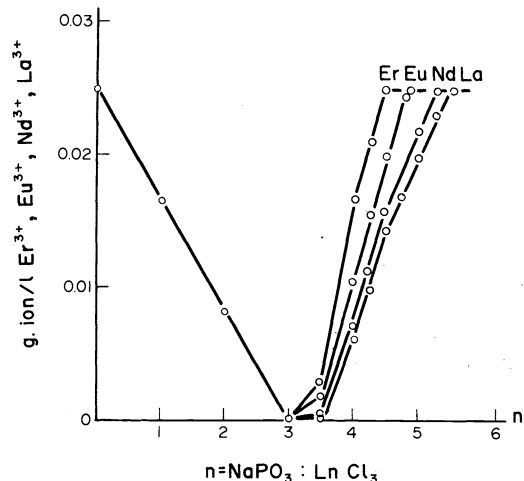


Fig. 8. The systems :
 $\text{LnCl}_3 - \text{NaPO}_3 - \text{H}_2\text{O}$ (0°C)
Ln = La, Nd, Eu, Er.

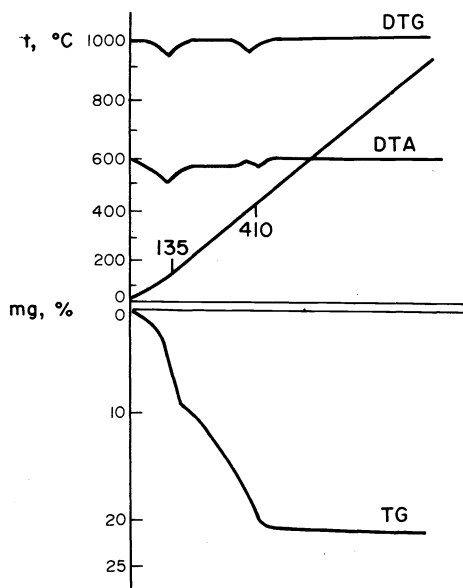


Fig. 9. The thermogram of $\text{La}(\text{PO}_3)_3 \cdot 6\text{H}_2\text{O}$.

From the above given data it follows that the chemical reactions of triphosphate anions with polyvalent cations, in the given case with the cations of rare-earth elements, proceed in a different manner than with the polyphos-

phate anions. With some simplification it may be assumed that in the formation of simple polyphosphates of rare-earth elements three long chains in the soda form, which had been in the disconnected state, "merge" at points where every three atoms of sodium (one from each chain) "give way" to one trivalent cation of rare-earth elements. In this case is formed as if a cross linked (structured) trihedral prism of polyphosphate chains. In mixed (double) polyphosphates of La, Nd a tetrahedral prism is formed, but in the compounds of composition $\text{Na}_3(\text{Ln}(\text{PO}_3)_6 \cdot n\text{H}_2\text{O})$ (Ln = La, Nd, Eu) (which are salted out from the aqueous solution of the corresponding mixture ($n=6$) by acetone), a hexahedral.

At present we are studying the interaction of cations of rare-earth elements with polymetaphosphates of other alkali metals.

Another method which is commonly used by us involves heating of the oxides of metals (or their salts with the anion of a volatile acid) with concentrated phosphoric acid. On heating the water gradually escapes out resulting in the increase of the concentration of H_2PO_4 , and finally phosphoric acids are formed. At each temperature are created definite conditions under which, depending on the nature of the cation, are formed phosphate compounds from ortho- to ultraphosphates. The heating range of similar systems ($\text{M}_x\text{O}_y - \text{P}_2\text{O}_5 - (\text{H}_2\text{O})$) varies from 100 to 500°C and above, therefore the precipitated solid phases in the system do not contain water. It is convenient to obtain them in the mono-crystalline state.

This method of precipitating phosphate compounds of polyvalent cations from the melt solutions of condensed phosphoric acids was time and again used for preparative purposes (6,7,8 and 9). This method with the application of the physico-chemical analysis procedure proved to be especially useful. With this point of view the considered systems have three components :

$\text{M}_x\text{O}_y - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$; the variations taking place in the composition of solid phases depend on the water content present in the air. A detailed study of this problem was made by N.N.Chudinova in (10), who obtained a polytherm of solubility determined at a constant pressure of water vapours. As may be seen from Fig.10, the usual stability diagrams determining the behaviour of the studied system are the projections of the polytherms of the solubility in the melt solutions of concentrated phosphoric acid on the lower plane by taking into account that the variations in the content of atmospheric moisture, within usual limits, at room temperature do not practically affect the results, and the corresponding "open" systems may be assumed to be existing at constant water content; the behaviour of the system in this case depends only on the temperature. A diagram of this type is shown in Fig.11 (10). Thus, the usual solubility diagrams in the $\text{M}_x\text{O}_y - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$ type systems (in particular, in the variant of residual concentrations method) can be visually combined into one with the melt-solution diagram following the second method. An example of such a diagram for the $\text{Bi}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$ system is shown in Fig.12 (10).

Up to now we have studied thoroughly in our laboratory numerous phosphate compounds of Group III elements obtained from the melt-solutions of concentrated phosphoric acid.

Much less attention in this respect was paid till now to the elements of Groups IV and V, in particular to transition metals. These elements are capable of varying the valent state depending on the relative excess of concentrated phosphoric acid, the temperature of the melt and the oxidation-reduction conditions created in this case. As a result it becomes possible to synthesize phosphate compounds containing oxocations very typical for transition elements of Groups IV, V and VI.

Below are given the data concerning the study of the regularities of formation, composition and crystal chemistry of the compounds formed in the $\text{M}_x^{\text{IV-VI}}\text{O}_y - \text{P}_2\text{O}_5 - (\text{H}_2\text{O})$ systems which have been studied in our laboratory by A.V.Lavrov, Yu.E.Gorbunova, S.A.Linde and V.G.Kuznetsov.

Thus, in the study of the $\text{MO}_2 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$ type systems it is shown that for small cations (M = Si, Ge, Ti and others) the formation of simple pyrophosphates, MP_2O_7 , with octahedral coordination of metal is quite natural. For the average and large size cations is observed, besides this, the tendency towards crystallization of polyphosphates, $\text{M}(\text{PO}_3)_4$, which increases with the increase of cation radius from Zr to Th.

The structural studies have shown that on transition from diphosphates (P : M = 2 : 1) to polyphosphates (P : M = 4 : 1) the octahedral coordination of metal changes to eight-fold coordination (square antiprism).

It has been shown that phosphate compounds of tetravalent metals with the common formula $\text{M}(\text{PO}_3)_4$ (M = Zr, Hf, Ce, U, Th) belong to four isostructural series. The structure of monoclinic modification $\text{Zr}(\text{PO}_3)_4\text{-I}$ (Fig.13) is characterized by unusual mutual orientation of polyphosphate chains which are twisted in double spiral-like chains instead of ordinary ones in the

orthorhombic modification $Zr(PO_3)_4$ -II (Fig.14).

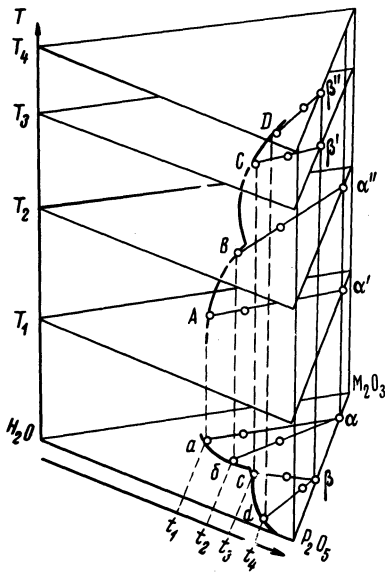


Fig.10. The solubility polytherm in the $M_2O_3 - P_2O_5 - H_2O$ system (projection on the $abcd$ plane).

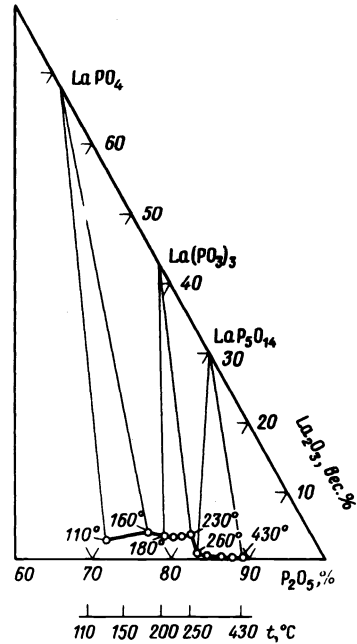


Fig.11. Solubility in the $La_2O_3 - P_2O_5 - (H_2O)$ system (140 - 400°C).

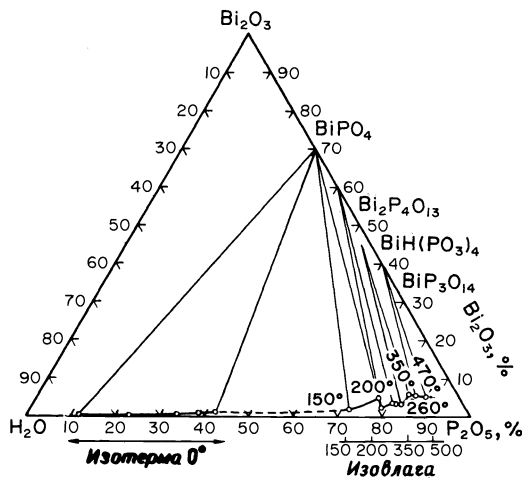


Fig.12. Equal-temperature and equal-moisture curves of the $Bi_2O_3 - P_2O_5 - H_2O$ system.

It should be noted that double spirals from polyphosphate chains do not have analogs among the phosphates and silicates as well. The eight-fold coordination of metal in the form of square antiprism is characteristic for both modifications; the links of polyphosphate chains of 8 PO_4 -tetrahedrons are retained. The three dimensional skeleton structure in both cases is obtained due to the participation of all the terminated atoms of oxygen. In the structures of above mentioned zirconium phosphates are present channels of diameter 4.5 Å, which makes possible their use as molecular sieves. The polyphosphate of zirconium and hafnium decompose at 600°C with the

escape of P_2O_5 and formation of diphosphates. In the triclinic and tetragonal modifications of U^{IV} and Th^{IV} phosphates the formation of other forms of the phosphate anion, including the cyclic ones, is not ruled out. These compounds are stable up to $1000^\circ C$. The formation of ultraphosphates in similar systems was not observed.

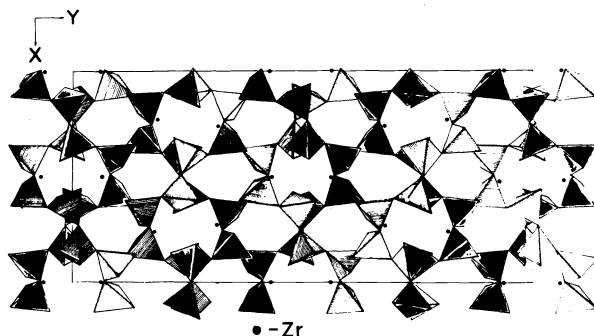


Fig.13. The projection of the $Zr(PO_3)_4$ -I structure on the (001) plane.

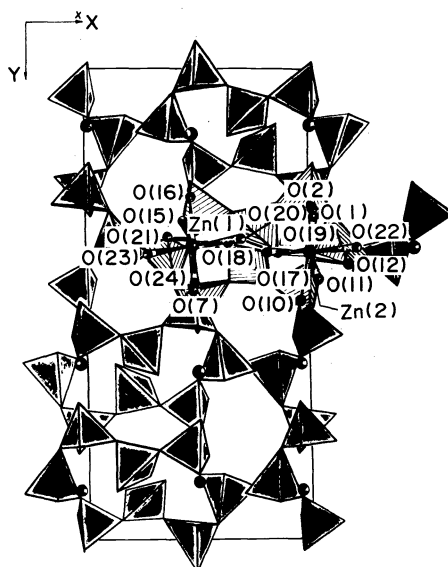


Fig.14. The projection of the $Zr(PO_3)_4$ -II structure on the (001) plane.

The specific nature of the phosphates of transition metals of Group V and VI (V, Nb, Mo, U) is determined by their tendency to form oxo- and dioxocations less stable in phosphate melts and concentrated phosphoric acid, as a result of which oxygen evolves and their low degrees of oxidation become stable. In the alkali metal pyrophosphate melts the uranyl ion was found to be highly stable to heat (up to $1000^\circ C$).

The properties of the structure of oxo- and dioxogroups in the phosphates of above mentioned metals affect the shape of their structures, in which the layered fragments dominate. But, the force and nature of interaction between them may differ significantly, and this determines the type of the structure. Characteristic for all the investigated phosphate compounds of transition metals of Group V is the octahedral coordination of metal independent of the P : M ratio in the compound. Only in $K_2VOP_2O_7$ the vanadium atom as an exception is coordinated by oxygen atoms in the form of a tetragonal pyramid. In M-octahedrons the M-O bond in the oxoion has, as a rule, increased strength, but with the trans-partner it is much weak. The lengths of M-O

bonds with equatorial ligands have an intermediate value. The M-octahedrons can be either isolated, or combined through axial apices into infinite chains by alternating the bond $O=M \dots O=M \dots$ and so on, found in particular in $(VO)_2P_2O_7$ and $VO(H_2PO_4)_2$. Thus, in the $(VO)_2P_2O_7$ structure (Fig.15) double columns (12,13,14) are formed as a result of dimerization of octahedrons through the common edge. The nonlinear pyrophosphate groups link such columns by the terminal atoms of oxygen in the three dimensional frame-work.

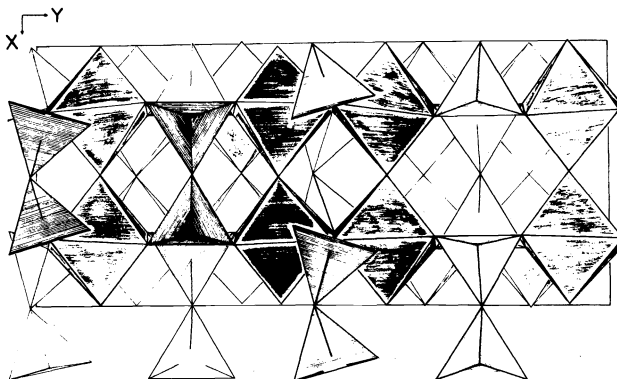
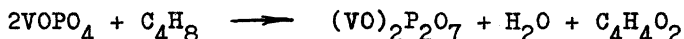


Fig.15. The projection of the $(VO)_2P_2O_7$ structure on the (001) plane.

The study of the $(VO)_2P_2O_7$ structure synthesized by G.Ladvig was carried out under the joint research programme of the Institute of General and Inorganic Chemistry, Academy of Sciences of USSR and the CIIC, Academy of Sciences, GDR (13,14). It was established that $(VO)_2P_2O_7$ was an effective catalyst for the oxidation of butene into maleic anhydride. $(VO)_2P_2O_7$ is formed as a result of the reduction of $VOPO_4$ as a catalyst :



Earlier the $(VO)_2P_2O_7$ was assumed to be formed in the process of crystal-IV lization of glasses in the $V_2O_5 + P_2O_5$ system, in which the presence of V^{IV} was proved by the electron paramagnetic resonance method, which was due to the unstability of V^V under these conditions.

Another known method of the synthesis of VOP_2O_7 is based on the dehydration of $VOHPO_4 \cdot 4H_2O$ at $350 - 400^\circ C$, which can be obtained by precipitating vanadyl ions in the aqueous solution of Na_2HPO_4 .

The chains of V-octahedrons show up in $VO(H_2PO_4)_2$ (Fig.16) (15), where they are linked by H_2PO_4 -groups. In this case a system of nonlinear hydrogen bonds is formed, where the O atoms of the OH-groups act simultaneously as donors and acceptors.

It should be noted that, unlike the isotope $Zr(HPO_4)_2 \cdot H_2O$, in the $VO(H_2PO_4)_2$ crystals the ionic exchange was not detected despite the presence of free channels (along the axis 4 perpendicular to the plane) (Fig.16) and sufficiently weak H-bonds due to steric hinderences; it is possible to replace four atoms of hydrogen by such small cations as Si, Ge only formally. The Si atoms can accomodate themselves in the free channels because in the corresponding solution of PO_4 -tetrahedrons is realized an original silico-phosphate anion on retaining the lattice symmetry and the general structural arrangement.

On heating $VO(H_2PO_4)_2$ is formed $VO(PO_3)_2$ which melts at $1180^\circ C$ with the formation of viscous glass acting as a cementing substance with respect to SiO_2 , Al_2O_3 and other difficulty fusible components.

The addition of potassium orthophosphate into the $VO(PO_3)_2$ melt results in the crystallization of $K_2VOP_2O_7$.

Vanadyl pyrophosphate may also be obtained by fusing $VO(PO_3)_2$ with K_2CO_3 in an inert atmosphere or under vacuum. In the structure of $K_2VOP_2O_7$ (Fig.17) are formed V-polyhedrons in the form of a tetragonal pyramid connected with the pyrophosphate groups in the layers bonded with potassium cations. Two oxygen atoms of each P_2O_7 group are bonded only with potassium.

In the study of interaction in the $Nb_2O_5 - P_2O_5 - (H_2O)$ system it is established that the tetrphosphate anion in the $(NbO)_2P_4O_{13}$ compound represents the

highest degree union of condensation in the system. On adding potassium ions (in the form of KNO_3) into the $\text{Nb}_2\text{O}_5 - \text{P}_2\text{O}_5$ system is formed the KNbOP_2O_7 . The degree of condensation of the anion decreases. The formation of polyphosphates Nb^{V} as well as of other metals prone to the formation of oxocations MO^{3+} is not typical.

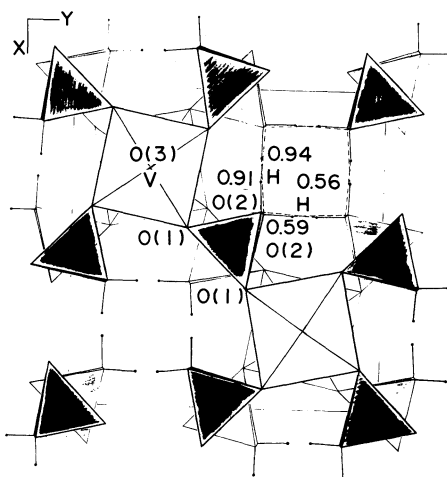


Fig.16. The projection of the $\text{VO}(\text{H}_2\text{PO}_4)_2$ structure on the (001) plane.

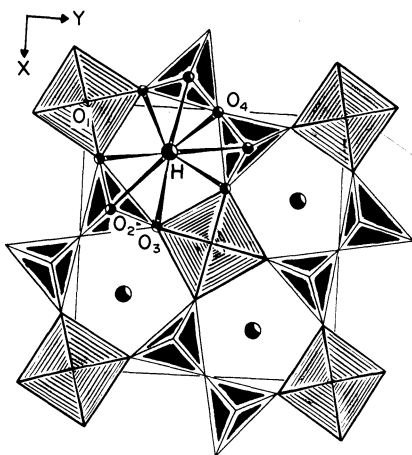
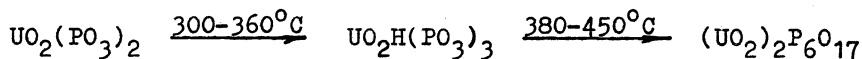


Fig.17. The projection of the $\text{K}_2\text{VOP}_2\text{O}_7$ structure on the (001) plane.

In the structure of KNbOP_2O_7 crystals (Fig.18) the Nb-octa hedra are isolated; the oxoniobium-phosphate layers are bonded by potassium cations and by the relatively weak Nb-O interaction (Nb-O bond with trans-partner). The oxygen atoms in each P_2O_7 group participate one by one in the bond only with potassium cations.

In the $\text{UO}_3\text{-P}_2\text{O}_5\text{-(H}_2\text{O)}$ system interaction takes place according to the scheme :



The acid polyphosphate of uranyl above 700° changes into ultraphosphate. Above 1000°C the latter splits off oxygen and changes into UP_2O_7 and $\text{U}(\text{PO}_3)_4$. The UP_2O_7 crystals are isostructural to the pyrophosphates of a number of tetravalent metals; the $\text{U}(\text{PO}_3)_4$ crystals belong to the $\text{Zr}(\text{PO}_3)_4\text{-I}$ type structure (Fig.13).

If the ions of alkali metals are present in the system, a number of non-isomorphous mixed phosphates of uranyl of the $MUO_2(PO_3)_3$ type are crystallized, where $M = Na, K, Rb, Cs$ (13,15,16,17). Thus, the UO_2^{2+} group in the phosphate systems behaves like bivalent metals, Sr, Cd, Ba, Pb, which are also prone to the formation of poly- and ultraphosphates.

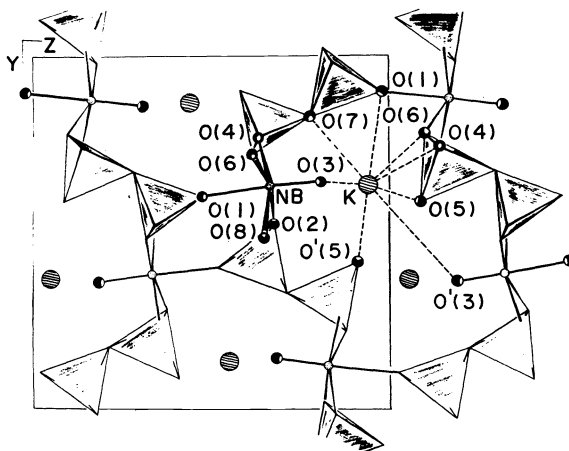


Fig.18. The projection of the $KNbP_2O_7$ structure on the (001) plane.

It should be noted that the linear or almost linear structure of the UO_2^{2+} group or the angular one of MoO_2^{2+} and WO_2^{2+} leads to anisomorphous changes in the isotype phosphates of molybdenum, tungsten and uranium in the total composition. Greater coordination possibilities for U^{VI} (4,5 and 6 atoms in the equatorial plane corresponding to a bipyramid compared with octahedral coordinated molybdenum are responsible for the large variety of structural types among uranyl phosphates. In the $UO_3-P_2O_5-(H_2O)$ system is also observed a more complicated interaction than in the $MoO_3-P_2O_5-(H_2O)$ system.

In 1955, Schulz in his studies of the $MO_3 - P_2O_5$ system showed that at $500^\circ C$ two types of compounds, $2MoO_3.P_2O_5$ and $MO_3.P_2O_5$, are formed. Based on the structural studies were established the formulas of the corresponding compounds: $MoOP_2O_7$ and $W_2O_3(P_2O_5)_2$ for the first type and $MoO_2(PO_3)_2$ and WOP_2O_7 for the second type. In the $MoO_3-P_2O_5-(H_2O)$ system the $MoO_2(PO_3)_2$ crystallizes easily at $220-500^\circ C$; the formation of molybdenyl does not take place at a higher degree of condensation of PO_4 -tetrahedra.

In accordance with our structural studies of condensed uranyl phosphates, pentagonal-bipyramidal coordination is preferred for U^{VI} (UO_2^{2+} for oxygen equals 5), and the uranyl group may be linear and symmetrical as well as slightly bent and asymmetrical. In natural minerals of uranyl phosphates the U-polyhedron has, as a rule, the shape of a tetragonal bipyramid with "unequal shoulder" of the uranyl group. The main reason of this, according to one of the interpretations, is that the "upper" and "lower" atoms of uranyl oxygen are unequally surrounded.

The uranyl orthophosphates ($P : UO_2 = 2$) have layered structures, unlike the cascade structures in its condensed phosphates ($P : UO = 3$). In the structures of the latter are clearly seen the laminated uranyl-phosphate fragments connected by $-P-O-P-$ bonds.

In crystal structures all the terminal atoms of oxygen of PO_4 -tetrahedrons can participate in the coordination of uranium or a part of them comes in contact with the alkali metal supplementing its coordination, or participates in the formation of H-bonds (in protonized phosphates).

With the increase in the size of the alkali metal atom the nature of the link of PO_4 -radicals varies, or the compounds different in composition and structure are crystallized. Thus, in the structure of $UO_2H(PO_3)_3$ (Fig.19) (18) and $NaUO_2(PO_3)_3$ (Fig.20) (19) are realized the phosphate chains, and for the larger cesium, hexametaphosphate cycles in $Cs_2(UO_2)_2P_6O_{18}$ (Fig.21) (16).

The structure of ultraphosphate, $(UO_2)_2P_6O_{18}$ (17) is characterized by the presence of an original highpolymer anion which is formed by 24-membered crimped phosphorous-oxygen cycles consisting of 14 "meta" (middle) and 10

"ultra" (bifurcation points) of three dimensional conjugated PO_4 -tetrahedra. A projection of the cycles conjugation on the (100) plane is shown in Fig. 22. The axonometric projection of the conjugation of two cycles in the direction of the (100) plane is shown in Fig.23. Apparently, the steric

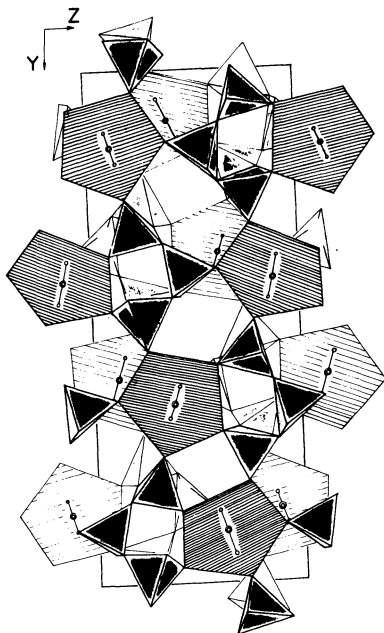


Fig.19. The projection of the $\text{UO}_2\text{H}(\text{PO}_3)_3$ structure on the (001) plane.

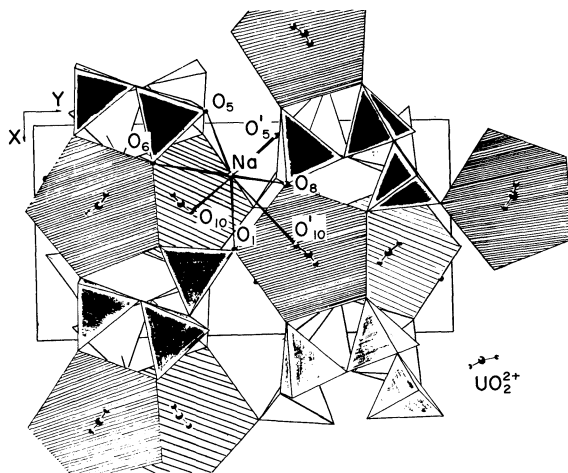


Fig.20. The projection of the $\text{NaUO}_2(\text{PO}_3)_3$ structure on the (001) plane.

factors and the nature of the coordination bond of UO_2^{2+} -ions play a significant role in the formation of such a spatial anion. It is necessary to point out that for the compounds $\text{M}_4\text{P}_2\text{O}_7$ ($\text{M} = \text{Ca}, \text{Mn}$) and $\text{M}_2\text{P}_5\text{O}_{17}$ ($\text{M} = \text{Sr}, \text{Cd}$) are typical the layered anion radicals of conjugated cycles. In the $\text{M}_4\text{P}_2\text{O}_7 - (\text{UO}_2)_2\text{P}_2\text{O}_7$ ($\text{M} = \text{Na}, \text{K}$) systems the mixed orthophosphates of uranyl and sodium (potassium), different in composition and structure, crystallize at 960°C : $\text{Na}_{6-x}(\text{UO}_2)_3(\text{H}_x\text{PO}_4)_3$, $x = 0.5$ (Fig.24) (20) and $\text{K}_4\text{UO}_2(\text{PO}_4)_2$ (Fig.25) (21). Both structures are laminated. In the first (sodium) salt are formed two layer uranyl-phosphate packets fastened by sodium cations which also fill the cavities both in the layers and within the

packets. Attention is drawn to the fact that uranium atoms have a different coordination number in the form of a tetragonal and pentagonal bipyramid. The presence of a proton in the structure was proved with the help of the

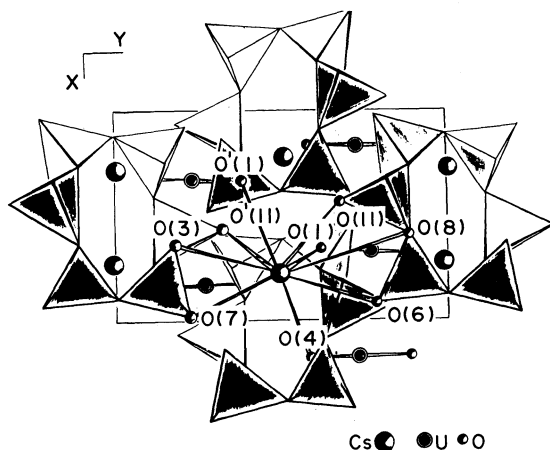


Fig. 21. The projection of the $\text{CsUO}_2(\text{PO}_3)_3$ structure on the (001) plane.

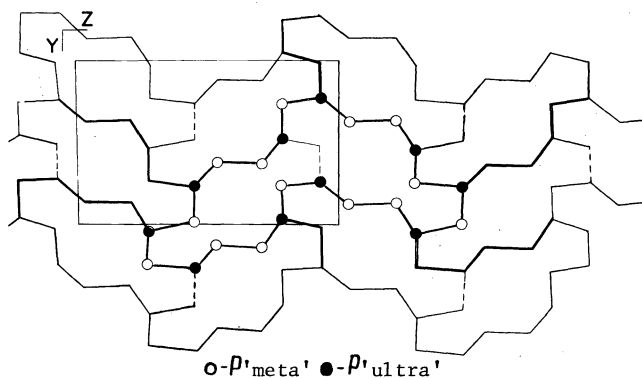


Fig. 22. The projection of the $(\text{P}_6\text{O}_{17})_3^{4-}$ anion on the (100).

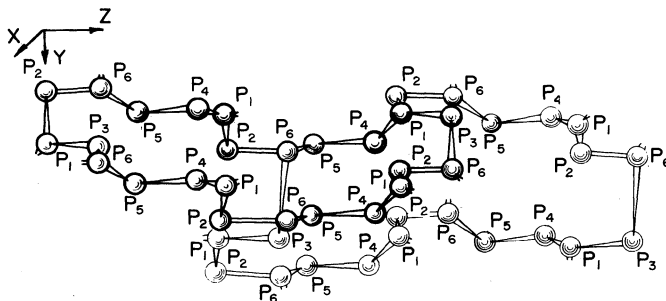


Fig. 23. The axonometric projection of the conjugation of two cycles in the direction of 100 .

Raman spectra and also from the loss of sodium in the more exact determination of the structure.

In the $K_4UO_2(PO_4)_2$ structure (Fig.25) the uranyl phosphate layers were formed by U-polyhedrons in the form of a tetragonal bipyramid and by the PO_4 -tetrahedrons. Two O atoms of each tetrahedron do not enter into the coordination of uranium, but supplement the coordination of potassium which fastens the layers in the structure (21).

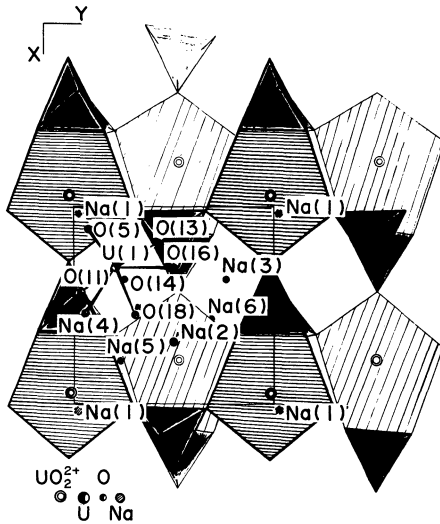


Fig.24. The projection of the $Na_{6-x}(UO_2)_3(H_xPO_4)(PO_4)_3$ structure on the (001) plane.

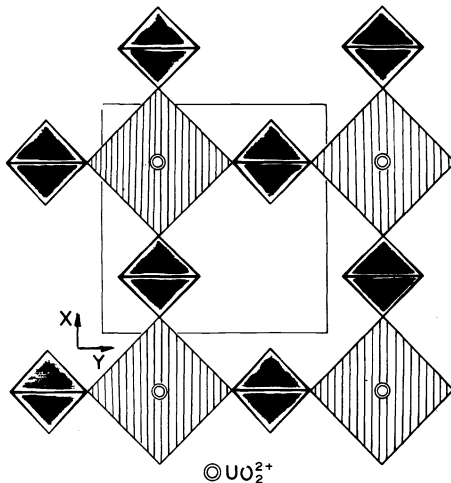


Fig.25. The projection of the $K_4UO_2(PO_4)_2$ structure on the (001) plane.

Now we sum up our views concerning general and particular features of the formation of phosphate compounds of V, Nb, Mo and U as follows. The general nature of the interaction of the oxides of Mo, Nb and V, which are prone to the formation of oxocations, results in the crystallization of tetraphosphates $MO_2P_4O_{13}$. The formation of poly- and ultraphosphates is not typical for them. Individual features show themselves up in the temperature range, where the crystallized compounds are stable. Thus, the oxotetraphosphate of vanadium crystallizes at 200°C, whereas the niobium and molybdenum ones crystallize only at 400°C. The differences in their crystal chemistry are also observed. The vanadium oxotetraphosphate is isostructural to Mo- and Nb-analogs. The phosphates of variable valency transition metals of the type V, Nb, Mo, U have certain general chemical and crystallochemical relationships with the phosphates of other cations of the corresponding

valency. In particular, the vanadium polyphosphate (III), $V(PO_3)_3$, (form C) only supplements the isostructural row of the phosphates of the trivalent Al, Sc, Cr, Fe, Mo, etc. The temperature conditions favourable for crystallization are maintained for all of them in analogous systems. In the vast isostructural row of phosphates of the MP_2O_7 type only vanadium (IV) has been represented by the polyphosphate, $VO(PO_3)_2$, whereas the pyrophosphates of tetravalent Mo, Nb and U fit into this row. They only supplement the row. The interaction of Mo, W and U in the $MO_3-P_2O_5-(H_2O)$ system has an individual nature for each element. Thus, the formation of $MO_2(PO_3)_2$ is typical for molybdenum in a sufficiently wide range of temperatures, but only in excess of P_2O_5 . Crystallization of $UO_2(PO_3)_2$ proceeds only when the ratio of the components is close to the stoichiometric one. The formation of the given type of compounds including W^{VI} is not typical in general.

As mentioned earlier, in the $UO_3-P_2O_5-(H_2O)$ system uranium behaves like bivalent metals (Sr, Ba, Cd, Pb), for which are typical the compounds with limiting polymerized shape of the phosphate anion - ultraphosphates. The formation of metaphosphates with alkali metals, typical for U^{VI} (uranyl), has not been ascertained neither for Mo^{VI} nor for W^{VI} . The analysis of the data on the chemistry and crystallochemistry of the phosphate compounds of transition metals makes it possible to conclude that the ratio between the metal and phosphorous, the degree of condensation of phosphate anion and the coordinated number of the metal together with other factors taking into account the dynamics of the process of formation of compounds in the $M_xO_y-P_2O_5-(H_2O)$ systems are interdependent. For a similar anion-composition of the melt of condensed acids, defined by its temperature, the formation of compounds with different degrees of condensation of PO_4 -tetrahedrons from ortho- to ultraphosphate is possible for different cations depending on the solubility of the separating out crystal phase.

On the other hand, in the presence of one or the other cation of a transition metal the degree of condensation of the phosphate anion to be associated with it may be varied by varying the temperature of the melt (or in other words, the amount of water present in it). A striking example of this is the successive crystallization of the phosphate compounds of uranyl from ortho- to ultraphosphates in the $UO_3-P_2O_5-(H_2O)$ system. This field was least studied before we undertook the investigations.

SOME DATA ON THE CHEMISTRY OF OXOPHOSPHATES OF RARE-EARTH METALS

At present the oxophosphates (phosphates of the metals for which the $M : P$ ratio is more than it should be for orthophosphates) are less studied. Mention may only be made of the investigations concerning the synthesis and X-ray study of oxophosphates of rare-earth elements (22,23) and the fusibility diagrams of the $MPO_4-M_2O_3$ ($M = Al, Cr, Y$) systems (24). Joint investigations into the synthesis, phase transition and the properties of oxophosphates of rare-earth elements are being carried out by us (V.P.Orlovskiy et al) and the laboratory of Refractory Materials CNRS (France). It is known that the latter on heating in air at high temperatures decompose with the liberation of P_2O_5 and with the formation of oxophosphates of the composition $xLn_2O_3 \cdot yP_2O_5$. By now has been recorded the formation of four types of oxophosphates of ligands with the ratio $x : y = 7 : 3, 3 : 1, 4 : 1, 6 : 1$ (22, 23).

The sun furnaces described in (25) and the method of direct analysis in a sun furnace (26) were employed for melting $LnPO_4$. Identification of the obtained substances was carried out by the X-ray analysis and the X-ray diffraction methods (27). The use of these methods enabled us to obtain data on melting and solidification temperatures of ortho- and oxophosphates of rare-earth elements, and also to control the variations taking place with time under isothermal conditions. The kinetic studies made it possible to reveal the basic effect of the nature of rare-earth elements on the thermal decomposition process of the corresponding ortho- and oxophosphates (28). For the purpose of establishing a correlation between the structure of the nearest enclosing of the rare-earth ion in the phosphates of different composition and the spectral-luminescent properties, we have undertaken the studies of vibrational and luminescent spectra of oxophosphates, Nd_3PO_7 , Sm_3PO_7 , Eu_3PO_7 , Gd_3PO_7 , and also of the activated oxyphosphates $(La, Nd)_3PO_7$, $(Gd, Nd)_3PO_7$, $(Er, Nd)_3PO_7$.

On comparing the general type IR-absorption spectra of ortho- and oxyphosphates of rare-earth elements an analogy is followed in the range of the frequencies of inherent vibrations of phosphate groups: the groups of bands in the ranges 950-1120 and 500-650 cm^{-1} are observed which correspond mostly to the valent and deformation vibrations of PO_4^{3-} , respectively. But there are significant differences in the spectra of ortho- and oxyphos-

phates of rare-earth elements. For the oxyphosphates are typical wide multiplet bands in the range $300-550\text{ cm}^{-1}$ which are observed in the spectra of Ln_2O_3 , while in the spectra of corresponding orthophosphates no bands are observed in this range. Apparently, these bands correspond chiefly to the valent vibrations of the $-\text{M}-\text{O}-\text{M}-$ bridge bands formed by "additional" atoms of oxygen present in oxyphosphates (29,30). Certain conclusions may be drawn from the results of preliminary investigations of spectroscopic parameters of neodymium oxyphosphates. In these compounds, apparently, one type of luminescence centres are formed. The life time of the metastable state of $4F_{3/2}$ neodymium in oxyphosphates is significantly less than in the corresponding meta- and ultraphosphates. Also the concentration of Nd in oxyphosphates is several times more. A strong intermolecular interaction at the expense of Nd-O-Nd bridge bonds increases the probability of radiationless transitions. This, apparently, is the main cause of Nd luminescence in oxyphosphates.

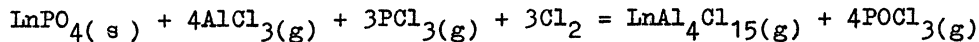
METHOD OF CHEMICAL TRANSPORT REACTIONS

The chemical transport reaction affects the formation of crystallochemical, structural and morphological properties of a crystal. The phase stability of the reaction mixture, as it is shown by us in (31), is one of the conditions that ensure the growth of perfect crystals and films by the method of chemical transport reactions. The phase stability of the reaction mixture may get disturbed at relatively high pressures of one of the gaseous components, in particular of the reaction substance, - the carrier. Thus the condensation of one of the components, for example of the lanthanide trichloride, may change the direction of transfer of LnPO_4 in the reaction



and may also suppress crystallization of the phosphate of rare-earth elements.

The linking of the condensed lanthanide trichlorides in the gaseous complexes $\text{LnAl}_3\text{Cl}_{12}$ and $\text{LnAl}_4\text{Cl}_{25}$, the existence of which has been proved by the spectroscopy and mass spectroscopy methods (32,33), enables the reaction (1) to be carried in the desired direction with a good yield :



The application of complexing principles to the systems containing liquid or solid metal halide enables the crystallization of solid substances like LnPO_4 to be carried out at much lower temperatures (at $400 - 500^\circ\text{C}$) than in the case of gaseous metal halides.

THERMOPHOSPHATE PAINTING

Probably there is no need to pay any stress in this report on the practical significance of inorganic phosphate compounds. They are used in engineering and construction to such an extent that it would be quite justified to mention about the industry supplying necessary phosphate materials. The basic component of these materials is the so called phosphate adhesive used in the form of acid phosphates of various metals, phosphoric acid or its condensed forms. All of them when mixed with the oxides of polyvalent metals ("fillers") form self-setting masses.

At present are available many acid metallophosphate adhesives (34), but out of them the aluminium dihydrophosphate (the grandfather of phosphate adhesives of this type) is extensively employed, and the acid alumochrophosphate is more stable under conditions of storage.

The distinctive property of hardened phosphate masses resides in that they after an appropriate thermal treatment (between 100 and 500°C depending on the kind of the adhesive) becomes very stable and moisture resistant. The number of possible combinations of composition and the variation of conditions (heating temperature, degree of dispersion and the nature of the filler, acidity, the ratio between the amounts of components to be mixed, etc.) is so large that they cannot be covered in one paper. In the present report we discuss the use of the mentioned systems of hardening which are used in fine arts. This new trend in the art known as "thermophosphate pictorial art" is being developed in the USSR by O.B.Pavlov for the last more than ten years. He has developed mineral as well as phosphate paints in three forms : thermophosphate paints, powder colors, pastel and artistic

colors. The palette of all these colors consists of 21 basic, most "rich" tints, and a pair of grades of each of them. Thus, the thermophosphate pastel is represented by 63 crayons.

The procedure of thermophosphate painting is very simple. The base material (asbestos-cement sheetings, fibre, cardboard, glass, ceramics, metal) is first coated with phosphate which is fixed by heating, then with phosphate colors (by a brush or by spraying). Thereafter, the color layer is treated (for example, pulverized) with a fixative containing phosphate adhesive. Finally it is heated for 2-3 minutes at 200-400°C using an electric shield (for large size paintings), or an ordinary gas burner or other modes of heating. The painting so obtained is moisture- and heat-proof and does not call for special conditions necessary for prolonged storage.

At present we have gained some experience in the "cold technology" without thermal treatment of ready artistic paintings.

Certain details concerning thermographic painting are available in the works of O.P.Pavlov (35,36).

In summary it may be said that the possibilities of theoretical and practical development of the chemistry of inorganic compounds of phosphorous (phosphates) are so wide that further investigations in this branch of inorganic chemistry and inorganic meteriology must be considered to be of current interest.

REFERENCES

1. I.V.Tananaev, The Formation Synthesis and some Properties of Phosphate Composition, XXIVth International Congress of Pure and Applied Chemistry, vol.3, Butterworths, London (1974).
2. I.V.Tananaev, Some Aspects of the Chemistry of Phosphates and their Practical Application, Problems of Chemistry and Chemical Technology, Nauka, Moscow (1977).
3. G.V.Rodicheva and N.M.Romanova, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials", XV, N6, 963 (1979).
4. Zh.A.Ezhova, I.V.Tananaev and E.M.Koval, Journ. Inorganic Chemistry (Russian), XXIII, N 11, 2987 (1978).
5. Zh.A.Ezhova, I.V.Tananaev, L.N.Zorina, E.M.Koval and N.P.Soshchin, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials", XIV, N 11, 2067 (1978).
6. F.Warschaner, Z. anorg. chem., B 36, 158 (1903).
7. E.Thilo and J.Grunze, Z. anorg. chem., B 290, 209 (1957).
8. D.Yvoir, Bull. Soc. Chim. France, 1224, 1237 (1962).
9. P.Remy and A.Bulle, Bull. Soc. Chim. France, 2287 (1972).
10. N.N.Chudinova, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials", XV, N 6, 933, 936 (1979).
11. Yu.E.Gorbunova, V.V.Ilyukhin, V.G.Kuznetsov, A.V.Lavrov and S.A.Linde, DAN AN SSSR, 228, N 6, 1339 (1976); 234, N 3, 628 (1977).
12. Yu.E.Gorbunova et al, DAN AN SSSR, 25, N 3, 584 (1979).
13. Kh.Zeebot, G.Ladvig et al, Ukr. Khim. Zhurnal, 43, N 8, 842 (1977).
14. G.Ladwig, Z. anorg. chem., (in press).
15. S.A.Linde, Yu.E.Gorbunova, A.V.Lavrov and V.G.Kuznetsov, DAN SSSR, 224, N 6, 1411 (1979).
16. S.A.Linde et al, DAN SSSR, 241, N 5, 1083 (1978).
17. Yu.E.Gorbunova, V.V.Ilyukhin, A.V.Lavrov, S.A.Linde and I.V.Tananaev, "Physical Methods of Investigation", Nauka, Moscow (in press).
18. S.A.Linde, Yu.E.Gorbunova, A.V.Lavrov and V.G.Kuznetsov, DAN SSSR, 230, N 6, 1376 (1976).
19. S.A.Linde, Yu.E.Gorbunova, A.V.Lavrov and V.G.Kuznetsov, DAN SSSR, 235, N 2 (1977).
20. Yu.E.Gorbunova, S.A.Linde, A.V.Lavrov and A.B.Pobedina, DAN SSSR, (1979) (in press).
21. S.A.Linde, Yu.E.Gorbunova, A.V.Lavrov, Zh. Inorg. Chem., (1979) (in press).
22. J.J.Serra, J.Cotures and A.Rounet, "High Temperatures - High Press", 8, 337 (1976).
23. J.J.Serra, Synthese et Identification de Nouvelles Familles des Composes les Oxyphosphates de Lanthanides, perpignen (1977).
24. I.V.Tananaev, E.V.Maksimchuk, Yu.G.Bushuev and S.A.Shestov, Trans. of Ac. of Sci. of USSR, series "Inorg. Materials", XIV, 719 (1978).
25. M.Foex, Bull. Soc. Chim. France, 137 (1962).
26. M.Foex, Rev. Inst. High. Temper. et Refract., 3, 309 (1966).
27. T.M.Badie, M.Faure and J.P.Traverse, Se Colloque sur les Methodes Analytiques Rayonnement x, Nice (1974).
28. J.J.Serra, A.Rounet, K.Allaf and V.P.Orlovskiy, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials" (in press).

29. V.P.Orlovskiy et al, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials", XV, 975 (1979).
30. Zh.A.Ezhova, Yu.I.Krasilov, V.P.Orlovskiy and A.V.Potemkin, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials", XIV, 2036 (1978).
31. V.P.Orlovskiy et al, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials", XIII, 1484 (1977).
32. M.A.Dye and D.M.Gruen, J. Amer. Chem. Soc., 91, 2229 (1969).
33. I.L.Agafonov, V.P.Orlovskiy et al, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials" (in press).
34. V.A.Kopeikin, A.P.Petrova, I.L.Rashkova, "Materials Based on Metallophosphates", Moscow (1976).
35. O.B.Pavlov, "Voprosy khudozhestvennogo obrazovaniya", Ibid., 14 (1975).
36. O.B.Pavlov, Trans. of Ac. of Sci. of USSR, series "Inorganic Materials", XV, N 6, 985 (1979).