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Uranium Phosphates

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The methods of preparation, stability in solution and in the solid state, and composition of the crystalline hydrates of uranyl and uranium(IV) orthophosphates and condensed phosphates have been reviewed. The structures of these compounds have been discussed; they are three-dimensional polymers with a uranyl-phosphate framework.
The polymerisation of the phosphate anion on thermal decomposition has been discussed. Condensed uranyl polyphosphates are unstable when kept, and are capable of undergoing dehydration, the extent of which increases with increase in the length of the phosphate chain and increase in the uranium concentration.
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I. INTRODUCTION

There is now a large amount of experimental and theoretical data on phosphates. The wide variety of these compounds is due to the high reactivity of the PO_4^{3-} group, and also the possibility of various combinations of phosphates. Phosphates have been the subject of a number of monographs[1-3] and reviews[4-6], in which the preparation, structural analysis, and spectral and thermal properties have been summarised. There are few publications, however, which systematise data on the phosphates of one element or several elements with similar properties, including orthophosphates and condensed phosphates (such as, for example, that devoted to the phosphates of quadrivalent metals[6]).

Extensive data on uranium phosphates have now accumulated, and require reviewing. The uranium compounds are mainly uranyl complexes containing the UO_2^{2+} group, of the oxo-group type MO_2^{2+} and MO^{2+}, which show a number of common structural and physicochemical properties.

In the present review, an attempt has been made to systematise available data on uranium phosphates. This has been done before, but the studies were incomplete. For example, in Ref.7, uranyl phosphates were examined from the viewpoint of the stability of their crystalline hydrates under isobaric conditions, and in Ref.8 the crystal chemistry of uranium minerals, including phosphorus-containing minerals, was discussed.

In the number of forms and variety of minerals, the class of uranyl phosphates is fairly representative[8]. Of 200 known minerals, it includes about 20 types, which can be divided into three crystal-chemical groups, on the basis of the $UO_2:PO_4$ ratio.

I. $UO_2:PO_4 = 1:1$ — autenite–meta-autenite or uranium phosphate micas.

II. $UO_2:PO_4 > 1$ — phosphuranylite.

III. $UO_2:PO_4 < 1$ — parsonsite.

The first group of minerals is made up of double uranyl phosphates with the alkali and alkaline earth metals, Cu, Mn,

Al, Fe, and hydrogen. The crystals of the minerals of the first group have a layer structure. The structure of meta-autenite $Ca[(UO_2)_2(PO_4)_2].6H_2O$ was studied in Ref.9, and later confirmed in Ref.10.

The second group includes minerals in which the ratio $UO_2:PO_4$ is most frequently 3:2 or 4:3. The crystal-chemical formulae of the minerals of this group have not been finally established, with the exception of dumontite $Ca(UO_2)_2(PO_4)_2.10H_2O$ and phosphuranylite $Pb(UO_2)_4(PO_4)_2(OH)_2.3H_2O$.[11] This group of minerals probably also includes the recently described phuralumite $Al_2(OH)_2(PO_4)_2(UO_2)_3(OH)_6.10H_2O$ and upalite $Al(UO_2)_3(PO_4)_2(OH)_3$,[12,13] whose structures are analogous to that of dumontite, and consist of $[(OH)_2(PO_4)_2.(UO_2)_3]_n$ layers. The crystal-chemical structures of the minerals of the parsonsite group have not yet been established.

Although considerable progress has been made in the crystal chemistry of uranium compounds, a number of problems relating to phosphorus-containing minerals have not yet been resolved. These include the question of the form in which uranium is present in the minerals, how to ensure the reliable determination of the $UO_2:PO_4$ ratio (errors in the determination of this ratio often lead to incorrect descriptions of chemical formulae), and how to systematise the nomenclature of the compounds. Since the study of minerals is often made difficult by such factors as the presence of impurities, the isomorphous replacement of elements, a low concentration of uranium, etc., the study of synthetic analogues of the natural compounds may help considerably in the determination of the degree of hydration and the form in which uranium is present in the compounds, and in establishing the regular features of the binding of the metal in different groups of atoms inside and outside the coordination sphere.

II. URANIUM ORTHOPHOSPHATES

1. Behaviour in Solution

The preparation of uranyl orthophosphates was the subject of lively discussion for a long time (until the nineteen-sixties). Some authors believed that the normal phosphate could not be isolated[14], and others that the dihydrogen phosphate could not be obtained[15]. The preparation of the compounds $P_2O_5.2UO_3.H_2O$, $P_2O_5.3UO_3$, and $P_2O_5.UO_3.2H_2O$, corresponding to the monohydrogen phosphate, the normal phosphate, and the dihydrogen phosphate, was reported[16]. It was noted that the composition of the precipitates is influenced by the $UO_3:P_2O_5$ ratio in the solution. The conditions of formation of uranium orthophosphate were studied most systematically by Schreyer and Baes[17,18], who examined the solubility of uranyl orthophosphates in phosphoric and perchloric acid solutions over a wide concentration range (0.001–15 M). They identified three stable phases at the following phosphoric acid concentrations:

$$[(UO_2)_3(PO_4)_2\cdot 6H_2O] < 0.014\,[PO_4^{3-}]\ M$$
$$[UO_2HPO_4\cdot 4H_2O] = (0.014 \div 6.1)\,[PO_4^{3-}]\ M$$
$$[UO_2(H_2PO_4)_2\cdot 3H_2O] > 6.1\,[PO_4^{3-}]\ M\ .$$

The dependence of the solubility of $UO_2HPO_4.4H_2O$ on the acid and salt concentrations was studied[18]. The existence in solution of the complexes $UO_2H_2PO_4^+$ and $UO_2H_3PO_4^{2+}$ was postulated.

Studies in solutions of constant ionic strength[19] confirmed the existence of the first complex, with formation constant 15.5, and also of $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)_2.H_3PO_4$ at PO_4^{3-} concentrations of ~ 1 M and 10 M respectively; their formation constants are 21.8 and 10.2 respectively. The solution of $UO_2HPO_4.4H_2O$ in perchloric acid (unlike that in phosphoric acid) is incongruent, depends on the surface area of the substance, and takes place via the formation of the sparingly soluble normal orthophosphate[20].

Pavkovic and co-workers[21,22] returned to the question of the formation and stability of orthophosphates in phosphoric acid solutions in a study of the precipitation and dissociation of complexes in aqueous solutions of phosphoric acid (2×10^{-6}–6 M) and uranyl nitrate (3×10^{6}–0.5 M). In an excess of the latter, the only product is the normal orthophosphate, which is present in equilibrium with solutions with a total PO_4^{3-} concentration of 3×10^{-3} M or less. Prolonged treatment of the normal orthophosphate (more than 24 d) converts it into the monohydrogen phosphate; the PO_4^{3-} concentration should be greater than 1.5×10^{-6} M. An important feature of this work[21,22] was the determination of the equilibrium conditions for the formation of the normal orthophosphate and the monohydrogen orthophosphate.

Comparison of the data of Refs.17 and 21 shows that they differ considerably at low and high phosphoric acid concentrations, and agree in the range 2×10^{-2}–2 M. The conversion of hydrogen phosphates into the normal phosphate is a common phenomenon, whereas the reverse process is comparatively rare. This characteristic feature of uranyl orthophosphates was noted by other workers[23], who converted the natural analogue trogerite $(UO_2)_3(PO_4)_2$ into the monohydrogen orthophosphate by keeping it in the equilibrium solution for six months. The normal phosphate is stable in air, whereas the monohydrogen phosphate is converted into the normal phosphate[16]. The compound $UO_2HPO_4.4H_2O$ is also stable when kept, and no changes were detected visually or by physicochemical methods in a specimen kept for 5 years. The best proof of its stability is the fact that it exists in nature as the mineral "hydrogen meta-autenite".

The synthesis from aqueous solutions of the so-called double uranyl phosphates containing other metal cations in addition to UO_2^{2+} is most complicated. A number of Soviet workers[24–26] have shown that normal and double phosphates may be formed under these conditions. The composition of the products depends on the concentration of the original solutions and the pH of the medium.

An attempt has been made to determine the relationship between the chemistry of the precipitation of the acidic, normal, and double orthophosphates[26,27]. A study of the conditions of precipitation of $NH_4UO_2PO_4$[26] showed that the reaction products may be normal ammonium orthophosphate and ammonium phosphatouranate, depending on the U:P ratio and the pH of the medium. A mechanism was proposed[26] for the formation of the phosphatouranate, including several stages. The uranyl ion is regarded primarily as the hydrolysed species $UO_2(OH)^+$,[28] so that formation of the normal orthophosphate is possible:

$$2UO_2(OH)^+ + UO_2^{2+} + 2HPO_4^{2-} + 4H_2O \rightarrow (UO_2)_3(PO_4)_2\cdot 6H_2O$$

$(UO_2)_3(PO_4)_2$ then reacts with the ammonium ion, giving a complex ammonium phosphatouranate

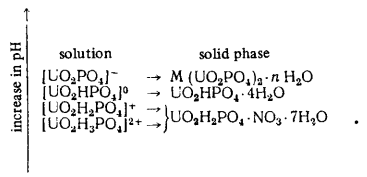
$$2(UO_2)_3(PO_4)_2\cdot 6H_2O + 2NH_4^+ \rightarrow (NH_4)_2(UO_2)_5(PO_4)_4\cdot 6H_2O + UO_2^{2+} + 6H_2O\ .$$

In an excess of ammonium phosphate, it is converted into $NH_4UO_2PO_4$:

$$(NH_4)_2(UO_2)_5(PO_4)_4\cdot 6H_2O + 3NH_4^+ + HPO_4^{2-} + 9H_2O \rightarrow 5NH_4UO_2PO_4\cdot 3H_2O\ .$$

It is believed[26] that the same reactions take place when uranyl salts are titrated with different phosphates (Na, K, Ca, etc.). It is suggested that the $(UO_2)_5(PO_4)_4^{2-}$ group is very stable, and forms part of a number of minerals. For a ratio U:P = 1:1, the following pH dependence of the stability

of the complexes was proposed:



Analysis of the data in Ref.26 reveals a number of discrepancies. First of all, it is not clear how the formation of ammonium phosphatouranate can be preceded by the formation of two compounds — $(UO_2)_3(PO_4)_2$, which is the least soluble uranyl orthophosphate (Table 1), and also a product containing the $(UO_2)_5(PO_4)_4^{2-}$ group, assumed[26] to be extremely stable—which are converted into ammonium phosphatouranate merely by titration. The statement[26] that $(UO_2)_5(PO_4)_4^{2-}$ is present in various minerals, in particular phosphuranylite, was not confirmed by later structural studies[11]. The dependence of the composition of the reaction products on the pH of the medium was also noted in Ref.29. Weigel and Hoffmann[7] regarded all double phosphates and hence minerals of uranium(VI) as salts of $HUO_2PO_4.4H_2O$ in which hydrogen is replaced by alkali and alkaline earth metals according to the schemes:

$$HUO_2PO_4 + M^+ \rightarrow MUO_2PO_4 + H^+$$
$$2HUO_2PO_4 + M^{2+} \rightarrow M(UO_2PO_4)_2 + 2H^+ \quad .$$

Table 1. Solubility products (SP) of uranyl orthophosphates.

Phosphate	SP	Refs.	Phosphate	SP	Refs.
UO_2HPO_4	$3{,}5 \cdot 10^{-12}$	[32]	$NH_4UO_2PO_4$	$4{,}36 \cdot 10^{-27}$	[33]
UO_2HPO_4	$2{,}14 \cdot 10^{-11}$	[33]	$NH_4UO_2PO_4$	$3{,}6 \cdot 10^{-26}$	[29]
UO_2HPO_4	$10^{-12{,}0 \pm 0{,}1}$	[30]	$(UO_2)_3(PO_4)_2$	$10^{-49{,}7 \pm 0{,}5}$	[30]
$LiUO_2PO_4$	$2{,}4 \cdot 10^{-26}$	[38]	$(UO_2)_3(PO_4)_2$	$8{,}2 \cdot 10^{-50}$	[34]
$NaUO_2PO_4$	$10^{-24{,}21 \pm 0{,}07}$	[30]	$(UO_2)_3(PO_4)_2$	$4{,}73 \cdot 10^{-47}$	[35]
$NaUO_2PO_4$	$6{,}4 \cdot 10^{-24}$	[38]	$Ca(UO_2PO_4)_2 \cdot 6H_2O$	$10^{-47{,}28 \pm 0{,}20}$	[31]
KUO_2PO_4	$10^{-25{,}5 \pm 0{,}1}$	[30]	$Sr(UO_2PO_4)_2 \cdot 7{,}5\ H_2O$	$10^{-48{,}30 \pm 0{,}15}$	[31]
KUO_2PO_4	$8 \cdot 10^{-24}$	[38]	$Ba(UO_2PO_4)_2 \cdot 6H_2O$	$10^{-49{,}62 \pm 0{,}15}$	[31]
KUO_2PO_4	$7{,}76 \cdot 10^{-2{,}}$	[33]	$Cu(UO_2PO_4)_2 \cdot 9H_2O$	$10^{-52{,}10 \pm 0{,}15}$	[31]
$RbUO_2PO_4$	$1 \cdot 10^{-27}$	[38]	$Zn(UO_2PO_4)_2 \cdot 7{,}8\ H_2O$	$10^{-46{,}77 \pm 0{,}35}$	[31]
$RbUO_2PO_4$	$10^{-25{,}72 \pm 0{,}15}$	[30]	$Co(UO_2PO_4)_2 \cdot 7H_2O$	$10^{-46{,}80 \pm 0{,}20}$	[31]
$CsUO_2PO_4$	$10^{-25{,}31 \pm 0{,}20}$	[30]	$Ni(UO_2PO_4)_2 \cdot 10H_2O$	$10^{-46{,}86 \pm 0{,}25}$	[31]

The difficulties of obtaining double uranyl phosphates were avoided[29] by treating powdered uranyl monohydrogen phosphate with 4 *N* solutions of the corresponding metal chlorides.

The conditions of preparation and solubility of uranyl orthophosphates have been studied by a number of authors[30-34,36-38]. Data on the solubility of uranyl orthophosphates are summarised in Table 1. The solubility of double uranyl phosphates with the alkali metals decreases in the order Na > Cs > K > Rb > NH_4, and that for bivalent metals in the order Zn ≅ Co ≅ Ni > Ca > Sr > Ba ≧ Cu.

2. Crystalline Hydrates of Uranyl Orthophosphates

In solubility studies, the composition of the crystalline hydrates is generally not discussed, and in the study of the physicochemical properties of solid specimens, the data obtained by different authors on the water concentration do not agree. Thus for the normal orthophosphate, the formation of $(UO_2)_3(PO_4)_2.6H_2O$,[17] and heptahydrate[16], and the trihydrate[24] has been reported. Methods for synthesising the hexa- and tetrahydrates have also been proposed[17,39]. For the monohydrogen orthophosphate, there is more agreement between different authors, who assign to it the composition $UO_2HPO_4.4H_2O$ (except for a report of the hydrate $UO_2HPO_4.2.5H_2O$[40]). The compositions of the crystalline hydrates of double uranyl phosphates differ considerably. The stability ranges of the crystalline hydrates with respect to isobaric thermal decomposition with a constant partial pressure of water vapour above the crystalline hydrates have been determined[7] (Table 2).

Table 2. Compositions of the crystalline hydrates of uranyl orthophosphates and the temperature range of their stability at a water vapour pressure of 92.5 ± 0.5 mmHg[7].

Original orthophosphate	Number of moles of water					
	6	4	3	2	1	0
$UO_2HPO_4 \cdot 4H_2O$	—	20—50	—	60—80	90—160	>170
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	—	20—120	—	—	160—220	>300
$LiUO_2PO_4 \cdot 4H_2O$	—	20—70	80—120	120—170	—	>190
$NaUO_2PO_4 \cdot 3H_2O$	—	—	20—70	—	90—160	>170
$KUO_2PO_4 \cdot 3H_2O$	—	—	20—70	—	(0,5 H_2O; 80—150)	>100
$NH_4UO_2PO_4 \cdot 3H_2O$	—	—	20—80	—	(0,5 H_2O; 130—140)	>140
$Mg(UO_2PO_4)_2 \cdot 9H_2O$	100	110	—	120—170	180—200	>230
$Ca(UO_2PO_4)_2 \cdot 10H_2O$	—	110	—	140—200	—	>240
$Sr(UO_2PO_4)_2 \cdot 8H_2O$	75—105	—	—	110—190	—	>200
$Ba(UO_2PO_4)_2 \cdot 8H_2O$	~60—70	—	—	100—180	—	>200

The processes of thermal dehydration of uranyl orthophosphates, in spite of differences in the data reported by different authors, can be examined from the simplified viewpoint of the formation of intermediate hydrates and anhydrous salts, and differ only in the stepwise character of the removal of water and the temperature ranges. This is confirmed by data on the dehydration of the monohydrogen orthophosphate. It has been reported[16] that $UO_2HPO_4.2H_2O$ is formed when the tetrahydrate is heated, and is stable up to 110°; the anhydrous phosphate exists in the range 150—500°. In Ref.41, the loss of 3.5 moles of water was observed in the range 30—180°, and complete dehydration at 230—250°. In Ref.42, three moles of water were removed up to 60°, to give the monohydrate, stable in the range 60—120°. In Ref.40, it is claimed that all the water of crystallisation is lost at 170°. Finally, in Ref.43 it is reported that 2.5 moles of water are lost at 60—70°, and all the water of crystallisation at ~220°. Published data on the dehydration of the normal and double phosphates are equally contradictory[16,29,39,44].

3. Uranium(IV) Orthophosphates

The synthesis of uranium(IV) phosphates has been described in detail[6], and these compounds will be discussed only briefly.

Attempts to prepare uranium(IV) orthophosphates were reported in the early nineteen-hundreds. Colani[45] described orthophosphates to which he assigned the compositions $U(HPO_4)_2.5H_2O$, $U_3(PO_4)_4.UCl_4.HCl$, and $M_2U(PO_4)_2$ (M = Na, K). They were obtained by fusing UO_2 with metaphosphates or pyrophosphates in molten alkali metal chlorides.

The synthesis and solubility of the monohydrogen orthophosphate were later studied by Schreyer[46], who isolated the gelatinous compound $U(HPO_4)_2.4H_2O$. When the compound was kept in equilibrium with phosphoric acid, it was converted into the hexahydrate, and at an H_3PO_4 concentration greater than 9.8 M into $U(HPO_4)_2.H_3PO_4.H_2O$. Blumenthal[47] reported the preparation of the hydrates $U(HPO_4)_2.2H_2O$ and $U(HPO_4)_2.5H_2O$. Moskvin and co-workers[48] studied the solubility of $U(HPO_4)_2.4H_2O$ in phosphoric acid solution, and found that it passes through a maximum due to the formation of the undissociated form of $U(HPO_4)_2$. The stability constants of the complexes $U(HPO_4)^{2+}$, $U(HPO_4)_2$, $U(HPO_4)_3^{2-}$, and $U(HPO_4)_4^{4-}$ were determined; lg β = 12.0, 22.0, 30.6, and 38.6 respectively.

The problem of the synthesis of the normal orthophosphate has not been resolved. It was noted above that in Ref.45 the normal phosphate could not be obtained by the reaction of solutions of UCl_4 and trisodium phosphate, whereas in Refs.49 and 50 it is stated that this compound is formed and is stable at 800°, and in Ref.51 it was found to be stable to 900–1200°. In Ref.39 it was shown that the normal orthophosphate does not exist at 600°, and the product, which has the same U:P ratio, is a mixture of the pyrophosphate and uranium dioxide.

Uranium orthophosphates with the general formula $MU_2(PO_4)_3$ (M = Na, K) are said to be obtained by the reaction of the uranium oxides UO_2 and UO_3 with zirconium pyrophosphate is molten sodium and sodium chlorides, and also by the reaction of the melts with uranium monohydrogen phosphate in an inert atmosphere according to the scheme[52]:

$$U(HPO_4)_2 + NaCl \xrightarrow{870°} NaU_2(PO_4)_3$$
$$U(HPO_4)_2 + KCl \xrightarrow{790°} KU_2(PO_4)_3 \quad .$$

4. Conditions of Preparation

In Ref.53, the phosphate $UO_2HPO_4.4H_2O$ was synthesised by the method of Schreyer and Baes[17], and had the composition given by this formula. The ranges of stability of its crystalline hydrated formed at room temperature were determined by keeping the specimens under equilibrium conditions at different saturated water vapour pressures. The tetrahydrate is stable down to pressures of 0.15 mmHg, the monohydrate exists at lower pressures, and the hydrates are interconvertible. The products with two and three water molecules are mixtures of the mono- and tetrahydrates. Thus the existence of the hydrate $UO_2HPO_4.2.5H_2O$[40] appears unlikely. A noteworthy feature of the interconversion of the crystalline hydrates is the rearrangement of the crystal structure, which involves the intermediate formation of an amorphous product which subsequently crystallises to give the new phase. This effect was detected by X-ray diffraction and thermal analysis, which showed the appearance of an exothermic effect on the DTA curve at 70° during the dehydration of the monohydrogen orthophosphate[53].

In Ref.54, the normal orthophosphate was obtained by various methods[17,24,39], including hydrothermal synthesis (Table 3). In the latter, an equimolar mixture of 0.1 M solutions of uranyl nitrates or stoichiometric quantities of UO_3 and 0.1 M H_3PO_4[54] were placed in ampoules, sealed, and kept at 150° for 3–4 d. The X-ray diffraction patterns of the products obtained under hydrothermal conditions and by hydrolysis of uranyl monohydrogen orthophosphate coincide, but do not agree with the data of Ref.55. The reaction of uranyl nitrate with Na_2HPO_4[24] gave a precipitate with the composition $NaUO_2PO_4.3H_2O$ (Table 3). Dilute (0.01 M) solutions of uranyl nitrate and phosphoric acid give the amorphous normal orthophosphate, which binds ~ 6 moles of water; it is stable in air, but in a dry atmosphere it gradually loses water to give the tetrahydrate. Crystalline $(UO_2)_3(PO_4)_2.4H_2O$ is stable at room temperature at different water vapour pressures in the range 0–12 mmHg.

Table 3. Compositions of uranyl orthophosphates obtained by different methods.

No.	Synthesis conditions	Concentration of the components in the solid phase, %				Composition
		U	P_2O_5	Na	H_2O	
1	0.001 M $UO_2(NO_3)_2$ and H_3PO_4; 25 °C (Ref.17)	63.4	13.2	—	9.7	$(UO_2)_3(PO_4)_2 \cdot 6H_2O$
2	Ditto (Ref.17)	62.4	12.5	—	6.9	$(UO_2)_3(PO_4)_2 \cdot 6,3H_2O$
3	Hydrothermal synthesis, 0.1 M $UO_2(NO_3)_2$ and H_3PO_4; 150 °C, 72 h (Ref.54)	66.8	13.4	—	6.9	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$
4	Hydrothermal synthesis, 0.1 M UO_3 and H_3PO_4 (U:P = 3:2); 150 °C, 72 h (Ref.54)	65.9	13.6	—	6.5	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$
5	Hydrolysis of $UO_2HPO_4.4H_2O$ by water; 100 °C, 2 h (Ref.39)	67.1	13.7	—	6.8	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$
6	0.001 M $UO_2(NO_3)_2$ and 0.015 M Na_2HPO_4; 25 °C (Ref.24)	53.4	15.6	4.0	12.5	$NaUO_2PO_4 \cdot 3H_2O$
7	0.01 M $UO_2(NO_3)_2$ and 0.15 M Na_2HPO_4; 25 °C (ref.24)	52.9	16.3	4.2	12.9	$NaUO_2PO_4 \cdot 3H_2O$
8	Hydrolysis of $NH_4UO_2PO_4.3H_2O$ by boiling with 0.8 M HNO_3 (Ref.17)	54.2	16.9	—	12.3	$NH_4UO_2PO_4 \cdot 3H_2O$

To obtain double uranyl phosphates, it is necessary to maintain strictly definite pH values in the solutions. Thus ammonium uranyl phosphate $NH_4UO_2PO_4.3H_2O$ can be obtained only at pH 4.6–4.8 from solutions of uranyl acetate and diammonium hydrogen phosphate[56]. In Ref.57 it was found that in the NH_3–UO_2–H_3PO_4–H_2O system there exist two uranyl phosphates, containing 3.8% and 8.8% NH_3 respectively.

The compound $U(HPO_4)_2.4H_2O$ obtained by the method of Ref.48 is a gelatinous product which does not crystallise on prolonged standing (20–30 d) in the equilibrium solutions at room temperature and higher temperatures[58]. To improve the mechanical properties of the product, it was salted-out with organic solvents. Best results were obtained using isopropyl alcohol in the ratio reduced solution:alcohol ≅ 1:4.[58] Although the precipitate obtained was amorphous towards X-rays, it was readily filtered, washed, and dried. Hydrates containing more or less than $4H_2O$ of crystallisation could not be obtained by the methods of Refs.46 and 47. Hydrates with 2.5 and 1.5 moles of water are obtained by keeping $U(HPO_4)_2.4H_2O$ under equilibrium conditions at different saturated H_2O vapour pressures. The tetrahydrate is stable down to p_{H_2O} = 5 mmHg, $U(HPO_4)_2.2.5H_2O$ is stable in the range 4–2 mmHg, and $U(HPO_4)_2.1.5H_2O$ is stable at lower water vapour pressures.

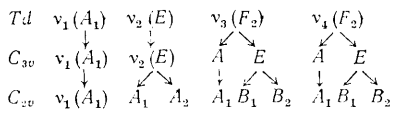
To resolve the question of the possibility of obtaining the normal orthophosphate[58], the conditions of its synthesis according to Ref.49 from solutions of UCl_4 and trisodium phosphate with subsequent heating of the precipitates to 600° were reproduced. At pH > 6, the precipitate is uranium hydroxide, and in acidic solutions, either the monohydrogen phosphate or chloride phosphates containing 58.6% U, 20.1% P_2O_5, 6.1% Cl, and 8.4% H_2O are formed; when the latter were heated at 600°, the product had a composition close to that of $U_3(HPO_4)_4$ (64.3% U, 23.6% P_2O_5), but consisted of a

mixture of the ortho- and pyrophosphates and uranium dioxide. The normal phosphate could not be obtained by the prolonged hydrolysis of $U(HPO_4)_2.4H_2O$ (20 d) at high temperatures. Thus the normal orthophosphate cannot be obtained, and products with a similar composition have been erroneously assumed to be normal uranium(IV) phosphate.

5. Physicochemical Properties

Until comparatively recently, there were few published papers on this topic[31,40,59,60]. A simplified interpretation of the bands in the infrared spectrum, involving their assignment to various vibrations of the uranyl ion and its overtones and combination tones, was carried out in Ref.59. The other papers do not give a detailed assignment of the bands of all the groups in the compound, and do not discuss the wavenumbers of the water vibrations, which make a significant contribution to the spectra of uranium complexes.

The characteristic ranges of absorption by each of the groups in uranyl orthophosphates are well known[3,61-63]. The free orthophosphate ion has a tetrahedral configuration, and has four fundamental vibrations with wavenumbers $\nu_1(A_1)$ ~ 940 cm^{-1}, $\nu_2(E)$ ~ 420 cm^{-1}, $\nu_3(F_2)$ ~ 1020 cm^{-1}, and $\nu_4(F_2)$ ~ 560 cm^{-1}, of which the two triply degenerate vibrations are infrared active[3,62]. On coordination to a metal, the symmetry of the PO_4^{3-} ion may be lowered from T_d to C_{3v} or C_{2v}, accompanied by the following changes in the spectral characteristics:



The infrared spectrum of $UO_2HPO_4.4H_2O$ in the range of the $\nu_3(F_2)$ vibrations shows two strong bands with maxima at 990 cm^{-1} and 1105 cm^{-1}; the $\nu_4(F_2)$ band is also split into two components. Thus the symmetry of the distorted phosphate tetrahedron is close to C_{3v}[64,65] (Table 4).

The ν(OH) stretching region contains a strong broad band with a maximum at about 3300 cm^{-1}, which merges with the band at 2200 cm^{-1}, and the $\delta(H_2O)$ region contains two bands, at 1640 cm^{-1} and 1750 cm^{-1}. From the broad bands of medium strength at 1750 cm^{-1} and 2200 cm^{-1}, it was first assumed that part of the water in the compound is present as hydroxonium ions H_3O^+,[66-68], formed by the transfer of protons from HPO_4^{2-} to H_2O. Evidence in support of this assumption was provided by the absence of δ(POH) absorption at 1200 cm^{-1} and 2400 cm^{-1}.[62,69]

A study of the ^1H NMR spectra of $UO_2HPO_4.4H_2O$,[70] however, showed the absence of the bands of width 10–15 G and 20 G characteristic of water of crystallisation and hydroxonium ions respectively[71-74]. Instead, the spectrum shows one narrow band of width only 0.1 G, which with decrease in temperature becomes broader, while retaining its singlet structure. This narrow line corresponds to weakly bound water molecules and protons with a high diffusion mobility, indicating that the proton is hydrated by water molecules to give the oxonium group $H_9O_4^+$. The criterion used to distinguish H_3O^+ and more complex oxonium groups was the absence of the totally symmetric deformations of H_3O^+ in the Raman spectra in the region of ~ 1200 cm^{-1}.[75] The extremely high mobility of the proton and water molecules in $UO_2HPO_4.4H_2O$ is indicated by the ease of deuteriation of the compound[70]. Treatment of a specimen in an atmosphere of D_2O vapour for 24 h is sufficient for complete isotopic replacement.

Thus the monohydrogen orthophosphate has a polymeric structure containing uranyl phosphate layers; water occupies the space between the layers, through which the mobile proton moves freely.

Table 4. Vibrational wavenumbers (cm^{-1}) of U^{VI} and U^{IV} monohydrogen orthophosphates*[64].

$UO_2HPO_4.4H_2O$	$UO_2HPO_4.H_2O$	$U(HPO_4)_2.4H_2O$	Assignment
254	250	—	$\nu_2(UO_2^{2+})$
290	287	—	$\nu(U-OPO_3)$
460	—	415	$\nu_2(HPO_4^{2-})$
544; 623	500; 533; 621	540; 610; 625	$\nu_4(HPO_4^{2-})$
825 (844)	850 (867)	—	$\nu_1(UO_2^{2+})$
923	926	—	$\nu_3(UO_2^{2+})$
—	990	920	$\nu_1(HPO_4^{2-})$
990 (990); 1105	1055; 1120	980; 1060; 1150	$\nu_3(HPO_4^{2-})$
—	1235	1265	δ(POH)
1640	1618	1625; 1700	$\delta(H_2O)$
1750; 2200	—	—	$H_9O_4^+$
—	2384±20	2400	ν(POH)
3300±20	3500±10	3200; 3400	ν(OH)

* The wavenumbers found in the Raman spectra are given in brackets.

On going to $UO_2HPO_4.H_2O$ there is an increase in the complexity of the infrared and Raman spectra; in the infrared spectra, the $\nu_3(F_2)$ band, as before, is split into two components (1055 cm^{-1} and 1120 cm^{-1}), which are displaced to larger wavenumbers by 65 cm^{-1} and 15 cm^{-1}. At the same time, the splitting $\Delta\nu_3$ decreases to 65 cm^{-1}. The $\nu_1(A_1)$ vibration is activated (990 cm^{-1}), and an additional $\nu_4(F_2)$ band appears at 500 cm^{-1}. An interesting feature is that the spectrum of the monohydrate contains bands at 1235 cm^{-1} and 2380 cm^{-1}, characteristic of the POH stretches and deformations of hydrogen orthophosphates. The ^1H NMR spectrum of $UO_2HPO_4.H_2O$ has the form typical of acid salts containing water of crystallisation and the proton of a hydrogen phosphate group. The molecules of water of crystallisation give a doublet of width 13.1 G. The calculated values of the second moment[76] and the distance between the protons[77] are 17.7 G^2 and 1.65 Å, typical of molecules of water of crystallisation. The central narrow component of width 1.3 G has a second moment of 2.2 G^2.

Thus the change from the tetra- to the monohydrate of uranyl monohydrogen orthophosphate leads to fixation of the mobile proton of the phosphate group and the formation of the acid salt, accompanied by a rearrangement of the structure[53].

Up to the present, relatively few solid compounds containing oxonium groups were known. Species of this kind with the general formula $H_{2n+1}O_n^+$ are extremely characteristic of solutions of strong acids[75,78-80]. In recent years, the improvement of physicochemical methods of study has made it possible to detect the dioxonium ion $H_5O_2^+$ in the hydrates of a number of complex acids: $H_3PWO_4.6H_2O$[81] and $H_2PtCl_6.nH_2O$[82]; $H_9O_4^+$ has been detected in $H_9O_4CF_3SO_3^+$[83] and $H_9O_4Cl.2H_2O$.[84]

The existence of the $H_9O_4^+$ group in uranyl monohydrogen orthophosphate distinguishes it from the series of acid phosphates with a fixed proton, and is responsible for its electrical conductivity. The presence of a proton gas, capable of moving along a line of hydrogen bonds, has been detected in studies of the electrical conductivity of various substances[85-90]. The conductivity, which is due to the migration of protons in the lattice, increases with increase in temperature. In fact, the electrical conductivity of a compressed disc of $UO_2HPO_4.4H_2O$ at a constant stabilised voltage of 3–6 V[70] begins to increase sharply at 72° by a factor of almost 10^6 compared with the original value (10^{-6} Ω^{-1} cm^{-1}), reaching a maximum of 0.2 Ω^{-1} cm^{-1} at 90°, after which it decreases equally sharply. A high proton conductivity in this phosphate was detected similarly by another group of workers[91] in the temperature range 20–60°. The anionic and electronic conductivity is negligibly small. The same authors[92] report that at 100 °C the proton conductivity of $UO_2HPO_4.4H_2O$ was 7×10^{-2} Ω^{-1} cm^{-1}, whereas the electronic conductivity is ~ 10^{-8} Ω^{-1} cm^{-1}. They discuss[92] the possibility of applying this phosphate in electrochemical devices, making use of such properties of the compound as the low solubility, corrosion resistance, ease of mechanical treatment, and ability to operate in the range 0–100°. According to their estimates[92], a cell having electrodes of CaH_2 and $TiFeH_2$ with uranyl monohydrogen phosphate as electrolyte will have an e.m.f. of 0.8 V and a theoretical specific energy of 294 W h kg^{-1}. The same authors[93,94] found by NMR that this compound in the temperature range 0–30° undergoes a phase transformation due to ordering of the hydrogen bonds in the structure; the diffusion of hydrogen at 20–70° has also been detected[95].

Comparison of data obtained by the present authors[53,64,70] with the data of Refs. 91–95 shows that the quantitative values of the electrical conductivity, the temperature range, and the explanation of the conductivity in terms of the migration of extremely mobile protons and water molecules for the most part agree; the views on the structure of the compound also coincide. The suggestion of the present authors that the substance has a layer structure involving a uranyl phosphate framework $(UO_2PO_4)_n^{n-}$ was confirmed by a calculation[96,97] for a fragment of the layer $[(UO_2)_nPO_4]^{5+}$ of symmetry D_{2d}, in which the heavy uranium atoms are practically at rest, and the kinematic interactions are weakly transmitted through them. The calculated vibrational wavenumbers show fairly good agreement with the experimental values for uranyl monohydrogen orthophosphate and double uranyl orthophosphates, and indicate that the calculation for the fragment of the layer model gives a sufficiently good qualitative description of the characteristic features of its structure. The conclusions about the structure of uranyl monohydrogen orthophosphate and double uranyl orthophosphates were confirmed by crystallographic data for $NH_4UO_2PO_4.3H_2O$,[98] the monohydrogen orthophosphate[99,100], and copper dioxophosphatouranate[101]. The structure of $UO_2HPO_4.4H_2O$ is made up of layers, containing UO_2^{2+} and PO_4^{3-} ions, and alternating two-dimensional networks containing water molecules. The U–O(PO_4) distance is 2.307 Å. In this compound there is a system of strong hydrogen bonds with O...O distances of 2.56–2.81 Å, which ensures proton migration and hence the electrical conductivity of the substance. When the proton is replaced by a metal or ammonium ion, the proton conductivity decreases sharply. The same result is achieved by removing part of the water, as for example in the monohydrogen orthophosphate monohydrate.

The structures of uranyl dihydrogen orthophosphate, normal uranyl orthophosphate, and uranium(IV) phosphates have not yet been determined. The spectra of these compounds have been analysed to determine their structural characteristics. On going from $UO_2(H_2PO_4)_2.3H_2O$ to $UO_2(H_2PO_4)_2.H_2O$ (the latter is stable at a water vapour pressure of 0.1 mmHg), the strength of the uranium–oxygen bond in the uranyl group increases (the ν_1 and ν_2 wavenumbers increase[102]). All the bands assigned to the $H_2PO_4^-$ vibrations are doublets (Table 5). It is suggested that the doublet structure of the bands is due to the existence of non-equivalent phosphate groups (see Table 5). A possible reason for the non-equivalence of the phosphate groups may be a difference in the influence of the hydrogen bonds of the water molecules on each $H_2PO_4^-$ group. In the monohydrate, where the influence of the water molecules is weaker, the splitting of the $H_2PO_4^-$ lines disappears.

Table 5. Vibrational wavenumbers (cm^{-1}) in the infrared spectra of hydrated uranyl dihydrogen orthophosphate*.

$UO_2(H_2PO_4)_2.3H_2O$	$UO_2(D_2PO_4)_2.3D_2O$	$UO_2(H_2PO_4)_2.H_2O$	$UO_2(D_2PO_4)_2.D_2O$	Assignment (Ref.102)
259	260	260	260	$\nu_2(UO_2^{2+})$
351 (365); 391 (400); 492; 536	346; 388; 503; 543	369; 430 (445); 505;	370; 423; 508	$\delta(PO_2)$
561; 631; 765	425; 465; 555	559; 672; 753	558	$\omega(H_2O, D_2O)$
836 (835)	836	(860)	—	$\nu_1(UO_2^{2+})$
900 (912)	900	900 (920)	900	$\nu_s(PO(H))$
921	924	933	933	$\nu_s(UO_2^{2+})$
973; 991	974; 999	999	999	$\nu_{as}(PO(H))$
1084 (1064)	1074	1064 (1058)	1070	$\nu_s(PO_2)$
1109	1103	—	—	$\nu_{as}(PO_2)$
1131 (1130)	1127	—	—	$\nu_s(PO_2)$
1183	1175	1163	1159	$\nu_{as}(PO_2)$
1220; 1280	825; 860	—	820	δ(POH, POD)
1600; 1627	1147	1588	1143	$\delta(H_2O, D_2O)$
2400	1800	—	—	ν(OH, O—H...O)
2700; 3000	2100; 2247	3137	2250	ν(PO—H, PO—D)
3200; 3360; 3530; 3572	2352; 2576; 2621; 2660	2522; 3577	2573; 2612; 2656	ν(OH, OD)

* The wavenumbers found in the Raman spectra are given in brackets.

The existence in $UO_2(H_2PO_4)_3.3H_2O$ of a system of strong hydrogen bonds and the participation of the phosphate anion in this system are indicated by the absorption in the ν(OH) region from 3600 cm^{-1} to 2600 cm^{-1}, the band of medium strength at 2550–2100 cm^{-1}, and the broad bands in the P–OH deformational region (1300–1100 cm^{-1}). The protons of the $H_2PO_4^-$ groups apparently form H-bonds with water molecules, giving bridged O...O structures[102-106]. Comparison of the spectra of dihydrogen orthophosphate specimens hydrated to different extents gives information on the state of the water in the compounds. The splitting of the $\delta(H_2O)$ band into two components at 1600 cm^{-1} and 1627 cm^{-1} in the spectrum of $UO_2(H_2PO_4)_2.3H_2O$, which increases with decrease in temperature, indicates that the water molecules in this compound are structurally non-equivalent. The spectrum of the monohydrate shows only one band at 1588 cm^{-1}, and the ν(OH) and δ(POH) bands tend to be narrower. At the same time, the broad range of absorption with a maximum at 2400 cm^{-1} disappears, and the two ν(OH) bands at 3572 cm^{-1} and 3530 cm^{-1} are preserved. The high values of ν(OH) and the low value of $\delta(H_2O)$ indicate that there is little distortion of the water molecule in the monohydrate under the influence of hydrogen bonds. At the same time, the difficulty of

removing the last H_2O molecule indicates that it is strongly bound in the structure, which is possible if it is coordinated to uranium. The infrared spectrum (Fig.1) shows bands due to the librational vibrations of water, which are sensitive to deuteriation and to decrease in temperature[102]. This separation of the protons was confirmed by ^1H NMR. The resonance lines of the water molecules were distinguished using the published atlas of crystalline hydrate spectra[107].

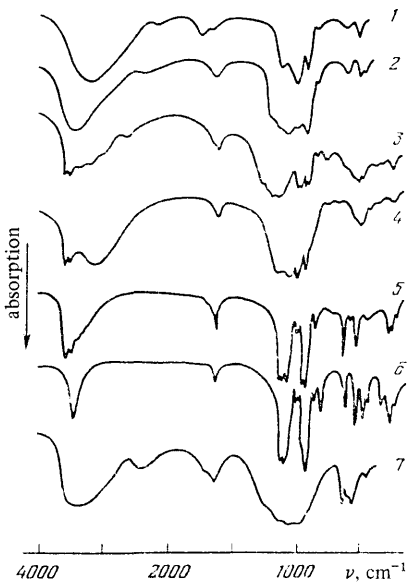
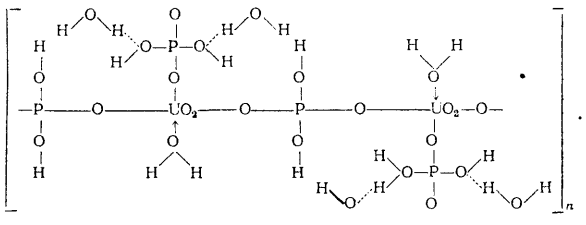


Figure 1. Infrared spectra of uranium orthophosphates: *1)* $UO_2HPO_4.4H_2O$;[64] *2)* $UO_2HPO_4.H_2O$;[64] *3)* $UO_2(H_2PO_4)_2.3H_2O$;[102] *4)* $UO_2(H_2PO_4)_2.H_2O$;[102] *5)* $(UO_2)_3(PO_4)_2.4H_2O$;[109] *6)* $(UO_2)_3(PO_4)_3.H_2O$;[109] *7)* $U(HPO_4)_2.4H_2O$.[58]

Like the monohydrogen orthophosphate, $UO_2(H_2PO_4)_2.3H_2O$ is a polymer in which one phosphate group binds the uranyl ions in a uranyl phosphate chain, while the other is terminal. One water molecule is coordinated directly to the uranium atom, and two others are joined by hydrogen bonds to $H_2PO_4^-$ groups:



The proposed scheme effectively explains the ease of hydrolysis of the dihydrogen orthophosphate with the removal of a terminal $H_2PO_4^-$ group under the influence of water and polar solvents, the reversible removal of two water molecules at low temperatures, and the decomposition of the compound when the last water molecule is removed. The coordination number of the uranyl group in this compound is probably four (the energy of the purely electronic transition is 20278 cm^{-1}[108]).

In the infrared spectrum of $(UO_2)_3(PO_4)_2.4H_2O$, the line corresponding to the $\nu_3(UO_2^{2+})$ vibrations is a doublet (Table 6)[109]. The totally symmetric $\nu_1(UO_2^{2+})$ stretch appears as a doublet. The observed splitting and activation of the $\nu_1(UO_2^{2+})$ band in the infrared spectrum indicate that the substance contains two types of uranyl group in environments with low symmetry. The nature of the absorption by the phosphate group indicates that it is extensively distorted, probably to C_{2v} symmetry. The $\nu_3(F_2)$ and $\nu_4(F_2)$ bands are split into three components[103]. The $\nu_1(PO_4^{3-})$ band is activated in the infrared spectrum. The spectra of the UO_2^{2+} and PO_4^{3-} ions of the hexahydrate are analogous to those for the tetrahydrate, although the bands are diffuse and broadened slightly. On the other hand, the spectrum of the PO_4^{3-} ion in the monohydrate (Table 6) has fewer bands, corresponding to an increase in the symmetry of this ion relative to the tetrahydrate.

Table 6. Vibrational wavenumbers (cm^{-1}) in the infrared spectra of crystalline hydrates of normal uranyl orthophosphate[109]*.

$(UO_2)_3(PO_4)_2.4H_2O$	$(UO_2)_3(PO_4)_2.4D_2O$	$(UO_2)_3(PO_4)_2.H_2O$	Assignment
217 (222)	220	225 (219)	$\delta(U{-}OPO_3)$
250	226	241 (245)	$\nu_3(UO_2^{2+})$
286 (285)	279 (289)	327	$\nu(U{-}OPO_3)$
(450)	—	428;461 (464)	$\nu_3(PO_4^{3-})$
450	375	—	$\omega(H_2O, D_2O)$
533;570 (576); 628 (625)	534;565 (575); 621 (620)	531;618 (615)	$\nu_4(PO_4^{3-})$
720 (736)	(583)	—	$\omega(H_2O, D_2O)$
852 (853,865)	850 (849,859)	804 (816);860 (850)	$\nu_1(UO_2^{2+})$
933;950	928;948	925;936;952 (950)	$\nu_3(UO_2^{2+})$
992(1002);1000(1028)	990 (1008);1000 (1031)	993 (1010);1000 (1037)	$\nu_1(PO_4^{3-})$
1076 (1105);1123; 1143 (1150)	1076 (1009);1123; 1143 (1152)	1080 (1072);1143 (1135)	$\nu_3(PO_4^{3-})$
1600;1618;1631; 1675	1126;1168;1209	1610	$\delta(H_2O, D_2O)$
3225;3325,3390; 3598;3575	2382;2498;2564; 2600;2650;2721	3450	ν(OH, OD)

* The wavenumbers found in the Raman spectra are given in brackets.

In normal uranyl orthophosphate, the PO_4^{3-} ions are probably coordinated to UO_2^{2+} as bridging bidentate anions to give uranyl phosphate layers.

The $\delta(H_2O)$ deformational wavenumbers for $(UO_2)_3(PO_4)_2.4H_2O$ indicate that the water molecules in the crystalline hydrates are non-equivalent, and the absorption at 460 cm^{-1} and 720 cm^{-1}, which is sensitive to decrease in temperature[110,111] and deuteriation ($K = 1.26$), corresponds to the librational vibrations of water.

It has been suggested[112] that the librational wavenumbers of water appear not only when H_2O is coordinated directly to the metal atom but also when a system of hydrogen bonds is formed. In the case of the tetrahydrate, however, and more particularly the monohydrate, for which the ν(OH) band has a half-width of only ~ 100 cm^{-1} with a maximum at 3450 cm^{-1}, the last effect is apparently slight. On the other hand, in the spectrum of the hexahydrate, the OH bands are broadened considerably (to 1300 cm^{-1}), apparently as a result of hydrogen bonding with excess water molecules. Analysis of the spectra indicates that in the uranyl phosphate

layer, one water molecule is coordinated to the uranyl ion, while the others are in the space between the layers.

On the whole, the spectrum of $U(HPO_4)_2.4H_2O$ shows diffuse bands due to PO_4^{3-} groups and water molecules[58] (see Table 4 and Fig.1). The ν(OH) range contains a very broad ($S_{1/2}$ = 500 cm^{-1}) band with a complex structure and maxima at 3400 cm^{-1} and 3200 cm^{-1}, against which it is possible to distinguish a band with a maximum at 2400 cm^{-1}. This band and the shoulder at 1265 cm^{-1} correspond to the P—OH stretches and deformations typical of acid phosphates[62,63].

6. Characteristic Features of the Thermal Decomposition

The thermal decomposition of the crystalline hydrates, which generally includes dehydration, depends on the state of the anion and the water molecules in the compound[5]. It was noted above that all the orthophosphates studied are three-dimensional polymers in which the PO_4^{3-} anion is coordinated to a uranium atom, and the water molecules either are mobile between the layers or complete the inner sphere of the complex. This is responsible for the great variety of forms of bonding of the water both to uranium and to the nearest groups by the formation of H-bonds of different types with the anions of neighbouring layers and with water molecules between the layers.

The dependence of the behaviour of uranyl orthophosphates when heated on these factors can be considered. The decomposition of uranyl monohydrogen orthophosphate is most complex, and shows a number of characteristic features.

1. The removal of water begins at relatively low temperatures, slightly above room temperature.
2. The dehydration of $UO_2HPO_4.4H_2O$ to the monohydrate involves a phase transformation.
3. On heating, the phosphate anion polymerises at 100° before all the water of crystallisation is removed. The quantity of polymeric forms increases with increase in temperature.
4. Up to ~ 6.5% free phosphoric acid is detected in the decomposition products.
5. Sublimation of phosphorus(V) oxide is observed at 500–600°.

The ease of removal of water is in good agreement with the assumption that the H_2O molecules lie between the layers, and with the increase in the mobility of the molecules with increase in temperature. At the same time, increase in temperature increases the probability of the movement of the protons through the system of hydrogen bonds, and in an electric field this movement becomes ordered. It may be noted that the temperature of the observed phase transformation coincides with the temperature range corresponding to the increase in the proton conductivity. A theory has been proposed[113,114] to explain the ordering of the motion of the protons in antiferroelectric orthophosphates and its relation to the phase transformation.

The increase in the mobility of the water molecules between the layers on heating may lead to the hydrolysis of the uranyl phosphate bonds and the removal of H_3PO_4 according to the schemes:

$$3UO_2HPO_4\cdot 4H_2O \rightarrow (UO_2)_3(PO_4)_2 + H_3PO_4 + 12H_2O$$

$$3UO_2HPO_4\cdot n\,H_2O \rightarrow (UO_2OH)_3PO_4 + 2H_3PO_4 + 3(n-1)H_2O\,. \qquad (1)$$

The concentration of free phosphoric acid reaches a maximum in the specimens heated to 150–200°. The appearance of H_3PO_4 during heating may create the impression that the increase in the electrical conductivity of the specimens is due to the electrolysis of H_3PO_4. The maximum on the electrical conductivity curve, however, does not coincide with the temperature range in which phosphoric acid is formed[70], and the conductivity in this range is low.

The formation of polyphosphates during the thermal decomposition of $UO_2HPO_4.4H_2O$ is probably the result of the superposition of a number of processes—the condensation of acid phosphate groups

$$2UO_2HPO_4\cdot n\,H_2O \rightarrow (UO_2)_2P_2O_7 + (2n+1)H_2O$$

and the decomposition of phosphoric acid with the subsequent reaction of pyrophosphoric acid with the components of the solid phase:

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$
$$2(UO_2)_3(PO_4)_2 + H_4P_2O_7 \rightarrow 3(UO_2)_2P_2O_7 + 2H_2O$$
$$2(UO_2OH)_3PO_4 + 2H_4P_2O_7 \rightarrow 3(UO_2)_2P_2O_7 + 7H_2O$$
$$5(UO_2)_3(PO_4)_2 + 4H_4P_2O_7 \rightarrow 3(UO_2)_5(P_2O_{10})_2 + 8H_2O \text{ etc.}$$

The reaction of H_3PO_4 with uranyl phosphates may explain the decrease in its concentration in the substance at 200–500°. Beginning at 550°, small quantities of phosphorus(V) oxide sublime into the gas phase[115].

Table 7. Stages in the removal of water from uranium orthophosphates under equilibrium conditions, and the thermodynamic characteristics of the process[116,54].

Compound	Dehydration temperature range, °C	Number of moles of H_2O	ΔH, kcal $mole^{-1}$	$\Delta S°$, e.u.
$UO_2HPO_4\cdot 4H_2O$	50–80	2.0	12.3±0.6	44.6±0.4
$UO_2HPO_4\cdot 4H_2O$	100–115	0.5	13.5±0.8	45.6±0.6
$UO_2HPO_4\cdot 4H_2O$	170–190	1.5	15.6±0.7	45.2±0.4
$UO_2HPO_4\cdot 4H_2O$	560–600	0.5	—	—
$(UO_2)_3(PO_4)_2\cdot 4H_2O$	180–210	3.0	12.0	37.3
$(UO_2)_3(PO_4)_2\cdot 4H_2O$	360–400	1.0	11.7	28.4
$U(HPO_4)_2\cdot 4H_2O$	30–150	3.0	—	—
$U(HPO_4)_2\cdot 4H_2O$	150–170	1.0	11.8	10.0
$U(HPO_4)_2\cdot 4H_2O$	180–205	0.5	38.6	33.8
$U(HPO_4)_2\cdot 4H_2O$	205–260	0.5	—	—

It was noted above that the data on the stepwise character of the removal of water and the temperature range of the dehydration given by different authors do not agree. This may be due to differences in the conditions of the experiments. To exclude the influence of such factors as the size and shape of the crystals, the rate of heating, etc., we studied[116] the thermal decomposition of the compounds under equilibrium conditions using a quartz membrane null manometer[117]. Table 7 gives data on the stepwise character of the dehydration under equilibrium conditions; it was found that it is different from that observed on heating in a stream of dry air. Throughout the entire range of temperatures studied, the anionic composition of the solid phase was restricted to ortho- and pyrophosphates (the latter was detected from 90°), whereas in the decomposition of the substance in a dry atmosphere, the heating products contained not less than six phosphate forms. A phosphorus-containing substance in concentrations of 10^{-2}–10^{-4} M was also detected in the gas phase. Increase in the water vapour pressure in the system increases the thermal stability of the substance slightly. Analysis of the infrared spectra of specimens kept under equilibrium conditions at 200° and 400° showed that the products contained uranyl hydroxo-complexes[110], whose appearance may be due to the reaction described by scheme (1). The value of $\Delta H \cong 14$ kcal $mole^{-1}$ obtained agrees with the ease of removal of water from the compound being studied, and the high value of $\Delta S°$ (45 e.u.) is apparently related to the high entropy of sublimation of water ($\Delta S° = 35.6$ e.u.), and also to the rearrangement of the crystal

structure of the substance during the decomposition. Thus these data do not agree with the statement[119] that the atmosphere has no influence on the extent of the decomposition of the phosphate anion in bivalent metal orthophosphates.

Ammonium dioxophosphatouranate $NH_4UO_2PO_4.3H_2O$, which is isostructural with the monohydrogen phosphate, loses three water molecules in a single stage when heated, but the removal of ammonia, like that of the last water molecule from $UO_2HPO_4.4H_2O$, takes place over a wide temperature range (280–800°) and is accompanied by polymerisation of the phosphate anion[56]. The product obtained after heating was found to contain a water-soluble phosphate compound containing no uranium, and consisting of ammonium phosphate, capable of dissociating and volatilising[119]. At low heating rates, this compound dissociates, and at high heating rates it volatilises. The product of the thermal decomposition of these phosphates is a compound with the overall composition $U_2O_3P_2O_7$,[54,56] whose formation is accompanied by the liberation of oxygen and the reduction of uranium.

The thermal decomposition of the dihydrogen orthophosphate $UO_2(H_2PO_4)_2.3H_2O$, which was studied in detail by Japanese workers[120], is also complex. Since the intermediate decomposition products are metaphosphates, the authors[120] were interested in their structure. A definite relationship exists between the structure of the metaphosphates and the magnitude of the charge and size of the cation[121]; phosphates with a metal ion of medium size are cyclic, and those with very small and very large metal ions are linear. It was shown[120] that the removal of two water molecules at 120° is not accompanied by the polymerisation of the phosphate anion. Up to 300° the products are pyro-, tri-, and tetrapolyphosphates, which at a temperature above 350° are converted into linear metaphosphates according to the scheme·

$$(UO_2)_n H_2P_{2n}O_{6n+1} \rightarrow [UO_2(PO_3)_2]_n + H_2O \ .$$

In the range 900–1000°, reduction of uranium takes place, and the composition of the substance becomes simpler. The final decomposition product is uranium(IV) pyrophosphate:

$$[UO_2(PO_3)_2]_n \rightarrow nUP_2O_7 + n/2O_2 \ .$$

The anionic composition and structure of $(UO_2)_3(PO_4)_2.4H_2O$ remain unchanged on thermal decomposition up to 950°. The loss of the last water molecule begins above 330°.[54] At 950–1000°, the orthophosphate is dehydrated completely, with the simultaneous liberation of oxygen and the formation of a mixture of uranium(IV) phosphate and U_3O_8, and not a phase with the composition $U_3O_8P_2O_7$.[39] Although the heating products obtained in the range 400–800° contain small quantities of water, their spectra are practically the same as those of the monohydrate. The stepwise character of the removal of water under thermodynamically equilibrium conditions is the same as in air (see Table 7). The low values of the entropy of dehydration indicate that the changes in the structure of the substance during the thermal decomposition are slight. The oxygen pressure over anhydrous $(UO_2)_3.(PO_4)_2$ on heating to temperatures above 800° has been measured[122].

The dehydration of uranium(IV) monohydrogen orthophosphate $U(HPO_4)_2 \cdot 4H_2O$ takes place in accordance with classical ideas to give pyrophosphate according to the scheme:

$$U(HPO_4)_2 \cdot 4H_2O \rightarrow U(HPO_4)_2 + 4H_2O$$
$$U(HPO_4)_2 \rightarrow UP_2O_7 + H_2O \ .$$

UP_2O_7 crystallises at ~ 760°.

Shchegrov[118] reviewed published data on the regular features of the mechanism of the dehydration of bivalent metal orthophosphates on the basis of the state of the water molecules present, in particular the strength of the hydrogen bonds with the phosphate anion. The dehydration of both acidic and normal orthophosphates takes place in three stages[118].

The first stage takes place at relatively low temperatures, and is accompanied by the removal of water molecules forming relatively weak hydrogen bonds with the anion, with energies up to 7–8 kcal mole^{-1}:

$$M_3(OH_2)_x(PO_4)_2(m-x)H_2O \rightarrow M_3(OH_2)_x(PO_4)_2 + (m-x)H_2O$$
$$[M(OH_2)_x HPO_4](m-x)H_2O \rightarrow [M(OH_2)_x HPO_4] + (m-x)H_2O \ .$$

The second stage, the removal of more firmly bound water (with hydrogen bond energies of 9–11 kcal mole^{-1}), is accompanied by extensive structural transformations such as the formation of a mixture of higher phosphates, hydroxides, or oxides of the metal:

$$n/2M_3(OH_2)_x(PO_4)_2 \rightarrow M_{(n+2)/2}P_nO_{3n+1} + (n-1)M(OH)_2 + \frac{nx-2n+2}{2}H_2O$$
$$n[M(OH_2)_xHPO_4] \rightarrow M_{(n+2)/2}P_nO_{3n+1} + \frac{n-2}{2}MO + \frac{n(2x+1)}{2}H_2O \ .$$

The third stage gives an intermediate dehydration product with a simpler composition, as a result of the following reactions:

$$M_{(n+2)/2}P_nO_{3n+1} + (n-1)MO \rightarrow \frac{n}{2}M_3(PO_4)_2$$
$$M_{(n+2)/2}P_nO_{3n+1} + \frac{n-2}{2}MO \rightarrow \frac{n}{2}M_2P_2O_7 \ .$$

The data in Refs.118 and 123–127 show some lack of agreement. Analysis of the infrared spectra of the dehydration products shows that the specimen first loses the water joined by "strong hydrogen bonds" (ν(OH) = 3030–3060 cm^{-1})[123–125], whose energy was estimated as 35–40 kJ mole^{-1}. At the same time, the high-wavenumber vibrations of the water molecules (above 3400 cm^{-1}, bond energies 10–15 kJ mole^{-1}) are preserved in the spectrum, while the OH stretching bands show an overall decrease in width. These bands generally remain in the spectrum up to fairly high temperatures.

In the discussion of the spectra in Refs.126 and 127, no account was taken of the possibility of the direct coordination of the phosphate group to the metal. Ideas about the aquocomplexes of a number of isostructural sulphates and perchlorates of bivalent metals (Co, Ni, Fe, Zn, Ca, Mg)[128,129], in which the water molecules are in the inner coordination sphere, and the anion is in the outer sphere and forms H-bonds with the water molecule, were applied to the phosphates. X-ray diffraction data on the phosphates of Ca^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Mg^{2+}, Al^{3+}, etc.[130–137] have shown that they are three-dimensional polymers, in which the polyhedron around the metal atoms is formed by the oxygen atoms of phosphate groups. The water molecules in hydrates with low water contents can act as bridges between metal atoms[131] or be coordinated to the metal or situated in the space between the layers[138,139], being held in the crystal lattice by hydrogen bonds. X-ray diffraction data indicate that the strength of the bonding of the water on dehydration is determined by the structure of the phosphate. The coordinated water molecules are naturally held much more strongly, as confirmed by the measured M–O(H_2O) bond lengths, which are equal to 2.0–2.2 Å and are comparable with the M–O(PO_4) distance. The formation of H-bonds with the outer-sphere anion will increase the force constant of the M ← OH_2 bond.

When extremely strong symmetrical H-bonds O...O with length 2.4–2.6 Å, which are formed extremely rarely in crystals, are produced, ν(OH) may reach 3000 cm^{-1} or less. When estimating the energy of hydrogen bonds from the lowering of the ν(OH) vibrational wavenumbers, however, care must be taken, since it is necessary to make allowance for a number of factors which displace the ν(OH) wavenumber in the same direction as hydrogen bonding. On coordination,

the displacement of ν(OH) to lower wavenumbers may reach 600 cm^{-1}, and it is complex in character and does not always depend on the strength of the bond formed with the metal. The displacement is also determined by the symmetry of the molecule, the perturbing influence of the field of the central atom, the nature of the hybridisation of the orbitals, Fermi resonance, etc.[140-143] The nature of the bonds formed by water is best deduced from the librational wavenumbers[141-143]; the wavenumbers of the rocking and wagging vibrations increase with increase in the strength of the M ← OH_2 bond.

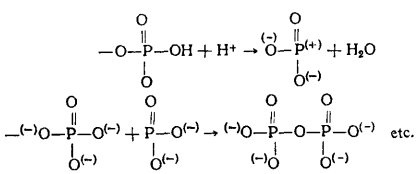
It is clear from the foregoing that without a knowledge of the structure of the compound, the estimation of the perturbing influence of the anion on the water molecules from the displacement of the ν(OH) wavenumbers is inaccurate. The situation is complicated by the fact that even in the anhydrous acidic compounds[132,138,144,145], the proton of the phosphate group is involved in a system of H-bonds with neighbouring layers, and in the case of the crystalline hydrates, the number of possible hydrogen bonds increases sharply.

Returning to the uranium phosphates, it can be seen that the dehydration of uranyl monohydrogen orthophosphate, which contains mobile water between the layers, involves the production of up to six forms of polyphosphate and free phosphoric acid, whose formation in the decomposition of bivalent metal phosphates has been related[118,123-127] to the existence of strong hydrogen bonds between the coordinated water molecules and the outer-sphere phosphate anion.

It can be seen from the case of $UO_2HPO_4.4H_2O$ that it is probably premature to reject the possibility of hydrolysis to explain the thermal decomposition of phosphates, particularly in view of the fact that many phosphates contain mobile water between the layers. On the other hand, in the decomposition of the normal orthophosphate monohydrate, which contains coordinated water (ν(OH) = 3450 cm^{-1}), the H_2O molecules are removed gradually up to a temperature of 900°, and polymeric forms of phosphate were not detected in the dehydration products. On the other hand, uranium(IV) monohydrogen orthophosphate, which gives extremely broad ν(OH) bands with a maximum at 3200 cm^{-1}, indicating strong hydrogen bonding, decomposes in accordance with classical ideas to uranium pyrophosphate.

Thus the ideas developed in Refs.5, 118, and 123–127 do not make possible a sufficiently reliable explanation of the mechanism of the dehydration of uranyl and uranium orthophosphates. A preferable concept was developed by the authors of Refs.146–149, who regard all crystalline hydrogen phosphates as proton semiconductors, which when heated above a definite temperature give free protons, capable of moving easily through interstices in the crystal lattice. The concentration of this "proton gas" increases with increase in temperature; the probability of its reaction with the phosphate tetrahedra also increases.

The condensation takes place by a series of successive processes involving ionisation of anionic sites:



The proton transfer is most effective when the compound contains a system of hydrogen bonds, and the degree of transfer depends on the crystal structure of the compound. With the formation of hydrogen orthophosphates, an increase in the strength of the P–OH bond and a decrease in the strength of the PO–H bond compared with the HPO_4^{2-} anion are assumed. The formula $[...(M-O)_3-P=O]^-H^+$ has been proposed to describe the structure of group IV metal phosphates[150].

III. CONDENSED URANIUM PHOSPHATES

A review of uranium phosphates would be incomplete without an examination of polymeric phosphates with different degrees of condensation. Uranium pyrophosphates in solution were studied in Refs.151–155, where it was shown that the reaction of uranyl nitrate with sodium pyrophosphate gives cationic complexes $[(UO_2)_nP_2O_7]^{2(n-1)}$, where n = 3–5. The composition of the pyrophosphates depends on the medium. The insoluble complex $[Na_4(UO_2)_8(P_2O_7)_5]$ and the soluble complexes $[Na_2UO_2P_2O_7]$, $Na_6UO_2(P_2O_7)_2$,[151] and $[UO_2H_q(P_2O_7)_x]^{(4x-q-2)-}$ (x = 1,2) were detected. At pH 0.83–3.00, $[(UO_2)_5H_2P_2O_7]^{8+}$ is formed[153]. Uranyl pyrophosphates including heavy metal cations (Ag^+, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}) have been prepared[155]. The possible formation of the uranyl hydroxide pyrophosphate $(RNH_3)_3UO_2OHP_2O_7$ in the extraction of uranium(IV) from pyrophosphate solution by alkylamines has been suggested[156].

The $UO_2(NO_3)_2$–$Na_4P_2O_7$–H_2O system has been studied[157], and the following salts isolated: the soluble $Na_6UO_2(P_2O_7)_2.6H_2O$ and the insoluble $Na_2UO_2P_2O_7.3H_2O$, $Na_2UO_2P_2O_7.2H_2O$, $Na_2(UO_2)_3(P_2O_7)_2.5H_2O$, and $(UO_2)_2P_2O_7.4H_2O$. Secondary processes gradually take place in the system, but their nature was not established[157].

The $Na_4P_2O_7$–$UO_2(NO_3)_2$–H_2O system was studied by the present authors by measuring the electrical conductivity, pH, and refractive index of isomolar series at concentrations of 0.001–0.2 M[158]. The existence in solution of complexes with ratios $P_2O_7^{4-}$:UO_2^{2+} of 2:1, 1:1, 1:2, and 1:6 was detected (some of these complexes were reported earlier[151,157]). To isolate the solid compounds, they were synthesised by mixing solutions to give the above component ratios. The pyrophosphates $Na_6UO_2(P_2O_7)_2.3H_2O$, $Na_2UO_2P_2O_7.5H_2O$ and $(UO_2)_2P_2O_7.8H_2O$ were obtained. The first of these is readily soluble in water, and it was salted-out with acetone or ether and dried in a desiccator over phosphorus(V) oxide. The pyrophosphate with ratio 1:6 could not be obtained[158]. When solutions to give this ratio were mixed, the precipitate, which formed 24 h after the solutions were mixed, contained up to 30% of the ortho-form. When the solutions were kept for a long time, the specific conductivity and refraction curves showed a displacement of some of the maxima, and in an excess of the uranyl ion (ratio > 1:2), changes were also observed visually; the external appearance and volume of the precipitates altered. To determine the reasons for these changes, the pyrophosphates were kept in equilibrium with the solution and then analysed by chromatography. After one month, the 1:1 and 1:2 compounds contained appreciable quantities of orthophosphate (~ 14 and 27), and at a ratio of 1:6 the system contained no pyrophosphate, and the precipitate consisted of $(UO_2)_3(PO_4)_2.4H_2O$.

Thus uranyl pyrophosphates in solution undergo appreciable degradation, which increases with increase in the uranium concentration. Thus the changes detected[157] in the system result from the decomposition of the polyphosphate anion. It was important to determine whether analogous degradation of the anion takes place in the solid phase. The chromatographic data showed that one month after the formation of the 2:1, 1:1, and 1:2 compounds, the first contained practically no ortho-form, and the others ~ 10% and 25% PO_4^{3-} respectively.

The $Na_4P_2O_7$–$UO_2(NO_3)_2$–H_2O system was also studied by other workers[159], who isolated the 1:1 and 1:2 complexes. The preparation of the 2:3 compound $Na_2(UO_2)_3(P_2O_7)_2.14H_2O$ has been reported[158]. The individuality of the last compound is doubtful, since its composition is extremely sensitive to slight changes in the $P_2O_7^{4-}:UO_2^{2+}$ ratio in the solution[158]. The infrared spectrum and heating curves of the product[159] are practically the same as those of the 1:1 compound. The authors[159], in spite of the reported[158] possibility of the degradation of uranyl pyrophosphates, studied the equilibrium in the system over a prolonged period. It will be shown below that with increase in the length of the polyphosphate chain, the ability of the uranyl phosphates to undergo degradation increases. The composition and structure of the compounds crystallising from melts of the $(UO_2)_2(P_2O_7)$–$Na_4P_2O_7$ system have been studied[160].

In the $Na_5P_3O_{10}$–$UO_2(NO_3)_2$–H_2O system, compounds with $P_3O_{10}^{5-}:UO_2^{2+}$ ratios of 2:1, 1:1, 1:3, 3:5, 1:2, and 2:5 exist in solution[161]; some of these compounds were reported earlier[162–166]. The ranges of stability of the crystalline hydrates of uranyl tripolyphosphates were determined by the present authors, and the following solid compounds isolated[161]: $Na_3UO_2P_3O_{10}.6H_2O$, $Na_4(UO_2)_3(P_3O_{10})_2.14H_2O$, $Na_5(UO_2)_5.(P_3O_{10})_3.22H_2O$, $Na(UO_2)_2P_3O_{10}.9H_2O$, and $(UO_2)_5(P_3O_{10})_2.21H_2O$.

The 1:1 and 2:5 compounds are obtained even with slight variation in the ratios of these components, but the 2:3, 3:5, and 1:2 complexes have these compositions in the solid state only with the appropriate stoichiometry in the solution.

The characteristics of the vibrational spectra of uranyl tripolyphosphates have been discussed[167]. On going from the 1:1 to the 2:5 compound, the $\nu_{as}(=PO_2)$ stretching wavenumbers tend to decrease from 1240 cm^{-1} to 1210 cm^{-1}, and $\nu_{as}(PO_3)$ from 1165 cm^{-1} to 1155 cm^{-1}. This can apparently be related to an increase in the degree of polymerisation of uranyl tripolyphosphates. A gradual increase in the strength of the binding of the water molecules in the complexes is observed in the same order (1:1 < 2:3 < 3:5 < 1:2 < 2:5). This can be seen from the thermal analysis data: water is removed at ~ 300° from the 1:1 compound, 500° from the 2:3 and 3:5 compounds, 700° from the 1:2 compound, and only at 800° from the 1:5 compound. The melting points of the dehydration products increase in the same order: the 1:1, 2:5, and 3:5 complexes melt in the range 800–850°; the 1:2 compound at 1150°, and the 2:5 compound at 1200°. On the other hand, the tendency of uranium to be reduced decreases: reduction takes place at 900° for the 1:1 complex, and at 700° for the 1:2 and 2:5 complexes. The final product of the thermal decomposition of uranyl polyphosphates at 1000° is a mixture of linear phosphates.

When considering the thermal stability of uranyl phosphates, mention must be made of the final decomposition products. The possibility of determining uranium as phosphates has been discussed many times. Different forms to be weighed have been proposed by different authors: $U(PO_3)_4$,[168] $U_2O_3P_2O_7$,[169–171,29] and $U_2O_5P_2O_5$.[172] In the description of the thermal stability of uranium orthophosphates, it was shown that the final decomposition products of the phosphates have different overall compositions. The decomposition products of the polyphosphates also have a different composition. The final products often contain a mixture of phosphates with different anionic compositions; the identification of the products is also complicated by the reduction of uranium on heating. Care must therefore be taken in the analytical determination of uranium by the published methods[29,169,171], and it should be remembered that the overall composition of the products formed on heating depends on the composition of the original specimen.

The tripolyphosphates, like uranyl pyrophosphates, are unstable when left to stand; Fig.2 illustrates their degradation at 0° and 25°. It can be seen from Fig.2 that the tendency to undergo degradation decreases with decrease in temperature. Unlike the pyrophosphates, for which the degree of degradation increases with increase in the uranium concentration, the degree of degradation of the tripolyphosphates shows a complex dependence on composition. In the series of compounds with the 1:1, 2:3, and 3:5 compositions, the degradation of the anion increases (the $P_3O_{10}^{5-}$ concentration after 100 d at 25° was 55, 25, and 5% respectively), whereas the 1:2 and 2:5 complexes after the same time interval contained 15% and 35% $P_3O_{10}^{5-}$.[173] In the 2:3 and 3:5 compounds there is probably considerable deformation of the phosphate anion. Thus the tendency of uranyl polyphosphates to undergo degradation increases with increase in the length of the phosphate chain, and depends on the structure of the phosphate. More complex linear polyphosphates should probably be even less stable.

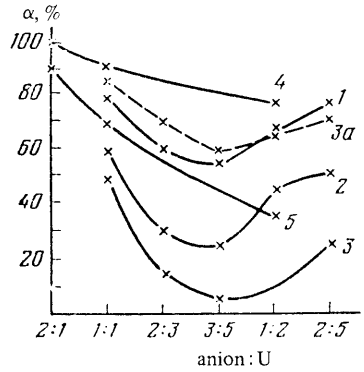


Figure 2. Dependence of the degree of degradation of uranyl pyro- and tripolyphosphates on the time for which they have been kept: *1, 2, 3*) tripolyphosphates at 25 °C after 10, 30, and 100 d respectively; *3a*) tripolyphosphates at 0 °C after 100 d; *4, 5*) pyrophosphates after 30 d; α is the concentration of the original phosphate[158,161].

In the discussion of the degradation of phosphate anions, it should be noted that there are practically no published data on the decomposition of solid polyphosphates. The dependence of the degradation of polyphosphates in solution on the pH of the medium and temperature has been studied[174,176]. It was shown only recently[177,178] that like uranyl phosphates, the tripolyphosphates of Co^{2+}, Ni^{2+}, and Cu^{2+} undergo degradation in the solid phase, the extent of the decomposition being greater for the copper phosphate.

Uranyl metaphosphates are much more stable than the polyphosphates. Japanese workers[179] have shown that uranyl tetrametaphosphate is more stable than the trimetaphosphate with respect to hydrolysis in the presence of UO_2^{2+} ions. α- and β-$U(PO_3)_4$ have been obtained and identified by X-ray diffraction[180].

The study of condensed uranyl and uranium phosphates was extended by Soviet workers[181–185]. The crystalline condensed phosphates formed in the UO_2–P_2O_5–H_2O and UO_2–P_2O_5–M_2O–H_2O systems (M = alkali metal), which contain

molten polyphosphoric acids, were synthesised and studied. The conditions of formation and crystallisation of the phosphates $UO_2(PO_3)_2$, $UO_2H(PO_3)_3$, and $(UO_2)_2P_6O_{17}$ were determined[181]. The synthesis of the hydrogen phosphate stimulated the search for analogous compounds with alkali metal ions, of the type $MUO_2(PO_3)_3$, where M = Na, K, Rb, or Cs; their optimum crystallisation temperature is 320°.[181]

$UO_2H(PO_3)_3$ is made up of spiral polyphosphate chains $[H_2P_6O_{18}]^{4-}$ of six PO_4^{3-} tetrahedra, extending along the (100) direction, and joined by uranyl ions to form a three-dimensional framework[183].

The behaviour in a melt of the uranyl ion with the cations Sr, Ba, and Pb, and oxocations MO_2^{2+}, has been compared[181]. Uranyl cations and the cations of these metals form ultraphosphates $M^{II}{}_2P_6O_{17}$.

The possibility of obtaining the metaphosphate $U(PO_3)_4$ by the reaction of metallic uranium or $UO_2(NO_3)_2.6H_2O$ with a melt of 87% H_3PO_4 in the presence of $NH_4H_2PO_4$ (which accelerates the reduction of UO_2^{2+} to U^{4+}) has been studied[184,185]. $U(PO_3)_4$ crystallises in two forms. The compound $U(PO_3)_4$(I) has a structure analogous to the zirconium phosphate structure. It consists of a framework of $[UO_8]$ eight-apex polyhedra and chains of PO_4 tetrahedra cross-linked into double spirals. The structural analysis of metaphosphates makes it possible to regard all uranyl phosphates as polymers with a uranyl phosphate framework in which the water molecules and other metal ions are situated in the space between the layers. In a number of phosphates, the water molecules are coordinated directly to the uranium atom.

Uranyl phosphites $UO_2HPO_3.3H_2O$,[186] $M_2UO_2(HPO_3)_2$ (M = Na, K, NH_4),[187] and the products of the reaction with amides[188] are also polymeric. The uranium(IV) phosphites $U(HPO_3)_2.2H_2O$ and $U(H_2PO_3)_4$[189] have also been obtained.

The reduction of $UO_2(PO_3)_2$ and vitreous $UO_3.1.5P_2O_5$ by hydrogen has been studied[190]. It is suggested that the reduction takes place according to the scheme:

$$UO_2(PO_3)_2 \xrightarrow{450-600^\circ} \supset P_2O_7\ (\text{cubic}) \rightarrow UP_2O_7\ (\text{orthorhombic}) \rightarrow (UO_2)_2P_2O_7 \rightarrow U_8O_{13}.$$

Cubic UP_2O_7 is stable up to 1000°. In $NaPO_3$–NaCl melts at 700–900° in the range rich in sodium metaphosphate, favourable conditions are created for the rapid solution of the sparingly soluble oxide UO_2.[191] The mechanism of the reaction in the system, and the form of the phosphate obtained, were not studied, however[191].

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The material examined deals with the synthesis of uranyl and uranium phosphates, the problems of studying their behaviour in solution, the stability of the crystalline hydrates, and the stability of the phosphate anion with increase in the length of the phosphate chain. Study of the thermal decomposition has shown that the behaviour of the compounds in these processes is determined by their structure and the mode of binding of the phosphate anion and the water molecules. When uranium phosphates contain mobile water molecules and protons, the decomposition processes become more complex: polymerisation of the phosphate anion, liberation of H_3PO_4, etc.

The study of uranium phosphates is opening up new possibilities for their further use in electrochemical devices, for dissolving sparingly soluble oxides, and also to solve the problems of improving the technology of the extraction of uranium from phosphate raw material, which is now acquiring increasing importance as rich uranium ores become exhausted. In the production of phosphoric acid by extraction, methods have been developed which make it possible to extract up to 10% of the total uranium produced[192–199].

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