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The physical chemistry of the compounds $M^IP(As)UO_6$ (M^I = H, Li, Na, K, Rb, Cs) and their crystalline hydrates

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Contents

I.	Introduction	913
II.	Discovery of the compounds $M^IP(As)UO_6 \cdot nH_2O$	913
III.	The structure of the compounds $M^IP(As)UO_6 \cdot nH_2O$	914
IV.	Thermographic study of the compounds $M^IP(As)UO_6 \cdot nH_2O$	918
V.	Thermodynamic properties of the compounds $M^IP(As)UO_6 \cdot nH_2O$	921
VI.	Standard enthalpies of formation of the compounds $M^IP(As)UO_6$ and their crystalline hydrates	921
VII.	Conclusion	925

Abstract. Problems concerning the structures of compounds of the series $M^IP(As)UO_6 \cdot nH_2O$ (M^I = H, Li, Na, K, Rb, Cs; n = 4 for M^I = H, Li and n = 3 for M^I = Na, K, Rb, Cs) are examined. The results of X-ray powder diffraction, thermographic, and IR spectroscopic studies on the above compounds are analysed. The experimental standard enthalpies of formation ($\Delta_f H^\circ$) of the compounds $M^IP(As)UO_6$ and their crystalline hydrates are discussed. The characteristic features of the variation of $\Delta_f H^\circ$ as a function of the structural characteristics of the compounds and of the physical properties of the Group I elements in the series of phosphorus and arsenic compounds are described. The enthalpies of dehydration and ion exchange involving the compounds investigated are presented. The bibliography includes 103 references.

I. Introduction

The compounds $M^IM^VUO_6 \cdot nH_2O$, where M^I = hydrogen or an alkali metal and M^V = phosphorus or arsenic, are of interest by virtue of a whole series of factors. The compounds include well-known, and fairly widely distributed in nature, uranium minerals with M^I = H, Na, or K, the rubidium compounds which have been much less investigated and are not encountered in nature, as well as the caesium compounds and natural uranium compounds with the same formula containing vanadium as the pentavalent element, which have not been investigated at all.

It is known that the compounds $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$ have a high proton conductivity and may be used in autonomous energy sources. The alkali metal derivatives are interesting from the standpoint of their electrophysical characteristics: for example, a high ionic conductivity is characteristic of these substances. Finally, the natural compounds $M^IP(As)UO_6 \cdot nH_2O$ are widely distributed objects of study in the geochemistry of uranium, in the development of processes for its extraction from natural raw material, and in the processing of uranium-containing waste.

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For the successful practical utilisation of the compounds $M^IP(As)UO_6 \cdot nH_2O$, it is necessary to have scientific information about the characteristics of their structure, their properties which depend on their physical state, and the energy characteristics of the chemical reactions and processes involving them. The foregoing suggests that a combined physicochemical study of the compounds $M^IP(As)UO_6 \cdot nH_2O$ is of current interest and desirable.

II. Discovery of the compounds $M^IP(As)UO_6 \cdot nH_2O$

The main element determining the nature of the structure of the compounds $M^IP(As)UO_6 \cdot nH_2O$ is uranium(VI). The crystal structures of compounds of uranium(VI) are on the whole determined by its pronounced tendency to form the O⩲U⩲O structural motif with two extremely strong and axially disposed uranium–oxygen bonds with increased [substantial? (Ed. of Translation)] multiplicity. This structural element is referred to as the uranyl group. The presence of the uranyl group in a compound usually gives rise to a layered structure.[1,2] The other elements — phosphorus, arsenic, and the alkali metal — have less influence on the overall structure. They perform a subsidiary function, 'building up' the structure of the compound and making it electrically neutral. The complex compounds containing uranium(VI) have therefore come to be referred to as the uranium compounds.

Information about the compounds $M^IPUO_6 \cdot nH_2O$ first appeared in the literature at the beginning of the XIXth century. The first studies have been reviewed in two publications.[3,4] These and other investigations (for example, those of Linau[5] and Rimbach[6]), carried out in France and Germany towards the beginning of the XXth century, were descriptive in character and contained no data about any kind of physicochemical measurements.

Scientific interest in the compound $M^IP(As)UO_6 \cdot nH_2O$ was not renewed until the 1930s–1940s in connection with the development of nuclear power. The enormous interest in uranium as a strategic raw material led to a vigorous search during these years for uranium deposits throughout the world. The study of uranium minerals showed that among them there are more than 20 varieties of the so-called phosphate and arsenate mica-like materials having the composition $M^m_{1/m}P(As)UO_6 \cdot nH_2O$, where $M^m_{1/m}$ are univalent or divalent elements.[2,7–14] $HPUO_6 \cdot 4H_2O$ (hydroautunite), $HAsUO_6 \cdot 4H_2O$

(hydrouranospinite), $NaPUO_6 \cdot 3H_2O$ (sodium autunite), $NaAsUO_6 \cdot 3H_2O$ (elvailerite), $KPUO_6 \cdot 3H_2O$ (metaankoleite), and $KAsUO_6 \cdot 3H_2O$ (abernathyite) have been found among the uranium mica-like materials. The corresponding rubidium and caesium compounds have not been found in nature. Naturally, the crude mineral material does not contain the pure individual phases but solid solutions, isomorphously substituted mixtures, and mechanical mixtures with other minerals, i.e. compositions with defective structures.

In order to determine the structure and to investigate the physicochemical characteristics, the compounds $M^IP(As)UO_6 \cdot nH_2O$ with M^I = H, Na, K, or NH_4 have been synthesised. The methods of synthesis, the conditions for isolation from solution, the solubilities, the dehydration conditions, and other properties of the compounds of the elements listed above have been discussed.[3,4,13,15-27] The studies published in the 1950s–1960s are extremely contradictory and approximate and refer solely to uranium(VI) phosphate derivatives.

The next period in the study of the properties of the compounds $M^IP(As)UO_6 \cdot nH_2O$ began in the 1970s and has continued to this day. It is difficult to establish who was the first to note the high proton conductivity of $HPUO_6 \cdot nH_2O$. Most probably this was done simultaneously by different investigators.[26,28,29] The conductivity of $HPUO_6 \cdot nH_2O$, which is 0.2 Ω^{-1} cm^{-1} at 90 °C, proved to be much higher than in the solid proton-containing materials known at the time.[26,29-31] The low solubility, corrosion stability, the ease of mechanical treatment, and the fairly high thermal stability, which are characteristic of crystalline $HPUO_6 \cdot 4H_2O$, make it an extremely promising electrolyte in autonomous electrochemical energy sources. These studies initiated more detailed structural investigations employing different physical methods and aroused interest in the arsenate derivatives of uranium(VI) and alkali metals having similar compositions and structures. In the 1980s, the number of studies devoted to the proton conductivity of $HP(As)UO_6 \cdot 4H_2O$ increased in an avalanche-like fashion. However, because this aspect is outside the scope of the problem with which we are concerned we shall confine ourselves here merely to presenting a brief bibliography[32-44] of the descriptions of the electrophysical properties of the compounds $M^IP(As)UO_6 \cdot nH_2O$. We shall note only that, together with the use in electrochemical energy sources,[44] reports have appeared on the employment of $HP(As)UO_6 \cdot 4H_2O$ as a sensor for the detection of protons,[38] in a solid-state electrochromic display,[40] and in luminescent materials.[45]

Towards the beginning of the 1990s, reports concerning the application of the compounds $M^IM^VUO_6 \cdot nH_2O$, where M^V = vanadium, niobium, tantalum, or antimony, for the fixation of ecologically dangerous radionuclides in order to immobilise them in the human habitat, began to appear.[35,36,46-50]

At the same time, studies were published[52,53] in which it was shown that neptunium(VI), plutonium(VI), and americium(VI) can replace uranium(VI),[51] whilst the lanthanides(III) and the actinides(III) can replace M^I in the compounds $M^IP(As)UO_6 \cdot nH_2O$. Natural and synthetic compounds having the composition $M^{II}_{0.5}P(As)UO_6 \cdot nH_2O$, where M^{II} = an alkaline earth metal or other divalent element, are also known.[54-57]

Comparison of the structural characteristics of the compounds $M^m_{1/m}P(As)UO_6 \cdot nH_2O$, where M^m represents univalent, divalent, or trivalent elements, on the one hand, and the compounds $M^n_{1/n}M^VM^{VI}O_6W \cdot nH_2O$, where M^V = vanadium, niobium, tantalum, or antimony and M^{VI} = neptunium, plutonium, or americium, on the other, showed that all the compounds have a layer structure and probably tend to form mixed crystals. This indicates the possibility of their employment for the retention of a wide range of radionuclides in different valence states in the form of a single thermally and chemically stable crystalline matrix.[52-57]

III. The structure of the compounds $M^IP(As)UO_6 \cdot nH_2O$

Numerous studies have been devoted to problems of the structure of the compounds $M^IP(As)UO_6 \cdot nH_2O$.[2,13,30,51,58-67] However, the functional composition of the compounds is treated in different ways by different investigators. In most reports, the phosphates and arsenates of uranium(VI) and univalent elements are regarded as double salts — disubstituted uranyl phosphates and arsenates having the compositions $UO_2M^IPO_4 \cdot nH_2O$ and $UO_2M^IAsO_4 \cdot nH_2O$. Such representation of the formula unit presupposes the existence of an anionic sublattice, made up of phosphate or arsenate tetrahedra, and a cationic sublattice, the sites of which contain the uranyl groups and the cations of the univalent element. However, such representation of the compounds is more a result of the tradition established by mineralogists in relation to uranium(VI) minerals[2] rather than reflecting the true situation corresponding to the experimental facts.

According to X-ray diffraction data, the uranium in the compound $UO_2HPO_4 \cdot 4H_2O$ [30] is in an octahedral environment comprising oxygen atoms, two of which actually form shortened O⋯U⋯O linkages with an increased multiplicity along one of the fourfold axes and these have in fact been interpreted as isolated uranyl groups UO_2^{2+}. However, the remaining four uranium–oxygen bonds in the octahedron are also distinguished by an appreciable strength and do not permit the isolation of the uranyl group without the disruption of the structure as a whole.

From our point of view, which is shared also by other investigators (see, for example, Weigel and Hoffman[51]), the compounds under consideration should be regarded as salts of phosphouranic and arsenouranic acids $M^IP(As)UO_6 \cdot nH_2O$. In these compounds, phosphorus and uranium or arsenic and uranium form a common anionic framework in the form of two-dimensional layers of the type $[P(As)UO_6]^{n-}_{2\infty}$ distinguished by an increased stability. The cations binding the layers play an appreciably smaller role in the formation of the crystal structure as a whole. They merely promote the imposition of a certain order in the interlayer space, ordering the disposition of the H_2O molecules and regulating their number.

The compounds $M^IP(As)UO_6 \cdot nH_2O$ can hardly be regarded as complex uranium(VI) oxides, because according to current ideas,[68] the cationic and anionic sublattices can be fairly readily isolated in their structures. Such separation is usually difficult in the structure of a complex oxide. Thus the most correct representation of the formula unit in the compounds under consideration is $M^IP(As)UO_6 \cdot nH_2O$, since it reflects most satisfactorily their functional properties and structural characteristics.

Direct structural studies on the compounds $M^IP(As)UO_6 \cdot nH_2O$ by X-ray diffraction and neutron diffractometric methods have been carried out in relation to the $HPUO_6 \cdot 4H_2O$,[30] $HAsUO_6 \cdot 4H_2O$,[60] $LiAsUO_6 \cdot 4H_2O$,[62] $KPUO_6 \cdot 3H_2O$,[61] and $KAsUO_6 \cdot 3H_2O$ [13] single crystals. Analysis of these data showed that the phosphouranic and arsenouranic acids are full structural analogues. As an illustration, Fig. 1 presents the crystal structure of $HPUO_6 \cdot 4H_2O$ in projection onto the 100 and 001 crystallographic planes.[30] According to these data, the structure is of the typical layered type. The uranium(VI) ions are located in an octahedral environment comprising oxygen atoms, two of which form shortened O⋯U⋯O linkages along an axis perpendicular to the $[P(As)UO_6]^{n-}_{2\infty}$ layer. The remaining four oxygen atoms belong to four different tetrahedral phosphate or arsenate groups. Water molecules, linked to one another by hydrogen bonds to form squares, the planes of which are parallel to the plane of the layer, are located between the layers. The centres of the squares are located on axes passing through the 'uranyl' groups. The protons compensating for the negative charge of the layer are located between two nearest water molecules belonging to neighbouring squares. Thus only two water molecules are linked

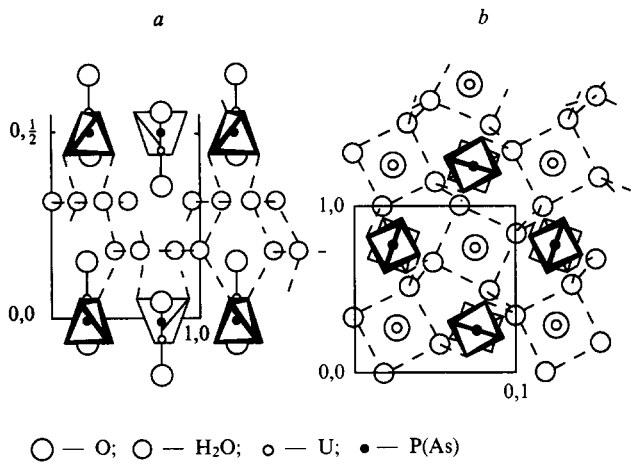


Figure 1. The crystal structure of the compound $HPUO_6 \cdot 4H_2O$ in projection onto the 100 (*a*) and 001 (*b*) planes.

to protons, forming the hydroxonium ions $H_5O_2^+$. Comparison of the crystal structures of the acids $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$ as well as the salts $LiAsUO_6 \cdot 4H_2O$, $KPUO_6 \cdot 3H_2O$, and $KAsUO_6 \cdot 3H_2O$ shows that both the hydrogen and salt forms have similar structures of the $[P(As)UO_6]^{n-}_{\infty}$ two-dimensional layer. The differences are manifested only in the positions of the alkali metal cations and the proton. Thus, when the proton is replaced by a lithium ion, no changes are observed in the structure and the number of water molecules is also retained. However, in the case of the larger K^+ ions, the H^+ or Li^+ positions become inaccessible. Therefore, when H^+ is replaced by K^+, the hydroxonium ion H_3O^+ is displaced from the structure and the K^+ cation occupies the position of one of the water molecules. As a result, the potassium salt contains one H_2O molecule less. This substitution mechanism probably operates also in the case of the sodium and rubidium compounds. However, direct structural studies on the above crystal phases have not been carried out. There are only numerous results of X-ray phase analysis and of the indexing of the X-ray diffraction powder patterns comprising the phospho- and arseno-uranate derivatives of hydrogen, lithium, sodium, potassium, and rubidium. The contradictory and ambiguous nature of the available results may be judged by analysing the crystallographic characteristics presented in Table 1 and calculated by different workers. The uncertainty in the available information applies both to the choice of the crystal system and symmetry space group and to the determination of the number of water molecules per formula unit of the compound. There is no information whatever in the literature about the composition and structure of the caesium derivatives.

The X-ray diffraction studies carried out on the $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$ single crystals at the beginning of the 1980s elucidated to a large extent the nature and position of the water in the above compounds. During the preceding period, frequent attempts were made to investigate the nature of the water in $M^IP(As)UO_6 \cdot nH_2O$ by means of other methods. One of the early publications[69] describes a simplified treatment of the IR spectra of $HPUO_6 \cdot 4H_2O$, in which bands belonging to the 'uranyl' group were differentiated. Another communication[70] gives a fuller description of the state of water based on the analysis of the IR spectra and it is concluded that the hydroxonium ion $H_9O_4^+$ is present in the $HPUO_6 \cdot 4H_2O$ structure. Kobets et al.,[28] who noted that the proton is localised in the hydroxonium ion, arrived at the same conclusion. It is noteworthy that this was an incorrect conclusion, because the IR spectra quoted in the above communications contained the band due to the deformation vibrations of H_2O in the region of 1625 cm^{-1}. This band shows that a proportion of the water does not belong to hydroxonium ions. Subsequent direct structural studies showed that only two out of the four water molecules are involved in the interaction with the proton, affording a hydroxonium ion of the type $H_5O_2^+$.[60]

Thus one may conclude that the characteristics of the structure and the state of the water molecules in $M^IP(As)UO_6 \cdot nH_2O$ have been established reliably only for a small number of compounds, namely for $HPUO_6 \cdot 4H_2O$, $HAsUO_6 \cdot 4H_2O$, $LiAsUO_6 \cdot 4H_2O$, $KPUO_6 \cdot 3H_2O$, and $KAsUO_6 \cdot 3H_2O$. Only X-ray phase analysis has been carried out for the compounds $NaP(As)UO_6 \cdot 3H_2O$ and $RbP(As)UO_6 \cdot \cdot 3H_2O$, indicating that they may belong to a single structural type. The analogous caesium compounds have not been investigated and there are no reports in the literature about their structure.

Studies on the structures of the crystalline phases of $HPUO_6 \cdot 4H_2O$, $HAsUO_6 \cdot 4H_2O$, and their derivatives with all the alkali metals (including the caesium derivatives which we obtained), carried out at the beginning of the 1990s (Tables 2 and 3), indicate that the X-ray diffraction patterns of all the compounds contain similar sets of reflection maxima with similar p ɔsitions and relative intensities. Lower relative intensities of a series of diffraction peaks and a reduction in the number of the latter have been observed only in the case of $CsPUO_6 \cdot 3H_2O$ and $CsAsUO_6 \cdot 3H_2O$. These findings may be a consequence of the steric strain arising in the crystal lattices after the incorporation in the latter of the large caesium ions.

Table 1. Crystallographic characteristics of the compounds $M^IP(As)UO_6 \cdot nH_2O$ with a tetragonal crystal system.

Compound	Space group	Unit cell parameters/Å		Z	Ref.	Compound	Space group	Unit cell parameters/Å		Z	Ref.
		a	*c*					*a*	*c*		
α-$HPUO_6 \cdot 4H_2O$	*P4/ncc*	6.995	17.491	4	30	$HAsUO_6 \cdot 4H_2O$	*P4/ncc*	7.153	17.607	–	67
$HPUO_6 \cdot 4H_2O$	*P4/ncc*	6.979	17.465	4	67	$HAsUO_6 \cdot 4H_2O$	–	7.12	8.77	2	51
$HPUO_6 \cdot 4H_2O$	*P4/ncc*	6.973	17.414	–	45	$HAsUO_6 \cdot 4H_2O$	–	7.157	17.612	–	45
$LiPUO_6 \cdot 4H_2O$	–	6.93	9.07	2	51	$LiAsUO_6 \cdot 4H_2O$	*P4/n*	7.097	9.190	2	62
$NaPUO_6 \cdot 3H_2O$	–	7.00	8.72	2	51	$LiAsUO_6 \cdot 4H_2O$	–	7.13	9.21	2	51
$NaPUO_6 \cdot (3-4)H_2O$	–	6.97	8.69	1	51	$NaAsUO_6 \cdot 3H_2O$	*P4/ncc*	7.152	17.292	4	67
$NaPUO_6 \cdot 4H_2O$	–	7.04	8.46	–	51	$NaAsUO_6 \cdot 3\frac{1}{2}H_2O$	–	7.15	8.73	2	51
$KPUO_6 \cdot 3H_2O$	*P4/ncc*	6.994	17.784	4	61	$NaAsUO_6 \cdot 4H_2O$	*P4/n*	7.12	8.70	–	51
$KPUO_6 \cdot 3H_2O$	–	6.99	8.9	2	51	$KAsUO_6 \cdot 3H_2O$	*P4/ncc*	7.176	18.126	4	13
$KPUO_6 \cdot 3H_2O$	–	6.99	8.89	1	51	$KAsUO_6 \cdot 3H_2O$	*P4/n*	7.17	9.07	2	13
$KPUO_6 \cdot 3H_2O$	*P4/ncc*	6.991	17.806	4	67	$KAsUO_6 \cdot 3H_2O$	*P4/ncc*	7.163	17.846	4	67
$RbPUO_6 \cdot 3H_2O$	*P4/ncc*	7.02	18.24	4	67	$KAsUO_6 \cdot 3H_2O$	–	7.19	8.99	2	51
$HAsUO_6 \cdot 4H_2O$	*P4/nmm*	7.16	8.80	–	51	$RbAsUO_6 \cdot 3H_2O$	*P4/ncc*	7.19	17.65	4	67

Table 2. X-Ray diffraction data for the compounds $M^IPUO_6 \cdot nH_2O$.[71]

$HPUO_6 \cdot nH_2O$			$LiPUO_6 \cdot nH_2O$			$NaPUO_6 \cdot nH_2O$			*hkl*	$KPUO_6 \cdot nH_2O$			$RbPUO_6 \cdot nH_2O$			$CsPUO_6 \cdot nH_2O$			*hkl*
d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)		d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)	
8.720	8.672	100	9.121	9.118	100	8.577	8.588	100	002	8.915	8.974	33	9.041	9.025	71	8.814	8.801	44	002
5.451	5.438	28	5.526	5.522	31	5.409	5.405	36	102	5.494	5.505	45	5.532	5.522	30	–	–	–	102
4.938	4.941	17	4.911	4.901	23	4.928	4.914	36	110	4.933	4.928	36	4.946	4.941	36	4.953	4.955	33	110
4.297	4.301	23	4.324	4.322	38	4.273	4.270	47	112	4.317	4.311	38	4.339	4.332	45	4.318	4.32	22	112
3.698	3.700	70	3.812	3.818	77	3.652	3.655	81	104	3.756	3.754	100	3.793	3.801	100	3.730	3.731	100	104
3.492	3.243	35	3.245	3.243	51	3.228	3.226	51	202	3.249	3.249	73	3.262	3.261	98	3.255	3.255	67	202
2.940	2.940	17	2.940	2.940	34	2.929	2.931	29	212	2.945	2.945	55	2.945	2.954	54	2.952	2.954	22	212
2.684	2.683	28	2.785	2.784	31	2.645	2.644	24	106	2.732	2.734	31	–	–	–	–	–	–	106
2.539	2.539	11	2.567	2.567	15	–	–	–	214	–	–	–	2.574	2.578	18	–	–	–	116
2.505	2.505	7	–	–	–	–	–	–	116	–	–	–	2.473	2.475	18	–	–	–	220
2.376	2.374	9	2.371	2.374	22	–	–	–	222	2.377	2.377	36	2.385	2.386	30	–	–	–	222
2.208	2.206	9	2.1967	2.198	28	2.204	2.204	24	310	2.206	2.209	31	2.212	2.214	36	–	–	–	310
2.141	2.141	7	–	–	–	2.134	2.134	21	312	2.142	2.146	45	–	–	–	–	–	–	312
2.128	2.129	21	2.173	2.173	29	–	–	–	216	–	–	–	2.151	2.151	36	–	–	–	108
2.081	2.080	10	–	–	–	–	–	–	108	2.062	2.062	27	–	–	–	–	–	–	304
2.054	2.053	11	–	–	–	–	–	–	304	1.831	1.831	17	–	–	–	–	–	–	306
1.1994	1.994	11	–	–	–	–	–	–	118										
–	–	–	1.842	1.841	17	–	–	–	306										
1.788	1.787	7	–	–	–	–	–	–	218										
1.746	1.746	7	–	–	–	–	–	–	400										
1.644	1.645	14	–	–	–	–	–	–	1.1.10										

Note. The following notation has been adopted: d_c and d_e are the calculated and experimental interplanar spacings and I is the relative intensity.

Table 3. X-Ray diffraction data for the compounds $M^IAsUO_6 \cdot n H_2O$.[72]

$HAsUO_6 \cdot nH_2O$			$LiAsUO_6 \cdot nH_2O$			$NaAsPUO_6 \cdot nH_2O$			*hkl*	$KAsUO_6 \cdot nH_2O$			$RbAsUO_6 \cdot nH_2O$			$CsAsUO_6 \cdot nH_2O$			*hkl*
d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)		d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)	d_c/Å	d_e/Å	I(%)	
8.797	8.801	100	8.904	8.845	100	8.560	8.547	100	002	9.069	8.845	100	8.797	8.715	100	9.187	8.801	100	002
5.544	5.539	25	5.575	5.574	7	5.484	5.488	10	102	5.625	5.574	9	5.562	5.556	7	–	–	–	102
5.049	5.039	12	5.055	5.039	5	5.050	5.049	5	110	5.072	5.071	4	5.076	5.007	5	–	–	–	110
4.379	4.385	22	–	–	–	–	–	–	112	4.427	4.440	22	4.397	4.396	43	4.430	4.428	80	112
–	–	–	4.452	4.439	24	4.280	4.301	22	004	3.883	3.788	22	3.750	3.746	31	3.865	3.762	33	104
3.745	3.746	53	3.779	3.778	19	3.671	3.685	36	104	3.586	3.576	7	3.589	3.590	8	3.576	3.583	13	200
3.570	3.569	22	3.575	3.576	5	3.571	3.596	10	200	–	–	–	3.324	3.326	14	–	–	–	114
3.308	3.308	34	3.317	3.314	12	3.295	3.296	14	202	3.335	3.320	9	–	–	–	3.332	3.314	20	202
3.001	2.998	16	3.009	3.010	5	2.993	2.993	5	212	–	–	–	3.016	3.013	8	–	–	–	212
2.772	2.771	6	2.787	2.789	5	–	–	–	204	2.023	2.003	4	–	–	–	–	–	–	006
2.713	2.710	16	–	–	–	2.650	2.663	13	106	2.786	2.743	9	2.715	2.718	10	–	–	–	106
2.584	2.662	9	–	–	–	2.560	2.560	5	214	2.597	2.596	4	2.539	2.543	8	–	–	–	116
–	–	–	2.559	2.560	5	–	–	–	116	2.536	2.537	4	–	–	–	–	–	–	220
2.524	2.529	14	–	–	–	2.525	2.527	5	220	–	–	–	2.439	2.442	5	–	–	–	22
2.426	2.426	11	2.432	2.433	6	–	–	–	222	–	–	–	–	–	–	2.221	2.219	33	303
2.199	2.196	12	2.226	2.225	31	2.484	2.151	12	008	–	–	–	2.199	2.201	32	–	–	–	008
2.160	2.161	12	2.175	2.176	7	–	–	–	216	–	–	–	2.165	2.163	10	–	–	–	216
2.093	2.017	16	2.037	2.040	12	1.940	1.918	10	118	2.162	2.176	5	2.103	2.103	8	–	–	–	108
–	–	–	1.781	1.780	7	–	–	–	0.0.10	–	–	–	2.018	2.019	10	–	–	–	118
1.661	1.661	12	1.680	1.681	10	–	–	–	1.1.10	2.029	2.040	9	–	–	–	2.029	2.032	15	314
1.578	1.576	16	–	–	–	–	–	–	2.0.10	1.814	1.812	4	–	–	–	–	–	–	0.0.10
										–	–	–	1.662	1.665	11	–	–	–	1.1.10
										–	–	–	1.580	1.581	7	–	–	–	2.0.10

The analytical indexing of the X-ray powder diffraction patterns presented in Table 4 shows that all the compounds have similar structures and have close unit cell parameters. Analysis of the IR spectra permits a fuller interpretation of the structures of the test compounds. The number of absorption bands, their positions, and their relative intensities are similar in the spectra of all the compounds in each of the series of phosphates and arsenates of the uranium derivatives. They confirm not only the structural similarity but also the similar functional composition and the identical nature of the distortion in the compounds of the principal coordination tetrahedra of phosphorus and arsenic (tetrahedra), uranium(VI) (octahedron), and the alkali metal. The assignment of the absorption bands in the spectra of the compounds $M^IPUO_6 \cdot nH_2O$ and $M^IAsUO_6 \cdot nH_2O$ is presented in Tables 5 and 6. The partial superposition of the stretching vibrations of the arsenate tetrahedron and of the shortened U⋯O⋯U linkages of the UO_6 octahedron in the 800–900 cm^{-1} region does not hinder their assignment because of their highly characteristic nature.

Table 4. The tetragonal unit cell parameters of the compounds $M^IP(As)UO_6 \cdot nH_2O$ (space group $P4/ncc$, $Z = 4$).[71,72]

Compound	a/Å	c/Å
$HPUO_6 \cdot 4H_2O$	6.984 ± 0.001	17.440 ± 0.004
$LiPUO_6 \cdot 4H_2O$	6.945 ± 0.002	18.242 ± 0.013
$NaPUO_6 \cdot 3H_2O$	6.949 ± 0.001	17.154 ± 0.007
$KPUO_6 \cdot 3H_2O$	6.977 ± 0.002	17.829 ± 0.010
$RbPUO_6 \cdot 3H_2O$	6.994 ± 0.002	18.083 ± 0.011
$CsPUO_6 \cdot 3H_2O$	7.005 ± 0.003	17.629 ± 0.014
$HAsUO_6 \cdot 4H_2O$	7.140 ± 0.002	17.594 ± 0.007
$LiAsUO_6 \cdot 4H_2O$	7.149 ± 0.006	17.808 ± 0.012
$NaAsUO_6 \cdot 3H_2O$	7.142 ± 0.002	17.119 ± 0.009
$KAsUO_6 \cdot 3H_2O$	7.172 ± 0.008	18.138 ± 0.042
$RbAsUO_6 \cdot 3H_2O$	7.178 ± 0.005	17.594 ± 0.018
$CsAsUO_6 \cdot 3H_2O$	7.151 ± 0.031	18.374 ± 0.080

The characteristic vibrations of the water of crystallisation can be distinguished in the spectra. The most striking feature is the separation into components of the ν_2 deformation vibration bands of water in the $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$ spectra. The ν_2 vibration of water in the $HPUO_6 \cdot 4H_2O$ spectrum at 1637 cm^{-1} is accompanied by a band with an intensity equal to that of the band at 1737 cm^{-1} corresponding to the deformation vibrations of the hydroxonium ion.[74] A similar separation of the ν_2 vibrations into bands at 1626 and 1737 cm^{-1} occurs in the $HAsUO_6 \cdot 4H_2O$ spectrum. The ν_2 doublets with comparable relative intensities permit the assumption that two water molecules form the hydroxonium ion $H_5O_2^+$, while the remaining water molecules retain their molecular individuality.[73]

The ν_2 vibrations of water in the IR spectra of $LiPUO_6 \cdot 4H_2O$ and $LiAsUO_6 \cdot 4H_2O$ are also represented by doublets at 1635 and 1675 cm^{-1} for the first compound and at 1614 and 1659 cm^{-1} for the second. The appearance of the doublets is a consequence of the nonuniformity of the water molecules in the lithium compounds and indicates the isolation of part of the water in the form of complex ions of the type $(H_2OLiOH_2)^+$ owing to the formation of the familiar Li bond. Thus the small size of the H^+ and Li^+ ions and their high electrostatic fields are the cause of the increased content of water molecules in the $HP(As)UO_6 \cdot 4H_2O$ and $LiP(As)UO_6 \cdot 4H_2O$ crystal lattices and are responsible for the incorporation of water molecules in the hydroxonium and 'lyonium' ions. The ν_2 deformation vibration bands of H_2O at 1600 cm^{-1} in the sodium, potassium, rubidium, and caesium compounds indicate the typically molecular form of water.

The ν_1 and ν_3 stretching vibrations of water in the region of 3400 cm^{-1} are not resolved in the spectra of any of the test compounds. They are represented in a broad band due to the presence of branched hydrogen bonds between the molecules of water of crystallisation.

The Cs^+ ions, among alkali metals, are characterised by the highest crystal-chemical radius and an extremely weak force field. Because of this, the X-ray diffraction patterns of the compounds $CsPUO_6 \cdot 3H_2O$ and $CsAsUO_6 \cdot 3H_2O$ reveal the disappearance of a series of diffraction peaks due to steric causes, indicating a degree of structural disorder.

Thus all the compounds considered with the composition $M^IP(As)UO_6 \cdot nH_2O$, where $M^I = H^+$, Li^+, Na^+, K^+, Rb^+, or Cs^+, are individual crystalline phases belonging to a single structural type. The composition of the coordination polyhedra of their structural-forming elements is based on the same principle and they differ from one another only in the number of molecules of water of crystallisation.

Table 5. Frequency assignments in the IR spectra of $M^IPUO_6 \cdot nH_2O$.[71]

Assignment	Vibration frequencies/cm^{-1}					
	$HPUO_6 \cdot nH_2O$	$LiPUO_6 \cdot nH_2O$	$NaPUO_6 \cdot nH_2O$	$KPUO_6 \cdot nH_2O$	$RbPUO_6 \cdot nH_2O$	$CsPUO_6 \cdot nH_2O$
$\nu(H_2O)$	3350 m	3390 m	3400 m	3440 m	3440 m	3390 m
$\delta(H_2O)$	1637 m	1675 m	1633 m	1640 m	1603 m	1645 m
		1635 m				
$\delta(H_3O^+)$	1737 m					
$\nu(PO_4)$	1090 w	1106 w	1103 w	1107 w	1106 w	1104 w
	985 s	993 s	997 s	997 s	997 s	993 s
$\delta(PO_4)$	600 w	610 w	610 w	590 w	590 w	590 w
$\nu(U{=}O)$	907 s	905 s	903 s	903 s	897 s	900 s
	809 w	800 w	803 w	800 w	783 w	803 w

Note. s = intense (strong), m = moderate, w = weak.

Table 6. Frequency assignments in the IR spectra of $M^IAsUO_6 \cdot nH_2O$.[72]

Assignment	Vibration frequencies/cm^{-1}					
	$HAsUO_5 \cdot nH_2O$	$LiAsUO_5 \cdot nH_2O$	$NaAsUO_5 \cdot nH_2O$	$KAsUO_5 \cdot nH_2O$	$RbAsUO_5 \cdot nH_2O$	$CsAsUO_5 \cdot nH_2O$
$\nu(H_2O)$	3350 m	3425 m	3395 m	3420 m	3400 m	3395 m
$\delta(H_2O)$	1626 m	1659 m	1626 m	1621 m	1618 m	1626 m
		1614 m				
$\delta(H_3O^+)$	1737 m					
$\nu(AsO_4)$	895 w	889 w	886 w	885 w	881 w	885 w
	803 s	805 s	802 s	805 s	804 s	802 s
$\delta(AsO_4)$	451 m	453 m	445 m	453 m	447 m	449 m
$\nu(U{=}U)$	916 m	918 m	917 m	919 m	921 m	919 m

IV. Thermographic study of the compounds $M^IP(As)UO_6 \cdot nH_2O$

The presence of water of crystallisation is responsible for important properties of the compounds $M^IP(As)UO_6 \cdot nH_2O$ with a layered structure. The capacity of compounds of this kind for hydration has two characteristic features: the unequal water contents for different alkali metals and the different nature of the water in the compounds under consideration. The same compound from the series considered can exist in states with different susceptibilities to hydration depending on the formation conditions. The number of water molecules changes stepwise on passing from one degree of hydration to another and the nature, location, and the role of water in the structure of each hydrate differ. The stability of a particular hydrate is determined by the size of the alkali metal cation. The removal of water from compounds with different cations under conditions where the water content is the same is accompanied by energy effects of different magnitude. This is associated with the nature of the ordered arrangement of the water molecules in the structure of the compound—their bonds both with the interlayer cation and the uranium phosphate (uranium arsenate) layer and with one another. Water determines in its turn the order in the packing of the anionic uranium layers and its removal leads to a shift of the layers relative to one another. The complete removal of water can lead to maximum disorder and hence to the retention of only two-dimensional order within the limits of the anionic uranium layer.

Despite the fact that the study of the dehydration of a number of the compounds $M^IP(As)UO_6 \cdot nH_2O$ has continued for more than 30 years, information about the temperature ranges in which water is removed is contradictory. Thus according to Karpov and Ambartsumyan,[75] 3.5 water molecules per formula unit are removed from $HPUO_6 \cdot 4H_2O$ in the temperature range 30–180 °C and four water molecules are removed at 230–250 °C. On the other hand, according to Weiss et al.,[76] three water molecules are removed from $HPUO_6 \cdot 4H_2O$ at 60 °C. The removal of 2.5 water molecules from the same compound at 60–70 °C and the removal of total water at 220 °C have been reported.[77] The most complete information about the dehydration of $HPUO_6 \cdot 4H_2O$ has been presented by Kobets and coworkers.[78,79] These results are presented in Table 7.

Table 7. Characteristics of the $HPUO_6 \cdot nH_2O$.[78,79]

Compound	Dehydration temperature range/K	Number of water molecules removed	$\Delta_r H°(T)$/ kJ mol^{-1}
$UO_2HPO_4 \cdot 4H_2O$	323–353	2	51.5 ± 2.5
$UO_2HPO_4 \cdot 2H_2O$	373–388	$\frac{1}{2}$	56.5 ± 3.3
$UO_2HPO_4 \cdot 1\frac{1}{2}H_2O$	443–463	$1\frac{1}{2}$	65.3 ± 2.9
$UO_2HPO_4 \cdot H_2O$	833–873	$\frac{1}{2}$	–

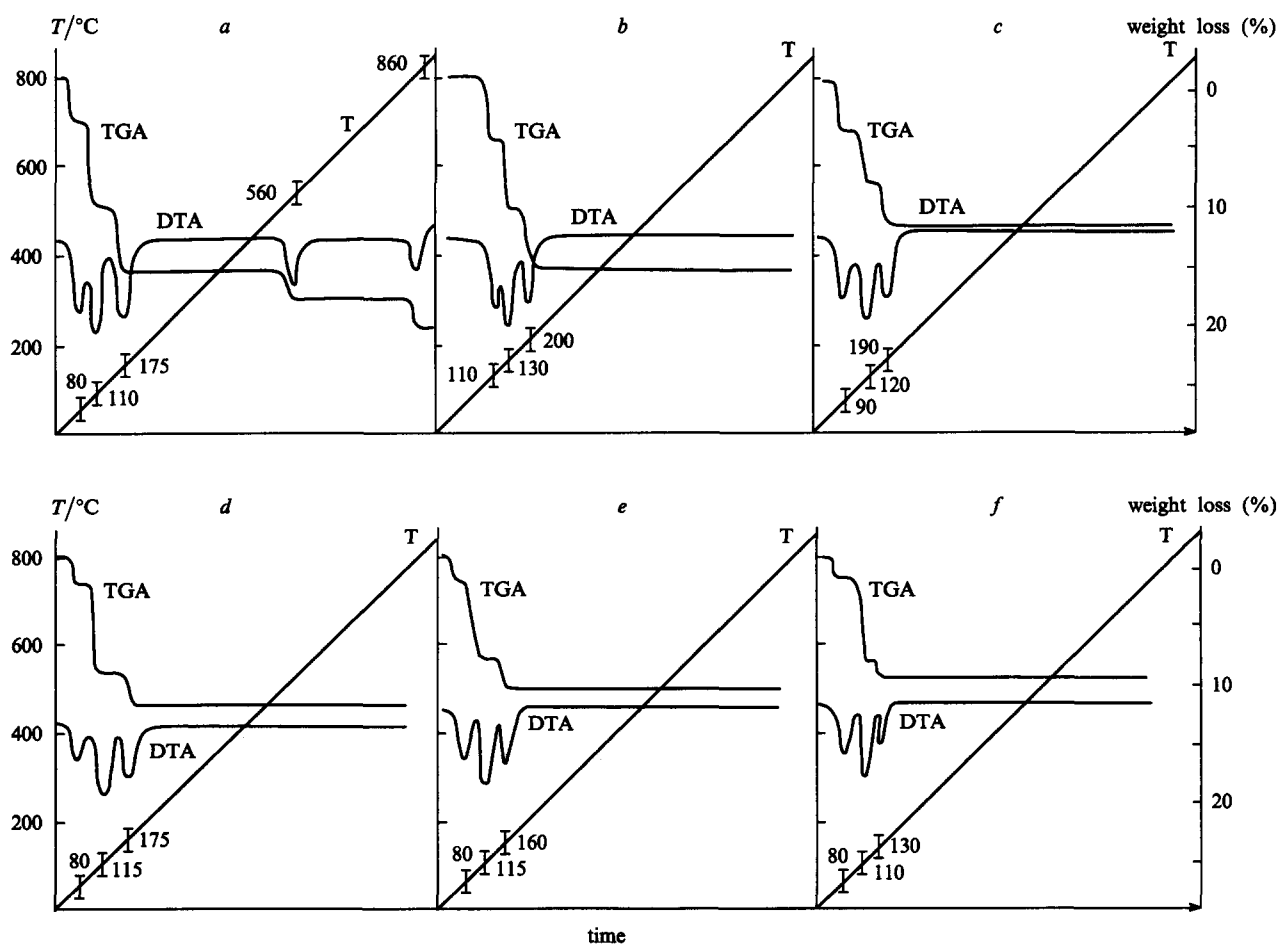


Figure 2. Derivatograms for the compounds $M^IPUO_6 \cdot nH_2O$: (*a*) $HPUO_6 \cdot 4H_2O$; (*b*) $LiPUO_6 \cdot 4H_2O$; (*c*) $NaPUO_6 \cdot 3H_2O$; (*d*) $KPUO_6 \cdot 3H_2O$; (*e*) $RbPUO_6 \cdot 3H_2O$; (*f*) $CsPUO_6 \cdot 3H_2O$.

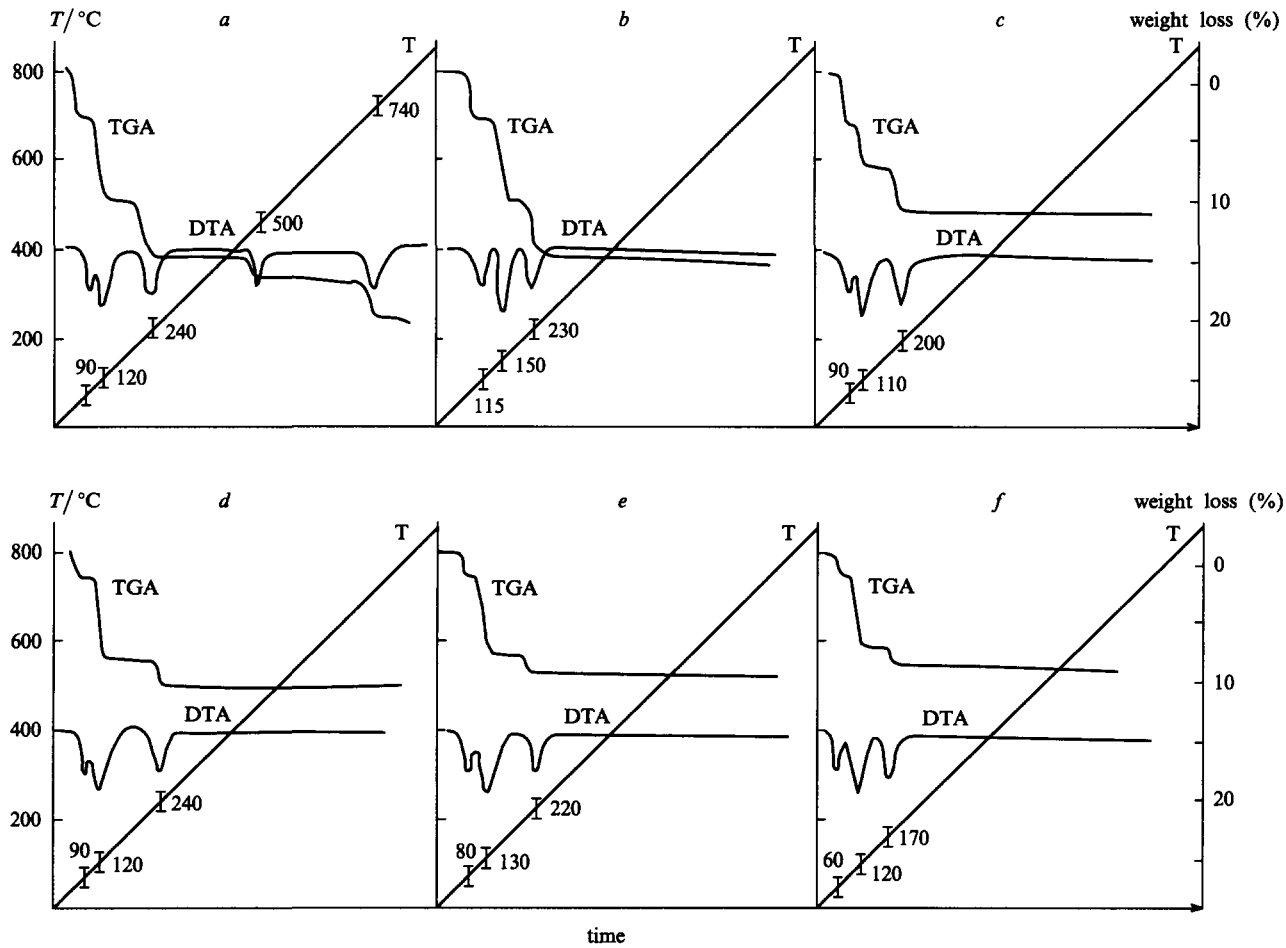


Figure 3. Derivatograms for the compounds $M^IAsUO_6 \cdot nH_2O$: (*a*) $HAsUO_6 \cdot 4H_2O$; (*b*) $LiAsUO_6 \cdot 4H_2O$; (*c*) $NaAsUO_6 \cdot 3H_2O$; (*d*) $KAsUO_6 \cdot nH_2O$; (*e*) $RbAsUO_6 \cdot 3H_2O$; (*f*) $CsAsUO_6 \cdot 3H_2O$.

The results quoted conflict with the data of other workers both as regards the temperature ranges and as regards the number of water molecules removed. However, they make it possible to estimate the enthalpy of the overall dehydration reaction of the crystalline compound $HPUO_6 \cdot 4H_2O$.

$$HPUO_6 \cdot 4H_2O \rightarrow HPUO_6(\text{solid}) + 4H_2O(\text{liq.}) \quad (1)$$

When account is taken of corrections for the enthalpy of vaporisation of water,[80] the enthalpy of the removal of four H_2O molecules calculated in terms of liquid water is $\Delta_r H^\circ_1(298)$ = 16.7 kcal mol^{-1} [69.9 kJ mol^{-1}]. The soundest available information (from the scientific point of view) about the dehydration reactions of the compounds $M^IP(As)UO_6 \cdot nH_2O$ is in essence restricted to these results. One may note in addition only isolated studies, carried out at different times, on the dehydration of $LiPUO_6 \cdot 4H_2O$,[3] $NaPUO_6 \cdot 4H_2O$, $NaAsUO_6 \cdot 4H_2O$, $KPUO_6 \cdot 4H_2O$, and $KAsUO_6 \cdot 4H_2O$.[2] However, the different experimental conditions, the uncertainty in the determination of the number of water molecules in the formula units of the same compounds, and the limited number of representatives of the $M^IP(As)UO_6 \cdot nH_2O$ structural series investigated have led to the problem of their dehydration being little studied.

The thermal stability of the compounds $M^IP(As)UO_6 \cdot nH_2O$ has been studied to an even lesser extent. Identical decomposition mechanisms have been put forward only for the compound $HPUO_6 \cdot 4H_2O$ by virtually all the workers who have investigated it (see, for example, Refs 25, 59, 79, and 81). The thermal stabilities of other compounds $M^IP(As)UO_6 \cdot nH_2O$ have not been studied.

The thermographic study of the compounds $M^IP(As)UO_6 \cdot nH_2O$ which we carried out by the derivatographic method combined with X-ray phase analysis of the intermediate and final dehydration thermal decomposition products showed that the acids $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$ are thermally least stable.[71-73] In conformity with the derivatograms presented in Figs 2 and 3, their thermal decomposition can be represented by the following reaction:

$$HPUO_6 \cdot 4H_2O \xrightarrow[-H_2O]{80\ ^\circ C} HPUO_6 \cdot 3H_2O \xrightarrow[-2H_2O]{110\ ^\circ C}$$
$$\rightarrow HPUO_6 \cdot H_2O \xrightarrow[-H_2O]{175\ ^\circ C} HPUO_6 \xrightarrow[-\frac{1}{2}H_2O]{560\ ^\circ C}$$
$$\rightarrow \tfrac{1}{2}(UO_2)_2P_2O_7 \xrightarrow[-\frac{1}{2}O_2]{>\ 860\ ^\circ C} \tfrac{1}{2}U_2O_3P_2O_7,$$

$$HAsUO_6 \cdot 4H_2O \xrightarrow[-H_2O]{90\ ^\circ C} HAsUO_6 \cdot 3H_2O \xrightarrow[-2H_2O]{120\ ^\circ C}$$
$$\rightarrow HAsUO_6 \cdot H_2O \xrightarrow[-H_2O]{240\ ^\circ C} HAsUO_6 \xrightarrow[-\frac{1}{2}H_2O]{500\ ^\circ C}$$
$$\rightarrow \tfrac{1}{2}(UO_2)_2As_2O_7 \xrightarrow[-\frac{1}{2}O_2]{740\ ^\circ C} \tfrac{1}{2}U_2O_3As_2O_7.$$

Analysis of the above data shows that the mechanisms of the dehydration and thermal decomposition of both compounds are the same with the sole difference that water is removed from $HAsUO_6 \cdot 4H_2O$ at a higher temperature and requires a larger

energy expenditure. On the other hand, the condensation of the acid group in $HAsUO_6$ takes place with a smaller energy expenditure than in the case of $HPUO_6$. The higher temperature ranges corresponding to the dehydration of $HAsUO_6 \cdot 4H_2O$ compared with $HPUO_6 \cdot 4H_2O$, despite their analogous composition and total structural similarity, may be due to the coordinative unsaturation of the arsenic in the AsO_4 polyhedron, which results in a redistribution of the electron density in the As ← O ← H chains, strengthening the hydrogen bonds. This property of arsenic(V) is characteristic of many arsenates[82] and is manifested even in As_2O_5, in the crystal lattice of which 50% of the arsenic atoms are involved in tetrahedral coordination, whilst the remaining 50% are involved in octahedral coordination,[77] which is completely uncharacteristic of oxygen compounds of phosphorus.

The higher temperatures of the condensation of the acid phosphate groups with formation of pyrophosphates are entirely reasonable and are a consequence of the coordinative saturation of the phosphorus in the PO_4 tetrahedron, which is responsible for the stability of the latter.

The compounds $M^IP(As)UO_6 \cdot nH_2O$, where M^I = Li, Na, K, Rb, or Cs, are distinguished by a higher thermal stability compared with the corresponding acids. After the multistage removal of molecular water, they all have the composition $M^IP(As)UO_6$. However, the elimination of water molecules from the coordination environment of the alkali metal cation leads to the disruption of the coordination polyhedron of the latter and to the breakdown of the structure of the compounds as a whole. The dehydration reactions of $M^IPUO_6 \cdot nH_2O$ and $M^IAsUO_6 \cdot nH_2O$ are presented below (Scheme 1).

Several trends are manifested in the dehydration reactions of the compounds $M^I(P)AsUO_6 \cdot nH_2O$, where M^I = H, Li, Na, K, Rb, or Cs, presented in Scheme 1. Firstly, the dehydration reactions of the phosphouranate and arsenouranate compounds of the same univalent element have the same stages. Secondly, lower temperature ranges of the dehydration reaction are characteristic of the phosphouranate derivatives, which may be a consequence of the weaker binding of water in these compounds. Thirdly, the temperature ranges of the dehydration reactions decrease on passing from lithium to caesium derivatives of both phosphouranate and arsenouranate compounds. This effect corresponds to a decrease in the enthalpies of dehydration of the alkali metal ions with increase in their size and indicates the inclusion of water molecules in the coordination environment of the univalent elements. Fourthly, the condensation of the acid groups in $HAsUO_6$ takes place with smaller energy expenditures than happens in the case of $HPUO_6$. This difference may be due to the coordinative unsaturation of the arsenic in the AsO_4 tetrahedron, which is the reason for its lower stability.

In connection with the thermal decomposition, it is necessary to consider yet another feature mentioned above. The complete dehydration of the compounds $M^IP(As)UO_6 \cdot nH_2O$ leads to their conversion into an amorphous form, i.e. to the breakdown of the long-range order and hence to the appearance of disorder in the crystal lattice. This is an extremely important feature because it involves a change in the energy state of the compounds and should influence their standard enthalpies of formation. The question arises of the reason for such conversion into an amorphous form. Direct structural studies on $KAsUO_6 \cdot 3H_2O$,[13] $KPUO_6 \cdot 3H_2O$,[61] and $LiAsUO_6 \cdot 4H_2O$ [62] single crystals have shown that the coordination environment of the alkali metal atoms includes the oxygen of the water of crystallisation. Since the oxygen atoms of the molecular water occupy the so-called crystallographic sites in the structure of the compounds, the removal of water leads to the disruption of the coordination polyhedra of the univalent elements and to the disordering of the structure as a whole. The possibility of the appearance of a new coordination environment around the alkali metal atoms is significantly hindered because the oxygen atoms present in the compounds $M^IP(As)UO_6$ now belong to the uranium octahedra and the phosphorus (arsenic) tetrahedra and are very rigidly fixed in the structure. As a result of this, instead of the stable lattice of the crystalline hydrate $M^IP(As)UO_6 \cdot nH_2O$, the less stable structure of the anhydrous compound with a highly polarised $M^{\delta+}[P(As)UO_6]^{\delta-}$ bond, similar to that which occurs in ionic melts, appears.

Scheme 1

$$LiPUO_6 \cdot 4H_2O \xrightarrow[-H_2O]{110\ ^\circ C} LiPUO_6 \cdot 3H_2O \xrightarrow[-2H_2O]{130\ ^\circ C} LiPUO_6 \cdot H_2O \xrightarrow[-H_2O]{200\ ^\circ C} LiPUO_6,$$

$$NaPUO_6 \cdot 3H_2O \xrightarrow[-H_2O]{90\ ^\circ C} NaPUO_6 \cdot 2H_2O \xrightarrow[-2H_2O]{120\ ^\circ C} NaPUO_6 \cdot H_2O \xrightarrow[-H_2O]{190\ ^\circ C} NaPUO_6,$$

$$KPUO_6 \cdot 3H_2O \xrightarrow[-\frac{1}{2}H_2O]{80\ ^\circ C} KPUO_6 \cdot 2.5H_2O \xrightarrow[-2H_2O]{115\ ^\circ C} KPUO_6 \cdot \tfrac{1}{2}H_2O \xrightarrow[-\frac{1}{2}H_2O]{175\ ^\circ C} KPUO_6,$$

$$RbPUO_6 \cdot 3H_2O \xrightarrow[-\frac{1}{2}H_2O]{80\ ^\circ C} RbPUO_6 \cdot 2.5H_2O \xrightarrow[-2H_2O]{115\ ^\circ C} RbPUO_6 \cdot \tfrac{1}{2}H_2O \xrightarrow[-\frac{1}{2}H_2O]{160\ ^\circ C} RbPUO_6,$$

$$CsPUO_6 \cdot 3H_2O \xrightarrow[-\frac{1}{2}H_2O]{80\ ^\circ C} CsPUO_6 \cdot 2.5H_2O \xrightarrow[-2H_2O]{110\ ^\circ C} CsPUO_6 \cdot \tfrac{1}{2}H_2O \xrightarrow[-\frac{1}{2}H_2O]{130\ ^\circ C} CsPUO_6,$$

$$LiAsUO_6 \cdot 4H_2O \xrightarrow[-H_2O]{115\ ^\circ C} LiAsUO_6 \cdot 3H_2O \xrightarrow[-2H_2O]{150\ ^\circ C} LiAsUO_6 \cdot H_2O \xrightarrow[-H_2O]{230\ ^\circ C} LiAsUO_6,$$

$$NaAsUO_6 \cdot 3H_2O \xrightarrow[-H_2O]{90\ ^\circ C} NaAsUO_6 \cdot 2H_2O \xrightarrow[-2H_2O]{110\ ^\circ C} NaAsUO_6 \cdot H_2O \xrightarrow[-H_2O]{200\ ^\circ C} NaAsUO_6,$$

$$KAsUO_6 \cdot 3H_2O \xrightarrow[-\frac{1}{2}H_2O]{90\ ^\circ C} KAsUO_6 \cdot 2.5H_2O \xrightarrow[-2H_2O]{120\ ^\circ C} KAsUO_6 \cdot 0.5H_2O \xrightarrow[-\frac{1}{2}H_2O]{240\ ^\circ C} KAsUO_6,$$

$$RbAsUO_6 \cdot 3H_2O \xrightarrow[-\frac{1}{2}H_2O]{80\ ^\circ C} RbAsUO_6 \cdot 2.5H_2O \xrightarrow[-2H_2O]{130\ ^\circ C} RbAsUO_6 \cdot 0.5H_2O \xrightarrow[-\frac{1}{2}H_2O]{220\ ^\circ C} RbAsUO_6,$$

$$CsAsUO_6 \cdot 3H_2O \xrightarrow[-\frac{1}{2}H_2O]{60\ ^\circ C} CsAsUO_6 \cdot 2.5H_2O \xrightarrow[-2H_2O]{120\ ^\circ C} CsAsUO_6 \cdot 0.5H_2O \xrightarrow[-\frac{1}{2}H_2O]{170\ ^\circ C} CsAsUO_6.$$

V. Thermodynamic properties of the compounds $M^IP(As)UO_6 \cdot nH_2O$

Before our investigations, there were virtually no literature data concerning the determination of the standard thermodynamic functions of formation of the compounds $M^IP(As)UO_6 \cdot nH_2O$. Attempts have been made in a number of studies[5,16,17,75,83–85] to calculate the standard Gibbs free energies of formation of a series of compounds of this type at 298.15 K ($\Delta_fG°$, kJ mol^{-1}) from the solubility products (K_s) in aqueous solutions. The calculation was based on the idea that the following equilibria exist at the precipitate ⇌ solution interface:

$$HP(As)UO_6 \cdot 4H_2O\,(cryst.) \rightleftharpoons UO_2^{2+}\,(soln) + HP(As)O_4^{2-}\,(soln) + 4H_2O, \quad (2)$$

$$M^IP(As)UO_6 \cdot nH_2O\,(cryst.) \rightleftharpoons M^+(soln) + UO^{2+}(soln) + P(As)O^{3-}(soln) + nH_2O, \quad (3)$$

where M^I are alkali metals.

Bearing in mind the low concentration of ions in solution and assuming that the activity of the solid phase is unity, one can postulate that the equilibrium constants of reactions (2) and (3) are equal to the solubility products of the corresponding compounds. Then we have

$$\Delta_rG^\circ_{2,3}(298) = 298.15 \times 8.314 \times \ln K_s/J.$$

The solubility products K_s of the compounds are listed in Table 8.

Table 8. The solubility products (K_s) of certain compounds $M^IP(As)UO_6 \cdot nH_2O$.

Compound	K_s	Ref.
$HPUO_6 \cdot 4H_2O$	2.14×10^{-11}	20, 23, 27
$HAsUO_6 \cdot 4H_2O$	3.17×10^{-11}	17
$LiPUO_6 \cdot 4H_2O$	2.4×10^{-26}	3, 21
$LiAsUO_6 \cdot 4H_2O$	1.5×10^{-19}	17
$NaPUO_6 \cdot 4H_2O$	6.4×10^{-24}	21, 27
$NaAsUO_6 \cdot 3H_2O$	1.35×10^{-22}	17
$KPUO_6 \cdot 3H_2O$	8×10^{-24}	21, 23, 27
$KAsUO_6 \cdot 3H_2O$	2.25×10^{-23}	17
$RbPUO_6 \cdot 3H_2O$	1×10^{-27}	21, 27

Table 9 presents the [standard] free energies [of formation] $\Delta_fG°(298)$ for a series of compounds calculated from the following relations:

$$\Delta_fG°[298,\ HP(As)UO_6 \cdot 4H_2O,\ cryst.] = \Delta_fG°(298, UO_2^{2+}, soln) + \Delta_fG°[298, HP(As)O_4^{2-}, soln] + 4\Delta_fG°(298,\ H_2O,\ liq.) + RT\ln K_s,$$

$$\Delta_fG°[298,\ M^IP(As)UO_6 \cdot nH_2O,\ cryst.] = \Delta_fG°(298, M^{I+}, soln) + \Delta_fG°(298, UO_2^{2+}, soln) + \Delta_fG°[298, P(As)O_4^{3-}, soln] + n\Delta_fG°(298, H_2O, liq.) + RT\ln K_s.$$

Langmuir[85] calculated the standard enthalpies of formation of $NaPUO_6$ (−2536 kJ mol^{-1}) and $KPUO_6$ (−2561 kJ mol^{-1}) from $\Delta_fG°(298)$ and the standard entropy of formation evaluated by the method of contributions. It is noteworthy that these values can be regarded as only estimates. For this reason, in the subsequent sections of the review we shall deal in greater detail with the determination of the standard enthalpies of formation of the compounds $M^IP(As)UO_6 \cdot nH_2O$ and their dehydration products.†

VI. Standard enthalpies of formation of the compounds $M^IP(As)UO_6$ and their crystalline hydrates

Detailed schemes for the determination of the standard enthalpies of formation of the compounds $M^IP(As)UO_6$, where M^I = H, Li, Na, K, Rb, or Cs, and their crystalline hydrates having the general formula $M^IP(As)UO_6 \cdot nH_2O$, where n = 4 for M^I = H or Li and n = 3 for M^I = Na, K, Rb, or Cs, have been put forward.[87–96] In the present review, we shall therefore consider only the general approach to the solution of the problem in relation to the calculation of the standard enthalpies of formation $\Delta_fH°(298)$ of the compounds $M^IP(As)UO_6$, where M^I = Li, Na, K, Rb, or Cs.

The standard enthalpies of the following processes were determined in an adiabatic calorimeter:

$$[KH_2P(As)O_4\,(cryst.) + UO_3\,(cryst.) + M^INO_3\,(cryst.)] + 4HF\,(soln) \rightarrow KF\,(soln) + UO_2F_2\,(soln) + M^IF\,(soln) + H_3PO_4\,(soln) + HNO_3\,(soln) + H_2O, \quad (4)$$

$$[M^IP(As)UO_6\,(solid) + KNO_3\,(cryst.)] + 4\,HF\,(soln) \rightarrow KF\,(soln) + M^IF\,(soln) + UO_2F_2\,(soln) + H_3PO_4\,(soln) + HNO_3\,(soln). \quad (5)$$

The design of the calorimeter and its use have been described in detail.[97] The standard enthalpies of reactions (4) and (5) are presented in Table 10.

The reactant ratios in reactions (4) and (5) were constant at 1 mol of the mixture: 260 mol of HF : 800 mol of H_2O.

† We carried out these investigations in 1990–1994, but unfortunately they cannot be compared with any other data because of the lack of the latter in the literature.

Table 9. The standard Gibbs free energies of formation of the compounds $M^IP(As)UO_6$ and their crystalline hydrates of 298.15 K.

Compound	$-\Delta_fG°$/kJ mol^{-1}	Ref.	Compound	$-\Delta_fG°$/kJ mol^{-1}	Ref.
$HPUO_6$	2112	83	$HAsUO_6$	1764	17
$HPUO_6$	2109	85	$HAsUO_6 \cdot 4H_2O$	2679	[a]
$HPUO_6$	2090	86	$LiAsUO_6 \cdot 4H_2O$	2950	84
$HPUO_6 \cdot 4H_2O$	3052	[a]	$NaAsUO_6 \cdot 4H_2O$	2941	84
$LiPUO_6 \cdot 4H_2O$	3358	84	$NaAsUO_6 \cdot 3H_2O$	2703	[a]
$NaPUO_6 \cdot 3H_2O$	3102	84	$KAsUO_6 \cdot 4H_2O$	2961	84
$KPUO_6$	2391	83	$KAsUO_6 \cdot 3H_2O$	2728	[a]
$KPUO_6 \cdot 3H_2O$	3102	83	$KAsUO_6$	2021	83
$RbPUO_6 \cdot 3H_2O$	3121	[a]			

[a] Calculated by the authors from literature data.

Table 10. The standard enthalpies of reactions (4) and (5).[87,88,94]

M^I	$-\Delta_r H_4^\circ(298)$/kJ mol^{-1}		$-\Delta_r H_5^\circ(298)$/kJ mol^{-1}	
	phosphates	arsenates	phosphates	arsenates
Li	107.4 ± 1.1	138.5 ± 1.2	82.2 ± 0.2	129.9 ± 0.8
Na	70.8 ± 0.8	125.3 ± 1.2	39.0 ± 0.9	116.4 ± 1.3
K	64.5 ± 1.9	112.1 ± 1.6	32.8 ± 0.1	99.2 ± 0.6
Rb	61.1 ± 0.8	112.5 ± 1.4	31.0 ± 1.2	95.4 ± 0.8
Cs	58.8 ± 2.4	107.0 ± 1.0	25.2 ± 1.0	89.5 ± 1.4

When Eqn (5) is subtracted from Eqn (4), we arrive at the following process:

$$KH_2P(As)O_4\,(cryst.) + UO_3\,(cryst.) + M^INO_3\,(cryst.) \rightarrow M^IP(As)UO_6\,(solid) + KNO_3 + H_2O\,(liq.), \quad (6)$$

the standard enthalpy of which is $\Delta_r H_6^\circ(298) = \Delta_f H_4^\circ(298) - \Delta_r H_5^\circ(298)$ according to Hess's law.

On the other hand, the quantity $\Delta_r H_6^\circ(298)$ is equal to the algebraic sum of the $\Delta_r H^\circ(298)$ of all the participants in reaction (6). The standard enthalpies of formation of the compounds investigated (Table 12) can then be calculated from the quantities $\Delta_r H_6^\circ(298)$ and the literature values of the standard enthalpies of formation of the corresponding reactants (Table 11).

Table 11. The standard enthalpies of formation of the reactants in reaction (6) at 298.15 K.

Compound	$-\Delta_f H^\circ(298)$/kJ mol^{-1}	Ref.
KH_2PO_4	1567.46 ± 2.32	83, 84, 98, 102
KH_2AsO_4	1184.79 ± 1.89	83, 84, 99
UO_3	1228.3 ± 3.0	83, 84, 100, 102
H_2O	285.83 ± 0.04	98
$LiNO_3$	483.2 ± 0.5	84
$NaNO_3$	468.2 ± 0.5	84
KNO_3	494.6 ± 0.5	84
$RbNO_3$	495.1 ± 0.5	84
$CsNO_3$	505.7 ± 0.5	84

Table 12. The standard enthalpies of formation of the compounds M^IPUO_6 and M^IAsUO_6.[87,88]

Compound	$-\Delta_f H^\circ(298)$/ kJ mol^{-1}	Compound	$-\Delta_f H^\circ(298)$/ kJ mol^{-1}
$HPUO_6$	2275 ± 7	$HAsUO_6$	1868 ± 7
$LiPUO_6$	2524 ± 8	$LiAsUO_6$	2125 ± 8
$NaPUO_6$	2515 ± 8	$NaAsUO_6$	2110 ± 8
$KPUO_6$	2539 ± 7	$KAsUO_6$	2140 ± 8
$RbPUO_6$	2541 ± 8	$RbAsUO_6$	2145 ± 8
$CsPUO_6$	2555 ± 10	$CsAsUO_6$	2156 ± 9

The following additional experiments were performed in order to test the results. Firstly, the enthalpies of reactions (4) and (5) were determined for two other reactant ratios (1 mol of mixture : 130 mol of HF and 1 mol of mixture : 520 mol of HF). It was established that the enthalpies $\Delta_r H_{4,5}^\circ(298)$ are independent of the molar reactant ratio within experimental error (1.5%–3.0%). Secondly, the enthalpies of reactions (4) and (5) were determined for two acids participating in the reaction — HF and HCl. It was established that the enthalpies of reaction (6) are identical within experimental error. This is in fact the reason why the products of reactions (4) and (5) are indicated as the most probable. Their chemical nature may be different but the important feature is that they are the same in the corresponding pairs of reactions.

Analysis of the results shows that reactions (4) and (5) are exothermic (Table 10); the absolute values of $\Delta_r H_4^\circ(298)$ for both phosphorus and arsenic compounds decrease on passing from lithium to caesium. Such variation of the enthalpies of the above processes in the series of alkali metals can be accounted for as follows.

Since the participants in reaction (4) — phosphorus or arsenic derivatives — differ only in the chemical nature of the alkali metal nitrate (M^INO_3) and the alkali metal ion in solution [$M^IF(soln) \rightleftharpoons M^+ + F^-$], the changes in the overall enthalpies $\Delta_r H_4^\circ(298)$ in the direction Li → Na → K → Rb → Cs are caused by the different crystal lattice energies of M^INO_3 and the different hydration energies of the M^+ ions in solution. The first term is always positive (endothermic process), diminishing on passing from lithium to caesium. Thus the endothermicity of this stage of the overall process (4) should decrease in the direction Li → Cs. On the other hand, the hydration of the M^+ ions in aqueous solutions is an exothermic process. With increase in the ionic radius of M^+, the hydration enthalpy diminishes (the exothermicity decreases in the direction Li → Cs). The experimental data therefore permit the following conclusions: the overall enthalpy $\Delta_r H_4^\circ(298)$ is negative, because the term associated with the enthalpy of hydration of the M^+ ions in aqueous solution exceeds the energy of the disruption of the M^INO_3 crystal lattice; the decrease in the absolute enthalpy of hydration of the M^+ on passing from lithium to caesium is the decisive factor governing the decrease in the exothermicity of the overall process (4) in the same direction.

The variation of the overall enthalpies $\Delta_r H^\circ(298)$ of reactions (5) can be accounted for similarly. The reactions differ only in the chemical nature of $M^IP(As)UO_6$ and the M^+ ion in aqueous solution.

The linear variation of the enthalpies of reactions (4) and (5) with increase in the ionic radius (r) of the alkali metal or with decrease in the hydration enthalpy [$\Delta_h H^\circ(298, M^+, soln)$] of the alkali metal ion in aqueous solution can be accounted for by the same causes. The corresponding relations assume the form

$$\Delta_r H^\circ(298) = a + b(X),$$

where X is a characteristic of the alkali metal or its ion (ionic radius, enthalpy of hydration). The quantities r and $\Delta_h H^\circ$ for alkali metals are presented in Table 13 and the coefficients a and b are listed in Table 14.

The significantly lower exothermicity of reactions (4) and (5) involving the same alkali metal in phosphorus compounds compared with arsenic compounds can be explained in the following manner. As a consequence of the greater, compared with arsenic, coordinative saturation of phosphorus in the oxygen compounds, the effective charge on the alkali metal atom is lower, which leads ultimately to an increase in the K–O bond energy in KH_2PO_4 [reaction (4)] or the M^I–O bond energy in M^IPUO_6 [reaction (5)] compared with the analogous arsenic compounds. On the other hand, the higher effective charge of the AsO_4^{3-} ion compared with PO_4^{3-} is responsible for the higher energy of dehydration of the AsO_4^{3-} ion in aqueous solution. Allowance for

Table 13. The characteristics X of the alkali metal according to Glushko and Pauling.[84,101]

M^I	r/Å	$\Delta_h H^\circ(M^+)$/ kJ mol^{-1}	$\Delta_f H^\circ(M^+)$/ kJ mol^{-1}	I_1/ eV[a]
Li	0.60	534	–	–
Na	0.95	426	609.60	5.138
K	1.33	341	513.91	4.339
Rb	1.48	316	490.16	4.176
Cs	1.69	284	458.81	3.893

[a] I_1 is the first ionisation potential.

Table 14. The coefficients a and b in the equations $\Delta_r H°(298) = a + bX$ for reactions (4) and (5).[103]

X	a		b	
	phosphates	arsenates	phosphates	arsenates
Reaction (4)				
r/Å	−122.8	−154.0	41.57	28.8
$\Delta_h H°(298, M^+, soln)$/ kJ mol^{-1}	−0.90	−71.12	0.188	0.126
Reaction (5)				
r/Å	−99.31	−152.3	47.32	38.16
$\Delta_h H°(298, M^+, soln)$/ kJ mol^{-1}	39.46	−43.53	0.214	0.165

these two factors actually makes it possible to understand the greater exothermicity of reactions (4) and (5) for the same alkali metal in the case of the arsenic compounds compared with the phosphorus compounds (Table 10).

The greater stability of the M^IPUO_6 structure compared with the M^IAsUO_6 structure is manifested by the fact that the absolute values of $\Delta_f H°(298)$ for the phosphorus compounds are higher than the corresponding values for the arsenic compounds. For all the alkali metals investigated (M^I = Li, Na, K, Rb, or Cs), the difference $\Delta_f H°(298, M^IAsUO_6) - \Delta_f H°(298, M^IPUO_6) = 400 \pm 5$ kJ mol^{-1} is virtually constant.

The absolute values of $\Delta_f H°(298)$ for the phosphorus and arsenic compounds exhibit a distinct tendency to increase in the direction Na → K → Rb → Cs. The linear relations $\Delta_f H°(298) = a + bX$, where X is a characteristic of the alkali metal, have been established. The corresponding coefficients a and b are presented in Table 15.

Table 15. The coefficients in the equation $\Delta_f H°(298) = a + bX$.

X	a		b	
	phosphates	arsenates	phosphates	arsenates
r, A	−2466	−2053	52.605	−62.279
$\Delta_f H°(298, M^+, gas)$/ kJ mol^{-1}	−2668	−2294	0.252	0.302
I_1/eV	−2673	−2299	30.83	36.84

Analogous schemes have been used to calculate the standard enthalpies of formation of the crystalline compounds of the $M^IP(As)UO_6 \cdot nH_2O$ series (Table 16).

Table 16. The standard enthalpies of formation of the compounds $M^IP(As)UO_6 \cdot nH_2O$.[90,91]

Compound	$-\Delta_f H°(298)$/ kJ mol^{-1}	Compound	$-\Delta_f H°(298)$/ kJ mol^{-1}
$HPUO_6 \cdot 4H_2O$	3473 ± 8	$HAsUO_6 \cdot 4H_2O$	3086 ± 7
$LiPUO_6 \cdot 4H_2O$	3707 ± 9	$LiAsUO_6 \cdot 4H_2O$	3311 ± 8
$NaPUO_6 \cdot 3H_2O$	3392 ± 9	$NaAsUO_6 \cdot 3H_2O$	2998 ± 8
$KPUO_6 \cdot 3H_2O$	3413 ± 8	$KAsUO_6 \cdot 3H_2O$	3022 ± 8
$RbPUO_6 \cdot 3H_2O$	3412 ± 9	$RbAsUO_6 \cdot 3H_2O$	3023 ± 7
$CsPUO_6 \cdot 3H_2O$	3423 ± 11	$CsAsUO_6 \cdot 3H_2O$	3030 ± 7

For example, the enthalpies of the reactions of equimolecular mixtures of $M^IAsUO_6 \cdot nH_2O$ and potassium nitrate with an aqueous solution at HF at 298.15 K have been determined for the ratios 1 mol of the mixture : 260 mol of the HF : 800 mol of H_2O.[91]

$$[M^IAsUO_6 \cdot nH_2O(\text{cryst.}) + KNO_3(\text{cryst.})] + 4HF(\text{soln}) \rightarrow KF(\text{soln}) + M^IF(\text{soln}) + UO_2F_2(\text{soln}) + H_3P(As)O_4(\text{soln}) + HNO_3(\text{soln}) + nH_2O \quad (7)$$

Subtraction of Eqn (7) from Eqn (4) yields the process

$$KH_2AsO_4(\text{cryst.}) + UO_3(\text{cryst.}) + M^INO_3(\text{cryst.}) + (n-1)H_2O \rightarrow M^IAsUO_6 \cdot nH_2O(\text{cryst.}) + KNO_3(\text{cryst.}), \quad (8)$$

the enthalpy of which $\Delta_r H°_8(298) = \Delta_r H°_4(298) - \Delta_r H°_7(298)$. The enthalpies $\Delta_f H°(298)$ for the crystalline hydrates investigated can be calculated from the values of $\Delta_r H°_8(298)$ and the standard enthalpies of formation of the corresponding reactants (Table 10).

$$\Delta_f H°(298, M^IAsUO_6 \cdot nH_2O, \text{cryst.}) = +\Delta_r H°_8(298) + \Delta_f H°(298, KH_2AsO_4, \text{cryst.}) + \Delta_f H°(298, UO_3, \text{cryst}) + \Delta_f H°(298, M^INO_3, \text{cryst.}) + (n-1)\Delta_f H°(298, H_2O, \text{liq.}) - \Delta_f H°(298, KNO_3).$$

Analysis of the quantities presented in Table 16 permits the following conclusions: the enthalpies $\Delta_f H°(298)$ for the phosphorus derivatives are greater in absolute magnitude, as in the case of anhydrous compounds, than the corresponding values for the arsenic derivatives. For all the alkali metals investigated, the difference $\Delta_f H°[298, M^IAsUO_6(\text{cryst.})] - \Delta_f H°[298, M^IPUO_6(\text{cryst.})]$ is almost constant and equal to 393 ± 3 kJ mol^{-1}; in the series of phosphorus and arsenic derivatives, the absolute value of $\Delta_f H°$ increases in the direction Na → K → Rb → Cs; the linear relations $\Delta_f H°[298, M^IP(As)UO_6 \cdot nH_2O] = a + bX$ have been established (Table 17); in the series of the phosphorus and arsenic compounds (M^I = Na, K, Rb, Cs), the difference between the enthalpies $\Delta_f H°(298)$ for the anhydrous compounds and their crystalline hydrates $\Delta_f H°[298, M^IP(As)UO_6] - \Delta_f H°[298, M^IP(As)UO_6 \cdot 3H_2O]$ per mole of the water of crystallisation is virtually constant and equal to 293 ± 3 kJ (mol H_2O)$^{-1}$; the analogous difference in the case of the hydrogen and lithium compounds is also constant but it exceeds the above value, i.e. $\Delta_f H°[298, M^IP(As)UO_6] - \Delta_f H°[298, M^IP(As)UO_6 \cdot 4H_2O] = 300 \pm 4$ kJ (mol H_2O)$^{-1}$, which emphasises yet again the stronger binding of the water of crystallisation in the hydrogen and lithium derivatives compared with other Group I elements.

Table 17. The coefficients in the equations $\Delta_f H°[298, M^IP(As)UO_6 \cdot 3H_2O, \text{cryst.}] = a + bX$ (M^I = Na, K, Rb, Cs).

X	a		b	
	phosphates	arsenates	phosphates	arsenates
r/Å	−3355	−2959	−40.441	−43.238
$\Delta_f H°(298, M^+, gas)$/ kJ mol^{-1}	−3511	−3128	0.196	0.213
I_1/eV	−3515	−3132	23.99	25.96

1. The enthalpies of the dehydration reactions of the compounds $M^IP(As)UO_6 \cdot nH_2O$

We shall examine the methods for the determination of the enthalpies of dehydration of the test compounds in relation to the phosphorus derivatives.

The enthalpies of the reactions of M^IPUO_6 or their crystalline hydrates with an aqueous solution of hydrofluoric acid have been determined calorimetrically.

$$M^IPUO_6(\text{solid}) + 3HF(\text{soln}) \rightarrow M^IF(\text{soln}) + UO_2F_2(\text{soln}) + H_3PO_4(\text{soln}), \quad (9)$$

$$M^{I}PUO_6 \cdot nH_2O\,(cryst.) + 3HF\,(soln) \rightarrow$$
$$\rightarrow M^{I}F\,(soln) + UO_2F_2\,(soln) + H_3PO_4\,(soln) \cdot nH_2O. \quad (10)$$

Subtraction of Eqn (9) from Eqn (10) yields the dehydration process [see Eqn (1)], the enthalpy of which is equal to the difference $\Delta_r H^\circ_{10}(298) - \Delta_r H^\circ_9(298)$ (Table 18).

Table 18. The standard enthalpies of reactions (1), (7), (9), and (10) (the $\Delta_r H^\circ$ are expressed in kJ mol^{-1}).[87,90]

M^I	$-\Delta_r H^\circ_9(298)$	$-\Delta_r H^\circ_{10}(298)$	$-\Delta_r H^\circ_1(298)$	$-\Delta_r H^\circ_7(298)$
H	65.5 ± 1.0	9.63 ± 0.08	53.8 ± 1.1	–
Li	89.0 ± 0.3	49.3 ± 0.2	39.7 ± 0.5	86.9 ± 0.8
Na	77.9 ± 0.3	58.4 ± 0.6	19.5 ± 0.9	85.4 ± 1.4
K	59.7 ± 0.6	43.0 ± 0.1	16.7 ± 0.7	75.1 ± 1.2
Rb	57.8 ± 0.3	44.4 ± 0.3	13.4 ± 0.6	74.7 ± 0.5
Cs	55.8 ± 0.2	45.2 ± 0.2	10.6 ± 0.4	72.7 ± 0.5

Since all the crystalline hydrates investigated differ in the amount of water of crystallisation, Table 19 presents the enthalpies of the dehydration reactions per mole of water evolved.

The higher binding energy of the water of crystallisation in the $M^{I}AsUO_6 \cdot nH_2O$ structures compared with $M^{I}PUO_6 \cdot nH_2O$ is striking. This happens despite their analogous functional composition and complete structural similarity, including identical locations of the water molecules around the univalent element. These results are fully consistent with the thermographic determinations of the temperature ranges in the stage-by-stage and complete elimination of water from the phosphorus and arsenic compounds (see Section IV). The cause of these differences, which consists in the unequal coordination capacities of phosphorus(V) and arsenic(V), was investigated in detail by the present authors in an earlier study.

Table 19. The enthalpies of the dehydration reaction[103] $(1/n)M^{I}P(As)UO_6 \cdot nH_2O(cryst.) \rightarrow (1/n)M^{I}P(As)UO_6\,(solid) + H_2O\,(liq.)$.

Compound	$-\Delta_r H^\circ(298)$/ kJ mol^{-1}	Compound	$-\Delta_r H^\circ(298)$/ kJ mol^{-1}
$HPUO_6 \cdot 4H_2O$	13.5	$HAsUO_6 \cdot 4H_2O$	19.0
$LiPUO_6 \cdot 4H_2O$	10.0	$LiAsUO_6 \cdot 4H_2O$	11.0
$NaPUO_6 \cdot 3H_2O$	6.5	$NaAsUO_6 \cdot 3H_2O$	10.0
$KPUO_6 \cdot 3H_2O$	5.5	$KAsUO_6 \cdot 3H_2O$	8.0
$RbPUO_6 \cdot 3H_2O$	4.5	$RbAsUO_6 \cdot 3H_2O$	7.0
$CsPUO_6 \cdot 3H_2O$	3.5	$CsAsUO_6 \cdot 3H_2O$	5.5

The significantly higher energy of the dehydration of the hydrogen forms compared with their salt analogues confirms the nonequivalent nature of the water in compounds $HP(As)UO_6 \cdot 4H_2O$, which is indicated by the results of an IR spectroscopic study of these compounds (see Section III). It has also been established that the decrease in the enthalpy of dehydration of the crystalline hydrates $M^{I}P(As)UO_6 \cdot nH_2O$ in the series of alkali metal compounds is equivalent to the decrease in this series of the enthalpies of dehydration (in kJ mol^{-1}) of the ions of the corresponding elements in aqueous solution:

$$\Delta_r H^\circ(298) = [-3.5 + 0.0245\Delta_h H^\circ(298,\ M^+,\ soln) \pm 0.2];$$

for the phosphates;

$$\Delta_r H^\circ(298) = [-3.0 + 0.0305\Delta_h H^\circ(298,\ M^+,\ soln) \pm 0.2].$$

for the arsenates.

2. Enthalpies of ion-exchange reactions

The substitution of a proton in the compounds $HP(As)UO_6 \cdot 2H_2O$ by alkali metal ions constitutes the basis of the synthesis of the crystalline compounds $M^{I}P(As)UO_6 \cdot nH_2O$. Knowledge of the energy relations governing the ion-exchange reactions is therefore necessary.

The standard enthalpies of the exchange reactions

$$M^+(soln) + HP(As)UO_6 \cdot 4H_2O$$
$$\rightleftharpoons M^{I}P(As)UO_6 \cdot nH_2(cryst) + H^+(soln) + (4-n)H_2O, \quad (11)$$

were calculated from the standard enthalpies of formation of the crystalline hydrates (Table 6) and the literature values of the standard enthalpies of formation of alkali metal ions in aqueous solution. The results are presented in Table 20.

Table 20. The ionic radii and standard enthalpies of formation of alkali metal ions and the standard enthalpies of reaction (11).[96]

M^I	R/Å	$-\Delta_r H^\circ(M^+)$/ kJ mol^{-1}	$\Delta_r H^\circ_{11}(298)$/kJ mol^{-1}	
			$M^{I}PUO_6 \cdot nH_2O$	$M^{I}AsUO_6 \cdot nH_2O$
Li^+	1.28	278.45 ± 0.21	44.5	54.5
Na^+	1.61	240.41 ± 0.13	35.5	42.5
K^+	2.01	252.25 ± 0.13	26.5	30.5
Rb^+	2.17	251.04 ± 0.13	26.0	28.5
Cs^+	2.42	255.56 ± 0.13	22.5	28.5

The standard enthalpies of the ion-exchange reactions presented are positive i.e. the above processes proceed with absorption of energy. The enthalpies $\Delta_r H^\circ(298)$ decrease on passing from lithium to caesium in the series of alkali metals. In order to establish the causes of such variation, we shall consider the energy relations for the ion-exchange reactions in greater detail.

The overall enthalpy of the ion-exchange reactions can be represented by the following terms:

$$\Delta_r H^\circ = \Delta H^\circ_{M^+} + \Delta \bar{H}^\circ_{M^+} + \Delta H^\circ_{H^+} + \Delta \bar{H}^\circ_{H^+} + \Delta H^\circ_{O-H}$$
$$+ \Delta H^\circ_{O-M} + \Delta H^\circ_{lat}, \quad (12)$$

where $\Delta H^\circ_{M^+}$ is the enthalpy of hydration of the M^+ ion in the crystalline $M^{I}P(As)UO_6 \cdot nH_2O$ phase, $\Delta \bar{H}^\circ_{M^+}$ is the enthalpy of dehydration of the M^+ ion in solution, $\Delta H^\circ_{H^+}$ is the enthalpy of hydration of the proton in solution, $\Delta \bar{H}^\circ_{H^+}$ is the enthalpy of dehydration of the proton in the crystalline $HP(As)UO_6 \cdot 4H_2O$ phase, ΔH°_{O-H} is the enthalpy of dissociation of the O–H bond in the crystalline $HP(As)UO_6 \cdot 4H_2O$, ΔH°_{O-M} is the enthalpy of formation of the O–M bond in the crystalline $M^{I}P(As)UO_6 \cdot nH_2O$ phase, and ΔH°_{lat} is the enthalpy of the disruption of the $HP(As)UO_6 \cdot 4H_2O$ crystal lattice and of the formation of the $M^{I}P(As)UO_6 \cdot nH_2O$ crystal lattice.

During the ion-exchange reaction, dehydration of the M^+ ion takes place before the transfer of the latter from solution to the crystalline $HP(As)UO_6 \cdot 4H_2O$ phase becomes possible. Such a process is associated with the expenditure of energy, so that $\Delta \bar{H}^\circ_{M^+} \gg 0$. In the series of alkali metal ions ranging from lithium to caesium, the enthalpy of dehydration diminishes from 534 kJ mol^{-1} for the lithium ion to 284 kJ mol^{-1} for the caesium ion.[101] A proportion of this energy expenditure is compensated by the energy of hydration of the corresponding M^+ ion in the crystalline $M^{I}P(As)UO_6 \cdot nH_2O$ phase ($n = 4$ in the case of M^I = Li and $n = 3$ in the case of all other alkali metals). In the stage involving the transfer of a proton from the crystalline $HP(As)UO_6 \cdot 4H_2O$ phase to the solution, the proton is hydrated with a considerable evolution of energy, amounting to $\Delta H^\circ_{H^+} = -1090$ kJ mol^{-1}.[84] Thus, from the standpoint of the ion hydration-dehydration processes, reaction (11) should be significantly exothermic. However, together with the energetic processes considered, other terms of Eqn (12) must also be taken into account.

As shown above, the four water molecules in $HP(As)UO_6 \cdot 4H_2O$ are not equivalent. Two of them form the hydroxonium ion $H_5O_2^+$, whilst the other two retain their molecular individuality. Whereas the removal of molecular water from $HP(As)UO_6 \cdot 4H_2O$ involves a considerable energy expenditure, at the level of the energy of hydrogen bonds, the decomposition of the hydroxonium ion into $2H_2O$ and H^+ is associated with an appreciable endothermic effect, i.e. $\Delta\overline{H}^\circ_{H^+} > 0$. An appreciable energy expenditure is also necessary for the dissociation of the P(As)O–H bond in the $HP(As)UO_6 \cdot 4H_2O$ crystals. Thus the average O–H bond dissociation energy is 463 kJ mol^{-1}. Finally, an energy expenditure is necessary to increase the interlayer distance on passing from the crystalline $HP(As)UO_6 \cdot 4H_2O$ phases to the crystalline $M^IP(As)UO_6 \cdot nH_2O$ phases. For example, this distance increases from 17.440 Å in the $HPUO_6 \cdot 4H_2O$ phase to 18.242 Å in the $LiPUO_6 \cdot 4H_2O$ phase. The analogous distances for the arsenic compounds are 17.594 and 17.808 Å (Table 4). Furthermore, it is necessary to take into account additional energy expenditures as a consequence of the structural rearrangement caused by the decrease in the number of water molecules from four to three in the $M^IP(As)UO_6 \cdot nH_2O$ formula unit on passing from lithium compounds to sodium, potassium, rubidium, and caesium compounds, i.e. $\Delta H^\circ_{lat} > 0$.

Thus the predominance of the energy expenditure over the exothermic effect, due to ion hydration processes ($\Delta H^\circ_{H^+} < 0$, $\Delta H^\circ_{M^+} < 0$) and the formation of new P(As)O–M bonds in the crystalline phase (ΔH°_{O-M}), is the cause of the endothermicity of the ion-exchange reactions (11). In this case, the quantities $\Delta_r H^\circ(298)$ decrease linearly with increase in the radius of the alkali metal ion (R) in aqueous solution (Table 20):

$$\Delta_r H^\circ(298) = [(67.5 - 19.35R) \pm 1.5]/\text{kJ}$$

for reactions involving $HPUO_6 \cdot 4H_2O$, and

$$\Delta_r H^\circ(298) = [(82.5 - 24.12R) \pm 3.0]/\text{kJ}$$

for reactions involving $HAsUO_6 \cdot 4H_2O$.

The observed greater endothermicity of the ion-exchange reactions (11) for arsenouranic acid compared with the analogous processes for phosphouranic acid is associated with the higher dehydration energy of $HAsUO_6 \cdot 4H_2O$ compared with that of $HPUO_6 \cdot 4H_2O$ and the lower packing density of the crystal lattice of the latter compound.

The considerable endothermicity of the reactions involving the exchange of hydrogen for alkali metal ions in the crystalline compounds $HP(As)UO_6 \cdot 4H_2O$ shows that the displacement of the equilibrium towards the formation of the exchange products requires that the entropy term $T\Delta_r S^\circ$ in the equation for the standard Gibbs free energy function $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ should be positive and should exceed the enthalpy term. However, an estimate of $\Delta_r G^\circ(298)$ for reactions (8) shows that the ion-exchange enthalpy makes the main contribution to the Gibbs free energy of the given process. For example, for the reaction

$$Li^+ \text{ (st. soln)} + HAsUO_6 \cdot 4H_2O \text{ (cryst.)} \rightleftharpoons LiAsUO_6 \cdot 4H_2O \text{ (cryst.)} + H^+ \text{ (st. soln)},$$

the free energy $\Delta_r G^\circ$ is given by

$$\Delta_r G^\circ(298) = \Delta_f G^\circ(298, LiAsUO_6 \cdot 4H_2O, \text{cryst.}) + \Delta_f G^\circ(298, H^+, \text{st. soln}) - \Delta_f G^\circ(298, HAsUO_6 \cdot 4H_2O, \text{cryst.}) - \Delta_f G^\circ(298, Li^+, \text{st. soln}).$$

If we employ the data presented in Table 18 and the quantity $\Delta_f G^\circ(298, Li^+, \text{st. soln}) = -292.29 \pm 0.46$ kJ mol^{-1},[84] we obtain $\Delta_r G^\circ(298) = 21$ kJ mol^{-1}. Consequently the equilibrium constant of the process, from the equation $\Delta_r G^\circ = -RT\ln K_e$, is $K_e(298) = 2 \times 10^{-4}$. The displacement of the equilibrium in reaction (11) towards the formation of the exchange products is possible either as a result of an increase in temperature or as a result of the employment of reactions occurring with liberation of energy. Table 21 presents the results of the calculation of the standard enthalpies of the reactions of $HP(As)UO_6 \cdot 4H_2O$ with aqueous solutions of alkali metal hydroxides and also the enthalpies of the ion-exchange reactions with participation of the anhydrous acids.[103]

$$M^IOH \text{ (st. soln)} + HPUO_6 \cdot 4H_2O \text{ (cryst.)} \rightarrow M^IPUO_6 \cdot nH_2O \text{ (cryst.)} + (n-1)H_2O \text{ (liq.)}. \quad (13)$$

$$M^+ \text{ (st. soln)} + HP(As)UO_6 \text{ (solid)} \rightleftharpoons M^IP(As)UO_6 \text{ (solid)} + H^+ \text{ (soln)}. \quad (14)$$

The reactions of $HP(As)UO_6 \cdot 4H_2O$ with solutions of alkali metal hydroxides are exothermic, which ultimately permits the quantitative formation of the crystalline compounds $M^IP(As)UO_6 \cdot nH_2O$. These results confirm the legitimacy of the use of ion-exchange reactions for the synthesis of the compounds $M^IP(As)UO_6 \cdot nH_2O$.

Table 21. The standard enthalpies of reaction (13) and (14).

M^I	$-\Delta_r H^\circ_{13}(298)$/kJ mol^{-1}		$\Delta_r H^\circ_{14}(298)$/kJ mol^{-1}	
	$HPUO_6 \cdot 4H_2O$	$HAsUO_6 \cdot 4H_2O$	$HPUO_6$	$HAsUO_6$
Li^+	11.5	2.5	29.5	21.5
Na^+	20.5	13.5	0.5	−1.5
K^+	29.0	25.5	−12.0	−19.5
Rb^+	29.5	27.0	−15.0	−26.0
Cs^+	33.5	27.5	−22.0	−30.0

It has been established on the basis of the results of X-ray phase analysis that the dehydration of the compounds $M^IP(As)UO_6 \cdot nH_2O$ leads to the disordering of their structures as a consequence of the disruption of the coordination environment of the ion of the univalent element. We used this finding to assess the role of structural factors from the standpoint of their contribution to the energy relations of the ion-exchange reactions.

The exclusion of contributions of the type ΔH°_{lat} from the energy relations of the ion-exchange reactions [see Eqn (12)] leads to a decrease in the overall energy expenditure in the processes under consideration and, in the case of the sodium, potassium, rubidium, and caesium compounds, the exchange reactions proceed with liberation of energy.

VII. Conclusion

The study of the crystalline compounds $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$ as well as their alkali metal derivatives by X-ray diffraction showed that the diffraction patterns of all the compounds have analogous sets of reflection maxima with similar positions and relative intensities. In terms of the results of the analytical indexing of the X-ray powder diffraction patterns, the compounds are structurally similar and have similar tetragonal unit cell parameters, which are virtually identical with the results of direct structural studies on $HPUO_6 \cdot 4H_2O$, $HAsUO_6 \cdot 4H_2O$, $LiAsUO_6 \cdot 4H_2O$, $KPUO_6 \cdot 3H_2O$, and $KAsUO_6 \cdot 3H_2O$ single crystals.

The numbers of bands, and their positions and relative intensities in the IR spectra of all the compounds in each of the series of phospho- and arseno-uranate derivatives are similar, which confirms not only the structural similarity of the compounds but also indicates their identical functional composition and the similar nature of the distortion of the principal coordination polyhedra: of phosphorus (tetrahedron), of arsenic (tetrahedron), and or uranium(VI) (octahedron).

A more detailed analysis of the IR spectra, especially in the region of the deformation vibrations of the so-called water of crystallisation, shows that its nature in the test compounds is not the same. In the compounds $HP(As)UO_6 \cdot 4H_2O$ and $LiP(As)UO_6 \cdot 4H_2O$, part of the water is present in the form of the complex hydroxonium ions $H_5O_2^+$ and the lyonium ions $(H_2OLiOH_2)^+$, whilst another part exists in the molecular form. In the compounds of other alkali metals, the entire water is molecularly homogeneous. The different nature of the water in the hydrogen and lithium derivatives, on the one hand, and the sodium, potassium, rubidium, and caesium derivatives, on the other, does not introduce fundamental differences into the structures of the principal coordination polyhedra of phosphorus, arsenic, and uranium or into the structures of the compounds as a whole.

The results of thermographic study of the compounds $M^IP(As)UO_6 \cdot nH_2O$ by the derivatographic method combined with X-ray phase analysis of the intermediate and final dehydration and thermal decomposition products showed that the temperature ranges corresponding to the dehydration of the $HAsUO_6 \cdot 4H_2O$ (363–513 K) are higher compared with $HPUO_6 \cdot 4H_2O$ (353–448 K), which is due to the excess force field of the arsenic in the coordinatively unsaturated AsO_4 polyhedron. On the other hand, the higher temperatures of the condensation of the phosphate groups in $HPUO_6$ with formation of pyrophosphates (833–1133 K) are a consequence of the coordinative saturation of the phosphorus in the PO_4 tetrahedron, which is responsible for the greater stability of the latter (the analogous condensation of the arsenic groups takes place in the range 773–1013 K). After the removal of water in stages, the alkali metal phospho- and arseno-uranate derivatives are converted into the compounds $M^IP(As)UO_6$. The elimination of water molecules from the coordination environment of the alkali metal cation leads in this instance to the conversion of the compound into an amorphous form, i.e. to the breakdown of the long-range order and hence to the disordering of the crystal lattices of the test compounds.

Higher dehydration temperature ranges are also characteristic of alkali metal arsenouranate derivatives compared with the corresponding phosphates, which is a consequence of the stronger binding of the water in $M^IAsUO_6 \cdot nH_2O$. A decrease in the dehydration temperature ranges is observed in both series of compounds on passing from lithium to caesium compounds. This effect is fully consistent with the decrease in the enthalpies of dehydration of alkali metal ions with increase in their size and indicates the incorporation of water molecules in the coordination environment of the univalent element.

The standard enthalpies of formation at 298.15 K of the compounds $M^IP(As)UO_6$ and their crystalline hydrates have been determined from calorimetric data. Quantitative rules governing the variation of the quantities $\Delta_fH°(298)$ for the compounds as a function of the physical characteristics of the alkali metal ions (ionic radius, enthalpy of formation of the ion in the gas phase, ionisation potential) have been established. The results have been compared with the structural characteristics of the same compounds. In particular, the structural similarity of the compounds is manifested by the fact that the standard enthalpies of formation of the phosphorus and arsenic derivatives obey the similarity principle proposed by M Kh Karapetyants.

$$\Delta_fH°(298, M^IPUO_6) = \{[-463.5 + 0.97\Delta_fH°(298, M^IAsUO_6)] \pm 2\}/\text{kJ mol}^{-1}$$

$$\Delta_fH°(298, M^IPUO_6 \cdot nH_2O) = \{[-351.5 + 1.01\Delta_fH°(298, M^IAsUO_6 \cdot nH_2O)] \pm 3\}/\text{kJ mol}^{-1}.$$

In the series of phosphates and arsenates with M^I = Na, K, Rb, or Cs, the difference between the $\Delta_fH°(298)$ for the anhydrous compounds and their crystalline hydrates per mole of water of crystallisation is virtually constant at 293 ± 3 kJ mol^{-1}. The analogous difference in the case of the hydrogen and lithium forms is also constant, but exceeds the above quantity and amounts to 300 ± 4 kJ mol^{-1}, which emphasises yet again the stronger binding of the water of crystallisation in the hydrogen and lithium derivatives compared with the derivatives of the other Group I elements. This is also indicated by the enthalpies of the dehydration reactions of the crystalline hydrates investigated.

The study of the energy relations of the ion-exchange processes showed that they are all endothermic. This is due to the predominance of the energy expenditure associated with the change in structure on passing from the compounds $HP(As)UO_6 \cdot 4H_2O$ to $M^IP(As)UO_6 \cdot nH_2O$ compared with the overall exothermic effect in the accompanying process involving the dehydration-hydration of the alkali metal ions and the proton in the aqueous phase. The enthalpies of the ion-exchange reactions decrease in this instance in the series of alkali metal derivatives from lithium to caesium for both $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$. The results lead to prospects for the practical use of the ion-exchange reactions in order to isolate the compounds and also to prevent the entry of the ecologically dangerous (including radioactive) elements into the human habitat.

References

1. V N Serezhkin, Doctoral Thesis in Chemical Sciences, Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 1985
2. G A Sidorenko *Kristallokhimiya Mineralov Urana* (Crystal Chemistry of Uranium Minerals) (Moscow: Atomizdat, 1978)
3. I A Murav'eva, O G Nemkova, Yu V Orlova, in *Issledovaniya v Oblasti Khimii Urana* (Investigations in Uranium Chemistry) (Ed. V I Spitsin) (Moscow: Izd. Mosk. Gos. Univ., 1961) p. 248
4. I A Murav'eva, O G Nemkova, R P Cherkasova, A S Orlova, in *Issledovaniya v Oblasti Khimii Urana* (Investigations in Uranium Chemistry) Ed. V I Spitsin (Moscow: Izd. Mosk. Gos. Univ., 1961) p. 240
5. H Linau Ph D, Berlin Univ, Berlin 1898
6. E Rimbach *Ber. Dtsch. Chem. Ges.* **37** 461 (1904)
7. E V Konchenova, K V Skvortsova *Dokl. Akad. Nauk SSSR* **114** 634 (1957)
8. Z D Nekrasova, in *Voprosy Geologii Urana* (Problems of the Geology of Uranium) (Moscow: Atomizdat, 1957) p. 67
9. O V Shchipanova, L N Belova, P V Pribytkov, A P Katargina *Dokl. Akad. Nauk SSSR* **197** 178 (1971)
10. M J Gallagher, D Atkin *Bull. Geol. Surv. Gr. Br.* (25) 49 (1966)
11. M Ross *Am. Mineral.* **35** 525 (1950)
12. M Ross *Am. Mineral.* **48** 1012 (1963)
13. M Ross, H Evans *Am. Mineral.* **49** 1578 (1964)
14. M Ross *Am. Mi*neral. **40** 917 (1955)
15. F G Zharovskii *Tr. Komissii po Anal. Khimii AN SSSR* **3** 101 (1951)
16. I G Zhil'tsova, L I Polupanova, E M Shmariovich, S A Perlina *Litologiya Polez. Iskopaemye* (6) 71 (1985)
17. I G Zhil'tsova, L I Polupanova, E M Shmariovich, S A Perlina *Litologiya Polez. Iskopaemye* (3) 44 (1987)
18. L S Itkina, I S Rassonskaya, N M Chaplygina *Zh. Neorg. Khim.* **3** 1675 (1958)
19. A E Klygin, D M Zavrazhnova, N A Nikol'skaya *Zh. Anal. Khim.* **16** 297 (1961)
20. A I Moskvin, A M Shelyakina, P S Perminov *Zh. Neorg. Khim.* **12** 3319 (1967)
21. I A Murav'eva, K B Zaborenko, O G Nemkova, Khan De Pin *Radiokhimiya* **6** 124 (1964)
22. V G Chukhlantsev, S I Stepanov *Zh. Neorg. Khim.* **1** 478 (1956)
23. V G Chukhlantsev, A K Sharova *Zh. Neorg. Khim.* **1** 36 (1956)
24. V Pekarek, M Benesova *J. Inorg. Nucl. Chem.* **26** 1743 (1964)
25. V Pekarek, V Vesely *J. Inorg. Nucl. Chem.* **27** 1151 (1965)
26. M G Shilton, A T Howe *Mater. Res. Bull.* **12** 701 (1977)
27. V Vesely, V Pekarek, M Abbrent *J. Inorg. Nucl. Chem.* **27** 1159 (1965)

28. L V Kobets, T A Kolevich, D S Umreiko *Koord. Khim.* **4** 1856 (1978)
29. P Childs, A Howe, M Shilton *J. Power Sources* **3** 105 (1978)
30. B Morosin *Acta Crystallogr.* **34** 3732 (1978)
31. A T Howe, M G Shilton *J. Solid State Chem.* **31** 393 (1980)
32. S B Auksyalis, G E Boyare, K S Pitre, A R Lusis, R A Vaitkus, A S Orlyukas, R A Mizeris *Lit. Fiz. Sb.* **28** 757 (1988)
33. L V Kobets, V A Filimonov *Izv. Akad. Nauk SSSR, Neorg. Mater.* **24** 1327 (1988)
34. R Baggio, M A R de Bengacar, H L de Dussel, P K de Petrazzo, L Schmirgeld, in *The Vth European Meeting on Ferroelectronics, Belmadena, Malaga, 1983* Vol. 4, p. 777
35. M Gasperin *J. Solid State Chem.* **67** 219 (1987)
36. A T Howe, M G Shilton *J. Solid State Chem.* **28** 345 (1979)
37. K D Kreuer, W Weppner, A Rabenau *Solid State Ion.* **3–4** 353 (1981)
38. S B Lyon, D J Fray, in *Solid State Ionics-83. The 4th International Conference, Grenoble, 1983* p. 1295
39. C M Mari, D Narducci *Chim. Ind.* **68** 70 (1986)
40. US P. 4 306 774; *Rocwell Intl. Corp.* 58 995 (1979)
41. J Schoonman, D R Franceschetti, J W Hanneken *Ber. Bunsenges. Phys. Chem.* **86** 701 (1982)
42. F Skou, I Cr Krogh Andersen, K E Simonsen, E Krogh Andersen, in *Solid State Ionics-83. The 4th International Conference, Grenoble, 1983* p. 1041
43. M V Susic, D M Minic *Solid State Ion.* **6** 327 (1982)
44. T Takahashi, S Tanase, O Yamamoto *J. Appl. Electrochem.* **10** 415 (1980)
45. P K Dorhout, G L Rosenthal, A B Ellis *Inorg. Chem.* **27** 1159 (1988)
46. N G Chernorukov, N P Egorov, E V Suleimanov *Zh. Neorg. Khim.* **34** 2995 (1989)
47. N G Chernorukov, N P Egorov, E V Suleimanov *Radiokhimiya* **4** 3 (1991)
48. N G Chernorukov, N P Egorov, E V Suleimanov *Zh. Neorg. Khim.* **38** 197 (1993)
49. M Gasperin *C. R. Acad. Sci.* **303** 1791 (1986)
50. M Gasperin *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **43** 404 (1987)
51. F Weigel, G Hoffman *J. Less-Common Met.* **44** 99 (1976)
52. P K Dorhout, D H Sabel, A B Ellis *J. Less-Common Met.* **156** 439 (1989)
53. G L Rosenthal, A B Ellis *J. Less-Common Met.* **139** 299 (1988)
54. R S W Braithwaite, J R Knight *Mineral. Mag.* **54** 129 (1990)
55. G R Dieckmann, A B Ellis, E E Hellstrom *J. Electrochem. Soc.* **137** 2331 (1990)
56. Y Marzoni Fecia di Cossato, P Orlandi *Rend. Soc. Ital. Mineral. Petl.* **42** 263 (1987)
57. Vochten Renaud *Am. Mineral.* **75** 221 (1990)
58. L V Volod'ko, A I Komyak, D S Umreiko *Uranilovye Soedineniya* (Uranium Compounds) (Minsk: Izd. Belorus. Gos. Univ., 1981)
59. L V Kobets, D S Umreiko *Usp. Khim.* **52** 897 (1983) [*Russ. Chem. Rev.* **52** 509 (1983)]
60. L Bernard, A N Fitch, A T Howe, A F Wright, B E F Fender *J. Chem. Soc., Chem. Commun.* **9** 784 (1981)
61. A N Fitch, M Cole *Mater. Res. Bull.* **26** 407 (1991)
62. A N Fitch, B E F Fender, A F Wright *Acta Crystallogr., Ser. B, Struct. Crystallogr.* **38** 1108 (1982)
63. M Pham-thi, Ph Colomban *Solid State Ion.* **17** 295 (1985)
64. M Pham-thi, Ph Colomban *J. Less-Common Met.* **108** 189 (1985)
65. M Pham-thi, Ph Colomban, A Novak *J. Phys. Chem. Solids* **46** 493 (1985)
66. M Pham-thi, Ph Colomban, A Novak *J. Phys. Chem. Solids* **46** 565 (1985)
67. E Schulte *Neues J. Mineral* **8** 242 (1965)
68. A F Wells *Structural Inorganic Chemistry* Vols 1–3 (Translated into Russian; Moscow: Mir, 1987, 1988)
69. K V Narasimham *Ind. J. Phys.* **34** 321 (1960)
70. M V Nikanovich, G G Novitskii, L V Kobets, T A Kolevich, V V Sikorskii, D S Umreiko *Koord. Khim.* **2** 253 (1976)
71. N G Chernorukov, N V Karyakin, E V Suleimanov, G N Chernorukov *Radiokhimiya* **36** 209 (1994)
72. N G Chernorukov, N V Karyakin, E V Suleimanov, G N Chernorukov *Zh. Neorg. Khim.* **39** 23 (1994)
73. N G Chernorukov, N V Karyakin, G N Chernorukov *Zh. Neorg. Khim.* **39** 1781 (1994)
74. G V Yukhnevich *Infrakrasnaya Spektroskopiya Vody* (Infrared Spectroscopy of Water) (Moscow: Nauka, 1973)
75. V I Karpov, Ts L Ambartsumyan *Zh. Neorg. Khim.* **7** 1838 (1962)
76. A Weiss, K Hartl, U Hoffman *Z. Naturforsch. B, Chem. Sci.* **12** 669 (1957)
77. M Jansen *Angew. Chem.* **89** 326 (1977)
78. L V Kobets, T A Kolevich, D S Umreiko *Zh. Neorg. Khim.* **23** 909 (1978)
79. L V Kobets, T A Kolevich, D S Umreiko, V N Yaglov *Zh. Neorg. Khim.* **22** 45 (1977)
80. I B Rabinovich *Vliyanie Izotopii na Fiziko-khimicheskie Svoistva Zhidkostei* (Influence of Isotopicity on the Physicochemical Properties of Liquids) (Moscow: Nauka, 1968)
81. L V Kobets, T A Kolevich, L P Savchenko, D S Umreiko *Koord. Khim.* **1** 499 (1975)
82. E Thilo *Rev. Chim. Mineral.* **5** 179 (1968)
83. G B Naumov, B N Ryzhenko, I L Khodakovskii *Spravochnik Termodinamicheskikh Velichin* (Handbook of Thermodynamic Quantities) (Moscow: Atomizdat, 1971)
84. V P Glushko (Ed.) *Termicheskie Konstanty Veshchestv* (Thermal Constants of Compounds) No. 10, Parts I–II Nauka Moscow 1981
85. D Langmuir *Geochim. Cosmochim. Acta* **42** 547 (1978)
86. R J Lemire, P R Tremaine *J. Chem. Eng. Data* **25** 361 (1980)
87. N V Karyakin, G N Chernorukov *Zh. Obshch. Khim.* **63** 1515 (1993)
88. N V Karyakin, G N Chernorukov *Zh. Obshch. Khim.* **64** 558 (1994)
89. N V Karyakin, G N Chernorukov *Zh. Obshch. Khim.* **64** 1082 (1994)
90. N V Karyakin, G N Chernorukov *Zh. Obshch. Khim.* **64** 1079 (1994)
91. N V Karyakin, G N Chernorukov *Zh. Obshch. Khim.* **64** 1077 (1994)
92. N V Karyakin, G N Chernorukov, in *Tez. Dokl. Pervoi Rossiiskoi Konf. po Radiokhimii, Dubna, 1994* (Abstracts of Reports at the First Russian Conference on Radioactivity, Dubna, 1994) p. 50
93. N G Chernorukov, E V Suleimanov, N V Karyakin, G N Chernorukov, in *XV Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Obninskii Simp. "Radioekologicheskie Problemy v Yadernoi Energetike i pri Konversii Proizvodstva"* (The XVth Mendeleev Congress on General and Applied Chemistry. Obninsk Symposium on "Radioecological Problems in Nuclear Power and Industrial Transformation") (Obninsk: Russian Scientific Centre, Physics and Power Engineering Institute, 1993) Vol. 2, p. 87
94. N V Karyakin, N G Chernorukov, G N Chernorukov, in *The VIth European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 1994* p. 161
95. N V Karyakin, N G Chernorukov, Ye V Suleimanov, G N Chernorukov, in *Czechoslovak-French-Polish Conference on Calorimetry and Experimental Thermodynamics; Application to Contemporary Problems, Prague, 1993* p. 161
96. N V Karyakin, N G Chernorukov, Ye V Suleimanov, G N Chernorukov, in *Annual Meeting on Nuclear Technology'94, Liederhalle, Stuttgart, 1994* p. 301
97. P N Nikolaev, I B Rabinovich *Tr. Khim. Khim. Tekhnol.* (2) 242 (1961)
98. CODATA Key Values *J. Chem. Thermodyn.* **3** 4 (1971)
99. V A Ryabin, M A Ostroumov, T F Svit *Termodinamicheskie Svoistva Veshchestv* (Thermodynamic Properties of Compounds) (Leningrad: Khimiya, 1977)
100. M Kh Karapet'yants, M L Karapet'yants *Osnovnye Termodinamicheskie Konstanty Neorganicheskikh i Organicheskikh Veshchestv* (Fundamental Thermodynamic Constants of Inorganic and Organic Compounds) (Moscow: Khimiya, 1968)
101. L Pauling *General Chemistry* (Translated into Russian; Moscow: Mir, 1974)
102. V N Yaglov, Doctoral Thesis in Chemical Sciences, Ivanovo Chemical Engineering Institute, Ivanovo, 1980
103. G N Chernorukov, Candidate's Thesis in Chemical Sciences, Nizhnii Novgorod State Technical University, Nizhnii Novgorod, 1995