THE CHEMISTRY OF URANIUM(VI) ORTHOPHOSPHATE SOLUTIONS: PART II, THE SOLUBILITY OF URANIUM(VI) ORTHOPHOSPHATES IN PHOSPHORIC ACID SOLUTIONS

J. M. Schreyer
C. F. Baes, Jr.
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PART II, THE SOLUBILITY OF URANIUM(VI) ORTHOPHOSPHATES IN PHOSPHORIC ACID SOLUTIONS

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ABSTRACT

The solubility behavior of uranium(VI) phosphates has been determined in aqueous solutions containing 0.001 to 15M total phosphate. Identification of the equilibrium solid phases has been made microscopically, chemically, and by X-ray diffraction analysis.
THE CHEMISTRY OF URANIUM(VI) ORTHOPHOSPHATE SOLUTIONS:

PART II, THE SOLUBILITY OF URANIUM(VI) ORTHOPHOSPHATES
IN PHOSPHORIC ACID SOLUTIONS

I. INTRODUCTION AND SUMMARY

This is the second in a series of reports describing an investigation of the uranium(VI) orthophosphate system. The preceding report (ORNL-1577) described a spectrophotometric study of uranium(VI) phosphate solutions under conditions of controlled acidity. In a subsequent report, the solubility behavior of uranium(VI) phosphates in perchloric acid solution will be presented. Also, all of the solubility results will be discussed in terms of the complex ionic species in solution.

The solubility data on uranium(VI) phosphates in pure phosphoric acid reported previous to the present work covered a limited range of molarities and in some cases the equilibrium solid phase was in question. Lord, Andrews, and Gates(1) studied the solubility of UO$_2$HPO$_4$.xH$_2$O as a function of phosphate concentration at pH 1 and 2. The pH of their solutions was adjusted with ammonia and nitric acid which suggests that their solubility data were probably for uranyl ammonium phosphate.(2) Their measurements were made without control of temperature, and data showing the attainment of equilibrium conditions were not presented. G. R. Leader(3) reported the solubility behavior of UO$_2$HPO$_4$.4H$_2$O in HNO$_3$ and H$_3$PO$_4$ over a range of 0.3 and 3.0M H$_3$PO$_4$. Phosphate determinations were made by precipitation of bismuth phosphate and were reported to be 5-10% high.

For the current solubility measurements, it was necessary to prepare several pure uranium(VI) phosphate salts in order to establish the range of stability of each solid phase. Three uranyl orthophosphates have been reported previously; they are UO$_2$HPO$_4$.4H$_2$O, \{UO$_2$\}$_3$(PO$_4$)$_2$.4H$_2$O and UO$_2$(H$_2$PO$_4$)$_2$.3H$_2$O.
Zachariasen\(^4\) examined \(\text{UO}_2\text{HPO}_4\cdot4\text H_2\text{O}\) by X-ray methods and showed this compound to be tetragonal with a calculated density of 3.41. Harris and Scott\(^5\) discussed the optical properties of \(\text{UO}_2\text{HPO}_4\cdot4\text H_2\text{O}\) and \((\text{UO}_2)_3(\text{PO}_4)_2\cdot4\text H_2\text{O}\). They reported that both these compounds are tetragonal, and \(\text{UO}_2\text{HPO}_4\cdot4\text H_2\text{O}\) was said to crystallize as tabular plates, usually four sided but occasionally as truncated squares. The \((\text{UO}_2)_3(\text{PO}_4)_2\cdot4\text H_2\text{O}\) was said to crystallize in needle-like crystals. They gave the density value of \(\text{UO}_2\text{HPO}_4\cdot4\text H_2\text{O}\) and \((\text{UO}_2)_3(\text{PO}_4)_2\cdot4\text H_2\text{O}\) as 3.399 and 3.213, respectively. Werther\(^6\) reported the preparation of crystals of \(\text{UO}_2(\text{H}_2\text{PO}_4)_2\cdot3\text H_2\text{O}\) by heating small amounts of \(\text H_3\text{PO}_4\) with \(\text{UO}_3\) to boiling and allowing to stand over \(\text H_2\text{SO}_4\). The crystal structure of this latter compound has not been previously determined.

The solubilities reported here were measured by shaking each phosphoric acid solution with an excess of the appropriate solid until equilibrium was reached, and analyzing the saturated solution. The present measurements were all made at 25\(^{\circ}\)C. The concentration of the aqueous phosphoric acid was varied from 0.001 to 15M \(\text H_3\text{PO}_4\). Through this range, the solubility of the uranium(\(\text{VI}\)) orthophosphates was found to increase with increasing phosphoric acid concentration from approximately 1x10\(^{-5}\)M uranyl at 0.001M phosphate to about 1.7M uranyl at 6.1M phosphate, and then to decrease to about 0.3M uranyl at 15M phosphate.

Chemical analysis of the equilibrium residues indicated three different stable solid phases at different phosphoric acid concentrations, as follows:

\[
\begin{align*}
(\text{UO}_2)_3(\text{PO}_4)_2\cdot6\text H_2\text{O}, \text{ total phosphate } & \leq 0.014\text M \\
\text{UO}_2\text{HPO}_4\cdot4\text H_2\text{O}, & \text{ } > 0.014\text M, < 6.1\text M \\
\text{UO}_2(\text{H}_2\text{PO}_4)_2\cdot3\text H_2\text{O}, & \text{ } > 6.1\text M
\end{align*}
\]

The existence of the normal uranyl phosphate as the hexahydrate was indicated by the uranium and phosphate analysis and corroborated by direct water determination. However, the X-ray diffraction pattern appeared to be the same as that for the normal uranyl phosphate tetrahydrate. This region of the phase diagram is confined to solutions of such low concentrations that the application of Schreinemaker's wet residue method to distinguish the degree of hydration is not practical.

The uranyl monohydrogenphosphate tetrahydrate was identified both by chemical analysis and by its X-ray diffraction pattern. The degree of hydration was confirmed by use of Schreinemaker's wet residue method.

The uranyl dihydrogenphosphate trihydrate was identified by chemical analysis, and corroborated by the density cal-
culated from X-ray diffraction data; the diffraction pattern for this compound has not been previously reported. The degree of hydration was also confirmed by use of Schreinemaker's wet residue method.

In addition to the compounds found to be in equilibrium with the saturated solutions, two lower hydrates were also prepared and identified - uranyl monohydrogenphosphate dihydrate and uranyl dihydrogenphosphate monohydrate.

II. EXPERIMENTAL

A. Methods of Analysis

1. Analysis for Uranium
   a. Volumetric Method

   Analysis for uranium in the various solutions was performed by the volumetric dichromate method described previously (7).

   b. Polarographic Analysis

   To facilitate the measurement of low uranium solubilities in dilute phosphoric acid solution, a procedure for polarographic analysis of the mother liquor was developed.

   Orthophosphate is known to interfere with the polarographic determination of uranium (8,9) presumably because of the precipitation of uranium(IV) phosphate at the dropping mercury electrode. However, it was found in the present work that by the addition of oxalic acid to the supporting electrolyte, well-formed waves are produced (E1/2 = ca. -0.08 v. vs. S.C.E.), the heights of which are independent of the phosphate concentration, at least in phosphoric acid solutions up to 0.01M. The maximum permissible phosphate concentration has not been determined.

   The procedure of analysis consisted in adding 20 ml of a stock solution, 0.6M in oxalic acid, 0.1M in sulfuric acid, and containing 0.015% gelatin, to 20 ml of the unknown solution in the dropping electrode cell. Purified hydrogen was then bubbled through the solution for at least twenty minutes to remove dissolved oxygen. A saturated calomel electrode was connected to the cell by means of an agar-saturated KCl salt bridge, and a polarogram was recorded from +0.15 to -0.35 volts. The diffusion current was measured
from the polarogram as follows: The current was read at 
-0.10 V and +0.30 V, and from the difference was subtracted
the residual current correction, determined from a solution
of the supporting electrolyte which contained no uranium.

The diffusion current was found to be proportional to
the uranyl concentration. The method was applicable to
uranyl concentrations as low as 1x10^-5 molar, though normal
accuracy (ca. 5% error) was limited to concentrations above
about 5x10^-5 molar, where the residual current correction
is not large compared to the diffusion current.

2. Analysis for Phosphate

In an investigation of the use of the magnesium ammonium
phosphate method(10) for the determination of phosphate, it
was found that uranium interfered in this analysis. A method
for removal of uranium from uranium(VI) phosphate solutions
by means of a cation exchange resin was developed by W. K.
Miller of the Analytical Division (Y-12) of the Oak Ridge
National Laboratory (unpublished data).

A glass column (1" by 15") containing 50 to 75 ml of
Dowex-50 resin, is washed with 200 ml of 3M HCl followed by
200 ml of H_2O at a flow rate of 2-3 ml per minute. A dilute
acid solution of uranium(VI) phosphate containing 100-150 mg
of phosphate is passed through the column at a flow rate of
1 ml per minute. The column is washed with water until the
washings are neutral to litmus, and the phosphate is
determined on the combined effluent by the magnesium ammonium
phosphate method.(10) Uranium may be eluted from the column
by washing with 3M HCl at a rate of approximately 3 ml per
minute.

An average deviation of 0.5% was obtained by this
method.

3. Analysis for Water

Water in the solid uranium(VI) phosphate samples was
determined* by heating at 300ºC for one hour, in an atmosphere
of helium, in a closed ignition tube connected to a weighed
absorption bulb containing anhydrous magnesium perchlorate.

*With UO_2(H_2PO_4)_2·3H_2O, decomposition of the orthophosphate to
pyro- or metaposphate apparently occurred; hence, the direct
water analyses were used only as supplementary to the indirect
determination by difference from uranium and phosphate
analyses.
B. Preparation of Salts

1. Preparation of UO₂HPO₄.4H₂O

Two samples of UO₂HPO₄.4H₂O (367 g each with 84% yields) were prepared by the following procedure.

One liter of 1.1M phosphoric acid solution was added with stirring to one Titer of approximately 1M uranium(VI) nitrate or perchlorate solution. The solution was seeded with a few crystals of UO₂HPO₄.4H₂O and precipitation occurred immediately. After stirring for 12 hours, the mother liquor was removed by centrifuging or filtering. The precipitate was reslurried in 1000 ml of approximately 0.01M HClO₄ solution for 12 hours, then filtered and washed with acetone. The dry sample was placed in a vacuum desiccator over a saturated solution of Na₂Cr₂O₇ (V.P. = 9.12 mm at 20°C) for 12 hours.

Under the microscope, tetragonal crystals characteristic of UO₂HPO₄.4H₂O were observed (see Photograph No. 1). X-ray diffraction analysis qualitatively identified the solid as UO₂HPO₄.4H₂O. Chemical analysis gave for the first sample 61.6% UO₂⁺⁺, 21.6% PO₄⁻³, and by difference 16.6% H₂O, while the second sample gave 61.9% UO₂⁺⁺, 21.6% PO₄⁻³, and by difference 16.3% H₂O. This corresponds to the formula UO₂HPO₄.4H₂O, for which the theoretical percentages are 61.63% UO₂⁺⁺, 21.68% PO₄⁻³ and 16.45% H₂O.

If the acetone-dried sample prepared by the above method is heated in an oven at 110°C, the UO₂HPO₄.4H₂O is converted to UO₂HPO₄.2H₂O. A typical analysis of a sample dried in this manner gave 67.7% UO₂⁺⁺, 23.1% PO₄⁻³, and by difference 9.0% H₂O, while the theoretical percentages for UO₂HPO₄.2H₂O are 67.16% UO₂⁺⁺, 23.6% PO₄⁻³ and 8.96% H₂O.

2. Preparation of (UO₂)₃(PO₄)₂.4H₂O

A 100 g sample of (UO₂)₃(PO₄)₂.4H₂O was prepared according to the directions of Ryon and Kuhn(11) by digesting UO₂NH₄PO₄.3H₂O in 0.8M HNO₃ at 100°C. The solid was then washed with hot water and acetone and dried in air. Conversion of UO₂NH₄PO₄.3H₂O to (UO₂)₃(PO₄)₂.4H₂O was easily observed by the change in physical appearance of the solid phase.

Under the microscope needle-like crystals were observed characteristic of (UO₂)₃(PO₄)₂.4H₂O, (see Photograph No. 2). X-ray diffraction analysis qualitatively identified the solid as (UO₂)₃(PO₄)₂.4H₂O. Chemical analysis of the solid
PHOTOGRAPH NO. 1

CRYSTALS OF $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$

MAGNIFICATION: 150 X

PHOTOGRAPHED BY R.S. CROUSE AND E.R. BOYD

METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
PHOTOGRAPH NO. 2

CRYSTALS OF $\text{(UO}_2\text{)}_3\text{(PO}_4\text{)}_2\cdot 4\text{H}_2\text{O}$

MAGNIFICATION: 150X

PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
gave 75.3% UO₂⁺⁺, 18.0% PO₄⁻³, and by difference 6.7% H₂O. This corresponds to a formula of (UO₂)₃(PO₄)₂·4H₂O, for which the theoretical percentages are 75.5% UO₂⁺⁺, 17.72% PO₄⁻³ and 6.72% H₂O.

3. Preparation of UO₂(H₂PO₄)₂·3H₂O

A sample (approximately 10 g) of UO₂(H₂PO₄)₂·3H₂O was prepared by the addition of approximately 30 g UO₂HPO₄·4H₂O to 100 ml 85% H₃PO₄. The sample was shaken for 13 days at 25°C and then filtered using the apparatus shown in Figure 1. Preliminary experimentation showed that the wet solid would dissolve immediately upon washing with a small amount of water. For this reason, the sample was washed only with acetone followed by carbon tetrachloride, and the dry sample was placed in a vacuum desiccator over CaCl₂ for 12 hours. X-ray powder diffraction analysis could not be made since a standard for this compound was not available, although a pattern was made for future reference. Chemical analysis of the solid gave 52.6% UO₂⁺⁺, 35.7% PO₄⁻³, and by difference 10.9% H₂O, while the formula UO₂(H₂PO₄)₂·3H₂O gives for the theoretical percentages 52.12% UO₂⁺⁺, 36.66% PO₄⁻³ and 10.4% H₂O.

If UO₂(H₂PO₄)₂·3H₂O is heated for 7 hours at 110°C, it is converted to UO₂(H₂PO₄)₂·H₂O. Werther(6) reported that part of the water in the trihydrate is lost upon heating and at red heat all of the water is removed without melting or loss of phosphorus. It is probable that he converted the compound to a pyrophosphate.

Bernard S. Borie, Jr.,(12) X-ray Laboratory, Oak Ridge National Laboratory, by private communication has reported a preliminary investigation of the crystal structure of UO₂(H₂PO₄)₂·3H₂O.

One of the yellow crystal platelets of a sample of UO₂(H₂PO₄)₂·3H₂O was mounted on a glass fiber with a little grease and then mounted on a precession camera. A series of photographs was taken with copper Kα radiation, which showed the crystals to be monoclinic: a = 10.83Å, b = 13.92Å, c = 7.48Å, and β = 105°45'.

If it is assumed that the unit cell contains four stoichiometric units, the density calculated from the formula weight and the dimensions given above is 3.17 for the formula UO₂(H₂PO₄)₂·3H₂O or 3.28 for the formula UO₂(H₂PO₄)₂·4H₂O. The measured density is 3.16, substantiating the trihydrate formula.
From the photographs, it was observed that reflections of the type OkO are absent except when k is even, and that reflections of the type h0l are absent except when l is even. No other extinction occurs. Therefore, the space group is \( \text{C}_{2h}^5 \cdot P2_1/C \). Since uranium is by far the heaviest element present in the compound, it should be possible to find parameters for the four uranium atoms in the cell from the intensities of the reflections recorded on the photographs. Approximate agreement between observed and calculated intensities result if the uranium atoms are in fourfold general positions, \( x \ y \ z; \ \bar{x} \ y \ z; \ x, 1/2 - y, 1/2 + z; \ x, 1/2 - y, 1/2 + z \), where \( x = 0.25, y = 0.4, \) and \( z = 0.25 \). The determination of the light atom positions would require quantitative intensity measurements.

C. Apparatus

1. Solubility Apparatus

The solubility measurements were carried out using solubility flasks of the type shown in Figure 1. The cap was fitted on the flask using Apiezon stopcock grease and a clamp. The solubility flasks were assembled on a mechanical shaker in a water bath thermostatically controlled at 24.9 ± 0.1°C. Agitation of the solution was accomplished by a pendulum-like motion with an arc of 80° and 36 strokes per minute. After equilibration, filtration was carried out by means of the pressure filter apparatus (Figure 1) which permitted maintenance of the constant temperature by immersion of the entire assembly under the water.

2. Polarograph

The polarograph used in these studies was an automatic recording instrument constructed at the Y-12 Instrument Shop according to the specifications of John Horton of the Oak Ridge National Laboratory and similar to the instrument described by Kelley and Miller.\(^{13}\) The instrument sensitivity ranged from 0.05 to 20 microamps per full scale deflection.

D. Solubility Studies in Phosphoric Acid

The solubility measurements were carried out by adding the desired uranium(VI) phosphate to a solution of phosphoric
FIGURE 1. SOLUBILITY APPARATUS
acid, placing the solution in the solubility apparatus and shaking the flask assembly in a water bath at 25°C for a period necessary to attain equilibrium conditions.

The attainment of solubility equilibrium in the various samples was established through experiments of varied shaking times. When \((UO_2)_3(PO_4)_2 \cdot 4H_2O\) was used as the added solid phase, the samples in the region of stability of \((UO_2)_3(PO_4)_2 \cdot 6H_2O\) were shaken from 7 to 11 days in order to attain equilibrium. In this region, the time required to convert \(UO_2HPO_4 \cdot 4H_2O\) to the stable \((UO_2)_3(PO_4)_2 \cdot 6H_2O\) was very long, making the use of \(UO_2HPO_4 \cdot 4H_2O\) as the added solid phase impractical (see Figure 2). In the region of stability of \(UO_2HPO_4 \cdot 4H_2O\) using \(UO_2HPO_4 \cdot 4H_2O\) as the added solid phase, equilibrium condition was attained in 2 to 12 days. Three determinations using \((UO_2)_3(PO_4)_2 \cdot 4H_2O\) as the added solid phase were run at 0.02, 2.495 and 5.527 initial \(H_3PO_4\) and complete conversions to \(UO_2HPO_4 \cdot 4H_2O\) occurred. Equilibration in the region of stability of \(UO_2(H_2PO_4)_2 \cdot 3H_2O\) using \(UO_2(H_2PO_4)_2 \cdot 3H_2O\) as the added solid phase was attained in 9 to 23 days. These values were used to definitely establish the solubility curve in this region. When \(UO_2HPO_4 \cdot 4H_2O\) was used as the added solid phase in the region of stability of \(UO_2(H_2PO_4)_2 \cdot 3H_2O\), the samples were shaken for 15 to 20 days with some question as to whether equilibrium had been attained, since chemical analysis of these solid phases indicated contamination with \(UO_2HPO_4 \cdot 4H_2O\) (see Table I). Although Figures 3 and 4 indicate that conversion of \(UO_2HPO_4 \cdot 4H_2O\) to \(UO_2(H_2PO_4)_2 \cdot 3H_2O\) in 7.3 to 2.5M \(H_3PO_4\) would be complete within these periods, it is evident from Figure 5 that much longer periods of shaking are required in more concentrated phosphoric acid solutions.

Microscopic examination of solids proved very useful in detecting the tetragonal crystals of uranyl monoacid phosphate (see Photograph No. 1) and the needle-like crystals of the normal uranyl phosphate (see Photograph No. 2). The crystal habit of the solid phase \(UO_2(H_2PO_4)_2 \cdot 3H_2O\), obtained in high phosphate concentrations, has not been characterized previously. These crystals varied from large monoclinic rods obtained at the transition point to indistinguishably small crystals in concentrated phosphate solutions (see Photographs Nos. 4, 5, 6, 7, 8, and 9).

In some of the solubility tests, chemical (see Table 1) and X-ray diffraction analyses (see Photograph No. 10) were made on the solid phases removed from the mother liquors.
FIGURE 2. CONVERSION OF UO$_2$HPO$_4$·4H$_2$O TO (UO$_2$)$_3$(PO$_4$)$_2$·6H$_2$O IN 0.01 M H$_3$PO$_4$
Table 1

CHEMICAL ANALYSES OF URANIUM(VI) PHOSPHATES
FROM PHOSPHORIC ACID SOLUTIONS

Theoretical Compositions:

\((\text{UO}_2)_(3)(\text{PO}_4)_2\cdot 6\text{H}_2\text{O}\): 73.10% \text{UO}_2^{++}, 17.10% \text{PO}_4^{-3}, 9.75% \text{H}_2\text{O}

\text{UO}_2\text{HPO}_4\cdot 4\text{H}_2\text{O}: 61.6 \% \text{UO}_2^{++}, 21.68\% \text{PO}_4^{-3}, 16.45\% \text{H}_2\text{O}

\text{UO}_2(\text{H}_2\text{PO}_4)_2\cdot 3\text{H}_2\text{O}: 52.13\% \text{UO}_2^{++}, 36.6 \% \text{PO}_4^{-3}, 10.42\% \text{H}_2\text{O}

<table>
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<th>Sample Number</th>
<th>Total Phosphate in Mother</th>
<th>Analysis of Solid Phases</th>
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<td>% Liquor moles/l</td>
<td>% \text{UO}_2^{++}</td>
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<td>71.81</td>
</tr>
<tr>
<td>*A-33</td>
<td>0.0140</td>
<td>65.90</td>
</tr>
<tr>
<td>A-27</td>
<td>0.0179</td>
<td>61.82</td>
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<td>A-10</td>
<td>0.103</td>
<td>61.70</td>
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<td>A-25</td>
<td>0.108</td>
<td>62.00</td>
</tr>
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<td>A-21</td>
<td>2.74</td>
<td>61.30</td>
</tr>
<tr>
<td>A-3</td>
<td>2.93</td>
<td>61.70</td>
</tr>
<tr>
<td>A-7</td>
<td>6.09</td>
<td>61.90</td>
</tr>
<tr>
<td>A-20</td>
<td>6.10</td>
<td>61.80</td>
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<tr>
<td>A-40</td>
<td>6.14</td>
<td>54.30</td>
</tr>
<tr>
<td>A-44</td>
<td>6.67</td>
<td>55.10</td>
</tr>
<tr>
<td>A-38-3</td>
<td>6.78</td>
<td>53.80</td>
</tr>
<tr>
<td>A-45</td>
<td>7.20</td>
<td>52.18</td>
</tr>
<tr>
<td>A-36</td>
<td>7.31</td>
<td>53.10</td>
</tr>
<tr>
<td>A-41</td>
<td>8.88</td>
<td>51.80</td>
</tr>
<tr>
<td>A-42</td>
<td>10.40</td>
<td>55.6</td>
</tr>
</tbody>
</table>

*Solid phase obtained at transition point between \text{UO}_2\text{HPO}_4\cdot 4\text{H}_2\text{O} and \((\text{UO}_2)_(3)(\text{PO}_4)_2\cdot 6\text{H}_2\text{O}\). See mixed crystals in Photograph No. 3.
Figure 3. Conversion of $\text{UO}_2 \text{HPO}_4 \cdot 4\text{H}_2\text{O}$ to $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ in 7.375M initial $\text{H}_3\text{PO}_4$ concentration
FIGURE 4. CONVERSION OF $\text{UO}_2\text{HPO}_4\cdot 4\text{H}_2\text{O}$ TO $\text{UO}_2(\text{H}_2\text{PO}_4)_2\cdot 3\text{H}_2\text{O}$ IN 8.5 M INITIAL $\text{H}_3\text{PO}_4$ CONCENTRATION.
CONCENTRATION OF UO$_2$ IN SOLUTION (gm-ion/LITER)

CONVERSION OF UO$_2$HPO$_4$·4H$_2$O

O UO$_2$(H$_2$PO$_4$)$_2$·3H$_2$O SOLUBILITY

FIGURE 5. SOLUBILITY OF UO$_2$(H$_2$PO$_4$)$_2$·3H$_2$O IN CONCENTRATED H$_3$PO$_4$ AND RATE OF CONVERSION OF UO$_2$HPO$_4$·4H$_2$O TO UO$_2$(H$_2$PO$_4$)$_2$·3H$_2$O
MIXTURE OF CRYSTALS OF $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ AND $\text{(UO}_2\text{)}_3\text{(PO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}$ AT TRANSITION POINT

MAGNIFICATION: 150 X

PHOTOGRAPHED BY R.S. CROUSE AND E. R. BOYD

METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
PHOTOGRAPH NO. 4

CRYSTALS OF $\text{UO}_2\left(\text{H}_2\text{PO}_4\right)_{2.3}\text{H}_2\text{O}$ FROM 6.1 M $\Sigma\text{PO}_4^{-3}$

MAGNIFICATION 125 X LARGE CRYSTALS IN FOCUS

PHOTOGRAPHED BY R.S. CROUSE AND E.R. BOYD

METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
PHOTOGRAPH NO. 5

CRYSTALS OF $\text{UO}_2\left(\text{H}_2\text{PO}_4\right)_2\cdot3\text{H}_2\text{O}$ FROM 6.1 M $\Sigma\text{PO}_4^{-3}$

MAGNIFICATION 125X, BACKGROUND CRYSTALS IN FOCUS

PHOTOGRAPHED BY R.S. CROUSE

METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
PHOTOGRAPH NO. 6

CRYSTALS OF \( UO_2(H_2PO_4)_2 \cdot 3H_2O \) FROM 6.67 M \( \Sigma PO_4^{-3} \)

MAGNIFICATION 125 X

PHOTOGRAPHED BY R.S. CROUSE AND E.R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
PHOTOGRAPH NO. 7.

CRYSTALS OF $\text{UO}_2\left(\text{H}_2\text{PO}_4\right)_{2/3}\text{H}_2\text{O}$ FROM $7.305 \text{ M } \Sigma \text{PO}_4^{3-}$

MAGNIFICATION 125 X

PHOTOGRAPHED BY R.S. CROUSE AND E.R. BOYD

METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
PHOTOGRAPH NO. 8.

CRYSTALS OF $\text{UO}_2\left(\text{H}_2\text{PO}_4\right)\cdot 3\text{H}_2\text{O}$ FROM 8.88 M $\Sigma \text{PO}_4^{-3}$

MAGNIFICATION 125X

PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD

METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
PHOTOGRAPH NO. 9

CRYSTALS OF $\text{UO}_2\left(\text{H}_2\text{PO}_4\right) \cdot 3\text{H}_2\text{O}$ FROM 10.4 M $\Sigma \text{PO}_4^{3-}$

MAGNIFICATION 125 X

PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD

METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY
REFERENCE PATTERN OF \((\text{UO}_2\text{)}_3\text{(PO}_4\text{)}_2\text{4H}_2\text{O})

TYPICAL SOLID PHASE IN 0.001 TO 0.014 M \(\text{H}_3\text{PO}_4\)

REFERENCE PATTERN OF \(\text{UO}_2\text{HPO}_4\cdot\text{4H}_2\text{O}\)

TYPICAL SOLID PHASE IN 0.014 TO 6.1 M \(\text{H}_3\text{PO}_4\)

REFERENCE PATTERN OF \(\text{UO}_2\text{(H}_2\text{PO}_4\text{)}_2\cdot\text{3H}_2\text{O}\)

TYPICAL SOLID PHASE IN 6.1 TO 14.6 M \(\text{H}_3\text{PO}_4\)

PHOTOGRAPH NO. 10
X-RAY DIFFRACTION PATTERNS

PATTERNS PREPARED BY H. W. DUNN, ISOTOPE ANALYSIS METHODS LABORATORY
OAK RIDGE NATIONAL LABORATORY
after attaining equilibrium.* The water analyses (see Table I) are not considered reliable in the case of \( \text{UO}_3(\text{H}_2\text{PO}_4)_2.3\text{H}_2\text{O} \). As noted previously, it is probable that some decomposition of the orthophosphate in this compound occurred, since percentages greater than 100% were obtained for the total analysis. More nearly constant values for water were obtained by calculations of differences assuming the values for uranium and phosphate to be correct.

III. RESULTS AND DISCUSSION

The solubility of uranium(VI) phosphate solids in phosphoric acid alone was measured in the range of 0.001 to 14.6M total phosphate at 25°C. Using \( \text{UO}_2\text{HPO}_4.4\text{H}_2\text{O} \) as the original solid added, it was found that a solid phase change occurred in both low and high phosphate concentrations. An extensive survey of the solid phases in equilibrium with the mother liquors was made, therefore, over the entire range of phosphate molarities.

The assembled data from the solubility measurements are shown in Table II. The calculated total phosphate concentrations for the saturated mother liquors were evaluated for dilute solutions (<0.5M) simply as the sum of the initial phosphoric acid concentration plus the phosphate derived from the dissolved salt.** In the more concentrated solutions, the method of calculation was altered to include the effect of the volume change which accompanied dissolution of the solid.

The data in Table I and II indicate the following solid phases to be in equilibrium with saturated solutions in phosphoric acid over the concentration ranges indicated:

\[ \left[ \Sigma \text{PO}_4^{3-} \right]_{\text{initial}} = \left[ \text{H}_3\text{PO}_4 \right]_{\text{initial}} + \left[ \Sigma \text{UO}_2^{++} \right]_{\text{final}} \]

and for \( (\text{UO}_2)_3(\text{PO}_4)_2.6\text{H}_2\text{O} \):

\[ \left[ \Sigma \text{PO}_4^{3-} \right]_{\text{final}} = \left[ \text{H}_3\text{PO}_4 \right]_{\text{initial}} + \frac{2}{3} \left[ \Sigma \text{UO}_2^{++} \right]_{\text{final}} \]

*The filtered solids were washed twice by slurrying in 500 ml of acetone, washed on the filter with 100 ml of carbon tetrachloride, and dried in a desiccator under continuous vacuum for 2 hours.

**For runs in which \( \text{UO}_2\text{HPO}_4.4\text{H}_2\text{O} \) was the stable solid phase.
### Table II

**The Solubilities of Uranium(VI) Orthophosphates in Phosphoric Acid Solutions**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Original MOLES/l</th>
<th>Solid Added</th>
<th>Analytical ( [\text{PO}_4^{3-}] )</th>
<th>Calculated ( [\text{PO}_4^{3-}] )</th>
<th>Analytical ( [\text{UO}_2^+ \cdot 3\text{H}_2\text{O}] )</th>
<th>SOLID IDENTIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-13</td>
<td>0.0100 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>0.000969</td>
<td>0.00100</td>
<td>0.0000109</td>
<td>Needles</td>
<td>Needles (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
</tr>
<tr>
<td>A-14</td>
<td>0.0100 UO(_2)PO(_4), (4\text{H}_2\text{O})</td>
<td>0.00242</td>
<td>0.00235</td>
<td>0.0000376</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-19</td>
<td>0.00100</td>
<td>0.00326</td>
<td>--</td>
<td>0.0000580</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-26</td>
<td>0.0006 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>0.00579</td>
<td>--</td>
<td>0.0000100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-29</td>
<td>0.00800</td>
<td>0.00789</td>
<td>0.00816</td>
<td>0.000156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-31</td>
<td>0.0130 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>0.01050</td>
<td>--</td>
<td>0.000252</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-33</td>
<td>0.0150 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>0.01348</td>
<td>0.0140</td>
<td>0.000345</td>
<td>Needles</td>
<td></td>
</tr>
<tr>
<td>A-34</td>
<td>0.0200 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>0.01797</td>
<td>--</td>
<td>0.000450</td>
<td>Needles</td>
<td></td>
</tr>
<tr>
<td>A-12</td>
<td>0.0483</td>
<td>0.0497</td>
<td>0.0497</td>
<td>0.001443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-10</td>
<td>0.0967</td>
<td>0.103</td>
<td>0.103</td>
<td>0.00330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-9</td>
<td>0.104</td>
<td>0.108</td>
<td>0.108</td>
<td>0.00407</td>
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<td></td>
</tr>
<tr>
<td>A-8</td>
<td>0.210</td>
<td>0.219</td>
<td>0.219</td>
<td>0.01035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-7</td>
<td>0.237</td>
<td>0.249</td>
<td>0.249</td>
<td>0.01237</td>
<td></td>
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</tr>
<tr>
<td>A-6</td>
<td>0.324</td>
<td>0.328</td>
<td>0.328</td>
<td>0.01860</td>
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<td></td>
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<tr>
<td>A-5</td>
<td>0.460</td>
<td>0.495</td>
<td>0.495</td>
<td>0.03523</td>
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<td>A-1</td>
<td>0.890</td>
<td>0.987</td>
<td>0.987</td>
<td>0.1099</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-2</td>
<td>1.105</td>
<td>1.459</td>
<td>1.459</td>
<td>0.2072</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-21</td>
<td>2.495 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>2.74</td>
<td>--</td>
<td>0.5054</td>
<td>Needles</td>
<td></td>
</tr>
<tr>
<td>A-38</td>
<td>2.495 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>2.93</td>
<td>2.990</td>
<td>0.0008</td>
<td>Needles</td>
<td></td>
</tr>
<tr>
<td>A-49</td>
<td>3.687</td>
<td>4.25</td>
<td>4.28</td>
<td>1.021</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-43</td>
<td>4.4</td>
<td>4.97</td>
<td>--</td>
<td>1.332</td>
<td></td>
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<tr>
<td>A-7</td>
<td>5.526</td>
<td>6.095</td>
<td>6.095</td>
<td>1.651</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-20</td>
<td>5.526 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>6.10</td>
<td>--</td>
<td>1.583</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-49</td>
<td>6.5</td>
<td>6.10</td>
<td>--</td>
<td>1.738</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-40</td>
<td>6.5</td>
<td>6.14</td>
<td>--</td>
<td>1.681</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-39**</td>
<td>6.9</td>
<td>6.30</td>
<td>6.36</td>
<td>1.768</td>
<td>Tetragonal</td>
<td></td>
</tr>
<tr>
<td>A-48</td>
<td>6.5</td>
<td>6.59</td>
<td>--</td>
<td>1.267</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-44</td>
<td>7.375</td>
<td>6.67</td>
<td>--</td>
<td>1.298</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-38-3</td>
<td>7.375</td>
<td>6.78</td>
<td>--</td>
<td>1.271</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-45</td>
<td>8.5</td>
<td>7.20</td>
<td>--</td>
<td>1.018</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
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</tr>
<tr>
<td>A-38**</td>
<td>8.5</td>
<td>7.31</td>
<td>--</td>
<td>0.959</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
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<tr>
<td>A-38-2</td>
<td>7.375</td>
<td>7.47</td>
<td>--</td>
<td>1.902</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-38-1</td>
<td>7.375</td>
<td>7.73</td>
<td>7.46</td>
<td>1.882</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-53</td>
<td>7.375 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>7.96</td>
<td>7.99</td>
<td>0.7525</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-41</td>
<td>10.4</td>
<td>8.88</td>
<td>--</td>
<td>0.5657</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-42</td>
<td>11.8</td>
<td>10.40</td>
<td>--</td>
<td>0.4347</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-52</td>
<td>13.3 (UO(_2))(_3), (3\text{H}_2\text{O})</td>
<td>12.91</td>
<td>--</td>
<td>0.3725</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-51-2</td>
<td>14.78</td>
<td>14.48</td>
<td>14.58</td>
<td>0.3019</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
<tr>
<td>A-51-1</td>
<td>14.78</td>
<td>14.60</td>
<td>14.62</td>
<td>0.3165</td>
<td>Monoclinic Rods (UO(_2))(_3), (3\text{H}_2\text{O}) &gt;90%</td>
<td></td>
</tr>
</tbody>
</table>

**Microscopic Appearance**: Needles, Mixtures, and others.

**X-ray Diffraction Analysis**: Needles, Tetragonal, and Monoclinic.

---

*Transition point where a mixture of crystals were observed.
**Solution was supersaturated with respect to UO\(_2\)\(_3\)\(\text{H}_2\text{O}\).
***Solution was saturated with UO\(_2\)\(_3\)\(\text{H}_2\text{O}\), then seeded with UO\(_2\)\(_3\)\(\text{H}_2\text{O}\).
(UO₂)₃(PO₄)₂·6H₂O, total phosphate <0.014M
UO₂HPO₄·4H₂O, " " >0.014, <6.1M
UO₂(H₂PO₄)₂·3H₂O, " " >6.1M

The degree of hydration of the normal uranyl phosphate in equilibrium with the dilute solutions is somewhat in doubt. The chemical analyses (Table I) are best fitted by formulation as the hexahydrate,* although the salt added was the tetrahydrate. A change in hydration on contact with the solution at 25°C is not surprising, since the tetrahydrate was prepared at 100°C. Photomicrographs of the higher hydrate, and also its X-ray powder diffraction pattern, appear similar to those of the tetrahydrate (see Photographs 2, 3, and 10).

The analyses listed in Table I for UO₂HPO₄·4H₂O and UO₂(H₂PO₄)₂·3H₂O samples separated from saturated mother liquors in general confirm the composition of the stable solid phases. The somewhat high uranium – low phosphate analyses obtained for the UO₂(H₂PO₄)₂·3H₂O samples suggest that these solids are contaminated with UO₂HPO₄·4H₂O, the initial solid phase in the runs listed here (cf. Table II).

If such contamination is involved, it has not seriously affected the resulting solubility values for these runs since they generally conform to a smooth curve which includes run Nos. A-51-1, 51-2, 52, and 53, for which the initial solid phase is the stable UO₂(H₂PO₄)₂·3H₂O. Other runs (A-14, 19, 20, 21, and 24) in which solid phase conversion has occurred also conform to the solubility curve, confirming that in general equilibrium values have been reached in the various measurements. In the case of run No. A-33, only partial conversion of the solid occurred (cf. Photograph No. 3), since a transition point had been reached, where two solid phases were in equilibrium with the same mother liquor.

A log-log plot of the solubility data is presented in Figure 6. Calculated total phosphate values are plotted where the original phosphate concentrations were known accurately since these were probably more nearly correct than those obtained by analyses of the mother liquors.

The solubility behavior in high phosphoric acid concentrations is expressed in the form of a three-component phase diagram in Figure 7. Included in the figure are several slurry analyses for the two stable solid phases UO₂HPO₄·4H₂O and UO₂(H₂PO₄)₂·3H₂O. In this method of plotting the data (Schreinemaker's wet residue method), the composition of the mother liquor, that of the slurry and that of the solid phase should be on the same straight line. Within the limit of experimental error, the data

*Since these samples were washed with acetone before analyses, the normal uranyl phosphate in equilibrium with the solution may have been a still higher hydrate.
Figure 6. Solubility of Uranium (VI) Phosphates in Phosphoric Acid Solutions
FIGURE 7. A PORTION OF THE ISOTHERMAL PHASE DIAGRAM FOR THE SYSTEM UO$_2$-H$_3$PO$_4$-H$_2$O AT 25°C: O - SATURATED SOLUTIONS; © - SLURRIES
are consistent with this requirement, indicating that the proposed solid phases are the correct ones. The range of stability of the normal uranyl phosphate is confined to solutions of too low concentrations to be shown on the diagram. Accordingly, the wet residue method cannot be applied here to establish the state of hydration of the equilibrium solid.

IV. ACKNOWLEDGEMENTS

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