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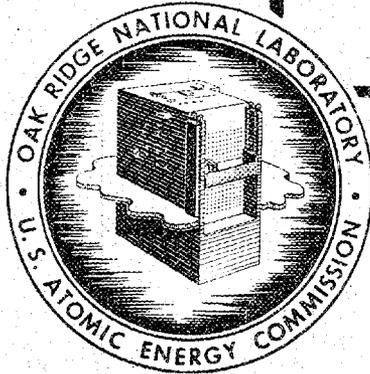
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THE CHEMISTRY OF URANIUM(VI) ORTHOPHOSPHATE
SOLUTIONS: PART II, THE SOLUBILITY
OF URANIUM(VI) ORTHOPHOSPHATES IN
PHOSPHORIC ACID SOLUTIONS

J. M. Schreyer
C. F. Baes, Jr.

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IN PHOSPHORIC ACID SOLUTIONS

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June 30, 1953

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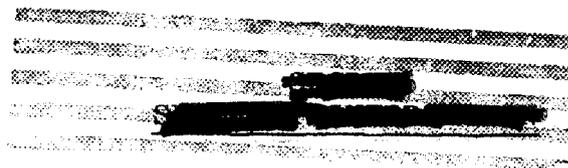
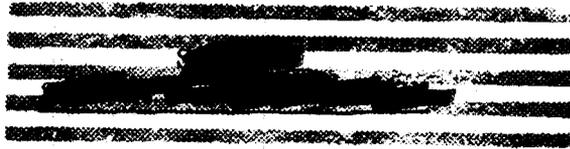


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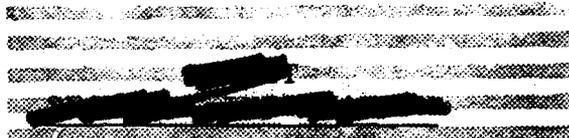
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ABSTRACT

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.



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Zachariassen⁽⁴⁾ examined $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ 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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. They reported that both these compounds are tetragonal, and $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ was said to crystallize as tabular plates, usually four sided but occasionally as truncated squares. The $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was said to crystallize in needle-like crystals. They gave the density value of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ as 3.399 and 3.213, respectively. Werther⁽⁶⁾ reported the preparation of crystals of $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ by heating small amounts of H_3PO_4 with UO_3 to boiling and allowing to stand over H_2SO_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°C. The concentration of the aqueous phosphoric acid was varied from 0.001 to 15M H_3PO_4 . Through this range, the solubility of the uranium(VI) orthophosphates was found to increase with increasing phosphoric acid concentration from approximately 1×10^{-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:

$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$,	total phosphate	<0.014M
$\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$,	" "	>0.014M, <6.1M
$\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$,	" "	>6.1M

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 Schreiner'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 ($E_{1/2} = \text{ca. } -0.08 \text{ v. vs. S.C.E.}$), 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 1×10^{-5} molar, though normal accuracy (ca. 5% error) was limited to concentrations above about 5×10^{-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 H₂O 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 300°C for one hour, in an atmosphere of helium, in a closed ignition tube connected to a weighed absorption bulb containing anhydrous magnesium perchlorate.

*With $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, decomposition of the orthophosphate to pyro- or metaphosphate 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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$

Two samples of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (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 liter of approximately 1M uranium(VI) nitrate or perchlorate solution. The solution was seeded with a few crystals of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ 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 HClO_4 solution for 12 hours, then filtered and washed with acetone. The dry sample was placed in a vacuum desiccator over a saturated solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ (V.P. = 9.12 mm at 20°C) for 12 hours.

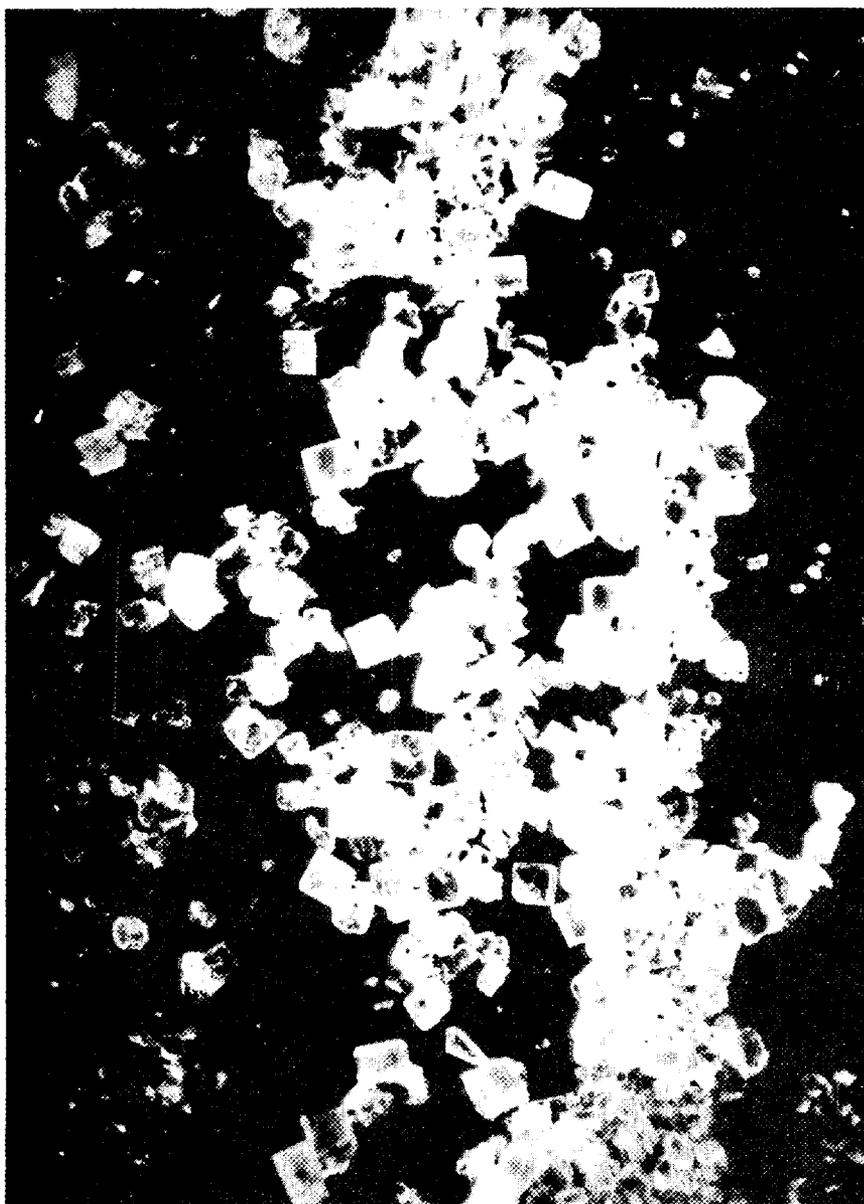
Under the microscope, tetragonal crystals characteristic of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ were observed (see Photograph No. 1). X-ray diffraction analysis qualitatively identified the solid as $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$. Chemical analysis gave for the first sample 61.6% UO_2^{++} , 21.6% PO_4^{-3} , and by difference 16.6% H_2O , while the second sample gave 61.9% UO_2^{++} , 21.6% PO_4^{-3} , and by difference 16.3% H_2O . This corresponds to the formula $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, for which the theoretical percentages are 61.63% UO_2^{++} , 21.68% PO_4^{-3} and 16.45% H_2O .

If the acetone-dried sample prepared by the above method is heated in an oven at 110°C, the $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ is converted to $\text{UO}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$. A typical analysis of a sample dried in this manner gave 67.7% UO_2^{++} , 23.1% PO_4^{-3} , and by difference 9.0% H_2O , while the theoretical percentages for $\text{UO}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ are 67.16% UO_2^{++} , 23.6% PO_4^{-3} and 8.96% H_2O .

2. Preparation of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

A 100 g sample of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was prepared according to the directions of Ryon and Kuhn(11) by digesting $\text{UO}_2\text{NH}_4\text{PO}_4 \cdot 3\text{H}_2\text{O}$ in 0.8M HNO_3 at 100°C. The solid was then washed with hot water and acetone and dried in air. Conversion of $\text{UO}_2\text{NH}_4\text{PO}_4 \cdot 3\text{H}_2\text{O}$ to $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was easily observed by the change in physical appearance of the solid phase.

Under the microscope needle-like crystals were observed characteristic of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, (see Photograph No. 2). X-ray diffraction analysis qualitatively identified the solid as $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. 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 $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

MAGNIFICATION: 150X

PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY

gave 75.3% UO_2^{++} , 18.0% PO_4^{-3} , and by difference 6.7% H_2O . This corresponds to a formula of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, for which the theoretical percentages are 75.5% UO_2^{++} , 17.72% PO_4^{-3} and 6.72% H_2O .

3. Preparation of $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$

A sample (approximately 10 g) of $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ was prepared by the addition of approximately 30 g $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ to 100 ml 85% H_3PO_4 . 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 CaCl_2 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% UO_2^{++} , 35.7% PO_4^{-3} , and by difference 10.9% H_2O , while the formula $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ gives for the theoretical percentages 52.12% UO_2^{++} , 36.66% PO_4^{-3} and 10.4% H_2O .

If $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ is heated for 7 hours at 110°C, it is converted to $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. 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 $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$.

One of the yellow crystal platelets of a sample of $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ 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 K_α radiation, which showed the crystals to be monoclinic: $a = 10.83\text{\AA}$, $b = 13.92\text{\AA}$, $c = 7.48\text{\AA}$, and $\beta = 105^\circ 45'$.

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 $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ or 3.28 for the formula $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. The measured density is 3.16, substantiating the trihydrate formula.

From the photographs, it was observed that reflections of the type $0k0$ 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 $C_{2h}^5 - P^2_1/C$. 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, $x \bar{y} z$; $\bar{x} \bar{y} \bar{z}$; $\bar{x}, 1/2 + y, 1/2 - z$; $x, 1/2 - y, 1/2 + z$, 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 $24.9 \pm 0.1^\circ\text{C}$. 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

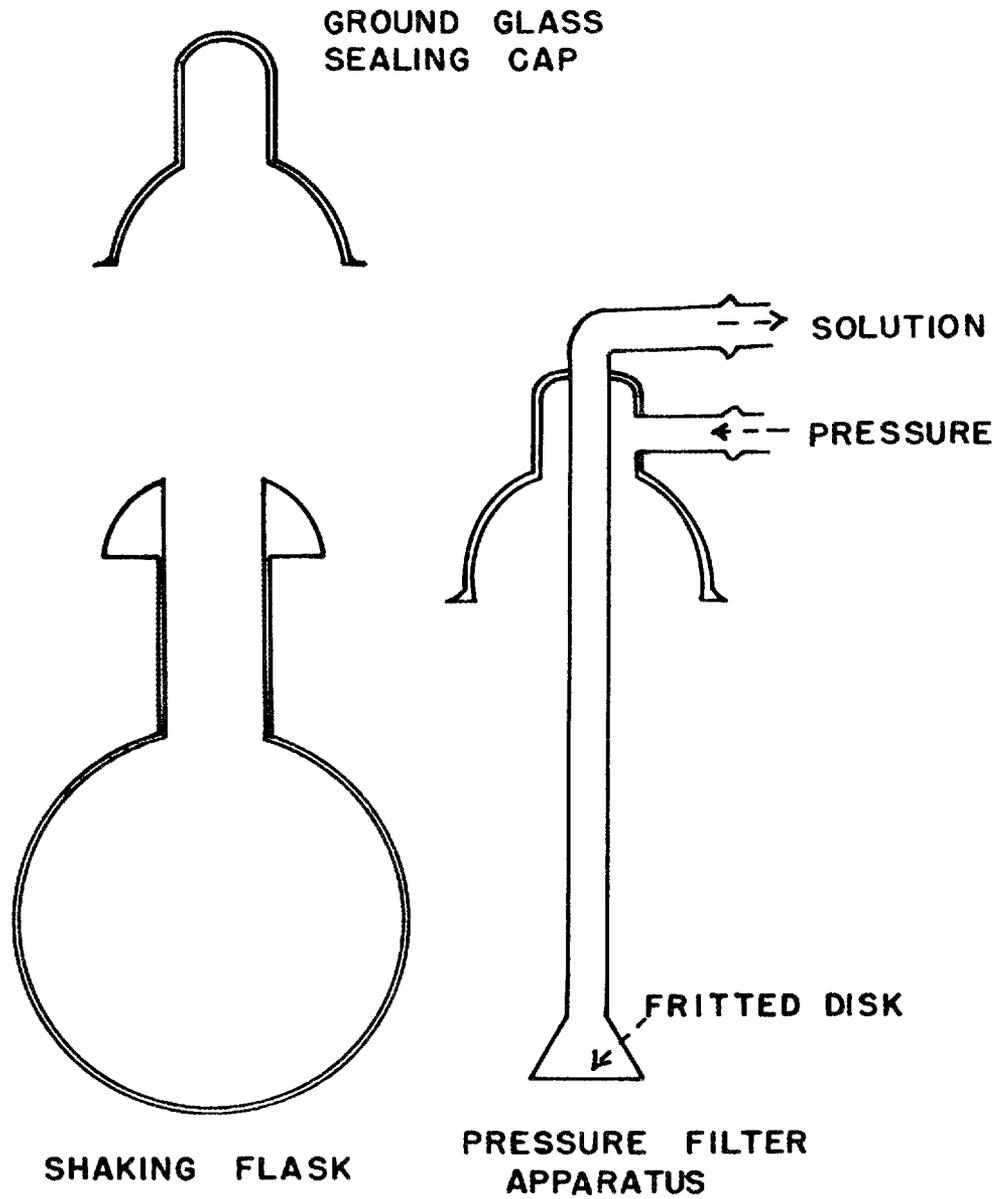


FIGURE 1. SOLUBILITY APPARATUS

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 $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was used as the added solid phase, the samples in the region of stability of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ were shaken from 7 to 11 days in order to attain equilibrium. In this region, the time required to convert $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ to the stable $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ was very long, making the use of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ as the added solid phase impractical (see Figure 2). In the region of stability of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ using $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ as the added solid phase, equilibrium condition was attained in 2 to 12 days. Three determinations using $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ as the added solid phase were run at 0.02, 2.495 and 5.527 initial $[\text{H}_3\text{PO}_4]$ and complete conversions to $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ occurred. Equilibration in the region of stability of $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ using $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ 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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ was used as the added solid phase in the region of stability of $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, 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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (see Table I). Although Figures 3 and 4 indicate that 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 7.3 to 8.5M 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 $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, 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

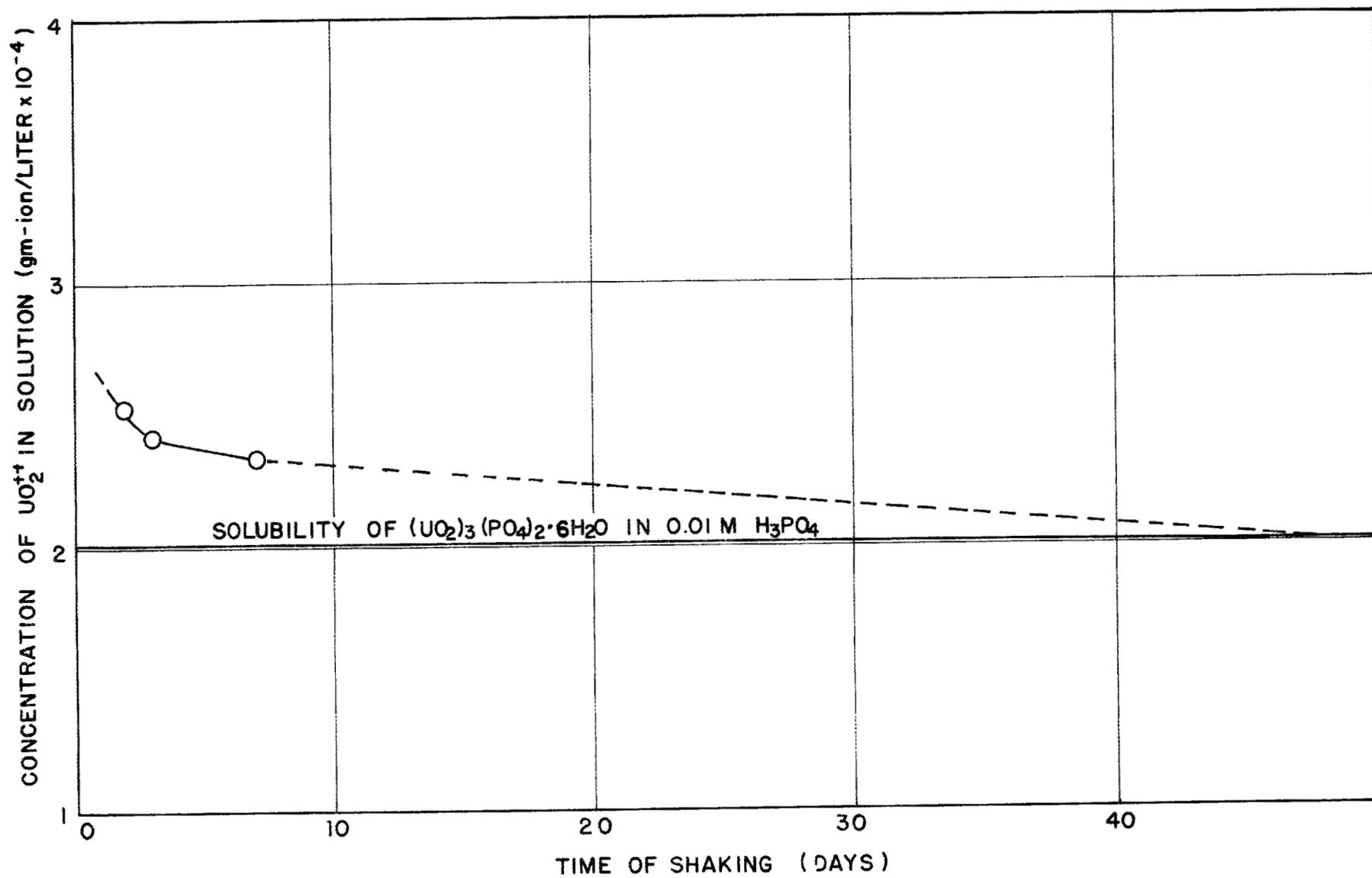


FIGURE 2. CONVERSION OF $UO_2HPO_4 \cdot 4H_2O$ TO $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ IN 0.01M H_3PO_4

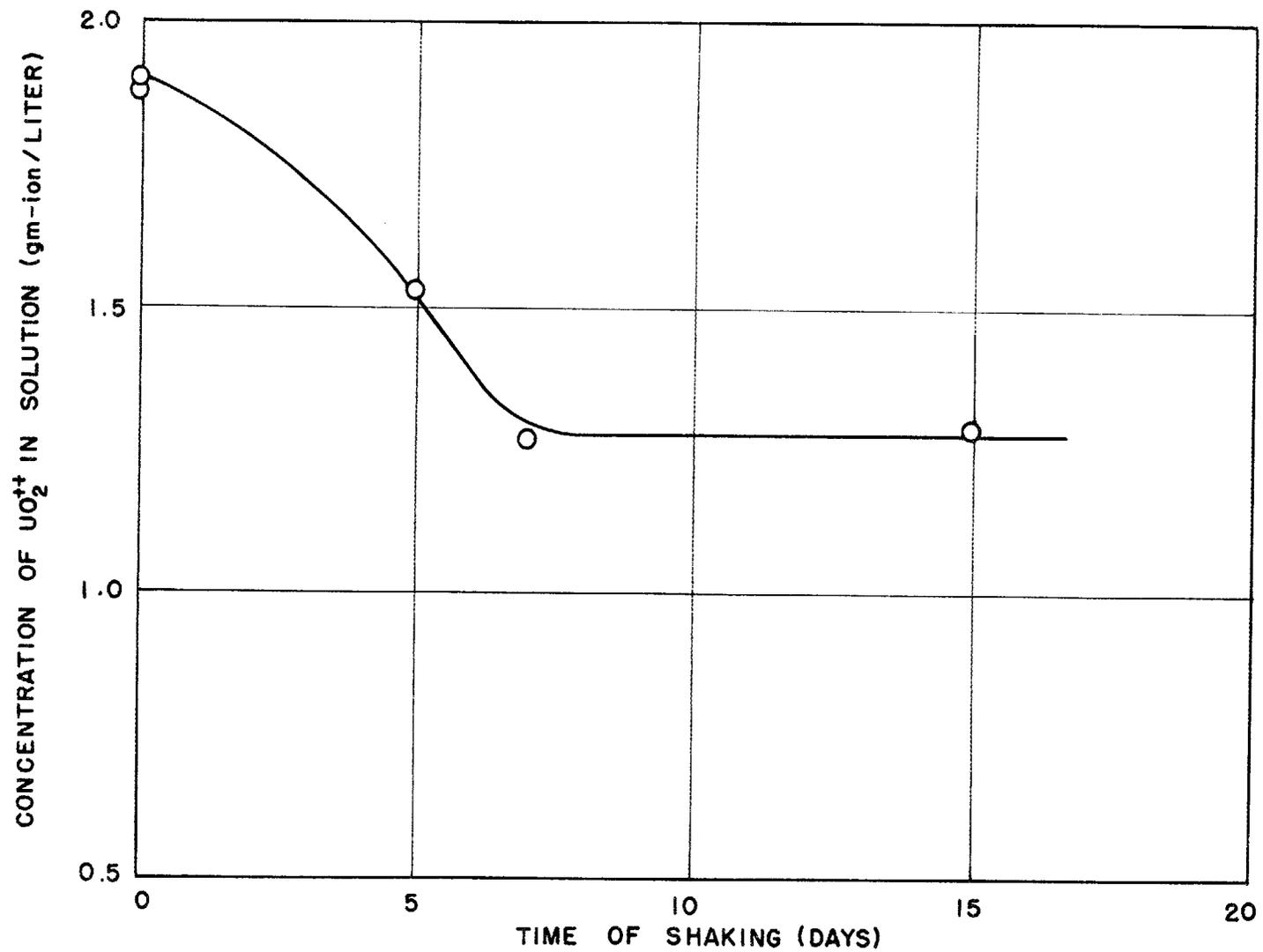
Table 1
CHEMICAL ANALYSES OF URANIUM(VI) PHOSPHATES
FROM PHOSPHORIC ACID SOLUTIONS

Theoretical Compositions:

$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$: 73.10% UO_2^{++} , 17.10% PO_4^{-3} , 9.75% H_2O
 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$: 61.6 % UO_2^{++} , 21.68% PO_4^{-3} , 16.45% H_2O
 $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$: 52.13% UO_2^{++} , 36.6 % PO_4^{-3} , 10.42% H_2O

Sample Number	Total Phosphate in Mother Liquor moles/l	Analysis of Solid Phases					
		% UO_2^{++}	% PO_4^{-3}	Assumed No. of Hydrogens	Theoretical % Hydrogen	% Water by Difference	% Water by Analysis
A-30	0.00100	73.17	17.4	0	0	9.43	--
A-26	0.00625	70.79	18.5	0	0	10.71	9.48
A-29	0.00816	71.24	18.3	0	0	10.46	9.41
A-28	0.0101	71.81	18.6	0	0	9.59	8.38
*A-33	0.0140	65.90	19.8	--	--	--	--
A-27	0.0179	61.82	22.0	1	0.23	15.95	16.5
A-10	0.103	61.70	21.5	1	0.23	16.57	--
A-25	0.108	62.00	21.7	1	0.23	16.07	16.5
A-21	2.74	61.30	21.6	1	0.23	16.87	--
A-3	2.93	61.70	21.6	1	0.23	16.47	--
A-7	6.09	61.90	21.6	1	0.23	16.27	--
A-20	6.10	61.80	21.0	1	0.23	16.99	--
A-40	6.14	54.30	34.6	4	0.78	10.32	14.6
A-44	6.67	55.10	33.8	4	0.78	10.32	10.1
A-38-3	6.78	53.80	35.9	4	0.78	9.52	13.2
A-45	7.20	52.18	36.5	4	0.78	10.54	7.6
A-36	7.31	53.10	36.1	4	0.78	10.02	15.1
A-41	8.88	51.80	37.0	4	0.78	10.42	16.7
A-42	10.40	55.6	34.5	4	0.78	9.12	14.6

*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.



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FIGURE 3. CONVERSION OF $UO_2HPO_4 \cdot 4H_2O$ TO $UO_2(H_2PO_4)_2 \cdot 3H_2O$ IN 7.375M INITIAL H_3PO_4 CONCENTRATION

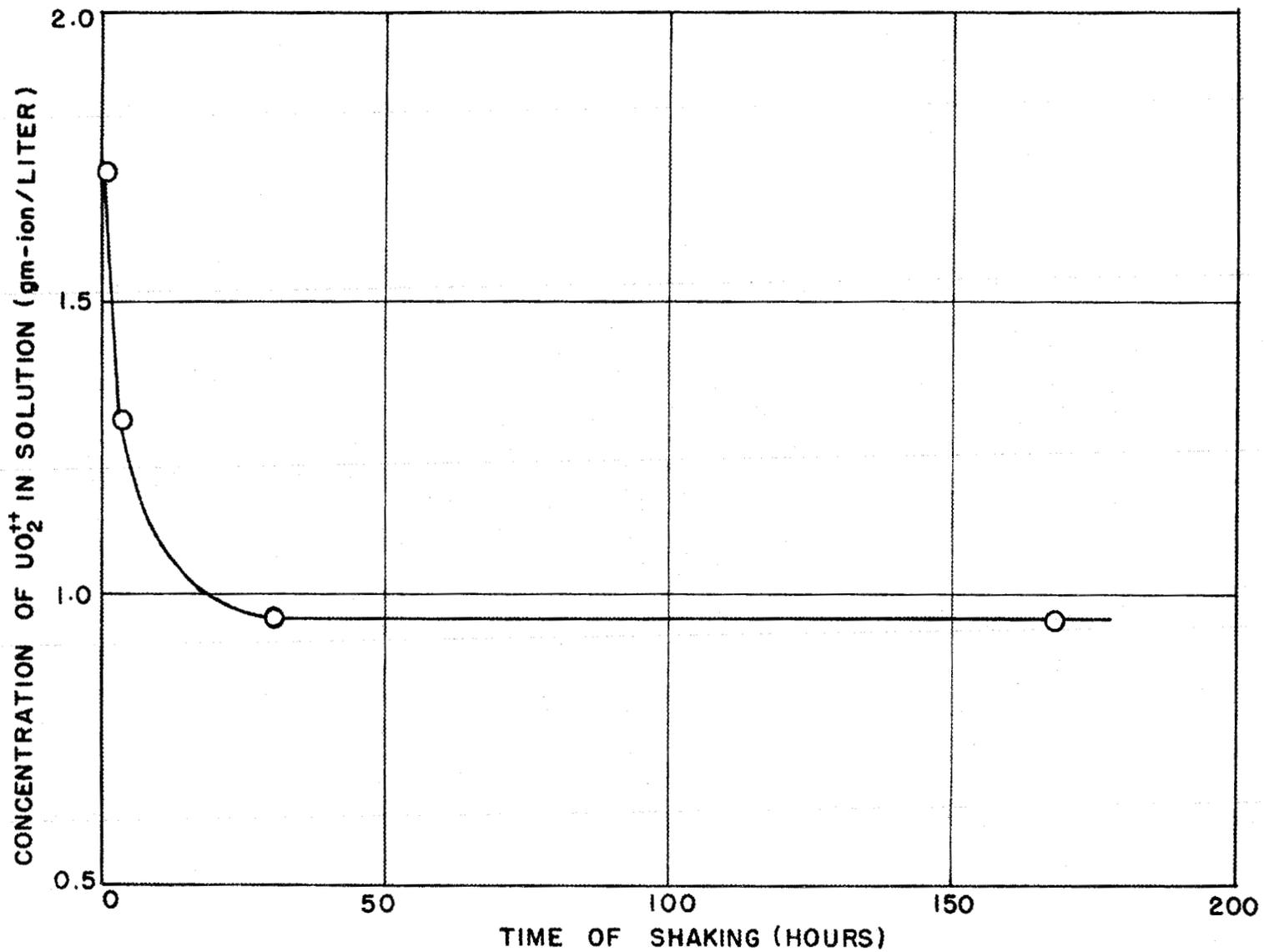


FIGURE 4. CONVERSION OF $UO_2HPO_4 \cdot 4H_2O$ TO $UO_2(H_2PO_4)_2 \cdot 3H_2O$ IN 8.5M INITIAL H_3PO_4 CONCENTRATION

DWG. 20231

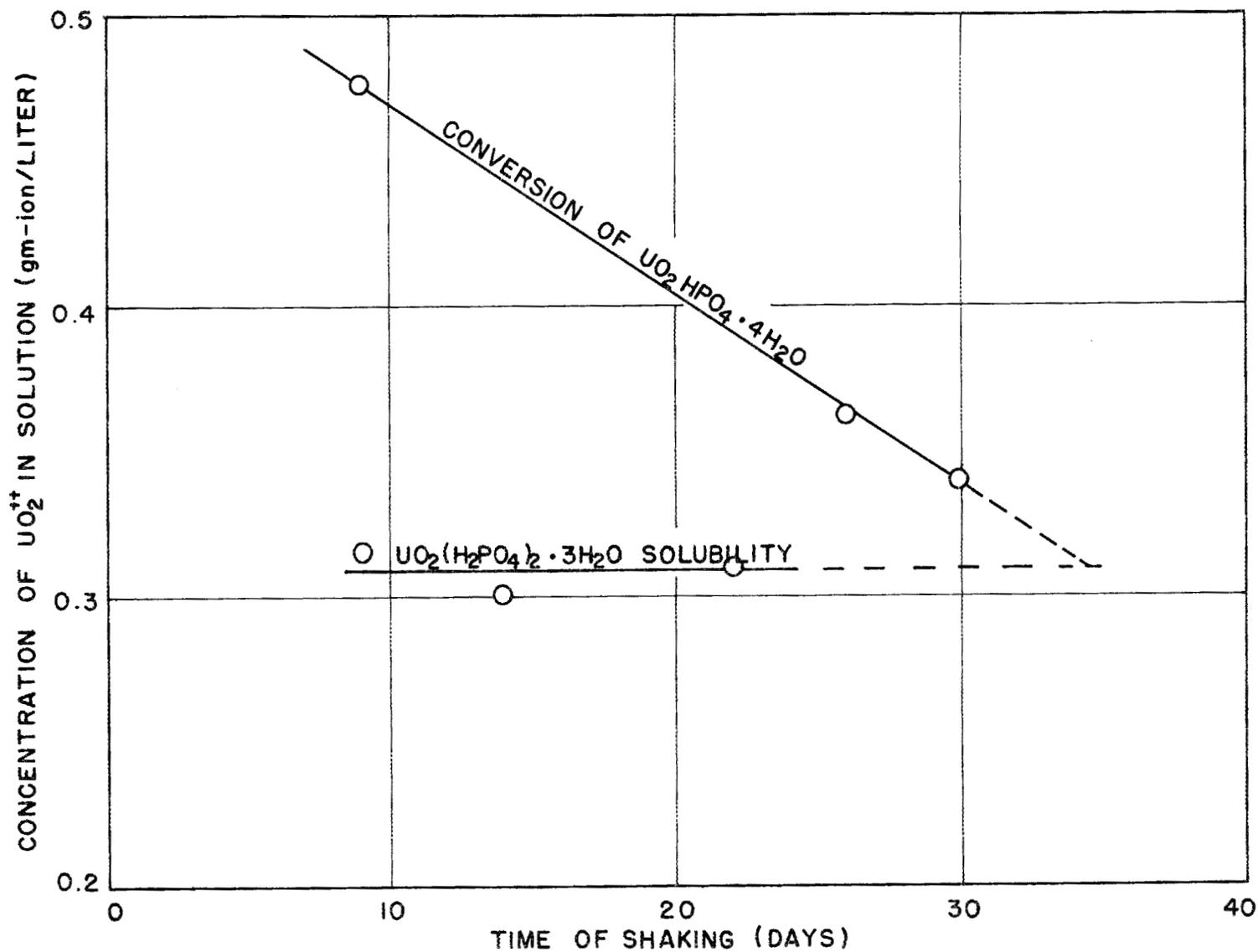
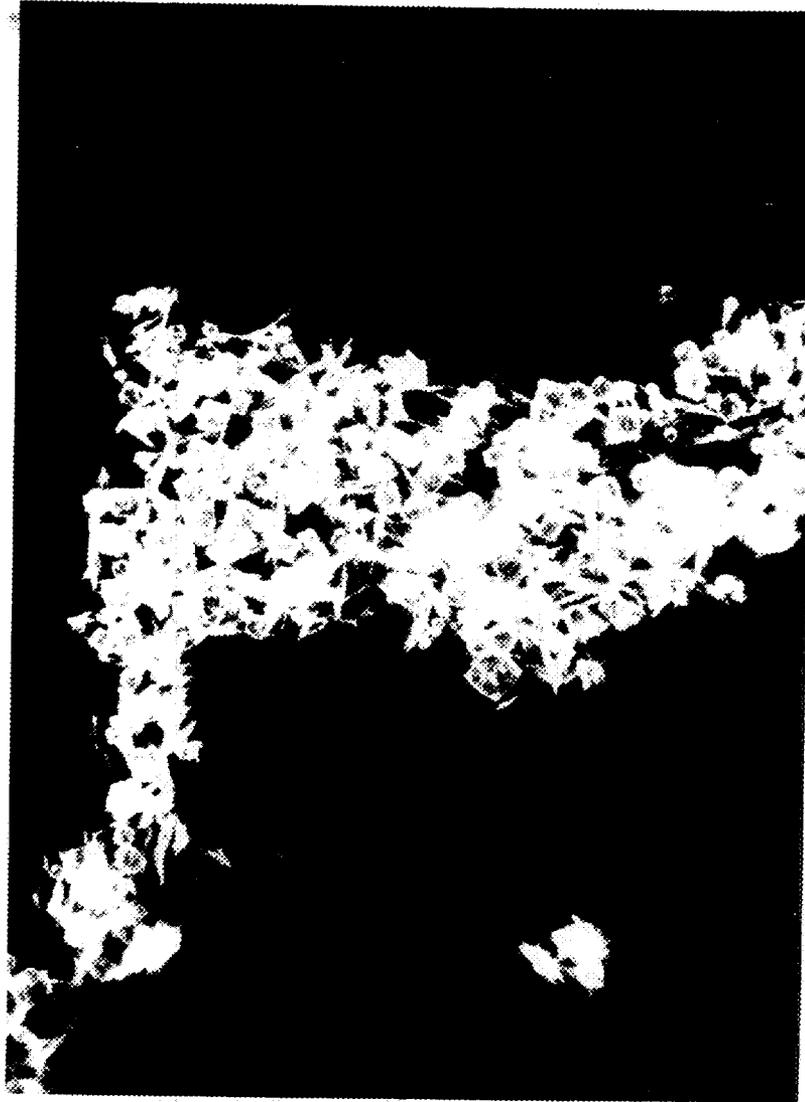


FIGURE 5. SOLUBILITY OF $UO_2(H_2PO_4)_2 \cdot 3H_2O$ IN CONCENTRATED H_3PO_4 AND RATE OF CONVERSION OF $UO_2HPO_4 \cdot 4H_2O$ TO $UO_2(H_2PO_4)_2 \cdot 3H_2O$



PHOTOGRAPH NO. 3

MIXTURE OF CRYSTALS OF $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ AND
 $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ AT TRANSITION POINT

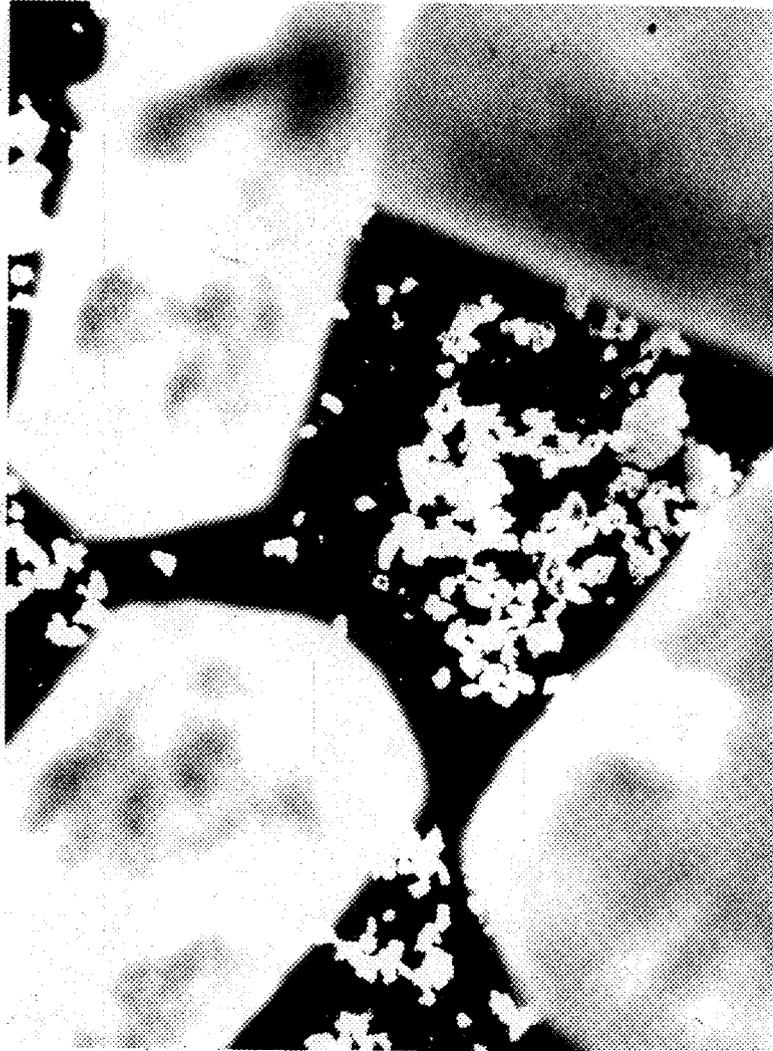
MAGNIFICATION: 150 X

PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY



PHOTOGRAPH NO. 4
CRYSTALS OF $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ FROM $6.1 \text{ M } \Sigma \text{PO}_4^{-3}$
MAGNIFICATION 125 X LARGE CRYSTALS IN FOCUS

PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY

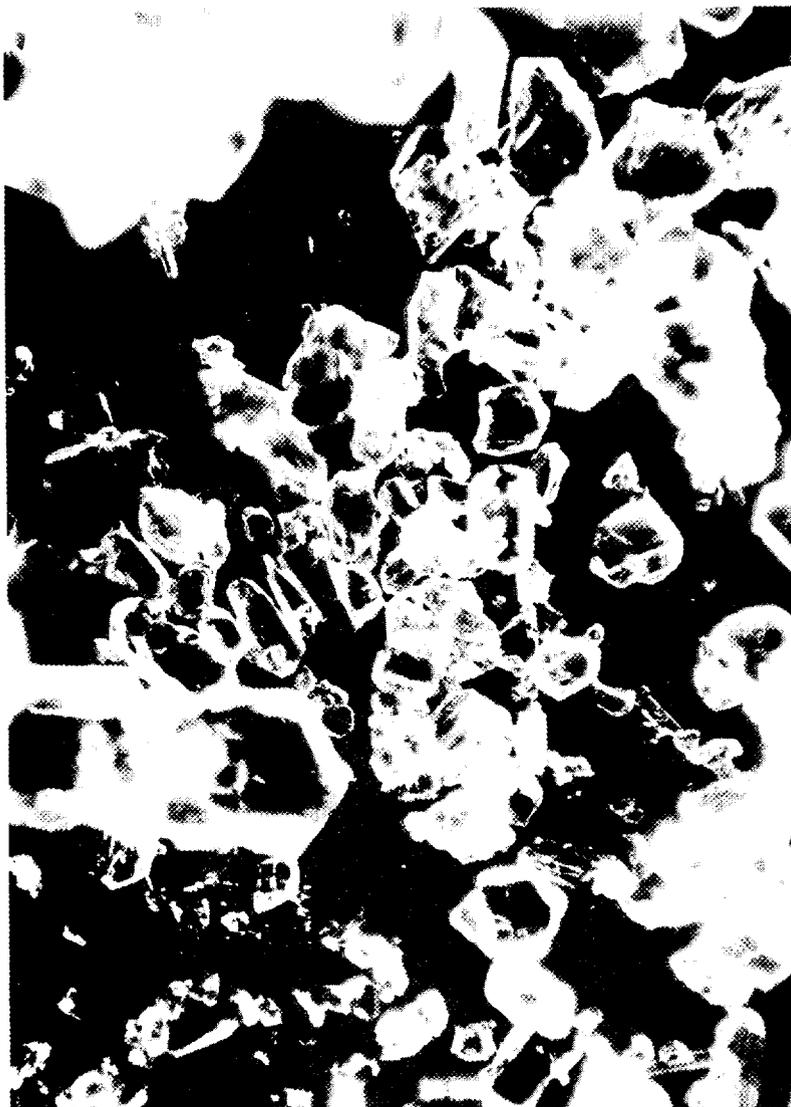


PHOTOGRAPH NO. 5

CRYSTALS OF $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ FROM 6.1 M ΣPO_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

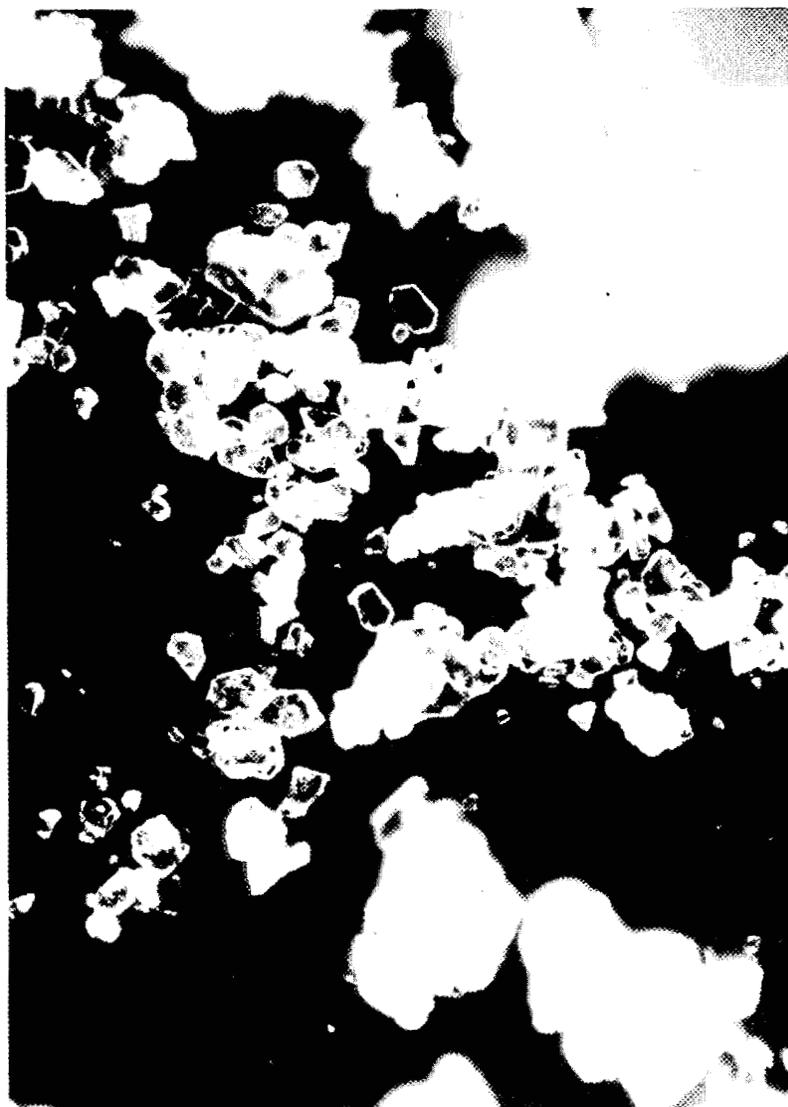


PHOTOGRAPH NO. 7.

CRYSTALS OF $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ FROM 7.305 M ΣPO_4^{-3}

MAGNIFICATION 125 X

PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY

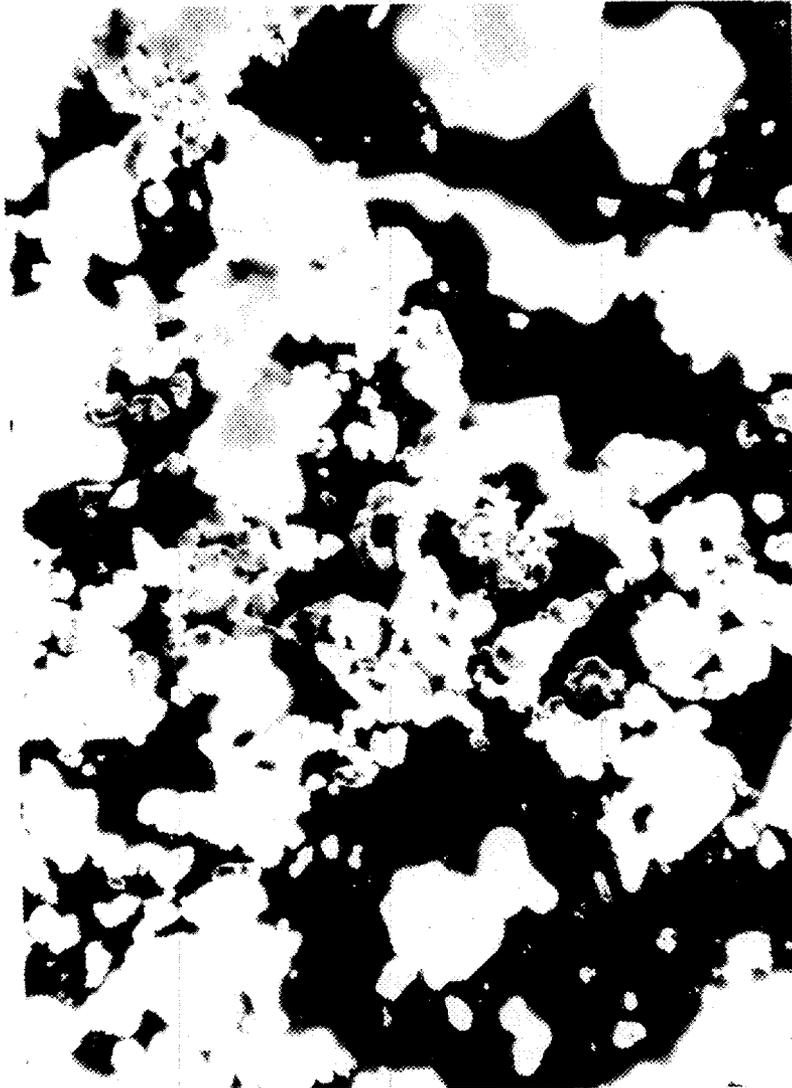


PHOTOGRAPH NO. 8.

CRYSTALS OF $\text{UO}_2(\text{H}_2\text{PO}_4)_{4/2} \cdot 3\text{H}_2\text{O}$ FROM 8.88 M ΣPO_4^{-3}

MAGNIFICATION 125 X

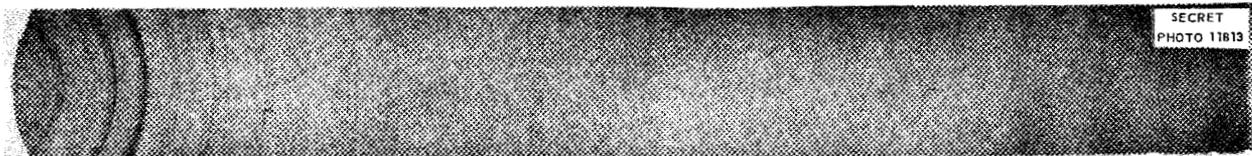
PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD
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PHOTOGRAPH NO. 9
CRYSTALS OF $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ FROM 10.4 M ΣPO_4^{-3}
MAGNIFICATION 125 X

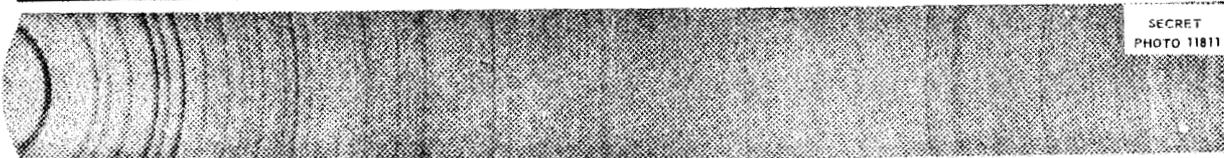
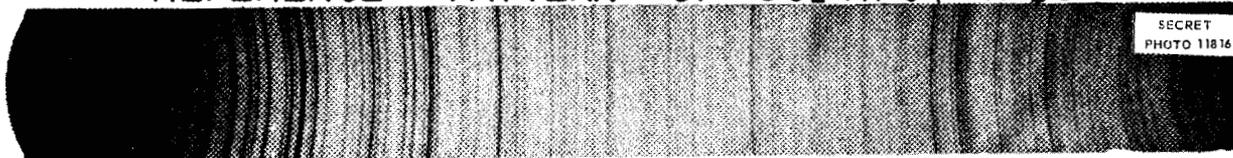
PHOTOGRAPHED BY R. S. CROUSE AND E. R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY

REFERENCE PATTERN OF $(UO_2)_3(PO_4)_2 \cdot 4H_2O$



TYPICAL SOLID PHASE IN 0.001 TO 0.014 M H_3PO_4

REFERENCE PATTERN OF $UO_2 HPO_4 \cdot 4H_2O$



TYPICAL SOLID PHASE IN 0.014 TO 6.1 M H_3PO_4

REFERENCE PATTERN OF $UO_2 (H_2PO_4)_2 \cdot 3H_2O$



TYPICAL SOLID PHASE IN 6.1 TO 14.6 M H_3PO_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 $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. 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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ 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:

*The filtered solids were washed twice by slurring 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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ was the stable solid phase:

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

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

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

Table II

THE SOLUBILITIES OF URANIUM(VI) ORTHOPHOSPHATES IN
PHOSPHORIC ACID SOLUTIONS

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Sample Number	Original $[H_2PO_4]$ moles/l	Solid Added	COMPOSITION OF MOTHER LIQUOR IN MOLES/l			SOLID IDENTIFICATION	
			Analytical $\sum PO_4^{-3}$	Calculated $\sum PO_4^{-3}$	Analytical $\sum UO_2^{++}$	Microscopic Appearance	X-ray Diffraction Analysis
A-30	0.00100	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	0.000969	0.00100	0.0000109	Needles	-----
A-24	0.00200	$UO_2HPO_4 \cdot 4H_2O$	0.00242	0.00235	0.0000376	"	-----
A-19	0.00100	"	0.00326	- - -	0.0000580	- - - -	-----
A-26	ca. 0.006	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	0.00579	- - -	0.000108	Needles	$(UO_2)_3(PO_4)_2 \cdot 4H_2O >90\%$
A-29	0.00800	"	0.00789	0.00816	0.000156	"	-----
A-28	0.00995	"	0.00979	0.0101	0.000206	"	-----
A-14	ca. 0.01	$UO_2HPO_4 \cdot 4H_2O$	0.0105	- - -	0.000252	- - - -	-----
A-31	0.0130	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	- - - -	0.0132	0.000282	Needles	-----
A-33*	0.0150	"	0.0134	0.0140	0.000345	Mixture	-----
A-27	ca. 0.02	"	0.0179	- - -	0.000450	Tetragonal	$UO_2HPO_4 \cdot 4H_2O >90\%$
A-13	0.0200	$UO_2HPO_4 \cdot 4H_2O$	- - - -	0.0205	0.000528	"	-----
A-12	0.0483	"	- - - -	0.0497	0.001443	"	-----
A-10	0.0967	"	- - - -	0.103	0.00330	"	$UO_2HPO_4 \cdot 4H_2O >95\%$
A-25	0.104	"	0.108	0.108	0.00407	"	-----
A-9	0.210	"	0.219	0.220	0.01035	"	-----
A-8	0.237	"	- - - -	0.249	0.01237	"	-----
A-6	0.310	"	0.324	0.328	0.01860	"	-----
A-5	0.460	"	0.498	0.495	0.03523	"	-----
A-1	0.890	"	0.980	0.987	0.1099	"	-----
A-4	1.305	"	1.459	1.477	0.2072	"	-----
A-2	1.705	"	1.948	1.970	0.3389	"	-----
A-21	2.495	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	2.74	- - -	0.5054	"	$UO_2HPO_4 \cdot 4H_2O >90\%$
A-3	2.495	$UO_2HPO_4 \cdot 4H_2O$	2.93	2.900	0.6008	"	-----
A-50	3.687	"	4.25	4.28	1.021	"	-----
A-43	ca. 4.4	"	4.97	- - -	1.332	"	-----
A-7	5.526	"	6.09	6.035	1.691	"	-----
A-20	5.526	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	6.10	- - -	1.583	"	-----
A-49	ca. 6.5	$UO_2HPO_4 \cdot 4H_2O$	6.10	- - -	1.738	Monoclinic Rods	$UO_2(H_2PO_4)_2 \cdot 3H_2O >90\%$
A-40	ca. 6.5	"	6.14	- - -	1.683	"	-----
A-39**	ca. 5.912	"	6.30	6.36	1.786	Tetragonal	$UO_2HPO_4 \cdot 4H_2O >90\%$
A-48	ca. 6.5	"	6.59	- - -	1.267	Monoclinic Rods	-----
A-44	7.375	"	6.67	- - -	1.298	"	-----
A-38-3	7.375	"	6.78	- - -	1.271	"	$UO_2(H_2PO_4)_2 \cdot 3H_2O >90\%$
A-45	ca. 8.5	"	7.20	- - -	1.018	"	-----
A-36***	ca. 8.5	"	7.31	- - -	0.959	"	$UO_2(H_2PO_4)_2 \cdot 3H_2O >90\%$
A-38-2	7.375	"	7.47	- - -	1.902	- - - -	-----
A-38-1	7.375	"	7.73	7.46	1.882	- - - -	-----
A-53	7.375	$UO_2(H_2PO_4)_2 \cdot 3H_2O$	7.96	7.99	0.7525	- - - -	-----
A-41	ca. 10.4	$UO_2HPO_4 \cdot 4H_2O$	8.88	- - -	0.5657	- - - -	-----
A-42	ca. 11.8	"	10.40	- - -	0.4347	- - - -	-----
A-52	ca. 13.3	$UO_2(H_2PO_4)_2 \cdot 3H_2O$	12.91	- - -	0.3725	- - - -	-----
A-51-2	14.78	"	14.48	14.58	0.3019	- - - -	-----
A-51-1	14.78	"	14.60	14.62	0.3165	- - - -	-----

*Transition point where a mixture of crystals was observed.

Solution was supersaturated with respect to $UO_2(H_2PO_4)_2 \cdot 3H_2O$.*Solution was saturated with $UO_2HPO_4 \cdot 4H_2O$, then seeded with $UO_2(H_2PO_4)_2 \cdot 3H_2O$.

$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$,	total phosphate	<0.014M
$\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$,	" "	>0.014, <6.1M
$\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$,	" "	>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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ 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 $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ samples suggest that these solids are contaminated with $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, 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 $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. 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 $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. 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.

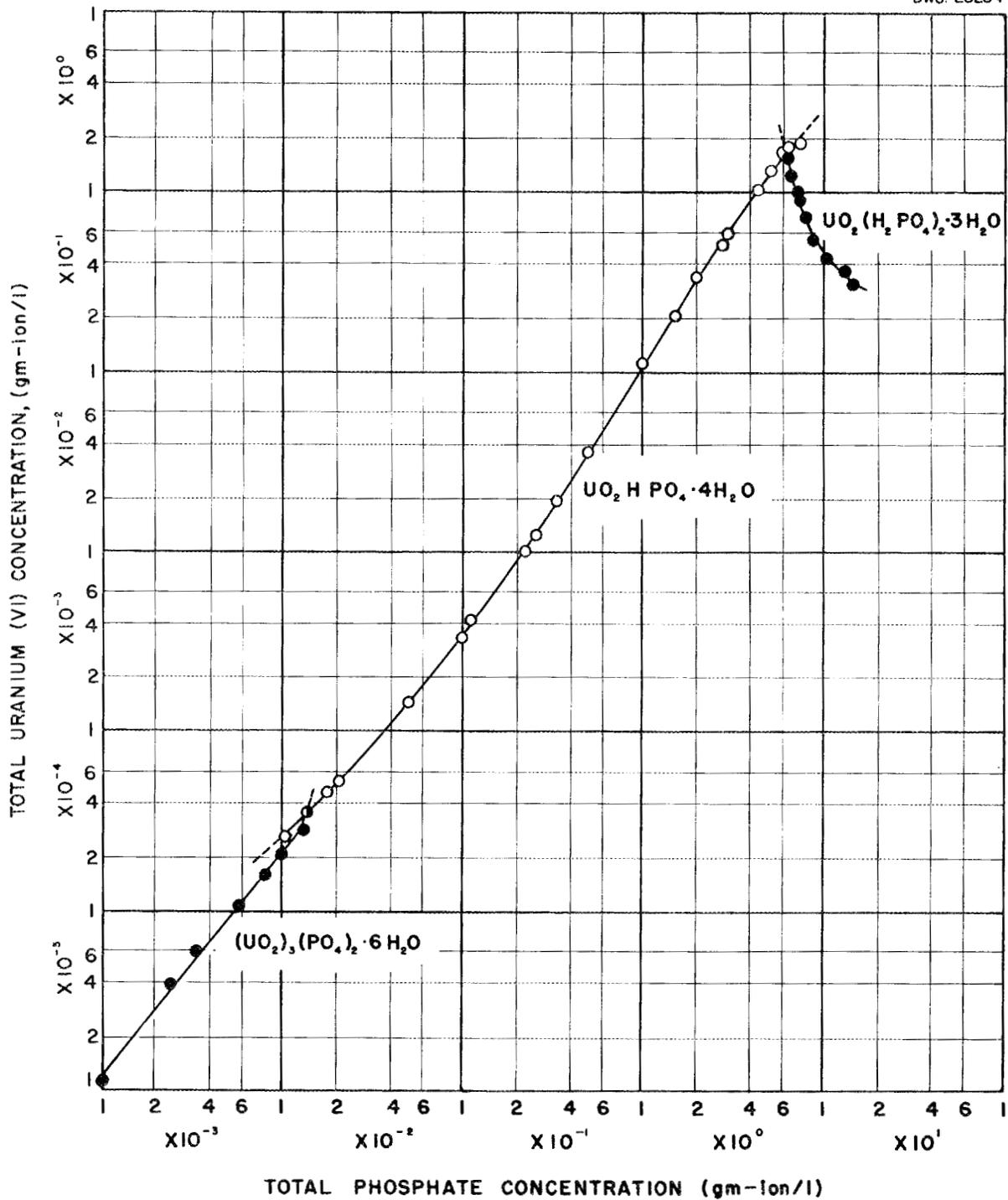


FIGURE 6. SOLUBILITY OF URANIUM (VI) PHOSPHATES IN PHOSPHORIC ACID SOLUTIONS

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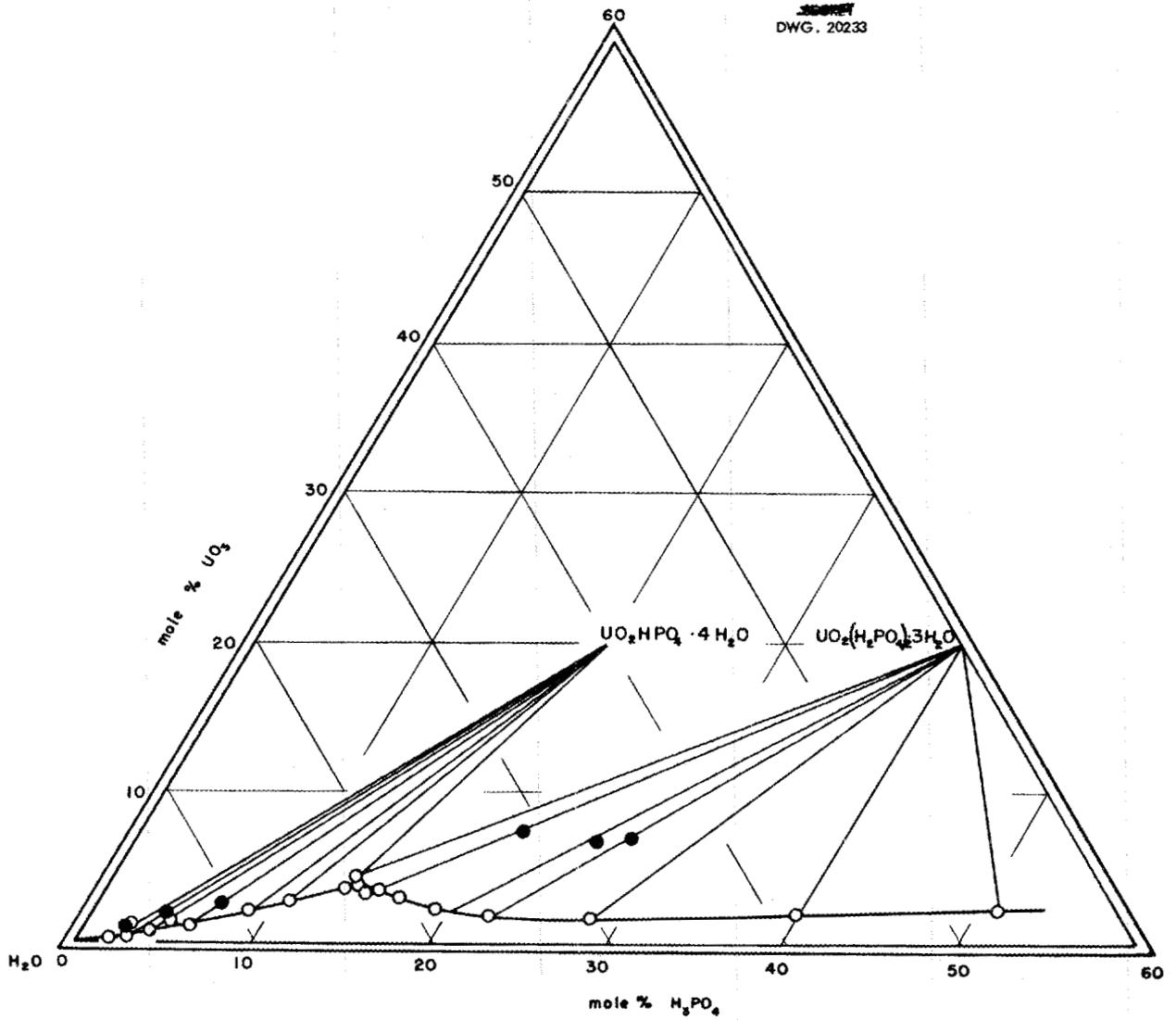


FIGURE 7. A PORTION OF THE ISOTHERMAL PHASE DIAGRAM FOR THE SYSTEM $\text{UO}_3\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ AT 25°C : ○ - SATURATED SOLUTIONS; ● - SLURRIES

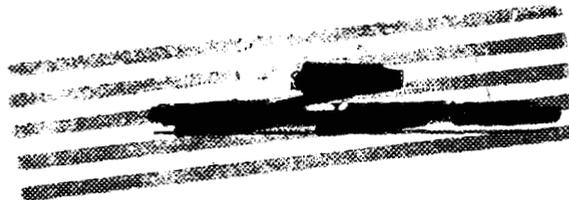
are consistent with this requirement, indicating that the proposed solid phases are the correct ones. The range of stability of the normal uranyl phosphate is confined to solutions of too low concentrations to be shown on the diagram. Accordingly, the wet residue method cannot be applied here to establish the state of hydration of the equilibrium solid.

IV. ACKNOWLEDGEMENTS

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