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The Solubility of Uranium(IV) Orthophosphates in Phosphoric Acid Solutions

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Solubility measurements in the UO_2–P_2O_5–H_2O system have been made at 25 ± 0.1° in the range from 1.5 to 15.24 *M* total dissolved phosphate. The existence of $U(HPO_4)_2 \cdot 6H_2O$ and $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ as the equilibrium solid phases has been demonstrated by use of the wet residue method of Schreinemakers. A method of preparation of $U(HPO_4)_2 \cdot 4H_2O$ is presented.

I. Introduction

Investigations in the uranium(IV) orthophosphate system reported prior to the present work are incomplete with regard to solubilities as well as the composition of the solid phases in equilibrium with the phosphate solutions. Some early investigators, Rammelsberg, Arendt and Knop, Chataing, Aloy,[1] and Schaap, Andrews and Gates,[2] reported the preparation of $U(HPO_4)_2 \cdot 2H_2O$ by various precipitation methods. Aloy[1] also reported the preparation of $U(HPO_4)_2\, 5H_2O$.

As a result of an investigation aimed at characterizing phosphates of tetravalent uranium, Pannell and Rubino[3] reported some solubility measurements of uranium(IV) phosphates in aqueous solutions of nitric, hydrochloric, sulfuric, phosphoric, perchloric and acetic acid in the *p*H range of 0.5 to 2.5. Unfortunately, the samples were shaken mechanically for 4.5 hours which the investigators recognized as an insufficient time to attain equilibrium. Milward[4] described the titration of uranium(IV) sulfate solution with 0.1 *M* Na_2HPO_4, and reported that an inflection point on the titration curve indicated the formation of $U_3(PO_4)_4$ under these conditions.

The present investigation was undertaken in order to determine the solubility of uranium(IV) orthophosphates in phosphoric acid solutions. For these measurements, it was expedient to characterize the starting solid, to study the rate of oxidation of uranium(IV) in phosphoric acid solutions and to determine the rate of attainment of equilibrium in the various solutions.

II. Experimental

A. Stability of Uranium(IV) Orthophosphate Solutions.—To obtain information on the stability of uranium(IV) toward air oxidation in phosphoric acid solutions, two solutions containing 0.02010 *M* U^{+4} in 8.50 *M* PO_4^{-3} and 0.003300 *M* U^{+4} in 3.18 *M* PO_4^{-3}, respectively (prepared by dissolving $U(HPO_4)_2 \cdot 4H_2O$ in the appropriate phosphoric acid solution), were vigorously aerated at 25°. Aliquots were removed at various time intervals for periods of 15 to 17 hours and analyzed for uranium(IV)[5] through the direct addition to ferric chloride solutions. No significant change in the concentration of uranium(IV) was found during these periods of aeration. The stability toward air oxidation of uranium(IV) in phosphoric acid solutions is greater than has been reported by Nichols[6] for uranium(IV) chloride solutions and by Sill and Peterson[7] for uranium(IV) sulfate solutions, indicating a comparatively stronger complex formation between uranium(IV) and phosphate in acid solutions. As a result, it was unnecessary to remove oxygen from the solubility mixtures above 3.18 *M* total phosphate prior to shaking, and the filtration of the equilibrium mixtures could be performed without protecting the mother liquors from air. Stability studies below 3.18 *M* total phosphate were not made because below this concentration the uranium(IV) phosphate solubility was found to be too low for detection of small changes in uranium(IV) by the available analytical methods. Operations in the solubility determinations in this region were carried out in a nitrogen atmosphere.

B. Analysis of Solids and Wet Residues.—Difficulty was encountered in dissolving the uranium(IV) phosphate solids and wet residues in sulfuric or perchloric acid. Nitric acid was not used because of interference with the determination of uranium when a Jones reductor is used for reduction.

It was found that these uranium(IV) phosphate solids and wet residues could be dissolved in sulfuric acid by the addition of a small amount of hydrogen peroxide. The excess hydrogen peroxide could not be removed from the resulting uranium(VI) solution by boiling. Analysis of these boiled solutions gave high results, probably because the hydrogen peroxide was not destroyed in the Jones reductor. This is in accord with the results of Sill and Peterson[7] who reported that hydrogen peroxide is formed in the Jones reductor in the presence of air.

The interference of hydrogen peroxide was eliminated in the following manner. The uranium(VI) solutions containing hydrogen peroxide were diluted to a desired volume. Aliquots were removed and titrated with a permanganate solution to a light pink end-point in order to destroy the hydrogen peroxide. The solution was then heated to boiling to remove the dissolved oxygen. If the pink color disappeared, more permanganate was added until the color returned. This solution, containing a slight excess of permanganate, was cooled and analyzed for uranium by the dichromate method.[5] It was found that permanganate or manganous ions as high as 0.001 *M* did not interfere with the uranium determination.

Phosphate determinations were made on these oxidized solutions by the modified magnesium ammonium phosphate method.[8]

C. Preparation and Purification of $U(HPO_4)_2 \cdot 4H_2O$.—Uranium(IV) orthophosphate is a light green hydrogel when freshly precipitated from aqueous solution. Except for the color, it resembles freshly precipitated hydrous aluminum oxide.

The detailed procedure for preparing samples of $U(HPO_4)_2 \cdot 4H_2O$ for use in the solubility studies is given below.

About 500 ml. of uranium(VI) phosphate solution containing approximately 0.25 *M* UO_2^{++}, 3 *M* H_3PO_4 and 3.5 to 4.5 *M* H_2SO_4 was reduced in a Jones reductor. In a previous report,[5] it was shown that under these conditions uranium(VI) is reduced quantitatively to uranium(IV). Uranium(IV) phosphate was precipitated from this reduced solution by slowly diluting with water until the concentration of sulfuric acid was approximately 1 *M*.

Vigorous stirring was required during the dilution and for several hours afterwards to produce a uniform product. The gelatinous precipitate was separated by filtering with suction through a coarse fritted glass filter.

The solid was washed twice with 2-liter portions of 1 *M*

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(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XII, Longmans, Green and Co., London, New York, Toronto, 1932, p. 128.

(2) W. B. Schaap, L. J. Andrews and J. W. Gates, Tennessee Eastman Corp., CD-4002.

(3) James H. Pannell and Emilia M. Rubino, Mineral Engineering Laboratory, MITG-245, September 15, 1950.

(4) G. L. Milward, CRL-AE-66, Chemical Research Laboratory, Teddington, August, 1950.

(5) J. M. Schreyer and C. F. Baes, Jr., Oak Ridge National Laboratory, Y-12, ORNL-1292, May 7, 1922; *Anal. Chem.*, **25**, 644 (1953).

(6) A. R. Nichols, Jr., BC-12, April 20, 1946.

(7) Claude W. Sill and Heber E. Peterson, Bureau of Mines, BM-RI-4882, June, 1952.

(8) J. M. Schreyer and C. F. Baes, Jr., Oak Ridge National Laboratory, Y-12, ORNL-1578, June 30, 1953; THIS JOURNAL, **76**, 354 (1954).

$HClO_4$ and five times with 1500-ml. portions of acetone. Each wash was performed with vigorous stirring for two hours followed by filtration. The solid was mixed on the filter with two 100-ml. portions of CCl_4, then placed in a vacuum desiccator with continuous suction for 3 hours. The resulting solid was a grayish green dusty powder. A yield of from 70 to 80 g. was obtained.

It was found that 5 acetone washes will remove the major portion of the sorbed perchlorate. In addition, the acetone dehydrates the solid from the hexahydrate, the equilibrium solid phase below 9.8 *M* total phosphate, at least to the tetrahydrate.[9]

Analyses of the $U(HPO_4)_2 \cdot 4H_2O$ preparations used in this study are shown in Table I.

TABLE I

ANALYSIS OF $U(HPO_4)_2 \cdot 4H_2O$ PREPARATIONS

U^{+4}, %	PO_4^{-3}, %	Mole ratio $U^{+4}/PO_4^{-3}/H_2O$[a]
47.3	38.2	1/2.02/3.94
48.1	37.2	1/1.93/3.93
47.2	37.4	1/1.99/4.19
48.1	38.6	1/2.01/3.55
49.4	36.2	1/1.84/3.74
48.7	38.8	1/2.00/3.28
48.8	38.9	1/2.00/3.22
47.2	37.6	1/1.99/4.14

[a] Water by difference.

The ratios of U^{+4}/PO_4^{-3} were in good agreement with the formula $U(HPO_4)_2 \cdot xH_2O$. It was observed that the preparations whose state of hydration was less than 4 very slowly approached the tetrahydrate when exposed to the atmosphere. All of the samples of $U(HPO_4)_2 \cdot 4H_2O$ gave the same X-ray pattern. Pannell and Rubino[3] detected no diffraction patterns in any of their unroasted uranium(IV) orthophosphate preparations.

D. Solubility of Uranium(IV) Orthophosphates in Phosphoric Acid Solutions.—The solubility behavior of uranium(IV) orthophosphate in phosphoric acid was studied over the range of 1.50 to 15.24 *M* total phosphate. The measurements were carried out by adding $U(HPO_4)_2 \cdot 4H_2O$ to a solution of known composition, placing the mixture in a round bottom Pyrex flask and shaking[8] in a water-bath at 25 ± 0.1° for a period which was sufficient to attain equilibrium conditions. In each experiment, the tetrahydrate was converted to the hexahydrate. In high concentrations of phosphoric acid the hexahydrate, in turn, was changed to $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$.

The attainment of solubility equilibrium in the various samples was demonstrated by studies of the rates of dissolution and by a comparison of solubilities obtained from both dissolution and precipitation runs. In the rate studies, $U(HPO_4)_2 \cdot 4H_2O$ was added to phosphoric acid solutions and aliquots were removed for analysis periodically. In 8.5 and 5.9 *M* total phosphate, equilibrium was attained in 12 and 18 days, respectively. These results suggested that a shaking time of two to three weeks would be sufficient to assure solubility equilibrium. It was found that in the region below 9.8 *M* total phosphate, this shaking time gave solubility results which were consistent with those obtained from the precipitation runs.

In the region above 9.8 *M* total phosphate, where $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ was found to be the stable solid phase, shaking times longer than three weeks were found to be necessary. In this region, $U(HPO_4)_2 \cdot 6H_2O$ was always found as a metastable intermediate solid phase in the conversion of $U(HPO_4)_2 \cdot 4H_2O$ to $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$, which probably explains the slower attainment of equilibrium. In an experiment with 11.8 *M* total phosphate, complete conversion and equilibrium were not attained until 23 days. In a rate study in 10.9 *M* total phosphate, $U(HPO_4)_2 \cdot 6H_2O$ was identified even after 21 days of shaking. The conversion of the hexahydrate to $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ between 9.8 and 11.76 *M* total phosphate was so slow that solubility values for $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ in this region were not obtained.

The rapid addition of water to any of the saturated uranium(IV) phosphate solutions precipitated $U(HPO_4)_2 \cdot 6H_2O$. Even upon slow addition of water, the precipitation of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ was difficult. In the only run plotted as a precipitation run above 9.8 *M* total phosphate, water was added dropwise with vigorous stirring in an attempt to minimize the local precipitation of $U(HPO_4)_2 \cdot 6H_2O$. In addition, this sample was shaken for 34 days in an attempt to ensure conversion of any $U(HPO_4)_2 \cdot 6H_2O$ that might have been formed.

In both the dissolution and precipitation studies, filtration was carried out by using a pressure filter apparatus[8] immersed in a water-bath at 25 ± 0.1°. The mother liquors were sampled by means of calibrated pipets or calibrated pycnometers, depending on the viscosity of the solution. After the determination of the densities of the mother liquors, they were analyzed for uranium(IV) and phosphate.[5,8]

The precipitation runs were much more difficult to filter than were the dissolution runs. This difficulty was probably due to the more gelatinous nature of the precipitated $U(HPO_4)_2 \cdot 6H_2O$.

The highest total phosphate concentration obtained from the solubility determinations in concentrated phosphoric acid was 14.97 *M*. The solubility curve was extended to 15.24 *M* total phosphate by dissolving P_2O_5 in 85% phosphoric acid and using this viscous liquid as the solvent. Although this solution may have contained some pyrophosphate, $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ was found as the equilibrium solid phase.

A log-log plot of the solubility data is shown in Fig. 1. The straight line representing the solubility curve of $U(HPO_4)_2 \cdot 6H_2O$ was drawn from the empirical equation

$$[U^{-4}] = 2.55 \times 10^{-5}[PO_4^{-3}]^{4.41}$$

which was determined by the method of least squares, assuming the uranium values to be more reliable than the phosphate.

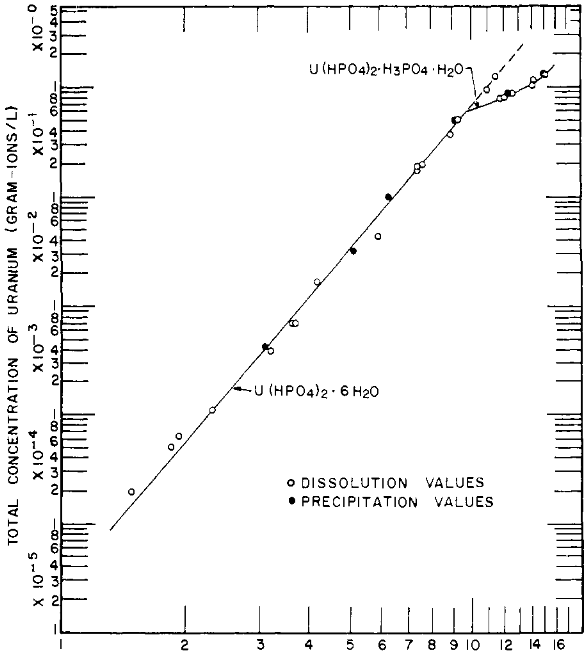

Fig. 1.—Solubility of uranium(IV) orthophosphate in phosphoric acid solution.

The system UO_2–P_2O_5–H_2O at 25° is graphically represented in Fig. 2 by reference to the two sides of a right isos-

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(9) Ethanol and water were also tested as washing agents. In one determination the perchlorate concentration was reduced to less than 0.03% by two ethanol washes, giving a product with a $U^{+4}/PO_4^{-3}/H_2O$ mole ratio of 1/2.01/3.91. However, because the ethanol slurry of the solid filtered very slowly, acetone was chosen as the washing agent. Pannell and Rubino[3] used water as a washing agent to remove impurities from their uranium(IV) phosphate preparations. In this investigation, water was found to be inadequate for removal of these impurities due to the hydrophilic nature of the product.

celes triangle.[10] The existence of $U(HPO_4)_2 \cdot 6H_2O$ and $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ as the equilibrium solid phases is demonstrated in Fig. 2 by use of the wet residue method of Schreinemakers.[11] The crystalline nature of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ made possible a more complete removal of mother liquor, resulting in a shorter extrapolation of tie lines and a more conclusive identification of the solid.

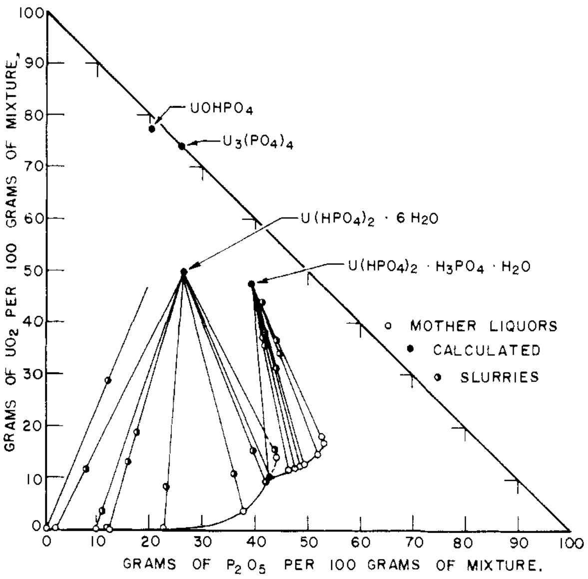

Fig. 2.—The system UO_2–P_2O_5–H_2O at 25°.

Additional information to substantiate the existence of the above-mentioned equilibrium solid phases was obtained from an X-ray diffraction pattern. All of the patterns obtained with slurries from 1.85 to 10.9 *M* total phosphate were identical, indicating the same solid phase over this range, but were different from the reference pattern for $U(HPO_4)_2 \cdot 4H_2O$. X-Ray patterns for slurries from 11.76, 12.42, 14.97 and 15.24 *M* total phosphate were identical with each other, but were different from the patterns for $U(HPO_4)_2 \cdot 4H_2O$ or $U(HPO_4)_2 \cdot 6H_2O$.

The concentrations of uranium(IV) and phosphate in the mother liquor at the transition point between $U(HPO_4)_2 \cdot 6H_2O$ and $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ were determined to be 0.62 ± 0.02 *M* and 9.8 ± 0.1 *M*, respectively, from an enlargement of Fig. 1. The density of the transition mother liquor (1.63 ± 0.03 g./ml.) was determined from a plot of densities as a function of the phosphate concentration. Calculations with these data give 42.6% P_2O_5 and 10.3% UO_2 in the mother liquor at this transition point.

Figure 2 shows that $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ is incongruently soluble in water since a line joining the H_2O apex with the point representing the solid does not intersect the solubility curve of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$. Since this line passes through the area of stability of the $U(HPO_4)_2 \cdot 6H_2O$, the conversion of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ to $U(HPO_4)_2 \cdot 6H_2O$ by water was predicted. X-Ray diffraction analysis confirmed that $U(HPO_4)_2 \cdot 6H_2O$ was produced upon washing $U-H_3PO_4 \cdot H_2O$ with water.

A sample of $U(HPO_4)_2 \cdot 4H_2O$ which was shaken in water for 50 days at 25° gave a slurry X-ray pattern which indicated that the solid produced was not pure $U(HPO_4)_2 \cdot 6H_2O$ and that probably another compound was present. The compositions of the wet residue and mother liquor from this run are plotted in Fig. 2. Analysis of the mother liquor showed the presence of a forty-five fold higher concentration of phosphate than uranium (1.47×10^{-4} *M* U^{+4} and 6.6×10^{-3} *M* PO_4^{-3}). It is suggested that hydrolysis occurred with the possible formation of a new product, such as $UOHPO_4$, or the normal salt, $U_3(PO_4)_4$.

III. Conclusions

As a result of solubility studies in 1.5 to 15.24 *M* total phosphate at 25°, two compounds were identified by Schreinemakers' wet residue method and X-ray diffraction analysis as stable solid phases in the system. These solid phases with their respective stability ranges are $U(HPO_4)_2 \cdot 6H_2O < 9.8 \pm 0.1\ M\ \Sigma\ PO_4^{-3}$; $U(HPO_4)_2 \cdot H_3PO_4 . H_2O > 9.8 \pm 0.1\ M\ \Sigma\ PO_4^{-3}$.

During this investigation, $U(HPO_4)_2 \cdot 4H_2O$ was prepared and identified by both chemical and X-ray diffraction analysis.

A graph is presented which depicts the solubility of uranium (IV) phosphate over the range of 1.5 to 15.24 *M* total phosphate.

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