TABLE II

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE EXCHANGE REACTIONS OF NpO_2^+ AND NpO_2^{++}, AND OF FERROUS ION WITH VARIOUS FERRIC SPECIES

	$E_{act.}$ kcal./mole	$\Delta S^{\ddagger}$, cal./deg./mole
NpO_2^+–NpO_2^{++}	8.3	−24
Fe^{++}–Fe^{+++}	9.9	−25
Fe^{++}–$Fe(OH)^{++}$	7.4	−18
Fe^{++}–$FeCl^{++}$	8.8	−24

and 6 d levels. Then the remaining electrons at the highest energy level at 5 f^1 and 5 f^2 for NpO_2^{+2} and NpO_2^+, respectively. Calculations based on the Fermi–Thomas model[7] indicate that the 5 f electron will have a second maximum in its radial distribution function at a distance of ~5 Å. from the nucleus. Since the effective potential energy of the second minimum is small there is a high probability for barrier penetration. Therefore, even if the somewhat naive assumptions made previously do hold, qualitatively there should be no decrease in the degree of probability for the exchange.

If the bonding and/or environment interaction does lead to promotion of the 5 f electrons to 6 d electrons, then the argument becomes more straightforward due to the greater extension of the 6d orbitals.

A satisfying explanation for the observed results is difficult to propose. If a direct electron transfer mechanism is postulated, it would appear that the probability for the penetration of the barrier is not primarily determined by the symmetry of the species (Franck–Condon principle). Furthermore, the small difference in the observed free energy of activation for the neptunium and iron cases is difficult to reconcile with the relatively large difference in free energy of rearrangement of the hydration spheres expected in the two cases. An explanation of the observed results can be made in terms of electron transfer if it is assumed that the determining factor is the low probability for the transfer of an electron through the intervening water molecules. Alternatively, an atom transfer mechanism could be proposed.[8,9] Decision as to the probable mechanism will have to await further investigation.

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[7] M. Mayer, *Phys. Rev.*, **60**, 184 (1941).

[8] H. Taube, H. Myers and R. L. Rich, THIS JOURNAL, **75**, 4119 (1953).

[9] J. Hudis and A. C. Wahl, *ibid.*, **75**, 4153 (1953).

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[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY, CARBIDE AND CARBON CHEMICAL DIVISION]

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

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

I. Introduction

The solubility data on uranium(VI) phosphates in pure phosphoric acid reported previous to the present work cover a limited range of molarities and in some cases the equilibrium solid phase is in question.

Lord, Andrews and Gates[1] studied the solubility of $UO_2HPO_4 \cdot xH_2O$ as a function of phosphate concentration at *p*H 1 and 2. The *p*H 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.

Leader[3] reported the solubility behavior of $UO_2HPO_4 \cdot 4H_2O$ in HNO_3 and H_3PO_4 over a range of 0.3 to 3.0 M H_3PO_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 $UO_2HPO_4 \cdot 4H_2O$, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ and $UO_2(H_2PO_4)_2 \cdot 3H_2O$. Zachariasen[4] examined $UO_2HPO_4 \cdot 4H_2O$ 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 $UO_2HPO_4 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$. They reported that both these compounds are tetragonal, and $UO_2HPO_4 \cdot 4H_2O$ was said to crystallize as tabular plates, usually four sided but occasionally as truncated squares. The $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ was said to crystallize in needle-like crystals. They gave the density values of $UO_2HPO_4 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ as 3.399 and 3.213, respectively. Werther[6] reported the preparation of crystals of $UO_2(H_2PO_4)_2 \cdot 3H_2O$ 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.

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[1] E. J. Lord, L. J. Andrews and J. W. Gates, Jr., Report CD-4035, June 16, 1945.

[2] W. B. Schaap and J. W. Gates, Jr., Report C-0.375.3, March 12, 1946.

[3] G. R. Leader, Report CN-2195, 1944.

[4] W. H. Zachariasen, Report CC-2768, March 12, 1945.

[5] W. W. Harris and Roberta H. Scott, Report AECD-2746, September 30, 1949.

[6] G. Werther, *J. prakt. Chem.*, [1] **43**, 321 (1848).

II. Experimental

A. Methods of Analysis

1. Analysis for Uranium(VI). a. Volumetric Method.—Analysis for uranium(VI) in the various solutions was performed by the volumetric dichromate method.[7] This method consists of the reduction of a uranium(VI) solution in a Jones reductor to uranium(IV) in the presence of 3–4 *M* phosphate and 4.5 *M* sulfuric acid. The reduced solution is diluted to approximately 1 *M* in phosphoric acid and a ferric chloride solution added. After the addition of phosphoric acid and sodium diphenylamine sulfonate, the solution is titrated with a standard dichromate solution. An average deviation of 2 to 3 parts per thousand was obtained by this method.

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 ($E_{1/2}$ = *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 0.01 *M*. The maximum permissible phosphate concentration has not been determined.

The procedure of analysis consisted in adding 20 ml. of a stock solution, 0.6 *M* in oxalic acid, 0.1 *M* 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 20 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 v. The diffusion current was measured from the polarogram as follows: The current was read at −0.10 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} *M*, though normal accuracy (*ca.* 5% error) was limited to concentrations above about 5×10^{-5} *M*, 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 3 *N* 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 3 *M* 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.—The determinations of water in the solid uranium(VI) phosphate samples were made as follows.

A weighed sample in a porcelain boat was placed in a closed ignition tube connected to a weighed absorption bulb containing a sample of G. Frederick Smith anhydrous magnesium perchlorate. The sample was heated at 300° in the presence of helium for 1 hour. The absorption bulb was then weighed and the water take-up calculated.

An average deviation of 2% is claimed for this method.

B. Preparation of Salts

1. Preparation of $UO_2HPO_4{\cdot}4H_2O$.—Two samples of $UO_2HPO_4{\cdot}4H_2O$ (367 g. each with 84% yields) were prepared by the following procedure.

One liter of 1.1 *M* phosphoric acid solution was added with stirring to one liter of approximately 1 *M* uranium(VI) nitrate or perchlorate solution. The solution was seeded with a few crystals of $UO_2HPO_4{\cdot}4H_2O$ 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 0.01 *M* $HClO_4$ solution for 12 hours, then filtered and washed with acetone. The dry sample was placed in a vacuum desiccator over a saturated solution of $Na_2Cr_2O_7$ (v.p. = 9.12 mm. at 20°) for 12 hours.

Under the microscope, tetragonal crystals characteristic of $UO_2HPO_4{\cdot}4H_2O$ were observed. X-Ray diffraction analysis indicated $UO_2HPO_4{\cdot}4H_2O$ to be present to >95% in each sample.[11] 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 $UO_2HPO_4{\cdot}4H_2O$, 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°, the $UO_2HPO_4{\cdot}4H_2O$ is converted to $UO_2HPO_4{\cdot}2H_2O$. 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 $UO_2HPO_4{\cdot}2H_2O$ are 67.16% UO_2^{++}, 23.6% PO_4^{-3} and 8.96% H_2O.

2. Preparation of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$.—A 100-g. sample of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ was prepared according to the directions of Ryon and Kuhn[12] by digesting $UO_2NH_4PO_4{\cdot}3H_2O$ in 0.8 *M* HNO_3 at 100°. The solid was then washed with hot water and acetone and dried in air. Conversion of $UO_2NH_4PO_4{\cdot}3H_2O$ to $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ was easily observed by the change in physical appearance of the solid phase.

Under the microscope needle-like crystals were observed characteristic of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$. X-Ray diffraction analysis indicated $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ to be present to >90% in the sample. Chemical analysis of the solid gave 75.33% UO_2^{++}, 17.97% PO_4^{-3} and by difference 6.70% H_2O. This corresponds to a formula of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$, for which the theoretical percentages are 75.5% UO_2^{++}, 17.72% PO_4^{-3} and 6.72% H_2O.

3. Preparation of $UO_2(H_2PO_4)_2{\cdot}3H_2O$.—A sample (approximately 10 g.) of $UO_2(H_2PO_4)_2{\cdot}3H_2O$ was prepared by the addition of approximately 30 g. of $UO_2HPO_4{\cdot}4H_2O$ to 100 ml. of 85% H_3PO_4. The sample was shaken for 13 days at 25° and then filtered. 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. The dry sample was placed in a vacuum desiccator over $CaCl_2$ for 12 hours. X-Ray 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 52.63% UO_2^{++}, 35.7% PO_4^{-3} and by difference 10.9% H_2O, while the formula $UO_2(H_2PO_4)_2{\cdot}3H_2O$ gives for the theoretical percentages 52.12% UO_2^{++}, 36.66% PO_4^{-3} and 10.4% H_2O.

If $UO_2(H_2PO_4)_2{\cdot}3H_2O$ is heated for 7 hours at 110°, it is converted to $UO_2(H_2PO_4)_2H_2O$. Werther[6] reported that part of the water in this compound is lost upon heating and at red heat all of the water is removed without melting or losing H_3PO_4. It is probable that he converted the compound to a pyrophosphate.

Bernard S. Borie, Jr.,[13] X-ray Laboratory, Oak Ridge National Laboratory, by private communication has re-

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[7] J. M. Schreyer and C. F. Baes, Jr., *Anal. Chem.*, **25**, 644 (1953).

[8] W. E. Harris and I. M. Kolthoff, This Journal, **67**, 1484 (1945).

[9] E. D. Marshall, F. S. Voss and E. M. Baer, Report K-585, March 31, 1950.

[10] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 563.

[11] This is the limit of accuracy of the X-ray diffraction analysis.

[12] A. D. Ryon and D. W. Kuhn, Report Y-315, January 10, 1949.

[13] Letter of October 14, 1952, from B. S. Borie, Jr., to J. M. Schreyer, Oak Ridge National Laboratory, Oak Ridge, Tenn.

ported a preliminary investigation of the crystal structure of $UO_2(H_2PO_4)_2 \cdot 3H_2O$.

One of the yellow crystal platelets of a sample of $UO_2(H_2PO_4)_2 \cdot 3H_2O$ 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 = 10.83 Å., b = 13.92 Å., c = 7.48 Å., and β = 105°45′.

If it is assumed that the unit cell contains four stoichiometric units, the calculated density of $UO_2(H_2PO_4)_2 \cdot 3H_2O$ is 3.17, in agreement with the measured value of 3.16. If the formula $UO_2(H_2PO_4)_2 \cdot 4H_2O$ is assumed, the calculated density is 3.28. The densities were calculated by using the formula weights and the unit cell value determined by the dimensions given above. The agreement between the calculated and experimentally determined density values substantiates the formula $UO_2(H_2PO_4)_2 \cdot 3H_2O$.

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 $C^5_{2h} - P^2 1/C$. 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 results if the uranium atoms are in fourfold general positions, xyz; $\bar{x}\bar{y}\bar{z}$; $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$; $x, {}^1/_2 - y, {}^1/_2 + z$, where $x \cong 0.25$, $y \cong 0.4$, and $z \cong 0.25$. The determination of the light atom positions would require quantitative intensity measurements.

C. Apparatus

1. **Solubility Apparatus.**—The solubility flasks were assembled on a mechanical shaker in a water-bath thermostatically controlled at 24.9 ± 0.1°. 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 which permitted the maintenance of a constant temperature by immersion of the entire assembly under 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.[14] The instrument sensitivity ranged from 0.05 to 20 microamp. per full scale deflection.

D. Solubility Studies in Phosphoric Acid

The solubility of uranium(VI) phosphate solids in phosphoric acid alone was measured in the range of 0.001 to 14.6 M total phosphate at 25°. Using $UO_2HPO_4 \cdot 4H_2O$ 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 solubility measurements were carried out by adding the desired uranium(VI) phosphate to a solution of phosphoric acid, placing the solution in the solubility apparatus and shaking the flask assembly in a water-bath at 25° for a period necessary to attain equilibrium conditions.

Microscopic examination of solids proved very useful in detecting the tetragonal crystals of uranyl monoacid phosphate and the needle-like crystals of the normal uranyl phosphate. 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. The crystals varied from large monoclinic rods obtained at the transition point to indistinguishably small crystals in concentrated phosphate solutions.

In some of the solubility tests, chemical (see Table I) and X-ray diffraction analyses were made on the solid phases removed from the mother liquors after attaining equilibrium. The water analyses (see Table I) are not considered reliable since it is not known what happens to the solid phases when heated at 300° for 1 hour. It is probable that some decomposition of the $UO_2(H_2PO_4)_2 \cdot 3H_2O$ 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.

TABLE I

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

Theoretical compositions: $(UO_2)_3(PO_4)_2 \cdot 6H_2O$—73.10% UO_2^{++}, 17.10% PO_4^{-3}, 9.75% H_2O; $UO_2HPO_4 \cdot 4H_2O$—61.6% UO_2^{++}, 21.68% PO_4^{-3}, 16.45% H_2O; $UO_2(H_2PO_4)_2 \cdot 3H_2O$—52.13% UO_2^{++}, 36.6% PO_4^{-3}, 10.42% H_2O.

		Analyses of solid phases					
Sample no.	Total phosphate in mother liquor, moles/l.	UO_2^{++}, %	PO_4^{-3}, %	Assumed no. of hydrogens	Theor. % H_2	H_2O by difference, %	H_2O by analysis, %
A-30	0.00100	73.17	17.4	0	0	9.43	...
A-26	.00625	70.79	18.5	0	0	10.71	9.48
A-29	.00816	71.24	18.3	0	0	10.46	9.41
A-28	.0101	71.81	18.6	0	0	9.59	8.38
A-33[a]	.0140	65.90	19.8	...	..	...	...
A-27	.0179	61.82	22.0	1	0.23	15.95	16.5
A-10	.103	61.70	21.5	1	.23	16.57	...
A-25	.108	62.00	21.7	1	.23	16.07	16.5
A-21	2.74	61.30	21.6	1	.23	16.87	...
A-3	2.93	61.70	21.6	1	.23	16.47	...
A-7	6.09	61.90	21.6	1	.23	16.27	...
A-20	6.10	61.80	21.0	1	.23	16.99	...
A-40	6.14	54.30	34.6	4	.78	10.32	14.6
A-44	6.67	55.10	33.8	4	.78	10.32	10.1
A-38-3	6.78	53.80	35.9	4	.78	9.52	13.2
A-45	7.20	52.18	36.5	4	.78	10.54	7.6
A-36	7.31	53.10	36.1	4	.78	10.02	15.1
A-41	8.88	51.80	37.0	4	.78	10.42	16.7
A-42	10.40	55.6	34.5	4	.78	9.12	14.6

[a] Solid phase obtained at transition point between $UO_2HPO_4 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 6H_2O$.

The data for the composition of the solid phase for the normal phosphate can more nearly be explained by assuming the formula $(UO_2)_3(PO_4)_2 \cdot 6H_2O$. There would be no reason to assume the tetrahydrate under these conditions since the recommended preparation of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ is carried out at 100°. These chemical analyses are the only evidence obtained for the formula $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ since application of the Schreinemaker's wet residue method was not practical because of the low solubilities in this range. It was observed by comparison of the X-ray patterns of the solids from 0.001 to 0.014 M H_3PO_4, *i.e.*, $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ compared with the standard for $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, that these two hydrates have virtually the same X-ray powder pattern. It is also of interest to note that the crystals of $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ are visually identical with those of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$.

Transition points between each solid phase were established through selected solubility runs and in the case of the transition between $UO_2HPO_4 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 6H_2O$, a mixture of well formed crystals was obtained.

The periods of shaking of the samples in order to attain equilibration were 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 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 much longer, making the use of $UO_2HPO_4 \cdot 4H_2O$ as the added solid phase impractical. In the region of stability of $UO_2HPO_4 \cdot 4H_2O$, the samples using $UO_2HPO_4 \cdot 4H_2O$ as the added solid phase were shaken for 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. The samples 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 were shaken for 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

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(14) M. T. Kelley and H. H. Miller, *Anal. Chem.*, **24**, 1895 (1952).

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). 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 runs for which the initial solid phase is the stable $UO_2(H_2PO_4)_2 \cdot 3H_2O$.

The low uranium concentrations in mother liquors below 0.017 *M* H_3PO_4 were determined polarographically as described in the section on analysis.

In solubility runs more dilute than 0.5 *M* H_3PO_4, wherein $UO_2HPO_4 \cdot 4H_2O$ was the stable solid phase, the final ΣPO_4^{-3} concentration was calculated to be simply the sum of the initial $[H_3PO_4]$ and the final ΣUO_2^{++}. For those runs in which $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ was the stable solid phase, ΣPO_4^{-3} was taken as the sum of $[H_3PO_4]$ and $^2/_3\Sigma UO_2^{++}$. In the range 0.5 to 15 *M* H_3PO_4, the final calculated ΣPO_4^{-3} was determined by taking into consideration the effect of volume change accompanying dissolution of the salt.

A log–log plot of the solubility data is presented in Fig. 1. Calculated ΣPO_4^{-3} values were plotted where the original phosphate concentrations were known accurately, since these were probably more accurate than those obtained by analysis of the mother liquors.

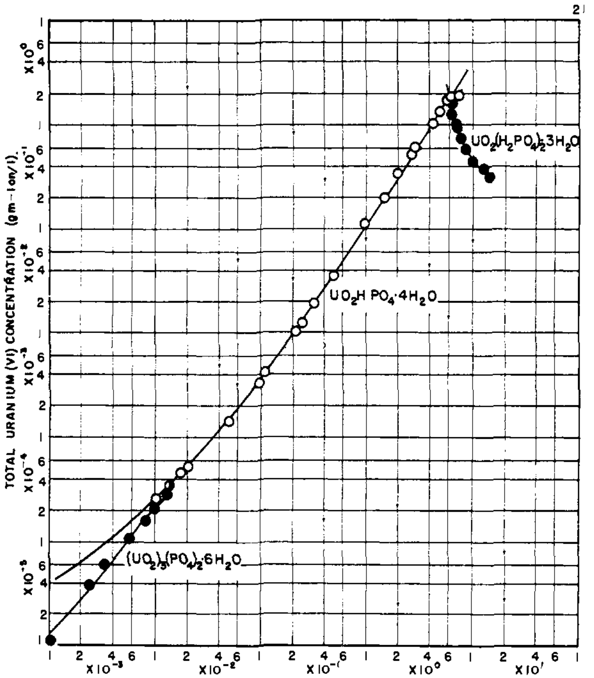

Fig. 1.—Solubility of uranium(VI) phosphates in phosphoric acid solutions.

The solubility behavior in high phosphoric acid concentration is expressed in the form of a three-component phase diagram in Fig. 2. Included in the figure are the data for both $UO_2(H_2PO_4)_2 \cdot 3H_2O$ and $UO_2HPO_4 \cdot 4H_2O$ (down to $\Sigma PO_4^{-3} = 1$ *M*). The range of stability of the normal phosphate is confined to solutions too dilute to be shown on the diagram.

Several slurry analyses of both solid phases are included in the phase diagram. In this method of plotting the data (known as Schreinemakers' wet residue method), the composition of the mother liquor, that of the slurry and that of the solid phase should lie on the same straight line. Within the limit of experimental error, the data are consistent with this requirement, indicating that these solid phases are the correct ones.

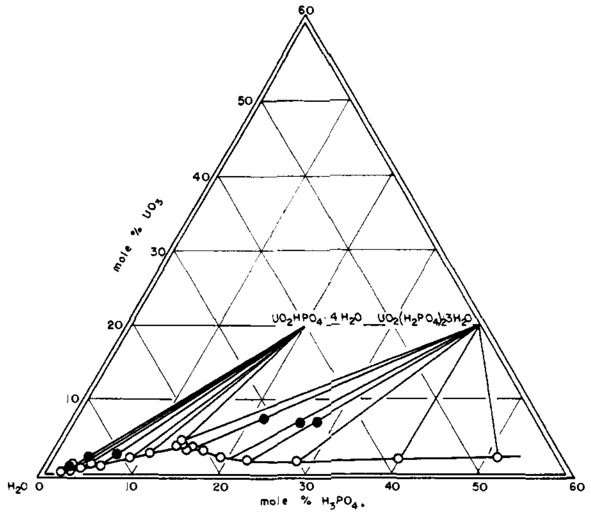

Fig. 2.—A portion of the isothermal phase diagram for the system UO_3–H_3PO_4–H_2O at 25°: ○, saturated solutions; ●, slurries.

III. Conclusions

As a result of solubility studies in 0.001–15 *M* phosphoric acid, three compounds were identified as stable solid phases in the system. These compounds with their respective stability ranges are

$(UO_2)_3(PO_4)_2 \cdot 6H_2O$	<0.014 *M* ΣPO_4^{-3}
$UO_2HPO_4 \cdot 4H_2O$	0.014–6.1 *M* ΣPO_4^{-3}
$UO_2(H_2PO_4)_2 \cdot 3H_2O$	>6.1 *M* ΣPO_4^{-3}

As described in the experimental section, identification of these salts was made microscopically, chemically, and by means of X-ray powder pattern.

A graph is presented which depicts the solubility of uranium(VI) phosphates over the range of 0.001–15 *M* phosphoric acid.

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