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The Solubility of Plutonium(IV) Phosphates
and the
Phosphate Complexes of Plutonium(IV)

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Edward L. King

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Charles W. Felt
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Abstract

The stability of the various complex species of phosphate and plutonium(IV) was determined by the measurement of the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ as a function of the H_3PO_4 concentration at constant nitric acid concentration. The existence of complexes involving from one to five phosphates per plutonium(IV) has been indicated by these measurements. Equilibrium constants for reactions involving the various complex species have been determined.

In connection with the work on the complex ions of plutonium (IV) and phosphate, a study was made of the composition of various solid plutonium (IV) phosphates. A gelatinous solid of the composition: $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ is precipitated when H_3PO_4 is added to a nitric acid solution of Pu(IV) at room temperature. The existence of two different crystalline plutonium (IV) phosphates of the compositions: $\text{Pu}_3(\text{PO}_4)_4 \cdot z\text{H}_2\text{O}$ and $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ has also been shown. These crystalline compounds are formed if the gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ is heated at 110°C in the presence of a $\text{HNO}_3\text{-H}_3\text{PO}_4$ solution.

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I. Introduction

Plutonium in the +4 oxidation state in aqueous solution readily forms complexes with many negative ions such as SO_4^{2-} , F^- , NO_3^- , Cl^- , phosphate, oxalate, etc. The chemistry of Pu(IV) is highly dependent on the stability of these complexes." In this research the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ has been determined in solutions of varying concentrations of H_3PO_4 . One can interpret these solubility data in terms of complex ion formation of Pu(IV) with phosphate ions.

II. Composition and Nature of Various +4 Metal Ion Phosphates

In order to interpret solubility data in terms of complex formation, it is necessary to know the composition of the solid phase present in equilibrium with the solution. There are many different types of orthophosphates for there are three different anions which may take part in compound formation with a metal ion. Thus, in the case of orthophosphates of a +4 metal ion one could conceivably have solids of the composition: $\text{M}_3(\text{PO}_4)_4 \cdot a\text{H}_2\text{O}$, $\text{M}_2(\text{HPO}_4)(\text{PO}_4)_2 \cdot b\text{H}_2\text{O}$, $\text{M}(\text{HPO}_4)_2 \cdot c\text{H}_2\text{O}$, $\text{M}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot d\text{H}_2\text{O}$, and $\text{M}(\text{H}_2\text{PO}_4)_4 \cdot e\text{H}_2\text{O}$. This list could be expanded even further if one wished to include formulas involving five or more metal ions or phosphates.

Before discussing the various precipitates of Pu(IV) phosphate which have been prepared, the composition and character of some of the other +4 metal ion phosphates will be mentioned.

A. Zirconium and Hafnium Phosphates

Zirconium and hafnium form similar gelatinous phosphates when precipitated from 6 N HCl. Hevesey and Kimura⁽¹⁾ have analyzed these solids and found them to correspond to the formulas: $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ and $\text{HfO}(\text{H}_2\text{PO}_4)_2$. Since the analysis merely determines the ratio of metal ion to phosphate in the precipitate, equally good representations of the compounds would be $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Hf}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. Two molecules of water are lost upon ignition of these compounds giving the anhydrous pyrophosphates, ZrP_2O_7 and HfP_2O_7 .

B. Ceric Phosphates

According to W. H. Hartley⁽²⁾ a yellowish precipitate is formed when a slightly acid solution of Ce(IV) is treated with sodium phosphate. He dried this compound in vacuo over H_2SO_4 and found its composition to correspond to the compound: $\text{Ce}_2\text{H}(\text{PO}_4)_3 \cdot \frac{25}{2}\text{H}_2\text{O}$. No other references to Ce(IV) phosphates were found in the literature.

Since Ce(IV) is very similar in many of its properties to Pu(IV), it seemed worthwhile to investigate the compounds precipitated when Ce(IV) phosphate was formed under conditions similar to those used in the experiments on Pu(IV).

In connection with this work it was desirable to have a rapid method of analysis for Ce(IV) and phosphate. The method used involved the reduction of the Ce(IV) with excess KI followed by a titration of the I_3^- liberated with a standardized sodium thiosulfate solution. The phosphate was then separated from the I^- , which would interfere with the phosphomolybdate analysis for phosphate. This was accomplished by the addition of $\text{Ba}(\text{NO}_3)_2$ and

excess NH_4OH (precipitating the phosphate as barium phosphate, or a mixture of barium phosphate and cerous phosphate). This solid was washed quite thoroughly with an $\text{NH}_4\text{OH}-\text{NH}_4\text{NO}_3$ buffer solution and dissolved in excess HNO_3 . The widely used phosphomolybdate analysis for phosphate⁽³⁾ was carried out on an aliquot of the dissolved precipitate. The ammonium phosphomolybdate was dissolved in an excess of standardized base and titrated with acid to the phenolphthalein end point (the end point is not very sharp in this solution)⁽⁴⁾. To check the accuracy of this analytical procedure, two blank experiments were run in which a mixture of known amounts of Ce(IV) and H_3PO_4 were analyzed. The results are presented in Table 1.

Table 1

Analysis of Solutions Containing Ce(IV) and H_3PO_4

Ce(IV) present	Ce(IV) found	H_3PO_4 present	H_3PO_4 found
0.49 millimoles	0.49 millimoles	1.20 millimoles	1.16 millimoles
0.50 "	0.50 "	0.90 "	0.94 "

The agreement between the amount of material present and the amount found is seen to be very good in the case of Ce(IV) , and while it is not so good in the case of the H_3PO_4 , it is accurate enough for the purposes desired.

If a solution of Ce(IV) in HNO_3 is treated with H_3PO_4 , a yellowish white gelatinous precipitate is formed. The precipitate will retain its gelatinous character for long periods of time when

kept at room temperature. However, if the mixture of solid and mother liquor is sealed in a tube and heated at 110°C , one observes the formation of crystals within the bulk of the gelatinous precipitate in a few days and after a week the material is completely converted to a crystalline form which is very light yellow in color.

Both the gelatinous substance which is precipitated initially and the crystalline material which results upon heating the gelatinous substance in the precipitation medium were analyzed by the method outlined previously.

The gelatinous solid was precipitated from a solution of the following composition:

1.5 M HNO_3

1.2 M H_3PO_4

0.16 M NH_4NO_3

The solid was stirred with the mother liquor for several days at room temperature. The solid was then allowed to stand with no stirring at room temperature for an additional two weeks before analysis. Two portions of solid were then washed with four ten milliliter portions of 0.5 M HCl (the oxidation of Cl^- by Ce(IV) under these conditions is negligible). These solids were then treated with dilute HCl and excess KI . The rate of oxidation of I^- by the Ce(IV) of the ceric phosphate precipitate is not very rapid; the reaction between Ce(IV) in solution and I^- is quite rapid. Further, the rate of oxidation of I^- by O_2 of the air under these conditions is sufficiently slow that the solid may be allowed to stand for one half hour in the presence of excess KI without an appreciable error being introduced. The analyses

of the gelatinous material prepared and analyzed as described indicated that the ratio of phosphate to ceric in the solid was 1.87 (two analyses were run; 1.85 and 1.89 were the results). The difference between the value 1.87 and 2.00 is within the experimental error of the analysis. Thus, the most reasonable formula to write for the compound which was precipitated is: $\text{Ce}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$.

The crystalline Ce(IV) phosphate was precipitated from a solution of the same composition as that from which the gelatinous material was precipitated. It was heated at 110°C in a sealed cone for about two weeks. The material was completely crystalline at that time. The analysis of this solid was carried out in the same manner as was the analysis of the gelatinous material. The reaction between the solid ceric phosphate and I^- is slower in the case of the crystalline material than it was in the case of the gelatinous material. One might expect this in view of the smaller surface area of the crystalline material. In spite of the longer time necessary for the reduction of the Ce(IV), the error introduced by the O_2 oxidation of I^- during the period of two hours while the I^- is reducing the Ce(IV) is small.

The ratio of phosphate to ceric in this crystalline material was found to be 1.54 (two analyses were run; 1.50 and 1.57 were the results). Therefore, the most reasonable formula of the crystalline substance is: $\text{Ce}_2\text{H}(\text{PO}_4)_3 \cdot x\text{H}_2\text{O}$. This compound has the same ratio of phosphate to cerium as did the compound reported by W. H. Hartley.⁽²⁾ Neither this compound nor the gelatinous material was analyzed for nitrate and therefore the formulas can not be considered as absolutely established. Mention will be made of the X-ray diffraction pattern of this crystalline ceric phosphate

in a later section of this paper.

C. Thorium Phosphates.

The literature concerning thorium phosphate is more abundant than is that of the other +4 metal ion phosphates. D'Ans and Dawihl⁽⁵⁾ have prepared several different thorium phosphates: $\text{Th}_3(\text{PO}_4)_4$, $\text{Th}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{ThHPO}_4 \cdot 2\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. These authors report that the first and second of these compounds are in equilibrium with one another in the presence of 2.4 M H_3PO_4 while the second and the third are in equilibrium in the presence of 3.6 M H_3PO_4 .

P. C. Cleve⁽⁶⁾ and C. Volck⁽⁷⁾ have prepared a gelatinous thorium phosphate of the composition: $\text{Th}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. They prepared the compound, which is a white gelatinous material, by mixing a H_3PO_4 solution with a thorium chloride solution.

It seemed desirable to investigate whether gelatinous thorium phosphate was converted to a crystalline material upon heating in a solution of HNO_3 and H_3PO_4 . A sample of gelatinous thorium phosphate was prepared. The solid was precipitated from a solution of the composition:

1.4 M HNO_3

1.0 M H_3PO_4 .

The solid which precipitated was much more gel-like than the gelatinous ceric phosphate. This solid was sealed in a tube with its mother liquor and heated at 110°C. After one week at the elevated temperature the material was still gelatinous. After three weeks heating it was completely converted to a crystalline substance. Neither the gelatinous thorium phosphate nor the

crystalline solid formed upon heating the gelatinous material was analyzed for the ratio of phosphate to thorium. However, it is seen that the behavior of the thorium phosphates has a certain similarity to the ceric phosphates reported. It is noteworthy that a much longer heating period was necessary before the thorium phosphate was converted to a crystalline substance. Mention will be made of the X-ray analysis of this crystalline thorium phosphate in a later section of this paper.

D. Uranous Phosphates

It is reported⁽⁸⁾ that a green gelatinous precipitate of the composition: $\text{U}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ is precipitated when NaH_2PO_4 solution is treated with UCl_4 . The solid is soluble in concentrated HCl and is reprecipitated upon dilution. If one cools this dihydrate, a crystalline pentahydrate $\text{U}(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$ is formed. Repeated washing of the dihydrate is said to fail to remove all of the sodium phosphate.

E. Plutonium (IV) Phosphate

The situation which exists in the case of plutonium (IV) phosphates is very similar to that observed in the phosphates of other +4 metal ions. If a solution of $\text{Pu}(\text{IV})$ in HNO_3 is treated with a H_3PO_4 solution, a very transparent gelatinous precipitate forms. If the phosphoric acid is added slowly with occasional stirring, this material, although gelatinous, is gathered together in small aggregates. If the entire amount of H_3PO_4 necessary to make the final concentration approximately 0.5 M is added at once and the mixture stands at room temperature without periodic stirring, the material becomes a gel, filling

the entire container. This material does not settle out upon standing for days. The gelatinous solid, when centrifuged to a more compact form, has a definite pinkish color.

If the gelatinous solid is sealed in a cone with its mother liquor and heated at 110°C , a red crystalline solid is formed.* The process is a very interesting one to watch. After

* The preparation of a crystalline plutonium (IV) phosphate has been reported previously by C. Smith, Report CN-1700, June 1, 1944, p. 38. The solid was formed upon heating for two weeks at $90^{\circ} - 95^{\circ}\text{C}$ a solution containing Pu(IV) and of the composition: 0.69 M HNO_3 , $1.35 \text{ N H}_2\text{SO}_4$, $0.9 \text{ M H}_3\text{PO}_4$.

the gelatinous solid has been held at the elevated temperature for two days, one can see red crystalline material present in the large mass of gel. As the heating proceeds, the gel is more and more converted to the crystalline substance and when conversion is complete, the dense crystals which occupy but a very small fraction of the volume of the gel are present in the bottom of the cone. The conversion generally requires a week at 110°C .

Since it was necessary that the composition of the solid used in the solubility measurements be known, a method for analyzing the various precipitates had to be devised. It was not practical to analyze the solid on a "macro" scale, for the amount of material available was smaller than would be required for a macro analysis. The most convenient method appeared to be a radioactive analysis for phosphate as well as plutonium. A very convenient isotope

of phosphorous for use in such a procedure is P^{32} , a beta particle emitting isotope of 14.30-day half life.⁽⁹⁾ The isotope is a pure beta emitter, having no gamma rays associated with its transition to S^{32} , one of the stable sulfur isotopes.⁽¹⁰⁾ The maximum energy of its beta particles has been reported as 1.69⁽¹¹⁾, 1.75⁽¹²⁾, and 1.71⁽¹³⁾ Mev. by different investigators. The P^{32} was prepared by an $n-p$ reaction on sulfur:

The material, along with inactive phosphate carrier, was worked up into its final form, a solution of 0.1 M Na_2HPO_4 , by Dr. Jacobsen and Dr. Overstreet of the Radiation Laboratory.

The specific alpha activity of Pu^{239} is 71,000 counts per minute per microgram at 52% counter geometry. There is also some other radiation associated with Pu^{239} .⁽¹⁴⁾ Soft X-rays, gamma rays and possibly beta particles are indicated by some measurements on highly purified plutonium. For the purposes of this work it was important in some of the analyses to know how many counts per minute on a Geiger counter would be associated with each microgram of Pu^{239} . This was determined by counting a sample of purified plutonium on a Geiger counter at the geometry under consideration.

The various solutions of H_3PO_4 containing P^{32} were prepared by mixing measured volumes of the 0.1 M Na_2HPO_4 containing P^{32} with measured volumes of carefully standardized 3.37 M H_3PO_4 . By mounting aliquots of these solutions and counting them at the same time and under the same geometry conditions as were used with the

samples being determined, it was possible to calculate the amount of phosphate present in the sample under consideration. This procedure eliminated all corrections due to decay of the P^{32} as well as changes in the counting characteristics of the Geiger counter used. In some of the analyses the solid was dissolved in concentrated HNO_3 and mounted directly on a platinum dish for counting for both alpha and beta activity. In this type of procedure it was necessary to apply a correction to the counting rate observed on the Geiger counter for the counts due to the radiation (other than the alpha particles) from plutonium. This was very important in the analyses performed because the correction was often an appreciable fraction of the counting rate observed on the Geiger counter. In other procedures the phosphate and plutonium were separated from one another and counted for activity separately. In such a case one did not have to make such a correction because the sample of phosphate counted for beta activity contained no Pu^{239} .

In the analysis of the various samples of gelatinous plutonium (IV) phosphate it was necessary to wash the precipitates quite well before analyzing. This was especially true in the case of solids precipitated from solutions containing a high concentration of H_3PO_4 . In some cases the solid was washed with dilute HCl and in other cases the solid was washed with dilute HNO_3 . After washing the solid, either of two alternative procedures was used:

- (I) The gelatinous solid was dissolved in concentrated HNO_3 and transferred to a platinum dish; 50-100 micrograms of $La(III)$ was usually added to the dish and LaF_3 was

precipitated by the addition of HF. The solution on the dish was then evaporated to dryness. The dish was not ignited for it was shown that some of the P^{32} activity was lost upon ignition. The LaF_3 was precipitated on the dish because it spreads out evenly on pre-ignited platinum and it is reasonable to suppose that the plutonium and phosphate are more uniformly distributed in such a case than when a solution of the plutonium and phosphate was directly evaporated on the platinum dish. In such a procedure a correction for the activity detected by the Geiger counter due to plutonium was made. In most of the analyses in which this procedure was used, this correction was 10 percent to 20 percent of the total beta activity measured. The factor relating the plutonium activity detectable by a Geiger counter to its alpha activity (and therefore its weight) was known to better than 5 percent accuracy. Therefore, the uncertainty in the corrected beta activity, which was used to calculate the amount of phosphate present, was small.

(II) Solids which contained phosphate of low specific activity were generally analyzed in a different fashion. The gelatinous solid was dissolved in concentrated HNO_3 and diluted with water. Sodium hydroxide solution was added and the plutonium (IV) hydroxide was centrifuged off. The solid was washed two times with water and dissolved in concentrated HNO_3 . The hydroxide precipitation was repeated once more. All of the supernatant solutions and washes were combined

and analyzed for phosphate while the final hydroxide was dissolved and diluted to a known volume; an aliquot of this was mounted and counted for alpha activity. The analysis of the combined washes and supernatant solutions for phosphate was carried out by acidification of the solution with concentrated HCl (NaCl precipitated out in most cases) followed by the precipitation of the phosphate with an excess of ZrO^{++} . The zirconium phosphate was heated with the mother liquor to aid in coagulation. It was then centrifuged off and dissolved in HF. This was transferred to a platinum dish for counting of the beta activity. The phosphate has been shown to be completely separated from the plutonium in the above outlined procedure by the following method. The solution of Pu(IV) formed upon dissolving the second hydroxide precipitate was treated with NaOH solution, again precipitating the hydroxide. The supernatant solution from this precipitation was analyzed for phosphate as described above. The activity was not distinguishable from the background. The effectiveness of the zirconium in removing all of the phosphate was also checked. In many of the analyses a second zirconium phosphate precipitation was made by adding a small amount of phosphate to the supernatant solution from the first precipitation. An excess of ZrO^{++} was present in this supernatant solution so the addition of phosphate caused further precipitation. The amount of phosphate added was such that an excess of ZrO^{++} was still present. It was supposed that this precipitate included all of the phosphate which was not precipitated in the first

precipitation. This supposition may not be strictly valid for the addition of phosphate to the ZrO^{++} containing solution causes a precipitate to form at the region of mixing, while the phosphate unprecipitated by the first precipitation presumably would be uniformly distributed throughout the solution. The zirconium phosphate formed was stirred and heated with the mother liquor before centrifugation. In ten such procedures it was found that an average of 3.4 percent of the total phosphate was not precipitated with the first precipitate (range of values 1.4 percent to 5 percent). The amount of phosphate found in analyses in which only one precipitation was made was multiplied by a factor: $100/97$.

The experimental error in the determination of the ratio of phosphate to plutonium in the washed plutonium (IV) phosphates is due to errors in determining the alpha and beta activity when method I is used, while in the use of method II, these uncertainties as well as those associated with the chemical separation of phosphate and plutonium must be considered. The probable error in the counting rate of the various samples due to statistical variations was kept below 1 percent, if possible. Only in the case of samples with very low activity was the contribution to the experimental error due to this cause larger than 1 percent. However, in determining the β activity of samples a certain amount of irreproducibility was observed. It was found that the relative activity of two different samples of P^{32} would vary by as much as 3 percent to 5 percent from time to time. Such a behavior was not the general rule, however. The cause for this behavior is not known. The

experimental error in the determination of the ratio of phosphate to plutonium in the washed solids is ± 3 percent. This figure does not include the error caused by changes in the composition of the solid which occur during its washing. This error is discussed later in this section.

Many different gelatinous solids were analyzed during the course of this research. Some were solids taken directly from solubility tubes, some were made on a small scale and analyzed at different times while others were analyzed before being introduced into solubility tubes in which the phosphoric acid contained no P^{32} , consequently eliminating the possibility of further analyses on such solids.

Detailed data will be presented on some of the solid composition determinations to indicate reproducibility, the effect of continued washing and the effect of changes in the precipitation medium.

Four analyses (run in two pairs) were performed on a solid which had been prepared in the following way. The gelatinous plutonium (IV) phosphate was precipitated from a solution of the composition:

1.2 M HNO_3

0.6 M H_3PO_4 .

It was allowed to stand with only an occasional stirring for two days at room temperature before the first pair of analyses were run. Then it stood for three days without stirring and finally was stirred with a mechanical stirrer for about 30 hours preceding the removal of the second pair of samples for analysis.

Some evaporation may have occurred during the last day while the sample was stirred. Several of the washes of these precipitates were mounted directly on platinum dishes for counting of both alpha and beta activity. The precipitate was analyzed by the first of the methods described, that is, by direct mounting of the dissolved precipitate. The results of these analyses are presented in Table 2.

The solid which was used in solubility sample number 20 (see Table 6) was analyzed at several different times during the course of its solubility determination in a solution of the composition: 2.06 M HNO_3 , 0.0322 M H_3PO_4 . After washing, the solid was analyzed by the second of the methods outlined. This was the method in which the phosphate and plutonium were separated by hydroxide precipitations. The procedure did not involve a second precipitation of zirconium phosphate from the supernatant solution from the first precipitation and therefore the ratios presented have been multiplied by a factor: 100/97. The results of these analyses are presented in Table 3.

Consideration will now be given to the data presented in Tables 2 and 3. From the data presented in Table 2 it would appear that four 0.10 ml washes of a precipitate containing ten micrograms of plutonium are necessary before the last wash and solid show the same ratio of phosphate to plutonium. This is a reasonable criterion for completeness of washing. Of course, the possibility exists that the composition of the solid is altered during the washing process. For the purposes of discussion it will be assumed that the solid phase when precipitated has a ratio of phosphate to plutonium of 2. The equilibrium between

Table 2

Analysis of Gelatinous Plutonium (IV) Phosphate

Precipitation Conditions:

2.10 M HNO_3 0.60 M H_2PO_4 Time of analysis (in
days after precipitation
(Pu))

	2 days	2 days	6 days	6 days
Ratio of phosphate/ plutonium in solid	1.85	1.86	1.80	1.95
Micrograms plutonium in solid	6.1	10	3.9	2.2
Total number of washes	5	5	6	6
Last wash (0.10 ml):				
Composition	2.1M HNO_3	2M HCl	2.1M HNO_3	2.1M HNO_3
Ratio phosphate/Pu(IV)	1.88	2.2	1.83	1.82
Micrograms Pu(IV)	4.5	1.6	10	8.2
Next to last wash (0.10 ml):				
Composition	2M HCl	2M HCl	2.1M HNO_3	2.1M HNO_3
Ratio phosphate/Pu(IV)	2.5	2.7	1.82	1.85
Micrograms Pu(IV)	1.5	1.6	22	20
Second to last wash (0.20 ml):				
Composition			0.5M HNO_3	0.5M HNO_3
Ratio phosphate/Pu(IV)			2.3	2.3
Micrograms Pu(IV)			2.4	2.3

Table 3

Analysis of Gelatinous Plutonium (IV) Phosphate
from Solubility Sample 20

Precipitation Conditions
2.06 M HNO₃
0.0322 M H₃PO₄

Time of analysis (in days after precipita- tion)	10	16	21	21
No. of washes (0.05 ml each)	4	3	7	7
Composition of washes	0.02M HCL	0.02M HCL	2M HCL	0.02M HCL
Micrograms plutonium in solid	17	15	7.2	7.6
Ratio of phosphate/ plutonium in solid	1.74	1.76	1.92	1.72

this solid and one in which the ratio was 1.5 is represented by the equation:

This equation is not valid if the phosphoric acid is not present mainly as H₃PO₄. In solutions of low hydrogen ion concentration the predominant species is H₂PO₄^{-*}. As long as one is in the

* K. S. Pitzer (J. Am. Chem. Soc., 59, 2365 (1937)) has made a critical selection of the ionization constants of phosphoric acid. He chooses:

$$K_1 = 7.5 \times 10^{-3}$$

$$K_2 = 6.2 \times 10^{-8}$$

$$K_3 = 10^{-12}$$

acid region in which the equation written is valid, the conversion does not have a hydrogen ion dependence but has a phosphoric acid dependence. As will be seen in a later section of this paper, the solubility of gelatinous plutonium (IV) phosphate is greater in solutions of higher acidity. Therefore, since washes of higher acidity dissolve more solid than washes of lower acidity, the wash of higher acidity has a higher concentration of H_3PO_4 . Thus the lower the acidity of a wash the greater is the tendency for a conversion from $Pu(HPO_4)_2 \cdot xH_2O$ to $Pu_2H(PO_4)_3 \cdot yH_2O$ to take place. This actually appears to be the case, for the data in Table 3 reveal that in a pair of duplicate analyses, the solid washed with 2 N HCl has a higher ratio of phosphate to plutonium than does the solid which was washed with 0.02N HCl (in 0.02N HCl approximately 60 percent of the phosphoric acid would exist as H_3PO_4). The data reported in Tables 2 and 3, as well as numerous unreported analyses, indicate that the ratio of phosphate to plutonium in the gelatinous solid precipitated from HNO_3 solutions of various concentrations of H_3PO_4 is 1.7 - 2.0. This variation could be due to one of three causes:

- 1) The solid is of an indefinite composition.
- 2) The solid precipitated is $Pu(HPO_4)_2 \cdot xH_2O$, the predominance of values of the ratio of less than 2 being due to the fact that the washes were always made with

solutions which could have a transition to some solid with a lower ratio.

- 3) The complete absence of colloidal Pu(IV) in the solutions used in the preparation of the various samples of gelatinous plutonium (IV) phosphate was not proved. If one precipitated gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ from a solution which contained some colloidal Pu(IV), the colloidal Pu(IV) would probably be coprecipitated. Such a solid would show a ratio of phosphate to plutonium of lower than 2.

While the first possibility is not unlikely in view of the nature of the precipitate, and the third certainly not impossible in view of the difficulty often experienced in the preparation of solutions of Pu(IV) free of colloidal Pu(IV), the second explanation seems to be the most reasonable. The fact that gelatinous phosphates of Hf(IV), Zr(IV), Ce(IV), Th(IV) and U(IV) have been prepared with the formula $\text{M}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ might also be considered as evidence in favor of the second explanation. Just as in the case of the ceric phosphates, none of these solids were analyzed for nitrate and therefore the formulas are not absolutely established although the ratio of phosphate to plutonium is certain.

The solubility of gelatinous plutonium (IV) phosphate in solutions containing NaNO_3 decreases as the solid is shaken with a solution containing NaNO_3 , H_3PO_4 and HNO_3 . This behavior was not noted when the solid was shaken with solutions containing H_3PO_4 and HNO_3 . Thus, it seemed desirable to determine whether or not this change in solubility was due to a change in the composition

of the solid phase. Gelatinous plutonium (IV) phosphate was precipitated from a solution of the composition:

0.84 M HNO_3

1.24 M NaNO_3

0.23 M H_3PO_4 .

This solid was stirred by a mechanical stirrer with its mother liquor for a long period of time. At various times aliquots were removed and analyses of the solid were performed. Some of these analyses were run by the first of the methods described while others were run by the second. The results of these experiments are presented in Table 4. It is interesting to note that as the time of stirring in the solution containing NaNO_3 is increased the composition changes. The ratio of phosphate to plutonium in the solid was 1.9 on the day of precipitation while it had dropped to approximately 1.65 after 19 days stirring. There was some evaporation in this three-week period and from time to time water was added to keep the volume approximately constant. This was done only roughly, however, and the best that can be claimed is that the concentrations of the various substances present did not change over 15 percent. The stirring was discontinued after 19 days. The solid which appeared to be of the same gelatinous nature as when prepared was allowed to stand in the presence of the mother liquor. After standing for two weeks another analysis was run. It is seen that the ratio of phosphate to plutonium was 1.8. This is a change in the opposite direction from what would be expected from the analyses performed at different times while the solid was being stirred with the mother liquor. However,

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Table 4

Analyses of Gelatinous Plutonium (IV) Phosphate Precipitated

in Presence of Sodium Nitrate

Precipitation Conditions:

0.84 M HNO_3 1.24 M NaNO_3 0.23 M H_3PO_4

Time of analysis (in days after precipitation)	0.5	0.5	2	5	13	13	19	19	32
Number of washes	5	5	5	5	5	5	5	5	5
Composition of washes	0.23M HCl	0.23M HCl	0.23M HCl	0.23M HCl	2M HCl	0.02M HCl	0.2M HCl	0.2M HCl	0.2M HCl
Method of analysis	II	II	I	I	I	I	I	I	II
Micrograms of plutonium in solid	9.2	8.7	8.7	10	5.1	2	7.5	7.0	18.7
Ratio phosphate/plutonium in solid	1.89	1.93	1.75	1.64	1.64	1.55	1.67	1.69	1.82

it was noted after the solid had stood for another couple of weeks that a definite amount of fine whitish crystalline material was present in the bottom of the cone; there was still gelatinous material present also. If there was a conversion of the gelatinous plutonium (IV) phosphate to some finely divided crystalline material in which the ratio of phosphate to plutonium is lower than in the gelatinous material, one might expect to find a decreasing ratio of phosphate to plutonium in the well stirred solid. The crystalline material which eventually settled out was quite fine and would probably have been fairly uniformly distributed throughout the gelatinous material while it was being agitated. However, when stirring ceased the crystalline material would tend to settle to the bottom of the cone leaving the upper part of the cone relatively rich in the gelatinous material which presumably has a ratio of phosphate to plutonium of about 2. Thus, the aliquot removed from the upper part of the cone two weeks after stirring ceased would show a higher ratio of phosphate to plutonium than one would expect on the basis of the results obtained on the well stirred solid. It should also be noted that the pair of duplicate analyses run after 13 days stirring show the same trend with the changing acidity of the wash solution as was pointed out in connection with the data in Table 3. That is, the ratio of phosphate to plutonium is lower in a sample which is washed with a wash solution of lower acidity.

Several samples of crystalline plutonium (IV) phosphate were prepared. These crystalline solids were prepared by the same method as was used in the preparation of the crystalline

thorium and ceric phosphates. The gelatinous plutonium (IV) phosphate was sealed in a Pyrex cone in the presence of the solution from which it was precipitated. This cone was heated at 110°C. As was mentioned previously, one could observe the tiny red crystals form within the bulk of the semi-transparent gelatinous solid. After heating for a period of a week, the material was completely crystalline. The results of the analyses of several samples of crystalline plutonium (IV) phosphate are presented in Table 5. The method used in these analyses was the first of the methods outlined. Duplicate analyses in which one of the samples was washed with 2 M HNO₃ and the other with 0.02 M HCl were performed on portions of Sample No. 64. The results were identical and are to be contrasted with the difference between analyses performed on the gelatinous solid using washes similar to those used here. An examination of the data in Table 5 indicates that there are at least two different crystalline plutonium (IV) phosphates. One has a ratio of phosphate to plutonium of 1.54 while for the other the ratio is 1.35. These ratios are within the experimental error equal to 1.50 and 1.33 respectively. Presumably the compounds would be:

It is seen that the solid with the lower ratio of phosphate to plutonium is formed at the lower concentration of H₃PO₄ as it should be. That these crystalline solids were formed at 110°C is no proof that they are stable at room temperature. In fact,

Table 5

Analysis of Crystalline Plutonium (IV) Phosphate

All samples were heated in sealed
pyrex cones at 110°C until crystal-
lization was complete.

	Sample No. 46	Sample No. 64	Sample No. 6
Precipitation Conditions:			
(HNO ₃) in moles per liter	1.45	1.45	1.82
(H ₃ PO ₄) in moles per liter	1.10	1.0	0.40
Number of analyses performed	2	4	2
Values of ratio of phosphate to plutonium in solid	1.54	1.55	1.36
	1.50	1.54	1.33
		1.59	
		1.49	

it will be shown in a later section of this paper that the crystalline material in which the ratio is 1.5 undergoes a transition at room temperature.

F. Crystal Structure and X-ray Analysis of Crystalline +4 Metal Ion Phosphates.

Portions of the several different crystalline phosphates prepared during the course of this research have been viewed with a microscope. All of the solids were viewed under 430 fold magnification.

The ceric phosphate which was analyzed and found to have a ratio of phosphate to cerium of 1.54 was composed of some very fine crystals which appeared to be needle-like although they were so small that their form cannot be stated with certainty. There was also present some larger agglomerations which showed no particular structure.

The thorium (IV) phosphate crystals were even finer than the ceric phosphate crystals and no definite crystal form could be discerned.

Both of the crystalline plutonium (IV) phosphates were viewed. Neither the $\text{Pu}_3(\text{PO}_4)_4 \cdot z\text{H}_2\text{O}$ nor the $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ form crystals of very large size. Crystals of a sample of $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ showed a needle-like form. The form was more definite than that observed in any of the other samples viewed. The sample of $\text{Pu}_3(\text{PO}_4)_4 \cdot z\text{H}_2\text{O}$ also contained some small needle-like crystals. There were present some larger agglomerates which appeared to be made up of the small needle-like structures.

Professor W. H. Zachariasen of the University of Chicago has made X-ray diffraction studies of several samples of crystalline phosphates. The samples of $Ce_2H(PO_4)_3 \cdot yH_2O$, $Pu_2H(PO_4)_3 \cdot yH_2O$ and the crystalline thorium phosphate prepared in connection with this work and described in this paper as well as the crystalline plutonium (IV) phosphate prepared by C. Smith *

* See footnote on page 11.

were studied by Professor Zachariasen. He found¹⁵ all of these compounds to be isomorphous. He did not make the detailed study of the X-ray diffraction pattern which would be necessary before an actual statement of the arrangement of the atoms could be made. The isomorphism of the compounds establishes the formulas of the crystalline thorium phosphate and the crystalline plutonium (IV) phosphate prepared by C. Smith as $Th_2H(PO_4)_3 \cdot yH_2O$ and $Pu_2H(PO_4)_3 \cdot yH_2O$ respectively.

III. Solubility Measurements on Plutonium (IV) Phosphates

A. Solubility Measurements on Crystalline $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$

Since crystalline $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ is apparently a well defined solid, it would be desirable to use this solid in solubility measurements. Several samples of crystalline $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ were shaken with HNO_3 solutions having various concentrations of H_3PO_4 . The solid was washed several times with a solution of the same composition as that used in the solubility measurement. It was then suspended in the solution and transferred to a long-necked Pyrex solubility tube. The solubility tube was stoppered with a tight fitting cork and this was covered with a small piece of "Parafilm"²³ which extended completely over

* "Parafilm" is a pliable semi-transparent material which is reputed to prevent the evaporation of solutions kept in containers which it covers. It is a product of The Menasha Products Co., Menasha, Wisconsin.

the cork onto the glass neck of the solubility tube. The solubility tube was then shaken in a water thermostat which was kept at $25.00 \pm 0.07^\circ\text{C}$. The solubility was measured at various times by the following technique: a portion of the solution was removed by dipping into the solution an air dried capillary

of moderately large bore. The solution and any suspended solid which may have accompanied it was then delivered into an air dried Pyrex cone which was at 25.0°C. The cone was covered with "Parafilm" and centrifuged for several minutes. The centrifuge cup in which the cone was placed was partially filled with water from the thermostat just before use. This precaution minimizes temperature variations in the solution between the time of removal of the sample and the time of removal of an aliquot of the solution from the cone after centrifugation. The use of an air dried cone and transfer pipet was also a precautionary measure. Several experiments have indicated that oven dried glassware has a tendency to adsorb Pu(IV) from quite acid solutions. The effect noted was quite small but could be important in samples of very low solubility. The glassware dried at room temperature did not seem to behave in such a fashion. Aliquots of the saturated solution above the centrifuged precipitate were taken with calibrated self-filling pipets. *

* A pipet of approximately this same type is described by A. A. Benedetti-Pichler, Introduction to the Microtechnique of Inorganic Analysis, (John Wiley and Sons Inc., New York, 1942) Figure 78B, p. 240.

In most of the solubility determinations a 0.000875 ml pipet was used; in the samples of extremely low solubility, however, 0.00485 ml and 0.0100 ml pipets were used. These aliquots were delivered into approximately 6 M HNO₃ on a platinum dish.

Approximately 50 micrograms of La^{+++} was also present on the dish and LaF_3 was precipitated by the addition of HF. As was mentioned previously, this produced a dish on which the activity is more uniformly distributed than when an aliquot is evaporated directly onto the dish. The solubilities observed in the different solutions are presented in Figure 1. It is seen that the solubility increases slowly as though it were approaching the value observed for the gelatinous plutonium (IV) phosphate in a solution of the same composition as indicated in Figure 1. The observed solubility is seen to continue rising even above the value observed for the gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$.

The appearance of the solid after it has shaken in these solutions for a month is not the same as it was at the time of preparation. The solid is extremely finely divided and lighter in color than the original $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$. No analyses have been carried out on these solids after they have been used in the long period solubility determinations.

It would be expected that some evaporation would take place in the period of over a month during which these samples were shaken. During that period of time numerous analyses of the supernatant solution were carried out; these necessitated opening the solubility tube which would tend to cause evaporation. The data presented in Figure 1 indicate that the solubility in this range of phosphoric acid concentration increases as the phosphoric acid concentration is increased. Data presented in Tables 6, 7, and 8 indicate that the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ increases as the acidity increases. Therefore, the solubility of $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ would also increase as the acidity

Figure 1

Solubility of Crystalline
Plutonium (IV) Phosphate
Initially $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$

.34

FL-1

CN-3360

FIGURE I

was increased. This follows directly from a consideration of the relative number of hydrogen ions per plutonium in the two solids. Thus, evaporation which increases both the phosphoric acid concentration and the nitric acid concentration would lead to increased values of the solubility of both $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ and $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$. The H^+ and H_3PO_4 dependences are such that an evaporation of 3% of the water would lead to a 10% to 15% increase in the solubility.

The most reasonable interpretation of the data in Figure 1 is that the solid in equilibrium with the solutions after shaking for a long time is $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$, the slightly greater solubility observed being due to the fact that some evaporation has occurred. The solubilities observed are all higher than that observed for gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ by about the same percentage. This is what would be observed if evaporation was occurring and $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ was the solid in equilibrium with the solution. The possibility that $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ might be the solid in equilibrium with the solutions and have an equilibrium solubility slightly lower than the value for $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ under one of the sets of conditions, the greater solubility observed being due to evaporation, is not reasonable. This follows from the fact that the solubility of $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ has a different H_3PO_4 concentration dependence than $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ and therefore the differences observed between the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ and that measured would change as the H_3PO_4 concentration was changed. If the rate of precipitation of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ were much slower than the rate of solution of $\text{Pu}_2\text{H}(\text{PO}_4)_3$, one might hypothesize

that $\text{Pu}_2\text{H}(\text{PO}_4)_3$ is the solid present and that equilibrium has not yet been established. If such were the case, $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ would be unstable with respect to $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ in the solutions used since it would have a greater solubility than $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$. Thus, it seems well established that $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ is unstable with respect to $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ in the solutions used and the slowly increasing solubility of the $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ is probably due to evaporation which increases the concentration of H_3PO_4 and HNO_3 . As was mentioned, the solid in these solubility tubes after 4 to 6 weeks shaking was quite finely divided and not gelatinous. Thus, if the solid present in these samples is $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$, it is in a much more compact form than the freshly precipitated gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$.

B. Solubility Measurements on Gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$

P. O'Connor¹⁶ has determined the solubility of plutonium (IV) phosphate in certain solutions of HNO_3 and H_3PO_4 . The plutonium (IV) phosphate which he used was prepared under conditions which would lead to the formation of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$. His measurements indicate that phosphate complexes of $\text{Pu}(\text{IV})$ exist in solutions in which the phosphoric acid concentration range is 0.1M to 0.6M.

In this paper the solubility of gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ in many different solutions containing HNO_3 and H_3PO_4 has been measured. Measurements of the solubility of this compound have

also been made in solutions containing HNO_3 , H_3PO_4 , and NaNO_3 . In all of the solubility samples run except four (Samples No. 3, 10, 14, and 20 (see Table 6)) the equilibrium was approached from the unsaturated side.

There were five different samples of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ prepared for use in the solubility measurements. Although Solid IV was the only one of the five which was analyzed, they were all prepared under conditions similar to those used in the preparation of solids which were shown to be $\text{Pu}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.

Samples of gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ containing approximately 0.5 - 1.0 milligrams of plutonium were used in each solubility determination. The solid was washed several times with the solution in which its solubility was to be determined. It was then suspended in this solution and transferred to a long-necked Pyrex solubility tube which had immediately before been rinsed several times with a solution of the same composition as that used in the transfer. The solubility tube was shaken in a thermostat at $25.00 \pm 0.07^\circ\text{C}$. The technique used in determining the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ in the various solutions was the same as that outlined previously in connection with the solubility determination of the crystalline plutonium (IV) phosphate. In the case of the samples run at 1.25 M NaNO_3 , there was an appreciable amount of NaNO_3 in the aliquots mounted. The amount present in a 0.000875 ml aliquot was 93 micrograms, while the 0.00485 ml aliquots contained 515 micrograms. This latter amount is enough to cause quite appreciable absorption of the alpha particles from plutonium,

especially when it distributes itself non-uniformly over the dish. It was found that one could wash the sodium hydroxide formed by the ignition of NaNO_3 off of an ignited platinum dish on which LaF_3 had been precipitated without removing over 1 to 2 percent of the plutonium. This water wash, which was allowed to stand on the dish for about five minutes, was then transferred to another platinum dish for counting. Since only 1 to 2 percent of the plutonium was on this second dish, even a large amount of absorption would not appreciably affect the result.

In practically all of the solubility determinations aliquots were removed at three or more different times. In the case of the samples run at 2.08 M HNO_3 , it was found over a three week period that the observed solubility did not change within experimental error in aliquots removed after the first day. After this had been shown to be true in several different samples, the practice adopted involved taking three or more aliquots within five days.

In the course of the solubility determinations, several of the supernatant solutions were analyzed for the amount of Pu(VI) present. The solutions were analyzed by the " LaF_3 holding oxidant" method.¹⁷ In none of the samples analyzed was the amount of Pu(VI) found to be greater than 1 to 2 percent of the total plutonium in solution. Thus, it appears that the rate of oxidation of Pu(IV) by NO_3^- or O_2 of the air under these conditions is very small.

It was observed that the solubility of gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ precipitated in the absence of NaNO_3 would slowly decrease over a period of six weeks when shaken at 25°C . in solutions containing sodium nitrate. Data presented in a previous section (Table 4) indicate that a change in the composition of the solid phase occurs when gelatinous plutonium (IV) phosphate is stirred with a solution containing NaNO_3 . It was found, however, that no appreciable trend in the solubility could be observed if 3 to 4 aliquots were removed over the time range $1/2$ to 4 days after preparation of the solubility tube. This would indicate that despite a small change in the average composition of the solid during this period, $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ was still the solid in equilibrium with the solution. The variation between the values of the solubility determined from successive measurements on the same sample was greater in the case of samples run at 1.25 M NaNO_3 than in those run with no salt present. This is probably due in part to the presence of some NaOH which is not removed by the washing of the dish and also in part to the fact that the LaF_3 precipitate doesn't seem to spread as evenly when NaNO_3 is present.

The values of the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ which have been determined are presented in Tables 6, 7, and 8. The maximum percent variation in the solubilities observed in the case of a given sample run at 2.08 M HNO_3 is seen to average ~ 4 percent if samples 3, 9, 16, and 25 are omitted

Table 6

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Solubility of Gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ at 25.0°C .

All samples: 2.08 M HNO_3

Sample Number	Solid Used	$(\text{H}_3\text{PO}_4)^h$ in moles per liter	Range in values of observed sol- ubility (in milli- grams of plutonium per liter)	Average Solubility	
				(in milli- grams of plutonium per liter)	(in moles per liter) $\times 10^4$
1	II	1.20	171. - 178.	175	7.33
2	IV	1.20	183. - 187.	185	7.74
3 ^a	g	1.09	160. - 186.	170	7.0
4	II	0.90	97. - 101.	98	4.10
5	III	0.90	100. - 106.	103	4.3
6	II	0.600	50. - 52.	51	2.14
7	III	0.400	31.7 - 32.9	32.3	1.35
8	IV	0.400	32.1 - 33.6	32.8	1.37
9	b	0.337	27.3 - 32.8	29.	1.2
10 ^a	g	0.33	28.2 - 30.3	29.	1.2
11	c	0.249	20.4 - 21.2	20.7	0.86
12	d	0.150	18.2 - 18.6	18.4	0.77
13	III	0.150	19.6 - 20.6	19.9	0.83
14 ^a	g	0.104	24.8 - 25.7	25.3	1.06
15	IV	0.100	21.6 - 22.4	22.1	0.92
16	I	0.073	30.4 - 35.2	32.	1.33
17	III	0.0600	27.0 - 28.1	27.5	1.15

Table 3 (cont.)

Sample Number	Solid Used	$(\text{H}_3\text{PO}_4)^h$ in moles per liter	Range in values of observed sol- ubility (in milli- grams of plutonium per liter)	Average Solubility	
				(in milli- grams of plutonium per liter)	(in moles per liter) $\times 10^4$
18	III	0.0404	38.7 - 38.8	38.8	1.62
19	IV	0.0404	41.7 - 43.9	42.5	1.78
20 ^e	g	0.028	69. - 72.	71.	3.0
21	III	0.0270	58.4 - 60.0	59.2	2.48
22	III	0.0135	137. - 144.	141.	5.9
23	III	0.0135	139. - 144.	141.	5.9
24	IV	0.0135	157. - 167.	162.	6.8
25	I	0.0120	185. - 240.	206.	8.6
26	IV	0.0071	268. - 275.	271.	11.3
27	III	0.0054	327. - 346.	339.	14.2
28	f	0.00268	483. - 490.	486.	20.4
29	I	0	740. - 820.	780.	33.

a $(\text{HNO}_3) = 2.10 \text{ M}$

b Solid used in Sample 9 was previously used in Sample 10.

c Solid used in Sample 11 was previously used in Sample 4.

d Solid used in Sample 12 was previously used in Sample 6.

e $(\text{HNO}_3) = 2.06 \text{ M}$

f Solid used in Sample 28 was previously used in Samples 22 and 23.

g Solid was precipitated directly in solubility tube.

h The concentration of H_3PO_4 listed is the concentration which would exist if no solid had dissolved. In the samples run at low H_3PO_4 concentration, an appreciable correction must be made for the phosphate in solution as a result of the precipitate dissolving. A discussion of this is given in the following section.

Table 7

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Solubility of Gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ at 25.0°C .

All samples: Solid No. III used
 0.832 M HNO_3
 1.25 M NaNO_3

Sample Number	(H_3PO_4) in moles/liter	Range in values of observed solubility (in milligrams of plutonium/liter)	Average Solubility	
			(in milligrams of plutonium per liter)	(in moles per liter) $\times 10^5$
30	1.21	62. - 68.	65.	27.
31	0.674	14.9 - 15.4	15.2	6.4
32	0.405	6.2 - 6.6	6.4	2.7
33	0.135	2.18 - 2.60	2.40	1.0
34	0.0405	1.90 - 2.06	2.03	0.85
35	0.0135	4.12 - 5.33	4.6	1.9
36	0.0081	5.8 - 7.3	6.7	2.8
37	0.00404	16.1 - 17.3	16.7	7.0

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Table 8

Solubility of Gelatinous $\text{Pu}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ at 25°C.

All samples: Solid Number V used
 $(\text{H}^+) = 0.35 \text{ M}$ (a)

Sample Number	Stoichiometric Concentration		(H_3PO_4) in moles/liter	Range in values of observed solubility (in milligrams of plutonium/liter)(b)	Average solubility	
	(HNO_3)	(H_3PO_4)			(in milligrams of plutonium per liter)	(in moles per liter) $\times 10^5$
38	0.269	1.50	1.42	28.8 - 29.4	28.8	12.0
39	0.301	0.90	0.852	8.06 - 8.17	8.12	3.40
40	0.318	0.60	0.568	3.14 - 3.54	3.32	1.38
41	0.334	0.39	0.284	0.71 - 0.77	0.74	0.31
42	0.342	0.150	0.142	0.34 - 0.42	0.37	0.16

(a) See Appendix for certain details of calculations made with regard to this series of experiments.

(b) In listing the range of observed solubilities some values which varied widely from the average were omitted. These very anomalous results were probably due to difficulties in analysis resulting from the large aliquot necessary to obtain samples of an appreciable counting rate.

from the average. It should be mentioned that these four samples which showed such wide variations were all run early in the course of this experimental work and the sampling and sample mounting technique were not as refined as in later measurements. The fact that we are dealing with a real equilibrium is evidenced by a comparison of the solubilities observed in samples 9 and 10. In sample 10 the equilibrium was approached from the super-saturated side; the solid used in determination No. 10 was then used in sample 9 which was run under essentially the same conditions. The solubilities are observed to check quite well, although it is unfortunate that sample 9 showed such a wide variation in values of the observed solubility. Comparison of samples 22 and 23 run at identical conditions and using solid prepared in the same lot indicates that the values of the solubility obtained with a given solid were quite reproducible. However, comparison of the values of the solubilities observed in the pair of samples 1 and 2, 4 and 5, 7 and 8, 12 and 13, 18 and 19, and 23 and 24 reveals that samples run under identical conditions except for the solid used generally do not agree as well as those run with the same solid. Definite trends are observed in these pairs. From the results of these determinations it may be said that the solubilities of the different solids show this trend:

Solid IV > Solid III > Solid II.

Only Solid IV was analyzed so nothing can be said concerning the composition of the different solids. It is to be noted

that the discrepancies are greater in the samples run at lower phosphoric acid. It must be admitted that the presence of several percent of colloidal Pu(IV) in the various solutions used in the preparation of the various solids is quite possible. What the behavior of a gelatinous plutonium (IV) phosphate containing some colloidal Pu(IV) would be is not known. In the solutions of higher H_3PO_4 concentration, where the Pu(IV) forms quite stable phosphate complexes, one might expect that the colloidal Pu(IV) in the precipitate of $Pu(HPO_4)_2 \cdot xH_2O$ would be more readily converted to the "normal" Pu(IV) than in solutions in which less stable complexes existed. This may be the explanation for there is better agreement between the pairs of analyses run on different solids in higher H_3PO_4 than at low concentrations of H_3PO_4 .

It does appear however that the solid in equilibrium with the various solutions is $Pu(HPO_4)_2 \cdot xH_2O$ and it will be seen that the theory developed on this basis is quite reasonable.

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IV Interpretation of the Solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ in Terms of Complex Ion Formation

Solubility data such as those presented in the preceding section of this paper may be quite readily interpreted in terms of complex ion formation. If one assumes that no species containing more than one Pu(IV) per molecule is formed, the equations for the net reactions occurring in the system under consideration are:

$$m = 0, 1, 2, \dots$$

$$n = 0, 1, 2, \dots, 3m,$$

for which the equilibrium constants are:

$$K_m = \frac{(\text{Pu}(\text{PO}_4)_m \text{H}_n^{+4+n-3m}) (\text{H}_3\text{PO}_4)^{2-m}}{(\text{H}^+)^{n+4-3m}}$$

Since the acidity of the solutions was kept constant throughout each series of measurements, it is convenient to define a new hydrogen ion dependent constant:

$$\begin{aligned} K'_m &= K_m (\text{H}^+)^{n+4-3m} \\ &= (\text{Pu}(\text{PO}_4)_m \text{H}_n^{+4+n-3m}) (\text{H}_3\text{PO}_4)^{2-m} \end{aligned}$$

Thus, it can be shown that if one would plot the logarithm of the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ in solutions of the same acidity against the logarithm of the H_3PO_4 concentration, the relationship between the slope and the number of phosphate groups attached to each plutonium would be given by:

$$\text{Slope} = \sum_m f_m (m-2) \quad 47$$

where f_m is the fraction of the dissolved plutonium present as $\text{Pu}(\text{PO}_4)_{m+1}^{+4+n-3m}$. Thus, if one were dealing with solutions in which but one molecular species was present, the slope of the curve would be 2 less than the number of phosphate groups attached to each plutonium.

The nitrate concentration is the same in all of the experiments run at 2.03 M H^+ and 0.832 M H^+ while it varies slightly in the series run at 0.35 M H^+ .^{*} This variation of the nitrate

* See appendix for certain calculations made in connection with the series of experiments run at $(\text{H}^+) = 0.35\text{M}$.

concentration in the solubility determinations run at 0.35 M H^+ would be undesirable if nitrate was present in any of the molecular species of plutonium (IV) present in these solutions. However, the samples of this series were all in solutions in which the species of plutonium (IV) present was highly complexed (by phosphate). Thus a reasonable assumption would be that the variation of the NO_3^- concentration has no effect on the solubility. In the solutions in which the degree of phosphate complexing of Pu(IV) is lower, nitrate may be present in some of the complexes. This fact does not interfere with the interpretation of the data in terms of phosphate complexes, since the NO_3^- concentration is the same in all of the solubility samples in which nitrate complexing might exist.

A preliminary examination of the data when plotted in the manner described enabled certain conclusions to be drawn.

Among these were:

- 1) There were present in solutions of high phosphoric acid concentration, species involving 4 or 5 phosphate groups per plutonium (IV). The solubility determination made at $(H^+) = 0.35 \text{ M}$ lead to the conclusion that a species involving at least 5 phosphate groups per plutonium (IV) must be present in solutions of high phosphoric acid concentration.
- 2) There was present in solutions of low phosphoric acid concentration the uncomplexed (by phosphate) Pu(IV) .
- 3) The combinations of molecular species:
 - a. Pu^{+4} and $\text{Pu(PO}_4)_4\text{H}_n^{+n-8}$
 - b. Pu^{+4} , $\text{Pu(PO}_4)_2\text{H}_n^{+n-2}$, and $\text{Pu(PO}_4)_4\text{H}_n^{+n-8}$
 could not explain the experimental results as these two combinations of possible species lead to symmetric curves whereas the experimental data are not symmetrically arranged.

With these restrictions placed on the possible combinations of species present and also ignoring the possibility of complexes existing which involve more than one plutonium atom, many calculations of various sets of equilibrium constants were made. The equilibrium constants calculated were of the form:

$$K_m^I = (\text{Pu(PO}_4)_m\text{H}_n^{+4+n-3m}) (\text{H}_3\text{PO}_4)^{2-m}$$

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The solubility may be expressed in terms of these constants:

$$\begin{aligned}\text{Solubility} &= \sum_m (\text{Pu}(\text{PO}_4)_m \text{H}_n^{+4+n-3m}) \\ &= \sum_m K_m' (\text{H}_3\text{PO}_4)^{m-2}\end{aligned}$$

The process of calculation of the constants from the solubility data presented in Tables 6, 7, and 8 involved assuming the presence of certain species. A number of points equal to the number of species assumed to be present were then selected through which the curve was to pass. This led to a set of b (where b was the number of species assumed) simultaneous equations in the b unknowns:

$$K_0', K_1', \dots, K_4' \text{ and/or } K_5'.$$

The b equations were:

$$(\text{Solubility})_1 = \sum_m K_m' (\text{H}_3\text{PO}_4)_1^{m-2}$$

$$\begin{array}{ccc} : & & : \\ : & & : \\ : & & : \end{array}$$

$$(\text{Solubility})_b = \sum_m K_m' (\text{H}_3\text{PO}_4)_b^{m-2} \quad : \text{ the summation, of course,}$$

was taken over the b different values of m . The deviation of this calculated curve from the remaining experimental points was a criterion of how correct an assumption was made regarding the species present.

The combinations:

led to curves which were all too steep on the high phosphoric

acid concentration side of the curve. The combination:

led to a negative value of appreciable magnitude for one of the equilibrium constants and therefore must be ruled out.

The combination:

led to a curve which was not steep enough on the high phosphoric acid concentration side.

The simplest combinations of assumed species which led to a satisfactory agreement between the experimental data of Tables 6 and 7 and a calculated curve were:

In the calculation of equilibrium constants for these two sets of assumed species the value of K'_0 and K'_1 are not determined as uniquely from the experimental data as one might expect. The phosphoric acid concentration in the samples run at low concentrations of phosphoric acid is appreciably affected by the choice one makes for the species which are formed when $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ dissolves. If $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ dissolves to give Pu^{+4} , the H_3PO_4 liberated is 2 times the solubility, while if it dissolves to give $\text{Pu}(\text{PO}_4)_n\text{H}_n^{+n+1}$, one H_3PO_4 molecule is liberated for each $\text{Pu}(\text{PO}_4)_n\text{H}_n^{+n+1}$ in solution. Not all of the experimental points at low phosphoric acid concentration would fall on any one theoretical curve. This fact, coupled with

the fact that a range of possible phosphoric acid concentrations existed for each experimental point depending on the values of K'_0 and K'_1 chosen, led to a wide variation of possible values for K'_0 and K'_1 which would still give fairly good agreement between the experimental points at the two different acidities and the theoretical curves. If one considers the reaction:

$$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O} + 4\text{H} = \text{Pu}^{+4}(\text{in HNO}_3 \text{ solution}) + 2\text{H}_3\text{PO}_4$$

one can see that $K_0 = \frac{(\text{Pu}^{+4})(\text{H}_3\text{PO}_4)^2}{(\text{H}^+)^4} = \frac{K'_0}{(\text{H}^+)^4}$.

Therefore, a 4th power hydrogen ion dependence should be observed for K'_0 . The two different series of experiments were run at an ionic strength of 2.08, the hydrogen ion concentration being 2.08 and 0.832 in the two series. If one assumes the absence of specific ionic effects on activities due to the change in media from a HNO_3 solution to a $\text{HNO}_3 - \text{NaNO}_3$ solution, a 39-fold difference in the values of K'_0 determined at the two acid concentrations should exist. All of the calculated sets of constants (for both assumed combinations of molecular species) led to a higher hydrogen ion dependence than 4th power. This can not be explained on the basis of a partially hydrolyzed $\text{Pu}(\text{IV})$ being the species present in solution, for such a picture would lead to a hydrogen ion dependence less than 4th power.

The sets of equilibrium constants chosen for presentation were picked such that the hydrogen ion dependence of K'_0 was but slightly greater than fourth power. Several sets of constants (assuming the same combinations of species) which would give equally good fits to the experimental points could be presented.

However, considering the scattering of the points as well as the desire to obtain values of K'_0 which do not lead to an impossible hydrogen ion dependence for K'_0 , the constants presented in Table 9 were selected.

Theoretical curves have been calculated on the basis of these constants. They are presented in Figures 2 and 3. The manner in which the species in solution changes as the phosphoric acid concentration is changed is also shown in these two figures. The abscissas of the points at low phosphoric acid concentration were determined by successive approximations using the values of the equilibrium constants given. For points which were found to agree very well with the theoretical curve, this was a very straightforward procedure. However, for points which do not lie on the curve, the abscissa still has a certain amount of uncertainty. This arises from the fact that the equilibrium constants are only valid for points on the curve and therefore should not be used to calculate the species present if the point cannot be brought into agreement with the curve. The values of the phosphoric acid concentration which were calculated for the experimental points at low phosphoric acid concentration using the chosen values of the constants are given in Table 10.

In the experiments run at 0.35 M H^+ the ionic strength was not made 2.08 and therefore these results are not to be compared with the two series in which the ionic strength was 2.08. This series of experiments should be useful, however, in ascertaining the complexing under conditions which would favor the complexes

Table 9

Equilibrium Constants for Various Reactions Involving
 $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ and Different Complex Molecular Species

	Assuming complexes involving 0, 1, 2 and 4 phosphates per plutonium (IV).		Assuming complexes involving 0, 1, 3 and 5 phosphates per plutonium (IV)	
	2.08 M HNO_3	0.832 M HNO_3	2.08 M HNO_3	0.832 M HNO_3
K'_0	3.5×10^{-8}	7.7×10^{-10}	3.0×10^{-8}	6.8×10^{-10}
K'_1	5.0×10^{-6}	1.3×10^{-7}	6.1×10^{-6}	1.7×10^{-7}
K'_2	3.5×10^{-5}	4.6×10^{-6}	0	0
K'_3	0	0	2.4×10^{-4}	5.6×10^{-5}
K'_4	5.0×10^{-4}	1.5×10^{-4}	0	0
K'_5	0	0	2.9×10^{-4}	1.08×10^{-4}

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Figure 2

Solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$

Solid line is theoretical curve assuming Pu^{+4} , $\text{Pu}(\text{PO}_4)\text{H}_n^{+n+1}$, $\text{Pu}(\text{PO}_4)_2\text{H}_n^{+n-2}$ and $\text{Pu}(\text{PO}_4)_3\text{H}_n^{+n-5}$ are species present in solution. 0, I, II and IV in lower figures refer to number of phosphate groups per plutonium (IV) in complexes.

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FIGURE II

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Figure 3

Solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$

Solid line is theoretical curve assuming Pu^{+4} , $\text{Pu}(\text{PO}_4)_2\text{H}_n^{+n+1}$, $\text{Pu}(\text{PO}_4)_3\text{H}_n^{+n-5}$ and $\text{Pu}(\text{PO}_4)_5\text{H}_n^{+n-11}$ are species present in solution. 0, I, III and V in lower figures refer to number of phosphate groups per plutonium (IV) in complexes.

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FIGURE III

Corrected H_3PO_4 Concentration in Samplesat Low H_3PO_4 Concentration

Sample Number	Assuming complexes involving 0, 1, 2 and 4 phosphates per plutonium (IV)			Assuming complexes involving 0, 1, 3 and 5 phosphates per plutonium (IV).		
	Solubility in moles/liter	$(\text{H}_3\text{PO}_4)_0^a$	$(\text{H}_3\text{PO}_4)_f^a$	Solubility in moles/liter	$(\text{H}_3\text{PO}_4)_0^a$	$(\text{H}_3\text{PO}_4)_f^a$
29	3.3×10^{-3}	0	4.8×10^{-3}	3.3×10^{-3}	0	5.1×10^{-3}
28	2.04×10^{-3}	2.68×10^{-3}	5.8×10^{-3}	2.04×10^{-3}	2.7×10^{-3}	5.8×10^{-3}
27	1.42×10^{-3}	5.4×10^{-3}	7.4×10^{-3}	1.42×10^{-3}	5.4×10^{-3}	7.4×10^{-3}
26	1.13×10^{-3}	7.1×10^{-3}	8.7×10^{-3}	1.13×10^{-3}	7.1×10^{-3}	8.7×10^{-3}
25	8.6×10^{-4}	1.20×10^{-2}	1.31×10^{-2}	8.6×10^{-4}	1.20×10^{-2}	1.31×10^{-2}
24	6.8×10^{-4}	1.35×10^{-2}	1.44×10^{-2}	6.8×10^{-4}	1.35×10^{-2}	1.45×10^{-2}
23	5.9×10^{-4}	1.35×10^{-2}	1.42×10^{-2}	5.9×10^{-4}	1.35×10^{-2}	1.43×10^{-2}
22	5.9×10^{-4}	1.35×10^{-2}	1.42×10^{-2}	5.9×10^{-4}	1.35×10^{-2}	1.43×10^{-2}
37	7.0×10^{-5}	4.04×10^{-3}	4.14×10^{-3}	7.0×10^{-5}	4.04×10^{-3}	4.15×10^{-3}

^a $(\text{H}_3\text{PO}_4)_0$ = H_3PO_4 concentration in moles per liter assuming no $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ dissolved.

$(\text{H}_3\text{PO}_4)_f$ = H_3PO_4 concentration in moles per liter corrected for H_3PO_4 formed upon dissolving $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ to give species calculated on the basis of the equilibrium constants given.

involving more phosphates. The experimental data have been graphed in the same fashion as was used with the data at higher acidity. Curves calculated assuming the two different combinations of species are shown. These curves and the experimental points are presented in Figure 4.

In selecting the constants to give the best agreement with the experimental points at the two higher acidities, the points corresponding to samples which were determined more recently were weighted more heavily. This seemed justified for the sampling and mounting techniques were more finely developed and greater precautions were taken to prevent the presence of colloidal Pu(IV) in the solution from which the solids were made. No reasonable explanation can be presented for the disagreement between some of the experimental points and neighboring points. This deviation is larger than the experimental error. The experimental error in these solubility determinations is actually less than 2 to 3 percent, for it arises mainly from errors in direct mounting of the samples and their counting. It is seen upon comparing the agreement of the experimental points with the theoretical curves calculated on the basis of the two assumed combinations of species that the one combination is just about as good as the other. The agreement between the experimental points at high H_3PO_4 concentration in the series at 0.835 M HNO_3 and the curve calculated assuming the species Pu^{+4} , $Pu(PO_4)H_n^{+1+n}$, $Pu(PO_4)_3H_n^{+n-5}$ and $Pu(PO_4)_5H_n^{+n-11}$ is a little better than that calculated assuming the other combination.

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Figure 4

Solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$

Solid line is theoretical curve assuming $\text{Pu}(\text{PO}_4)_3\text{H}_n^{+n-5}$ and $\text{Pu}(\text{PO}_4)_5\text{H}_n^{+n-11}$ are the species in solution while the broken line is based on the assumption that $\text{Pu}(\text{PO}_4)_2\text{H}_n^{+n-2}$ and $\text{Pu}(\text{PO}_4)_4\text{H}_n^{+n-8}$ are in solution.

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FIGURE IV

An examination of the curves shown in Figure 4 also indicates that a better agreement with the experimental data is observed if the combination involving a complex with five phosphates is assumed. However it is seen that neither of the calculated sets of constants gives too good a fit with all of the experimental points. It should be mentioned that if there are present on these higher complexes a nitrate group as well as the phosphate groups, the points at higher H_3PO_4 concentrations should be lowered with respect to those at lower values of H_3PO_4 . This is because of the fact that the nitrate ion concentration is not constant throughout this series at $0.35 \text{ M } H^+$. This would tend to improve the agreement between the experimental points and the curve calculated assuming the set of species: Pu^{+4} , $Pu(PO_4)H_n^{+1+n}$, $Pu(PO_4)_2H_n^{+n-2}$ and $Pu(PO_4)_4H_n^{+n-8}$.

It has been shown that the data can be represented within the experimental error by either of two sets of four species. However, this does not rule out combinations of more than four species. An interpretation which seems more reasonable is that the actual state of affairs involves the existence of all of the species: Pu^{+4} , $Pu(PO_4)H_n^{+n+1}$, $Pu(PO_4)_2H_n^{+n-2}$, $Pu(PO_4)_3H_n^{+n-5}$, $Pu(PO_4)_4H_n^{+n-8}$, and $Pu(PO_4)_5H_n^{+n-11}$. There is certainly no obvious reason why some of the intermediate species should be absent. The fact that the only difference in the two combinations of species is the presence of $Pu(PO_4)_2H_n^{+n-2}$ and $Pu(PO_4)_4H_n^{+n-8}$ in the one set, while $Pu(PO_4)_3H_n^{+n-5}$ and $Pu(PO_4)_5H_n^{+n-11}$ are assumed in the other, indicates that a combination of these constants could

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also explain the experimental points very nicely. This was evident when two different sets of constants which were chosen by merely inspecting the values of the constants for the solubility reactions at 2.08 M HNO_3 given in Table 9 were found to give quite good agreement with the experimental data. There seems to be no reason why numerous other sets of constants which would give equally good agreement with the experimental data could not be calculated. The only difference between these different set of constants would be the importance of $\text{Pu}(\text{PO}_4)_2\text{Hn}^{+n-2}$ and $\text{Pu}(\text{PO}_4)_4\text{Hn}^{+n-8}$ relative to $\text{Pu}(\text{PO}_4)_3\text{Hn}^{+n-5}$ and $\text{Pu}(\text{PO}_4)_5\text{Hn}^{+n-11}$.

It should be noted that the equilibrium constants calculated assuming the simpler "four-species combinations" have the maximum value possible. If one assumes more complicated combinations of species, a given equilibrium constant could not exceed its value calculated on the basis of a smaller number of assumed species.

The hydrogen ion dependence of the various constants (K'_i 's) is of interest. The equations which will concern us are:

As was mentioned previously, the values of the constants were chosen such that K'_0 had approximately a 4th power hydrogen ion dependence. The actual dependence is 4.16 in the case of the combination: K'_0 , K'_1 , K'_2 , and K'_4 while it is 4.13 in the

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case of the combination K_0^0 , K_1^0 , K_3^0 and K_5^0 . The values of the constants given in Table 9 lead to the values for the number of added hydrogen's in the various complexes given in Table 11.

The results of calculations presented in Table 11 indicate that in the complex involving one Pu(IV) and one phosphate, the phosphate has three hydrogen ions attached. These calculations show the complexes involving more phosphates per plutonium (IV) have an average of more than two hydrogen ions per phosphate, which would indicate that some phosphates would have three hydrogen ions. The possibility that H_3PO_4 , as such, would form complexes with a metal atom is not too unreasonable for there is still one oxygen present in H_3PO_4 which is not bonded to hydrogen. However, the manner in which the number of hydrogen ions per phosphate changes as one considers the complexes involving more phosphates is not very reasonable. One would expect that the first H_3PO_4 added to a highly charged positive ion would have its acid strength the most greatly enhanced. Such would not be true if the calculations presented in Table 11 are valid.

Dixon and McLane⁽¹⁸⁾ have determined the sign of the average charge existing on the predominant species of plutonium (IV) present in a solution of 2 M $HClO_4$ and 1.2 M H_3PO_4 . In a transference experiment, they found the plutonium traveled toward the cathode. This would indicate that the species present in such a solution was positively charged. All of the formulas derived from considerations of the solubility data presented here would also correspond to positively charged particles.

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Table 11

The Number of Hydrogen Ions Present in the
Various Complex Molecular Species
Involving Phosphate and Plutonium (IV)

	Assuming complexes involving 0, 1, 2 and 4 phosphates per plutonium (IV)		Assuming complexes involving 0, 1, 3 and 5 phosphates per plutonium (IV)	
	Number of H ⁺ s per complex	Number of H ⁺ s per PO ₄ ⁼	Number of H ⁺ s per complex	Number of H ⁺ s per PO ₄ ⁼
$\text{Pu}(\text{PO}_4)\text{H}_a^{+a+1}$	3.0	3.0	2.9	2.9
$\text{Pu}(\text{PO}_4)_2\text{H}_b^{+b-2}$	4.2	2.1		
$\text{Pu}(\text{PO}_4)_3\text{H}_c^{+c-5}$			6.6	2.2
$\text{Pu}(\text{PO}_4)_4\text{H}_d^{+d-8}$	9.3	2.3		
$\text{Pu}(\text{PO}_4)_5\text{H}_e^{+e-11}$			12.1	2.4

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If the $\text{Pu}(\text{PO}_4)_4\text{H}_n^{+n-8}$ is to be a positively charged ion, n must be greater than 8; a value of 9.3 is observed. If the species $\text{Pu}(\text{PO}_4)_5\text{H}_n^{+n-11}$ is to be a positively charged ion, n must be greater than 11; a value of 12.1 is observed. One or the other of these species would predominate in a solution of the composition: 2 M HClO_4 and 1.2 M H_3PO_4 . In either case, it is to be noted that a positively charged particle is impossible unless some of the phosphate groups attached to Pu(IV) have more than two H^+ s per phosphate group.

The assumption that no change in the ionic effect of the solvent on the activities occurs upon going from a solution of 2.08 M HNO_3 to a solution of 1.25 M NaNO_3 and 0.832 M HNO_3 is not strictly valid even though the ionic strength is maintained constant. The activity coefficient of NaNO_3 is lower than that of HNO_3 . The mean activity coefficient of HNO_3 in 2 M HNO_3 is 0.783 while that of NaNO_3 in 2 M NaNO_3 is 0.48.⁽¹⁹⁾ It has been shown that the activity coefficient of HCl in various salt solutions follows the trend: $\gamma_{\text{HCl}} > \gamma_{\text{HCl}}$ in $\text{LiCl} > \gamma_{\text{HCl}}$ in $\text{NaCl} > \gamma_{\text{HCl}}$ in $\text{KCl} > \gamma_{\text{HCl}}$ in CsCl .⁽²⁰⁾ The activity coefficients of the solutions of the pure salts follow the trend: $\gamma_{\text{LiCl}} > \gamma_{\text{NaCl}} > \gamma_{\text{KCl}} > \gamma_{\text{CsCl}}$.⁽²⁰⁾ The same sort of trend is found for the activity of H_2SO_4 in solutions of various sulfates while the opposite trend is observed for the activity coefficient of the alkali metal hydroxides in halide solutions. Assuming that HNO_3 behaves like HCl and H_2SO_4 , one would say that the activity coefficient of HNO_3 in a solution of HNO_3 and NaNO_3 would be lower than its activity coefficient in a HNO_3 solution. The activity coefficients

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of HNO_3 in solutions of NaNO_3 have not been determined. Thus, in order to make a recalculation of the hydrogen ion dependence of the various reactions:

$$m = 0, 1, 2, \dots\dots\dots$$

making the appropriate corrections of activity changes in going from the one medium to the other, it is necessary to make some very crude approximations. If one examines the activity coefficient of HCl in HCl solutions and in HCl-NaCl solutions⁽²⁰⁾ and compares the change one encounters in going from one system to the other with the change in the solubility of TlCl ⁽²¹⁾ in KCl and HCl solutions, it is apparent that the effect of changing the medium is much more apparent in the variation of the activity coefficient of HCl than in the solubility of TlCl . This would lead one to expect that the activity of HNO_3 would be more appreciably affected than the activity of the nitrate of $\text{Pu}(\text{PO}_4)_m\text{H}_n^{+4+n-3m}$ in changing from a solution of HNO_3 to a solution of HNO_3 plus NaNO_3 of the same ionic strength. Laboring under this assumption, it will be assumed that no change in the activity coefficient of $\text{Pu}(\text{PO}_4)_m\text{H}_n^{+4+n-3m}$ occurs in changing the medium while the activity coefficient of H^+ will be assumed to be equal to the mean activity coefficient of HNO_3 in these solutions. The mean activity coefficient of HNO_3 in 2 M HNO_3 is 0.783 and it is estimated that it is 0.70 in the mixed electrolyte solution. This estimation was made by comparison with the HCl-NaCl system. If such approximations are made, the ratio of the hydrogen ion activities in the two different solutions is 2.8. The use of this figure instead of the concentration ratio

of 2.5 in the recalculation of the results presented in Table 11 leads first of all to a hydrogen ion dependence of K_O' of 3.7 power (this should be 4). The number of hydrogen ions per phosphate is reduced by the use of this activity ratio. The use of the equilibrium constants presented in Table 9 still lead to values greater than two for the number of hydrogen ions per phosphate in the various complex molecular species.

If one calculates a new set of constants adjusting the values of K_O' such that a fourth power hydrogen ion activity dependence exists, one finds that the hydrogen ion activity dependence of the other constants is such that the number of hydrogen ions per phosphate is lowered to a value slightly greater than 2. The trend found, when such calculations were made, is as one would expect. That is, the number of hydrogen ions per phosphate increases as the number of phosphates per Pu(IV) increases.

In conclusion with respect to the hydrogen ion dependence of the various reactions, it may be said that the approximations necessary in making a calculation involving activities are such that one can not be confident of the results and it is certain that the calculations using concentrations are an oversimplification. It appears certain, however, that there are present phosphates on the more highly complexed Pu(IV)'s which have three hydrogen ions attached. This would lead to the conclusion that at least some of the phosphates are coordinated by but a single oxygen with Pu(IV).

It has been the purpose of this research to determine the formulas and stabilities of the various complex species of

plutonium (IV) and phosphate. This has been accomplished using data on the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ in solutions of nitric acid and phosphoric acid. Unique values of the equilibrium constants for the reactions involving the various complex species have not been obtained, however. It has been shown that different sets of assumed species will lead to a good agreement between the experimentally determined solubilities and those calculated on the basis of the equilibrium constants for reactions in which these species take part. Uncertainties in the activity coefficients of hydrogen ion and the complex phosphates of plutonium (IV) make it quite difficult to establish the exact number of hydrogen ions present in the various species. It does appear certain, however, that in the more highly complexed species there are phosphate groups with three hydrogens attached.

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VI. Appendix

If one wishes to interpret solubility data in terms of complex ion formation, it is necessary that the ionic strength and hydrogen ion concentration remain constant throughout each series of measurements. Both the hydrogen ion concentration and the ionic strength will remain constant if the concentration of nitric acid is kept at some relatively high constant value. In the case of measuring the solubilities of phosphates in solutions of nitric and phosphoric acids, the situation changes at lower concentrations of nitric acid. At lower concentrations of nitric acid, the H_3PO_4 present will dissociate appreciably into H^+ and H_2PO_4^- . The degree of dissociation will depend upon the concentration of phosphoric acid and therefore, in a series of solutions of constant nitric acid concentration but varying concentration of phosphoric acid, neither the hydrogen ion concentration nor the ionic strength will remain constant. In the series of measurements run at 2.08M HNO_3 and at 0.832M HNO_3 -1.25M NaNO_3 , the variation in the ionic strength and hydrogen ion concentration is quite small. However, it was desired to run a series of measurements at still lower acidity under which conditions the dissociation of H_3PO_4 makes an appreciable change in the hydrogen ion concentration and the ionic strength.

In a series of solutions of nitric acid and phosphoric acid the concentration of H^+ and the ionic strength (which is numerically equal to the concentration of H^+ which shall be designated by "a") will be constant if:

$$(\text{HNO}_3) = a - \frac{K(\text{H}_3\text{PO}_4)}{a}$$

where K is the first dissociation constant of phosphoric acid. The dissociation constant used in this expression should be one which applies to the solution under consideration and not a value obtained in solutions of very low ionic strength (i.e. solutions of phosphoric acid containing no other acid or salt). Approximate values of the first dissociation constant of phosphoric acid in a medium of ionic strength 0.5 and 0.3 were determined. The determination was made by measuring the pH of H_3PO_4 solutions and $\text{H}_3\text{PO}_4\text{-H}_2\text{PO}_4^-$ buffer solutions in the presence of lithium nitrate. Lithium nitrate was used to furnish the ionic strength as it would be expected to have approximately the same effect on the ionization constant of phosphoric acid as the same concentration of nitric acid would have. It is known that a pH meter will not measure the concentration of hydrogen ion if the solution is of appreciable ionic strength. However, if one assumes that nitric acid is completely dissociated and measures the pH of dilute solutions of nitric acid in lithium nitrate solution, the factor by which the $\log^{-1}(-\text{pH})$ must be multiplied in order to obtain the hydrogen ion concentration, can be determined. This factor is defined by the following equation:

$$(\text{H}^+) = \frac{1}{\gamma_{\text{H}^+}} \log^{-1}(-\text{pH}). \quad (22)$$

The results of the determination of the value of $\gamma^{\pm}$ at two different concentrations of lithium nitrate are presented in Table 12.

Table 12

pH of Solutions of HNO_3 at Different Concentrations of LiNO_3

Solution Composition

Concentration in moles/l

(HNO_3)	($\text{Li}(\text{NO}_3)$)	pH	$\gamma^{\pm}$
9.35×10^{-3}	0.48	1.88	1.41
9.35×10^{-3}	0.32	1.91	1.31

If one assumes that a linear relationship exists between $\gamma^{\pm}$ and μ (the ionic strength) over a short range of values of μ , the equation:

$$\gamma^{\pm} = 1.31 + (\mu - 0.32) \frac{0.10}{0.16}$$

is valid. Using this expression for $\gamma^{\pm}$, the hydrogen ion concentration of various solutions containing H_3PO_4 , H_2PO_4^- and LiNO_3 was determined by measurement of the pH with a Beckman pH meter (Laboratory Model G). From the values of the H^+ concentration determined in this way it was possible to calculate the first dissociation constant for phosphoric acid. The constants calculated in this manner were not in too good agreement nor did they show a noticeable trend with ionic strength. The values varied from 1.5×10^{-2} to 2.1×10^{-2} .

In the preparation of the solutions for use in the series of experiments run at a H^+ concentration of 0.35M, it was assumed

* K. S. Pitzer (J. Am. Chem. Soc. 59, 2365 (1937) chooses a value of 7.5×10^{-3} as the best value for K, at infinite dilution.

that the first dissociation constant of phosphoric acid is 2.0×10^{-2} , this value being a weighted mean of the determined values. Using this value for the constant one can calculate the amounts of phosphoric acid and nitric acid one must use in order to prepare solutions in which the hydrogen ion concentration is 0.35M. Since the value of the dissociation constant is none too certain it is of interest to calculate the variation in the hydrogen ion concentration and the H_3PO_4 concentration if the true equilibrium constant was different from the assumed value of 2.0×10^{-2} . The results of such calculations are presented in Table 13.

Table 13

Concentration of H_3PO_4 and H^+ in Solutions containing
 HNO_3 and H_3PO_4

(Concentration in moles per liter)

Stoichio- metric conc.		$K_1 = 2.0 \times 10^{-2}$		$K_1 = 1.3 \times 10^{-2}$		$K_1 = 3.0 \times 10^{-2}$	
(HNO_3)	(H_3PO_4)	(H^+)	(H_3PO_4)	(H^+)	(H_3PO_4)	(H^+)	(H_3PO_4)
0.269	1.50	0.35	1.42	0.33	1.44	0.38	1.39
0.342	0.150	0.35	0.142	0.35	0.145	0.354	0.138

Thus it is seen from the results of the calculations presented in Table 13 that even if the true value of the equilibrium constant differed from the assumed value by about 50 percent, the hydrogen ion concentration will differ only 6 percent between the two solutions at opposite ends of the phosphoric acid concentration range of the measurements. Similarly the

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difference between the H_3PO_4 concentration calculated assuming $K_1=2.0 \times 10^{-2}$ and the value calculated assuming quite different constants is of the order of 2 percent. Thus in solutions used in the solubility determination at 0.35M H^+ the ionic strength and H^+ concentration are constant but the NO_3^- concentration is not constant. The NO_3^- concentration varies from 0.27 to 0.34 in the series of experiments run.

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