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EXTRACTION OF PLUTONIUM BY HEXONE FROM AQUEOUS SOLUTIONS CONTAINING NITRIC ACID

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by

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Chalk River, Ontario

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ABSTRACT

A general study has been made of the chemistry of plutonium-hexone systems containing nitric acid. The greater part of the work consisted of investigating the extent to which hexone extracted plutonium from aqueous solutions. A study of aqueous Pu(III) solutions in contact with hexone showed that the small amount of plutonium appearing in the hexone phase was in the 4-valent state. The partition coefficients for pure Pu(IV) and Pu(VI) have been determined under a variety of conditions in aqueous-hexone systems containing no salting-out agent, and containing the salts ammonium, zinc, aluminum and uranyl nitrate. A necessary preliminary to these studies was the preparation of plutonium in pure valence states, and the determination of the absorption spectra of these states in aqueous and hexone solutions of different acidities. The decomposition of hexone under the chemical influence of dissolved plutonium was observed and has been investigated in a qualitative manner.

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I: INTRODUCTION

Methyl isobutyl ketone, or hexone, is one of the solvents used for plutonium extraction in the Chalk River chemical extraction plant. At the time the work covered in this report was being considered, work was known to be going on in the U.S. on development of a large scale column process for plutonium extraction using hexone as the only solvent. Because of the interest in hexone in the U.S. and the advantage to the Chalk River plant of having a reasonably complete picture of the chemistry of Pu-hexone systems, a general investigation of this subject was begun.

Plant scale organic solvent extraction processes will, in general, be limited to the use of nitrate solutions, since nitrates are the only inorganic salts of plutonium which extract well into organic solvents. Hence, in the laboratory investigation it was planned to use systems containing nitric acid and to study the effect of various nitrate salts on plutonium extraction. As a preliminary, the extraction properties of hexone for nitric acid were investigated(1), using the same systems (except for plutonium) as planned for the studies with active solutions. Besides yielding necessary data for plutonium experiments, which would be difficult to obtain with the highly active systems, it was felt that the inactive experiments would give information of value in interpretation of results.

Earlier work on the extraction of plutonium with hexone(2,3) suffered from the disadvantage that only tracer amounts of plutonium were available, so that it was not possible to be certain of its valency state. In many cases, also, adsorption effects caused fairly large uncertainties in results. When the present investigation started, plutonium was readily available in macro amounts, and the above problems no longer existed. Thus it was decided to prepare each valence state in as high as possible a degree of purity and investigate its extraction by hexone. In order to check the purity of experimental solutions, a knowledge of the absorption spectra of the pure valence states in aqueous and hexone solutions containing nitric acid was indispensable.

Pu(V) disproportionates fairly rapidly even at low acidity(4). It was intended to work with acidic solutions, in which Pu(V) was, therefore, unlikely to be formed during preparation of other valence states. Also, using prepared Pu(V) solutions (stable at pH 3.5), there would be little point in determining partition coefficients for Pu(V) in acidic media since results would vary with time of shaking*. Accordingly, no attempt was made to prepare Pu(V) or study its spectrum.

II: PREPARATION OF PURE VALENCE STATES

A: General Procedure

Solutions of single valence states in a high degree of purity were prepared under conditions that were known from other data (such as e.m.f. data) to yield products containing amounts of other valence states well below the limit detectable spectrophotometrically (which is about 1%). The spectra of these solutions were first compared, at the proper acidities, with the published spectra(6,7), then were used to obtain spectral data under other conditions of acidity and salt concentration than those given in the literature. Solutions prepared by any other methods could then be checked for purity of valence state by referring to these data.

B: Pu(IV)

Plutonium solutions were received from Isotopes Branch as $Pu(NO_3)_4$

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*A K.A.P.L. report(5) received after this work was completed, gives data for acidic solutions on rates of extraction of total Pu, as Pu(V) disproportionates. It also discloses that hexone extracts very little Pu(V) from aqueous aluminum nitrate solutions in which it is stable (i.e., slightly acid deficient).

with free nitric acid ranging from 3.4 to 6.2 M. Spectrographic analysis showed the presence of a few other elements (such as Fe, Al, and U) in amounts of the order of 0.01 to 0.1% of the Pu and traces of a few others. Silicon varied from 1 to 3% and was the only impurity present in amount $> 0.1\%$.

Spectrophotometric analysis of the plutonium in the solutions showed no detectable[*] Pu(III) or Pu(VI) present. These solutions were therefore used without further treatment for spectrophotometric work and for making up experimental solutions of "pure" Pu(IV). Those in 6 M HNO_3 were so stable to reduction and disproportionation that no change was observed in the spectrum in over a year.

C: PU(VI)

Pu(VI) was prepared by three principal methods which are described below.

1. Oxidation of Pu(IV) with Ag(II)

This method has been described elsewhere$^{(6)}$ and gives very pure Pu(VI). Accurate spectrophotometric determinations were made with this material to obtain reference data.

Amounts of Ag(I) greater than those of plutonium are introduced into the solutions by this method. For extraction studies, it was desired to produce Pu(VI) solutions without introducing foreign ions, so that method 2) was tried.

2. Electro-Oxidation of Pu(IV) at a Platinum Anode

This anodic oxidation was carried out at low current density and in dilute nitric acid solution (0.65 M). Low acidity was considered advisable to ensure that most of the Pu(IV) would be in uncomplexed form[**]. The solution electrolysed contained 8.0 mg. Pu(IV)/ml.

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[*] See previous section and section III, A.

[**] See concluding paragraph of Reference 8.

Oxidation was very slow, indicating a low current efficiency for the process (at least under these conditions). After thirty hours only about 60% of the Pu(IV) had been oxidized. There seems no reason why complete oxidation should not occur in time, but a faster method is desirable for routine preparation of Pu(VI) solutions.

3. Heating Pu(IV) in Dilute Nitric Acid

This method, reported by Kraus(8), proved successful in producing at least 99% Pu(VI) (which is the limit of precision of the spectrophotometric method). Accordingly it was used for preparing Pu(VI) from which experimental solutions were made up. Pu(IV) solutions for treatment were made 0.5 N in nitric acid. Ten to twelve hours heating at 95 - 100°C were required for "complete" oxidation. Solutions were then evaporated until the nitric acid concentration was in the range 2 - 3 M.

Solutions of Pu(VI) left standing in nitric acid of this concentration were found to contain considerable Pu(IV) after a week or ten days. However, if made up to 7 - 8 M by addition of concentrated nitric acid to the cool solution immediately after preparation, only 2 - 3% Pu(IV) formed in 40 days, and it was barely observable after 20 days (slightly greater than 1%).

D: Pu(III)

1. Reduction of Pu(IV) with Hydrogen

Using platinized platinum as a catalyst, Pu(III) had been prepared in $\sim$2 M HNO_3 solution by reducing Pu(IV) in a stream of hydrogen. However, the Pu(III) was rapidly oxidized back to Pu(IV), so that such solutions were useless for extraction studies, and a holding reductant method had to be used for Pu(III) preparation.

2. Holding Reductant Method

Since pure Pu(III) cannot be kept for an appreciable length of time in nitric acid solutions, an excess of some reducing agent stable to nitric acid must be used to hold the plutonium in the reduced state. Pu(III) solutions for experimental work were prepared using two different reducing agents, a) hydroxylamine and b) ferrous sulfamate.

a) Hydroxylamine nitrate 0.7 M was used to reduce 0.08 M Pu(IV) in 1.8 M HNO_3. The spectrum showed no detectable Pu(IV) or Pu(VI).

b) Reduction of 0.04 M Pu(IV) in 1.9 M HNO_3 was carried out using 0.20 M ferrous sulfamate. To simulate reduced cycle plant conditions the solution was made 7.7 M in ammonium nitrate. The equilibrium $[Fe(II)]/[Fe(III)]$ was 0.164/0.04 = 4.1. No data for the potentials of the Fe(II) - Fe(III) and Pu(III) - Pu(IV) couple under these exact conditions were available, but Bunce and Nye have made precise determinations in solutions 8 M in ammonium nitrate and 0.5 M in nitric acid(9). Assuming that the values will not be greatly different under the conditions employed here, the equilibrium $[Pu(III)]:[Pu(IV)]$ should be of the order of 10^3, i.e., Pu(IV) should have been present to the extent of one part in a thousand of Pu(III). Spectrophotometric measurements showed, in fact, no Pu(IV) or Pu(VI).

III: SPECTROPHOTOMETRY

A: Introduction

The spectrophotometer was used first, as explained in section II, A, to obtain spectral reference data for pure valence states of plutonium, and then for analyzing the solutions used in extraction experiments.

The uncertainties involved in spectrophotometric measurements are such that analyses cannot usually be made to closer than ± 1%. With nearly pure valence states, the differences between the spectra of a pure and a 99% pure valence state are, in general, within experimental error. In the case of Pu(VI), however, the sharp absorption band at 834 mμ is so strong that probably 0.5% or less Pu(VI) can be detected in solutions of Pu(III) or Pu(IV).

B: Experimental Details

The spectral data were obtained using a Beckman DU model spectrophotometer with 10 mm. path length corex cells. The lamp, cell holder, and phototube housing were inclosed in the end chamber of a dry box so that samples could be handled without contaminating the laboratory. Measurements were made at 25 ± 1°C. Blank solutions were made up with the same concentrations of all components (except plutonium) as in the unknown.

C: Aqueous Solutions

A good deal of work has been reported on the spectra of aqueous plutonium solutions containing different mineral acids, and on measurement of the proportions of the different valence states present in mixtures of two or more(6,7,10). In order to calculate these proportions, accurate values must be known for the extinction coefficients of the pure valence states at a number of key wave lengths. Kasha(10) gives these key wave lengths and extinction coefficients for weakly acidic solutions, in which the plutonium is essentially uncomplexed.

Due to complexing by nitric acid, marked changes occur in the spectra of the different valence states of Pu (especially the IV and VI) as $[HNO_3]$ increases. Hence, in nitric acid concentrations up to about 4.6 M, extinction coefficients at the key wave lengths continually change in value. Above this normality both the extinction coefficients and the wave lengths which must be used for analytical calculations keep shifting with nitric acid concentration. Thus, in order to analyze a nitric acid solution of plutonium for the various valence states, the spectrum of each valence state in that particular strength of acid must be known.

The main requirement, then, was to obtain as nearly pure valence states as possible from which these "reference" spectra might be determined. The methods employed for obtaining pure valence states have been given in section II under the appropriate headings.

Since Pu(III) was present to only a negligible extent in Pu(IV) stock solutions, and presumably also under the strong oxidizing conditions used in preparing Pu(VI), it was considered that a negligible error would be introduced by omitting to calculate for its presence in Pu(IV) and Pu(VI) solutions in strong acid. Thus spectral data were obtained for Pu(III) only in weak acid solutions (up to 2 M).

D: Hexone Solutions

Very little information was available on the spectra of plutonium in hexone, so a study was made of the spectra of Pu(IV) and Pu(VI) in hexone-nitric acid solutions. These solutions were prepared by extracting the Pu from aqueous solutions of "pure" valence states, under a number of different conditions of acidity, and using different salting-out agents. Pu(III), as will be explained in some detail in section IV, is not extracted to a measurable extent by hexone in systems containing nitric acid.

It appeared that there were slight differences in the positions of the key Pu(IV) peaks and their extinction coefficients at maximum absorption, for different nitric acid concentrations in the hexone phase. However, it was found that the spectra changed slowly with time, especially at the violet end. This was undoubtedly due to reactions involving nitric acid and organic material, since a light pinkish-brown colour was observed in the hexone-nitric acid solutions used as blanks in the spectrophotometer. It proved impossible to find conditions which would yield reproducible results, so further attempts to obtain accurate extinction coefficients for analytical work were abandoned.

The spectra of Pu(IV) and Pu(VI) in hexone are somewhat similar at the violet end, as shown by the typical curves in Fig. 1. However, by running

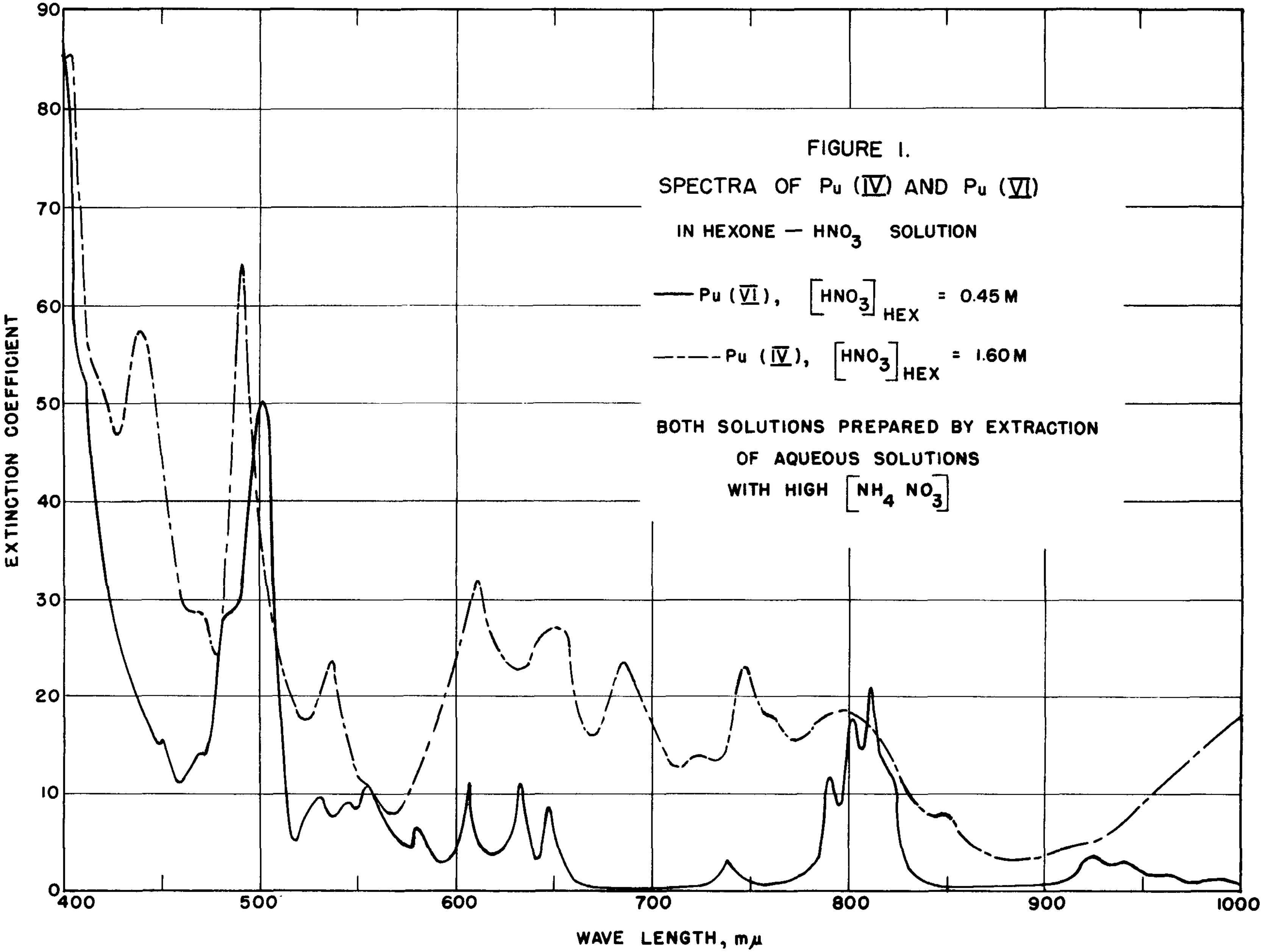

FIGURE 1.

SPECTRA OF Pu ($\overline{\underline{IV}}$) AND Pu ($\overline{\underline{VI}}$)

IN HEXONE — HNO_3 SOLUTION

BOTH SOLUTIONS PREPARED BY EXTRACTION
OF AQUEOUS SOLUTIONS
WITH HIGH $[NH_4NO_3]$

through characteristic portions of the spectrum in other regions (e.g., around 700 mμ), one can easily tell whether or not one of the valence states is in nearly pure form. It was felt that this would probably be all the information required for extraction experiments using initially pure and stable valence states in the aqueous phase.

IV: PARTITION EXPERIMENTS

A: General

The partition of Pu(IV) and Pu(VI) was studied both in the salt-free nitric acid-hexone-water system and in systems containing the same salting-out agents as used in the study of nitric acid partition(1) (ammonium, zinc, aluminum, and uranyl nitrates). Results are expressed in terms of partition coefficients, which are written as

$$K_{Pu} = \frac{[Pu]_{Hexone}}{[Pu]_{aqueous}}$$

Because of the instability of Pu(III) toward oxidation in the presence of nitric acid, it was considered likely that other states besides the 3-valent would be present in the hexone after extraction from a Pu(III) aqueous solution. Then merely analyzing the phases by α-counting would not give true partition coefficients for Pu(III): the proportions of the counts in the hexone due to Pu(III) would have to be known as well.

It was hoped that the proportions of Pu(III) in the hexone could be estimated by means of the spectrophotometer. This proved impossible, since under all experimental conditions used, Pu(IV) was present in very great excess. Thus no precise values could be obtained for $K_{Pu(III)}$ although it was possible to set an upper limit for any given conditions.

B: Experimental

1. Pu(III)

Due to the nature of the results of experiments employing Pu(III), the experimental procedure is probably best given along with the results in a single section. This is done under the heading "Experiments with Pu(III)" (Section IV,C).

2. Pu(IV) and Pu(VI)

For experiments with Pu(IV) and Pu(VI), equal volumes of hexone and aqueous plutonium solutions were shaken for three minutes in 5 ml. centrifuge tubes fitted with ground glass stoppers. Separate experiments showed that equilibrium was reached in that time. After shaking, the mixtures were thoroughly centrifuged before separating phases for analysis and spectrophotometric study. Plutonium concentrations were determined by α-counting, details of which are given in the Appendix. Methods for determination of acidity are also described in the Appendix.

Shell Oil Co. hexone further purified by fractionation(1) was used throughout. The hexone was not "preconditioned" with nitric acid, since all the data for inactive systems had been obtained for the unconditioned solvent. After the first few experiments with no added salt, and throughout the experiments with salting-out agents, the concentration of plutonium in the initial aqueous solutions was kept as close as possible to 2 mg./ml.

C: Experiments with Pu(III)

In order to analyze hexone solutions for Pu(III), the spectrum of Pu(III) in hexone containing nitric acid had to be known. In an effort to determine this, 4 ml. of the Pu(III) solution prepared with hydroxylamine nitrate (see section II,D) were shaken with 2.5 ml. hexone. The separated hexone phase was transferred to a Beckman cell and thence to the spectrophotometer as quickly as possible and the spectrum determined. The hexone had a pale greenish-yellow colour as soon as it was shaken with the aqueous phase and the spectrum showed it to contain Pu(IV) only. The equilibrium aqueous phase still contained Pu(III) only.

Several other experiments carried out with the hydroxylamine-Pu(III) solutions showed that the concentration of Pu(IV) in the hexone was an equilibrium value, independent of shaking time up to a time of one hour. The same conclusions were reached from experiments using Pu(III) solution prepared with ferrous sulfamate as a holding reductant (see section II:D for preparation) and the solvents trigly* and T.B.P.-turpolene** as well as hexone. In all cases only Pu(IV) could be detected in the organic phase.

Thus we have aqueous solutions containing Pu(III) in roughly a thousand-fold excess over Pu(IV), in equilibrium with hexone solutions containing only Pu(IV) or at least a large excess of Pu(IV) over Pu(III). If it is assumed that an upper limit of 1% Pu(III) could be present but undetected in hexone solution of Pu(IV), an upper limit can be set for the values of $K_{Pu(III)}$ in these systems of 10^{-4} to 10^{-5}, depending on acidity and concentration of salting-out agent. (This is opposed to a "total Pu" partition coefficient of 10^{-2} to 10^{-3}.)

The equilibrium concentration of Pu(IV) in the hexone phase increases with increasing acidity and total ionic strength. Thus, to have as little plutonium as possible extracted by hexone under reduced conditions, acidity (and salt concentration, if possible) must be kept low.

D: Pu(IV) and Pu(VI)

1. In the Hexone-Nitric Acid-Water System

a) Effect of Plutonium Concentration on K_{Pu}

The effect of [Pu] on K_{Pu} at constant acidity was determined for both Pu(IV) and Pu(VI) in solutions of moderate acid strength. The results are summarized in Table I.

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*Triglycol dichloride: $CH_2Cl-CH_2-O-CH_2-CH_2-O-CH_2-CH_2Cl$

**30% solution of tributyl phosphate in turpolene.

TABLE I

Effect of [Pu] on K_{Pu}

	Pu (mg/ml)	K_{Pu}
Pu(IV) in 2.6 N HNO_3	0.022	0.43
	0.22	0.46
	1.8	0.525
Pu(VI) in 1.8 N HNO_3	0.01	0.226
	0.1	0.287
	1.0	0.292
	10	0.384

TABLE II

Effect of $[HNO_3]$ on K_{Pu}

	$[HNO_3]_{Hex}$ (moles/l)	K_{Pu}	Orig $[Pu]_{aq}$ (mg/ml)	K_{Pu} corrected to 2 mg Pu/ml
Pu(IV)	0.043	0.00815	6.2	0.0077
	0.059	0.0090	0.8	0.0094
	0.067	0.0146	2.0	
	0.165	0.051	1.8	
	0.20	0.058	1.8	
	0.36	0.175	2.5	
	0.76	0.80	2.0	
	1.30	2.19	4.8	2.1
	1.64	3.38	2.0	
	2.70	4.1	8.0	3.8
	3.7	3.88	1.9	
	3.95	2.58	0.2	2.9
	4.9	1.60	2.0	
Pu(VI)	0.060	0.0366	1.0	0.039
	0.145	0.086	1.7	
	0.29	0.26	1.8	
	0.40	0.292	1.0	0.31
	0.74	0.855	1.8	
	1.62	2.38	1.8	
	2.85	3.16	1.8	
	5.6	1.79	2.0	

The results are not precise enough to yield exact relationships between K_{Pu} and plutonium concentration. The poorness of fit of the experimental points to a reasonable curve is partly due to small differences in acidity between experiments of the same series, caused mainly by inaccurate measurement of the small volumes of hexone and aqueous solution. This lack of precision coupled with the usual errors in preparing sources is quite sufficient to cause the scattering obtained. It is obvious, however, that in this concentration range and under the conditions of acidity used, the values of $K_{Pu(IV)}$ and $K_{Pu(VI)}$ increase with increasing concentration of plutonium.

b) Effect of Nitric Acid Concentration on K_{Pu}

(i) Results: The change in K_{Pu} with change in nitric acid concentration was studied over the range 0.5 to 13.5 M in the original aqueous phase. Initial concentration of plutonium was kept at about 2 mg/ml for most of the experiments. In cases where it was not convenient to use this concentration, the resulting K_{Pu} values were corrected for the effect of plutonium concentration, using the data given in the last subsection. These corrections were at best very rough estimates, since they assumed the same plutonium concentration dependence over the complete range of nitric acid concentrations. However, they were never very large, for in only one case did the concentration differ from 2 mg./ml. by a factor of more than 4.

Table II gives a summary of the results obtained. Values of $[Pu]$ in the original aqueous phase are given for each experiment, together with the corrected values of K_{Pu} where deviations from 2 mg./ml. in $[Pu]$ are significant. The equilibrium concentration of nitric acid in the hexone phase (equil$[HNO_3]_{Hex}$) has been chosen to express the acidity. Although the original nitric acid concentration in the aqueous phase (orig$[HNO_3]_{aq}$) or the equilibrium concentration (equil$[HNO_3]_{aq}$) would do as well in this particular system, they seemed

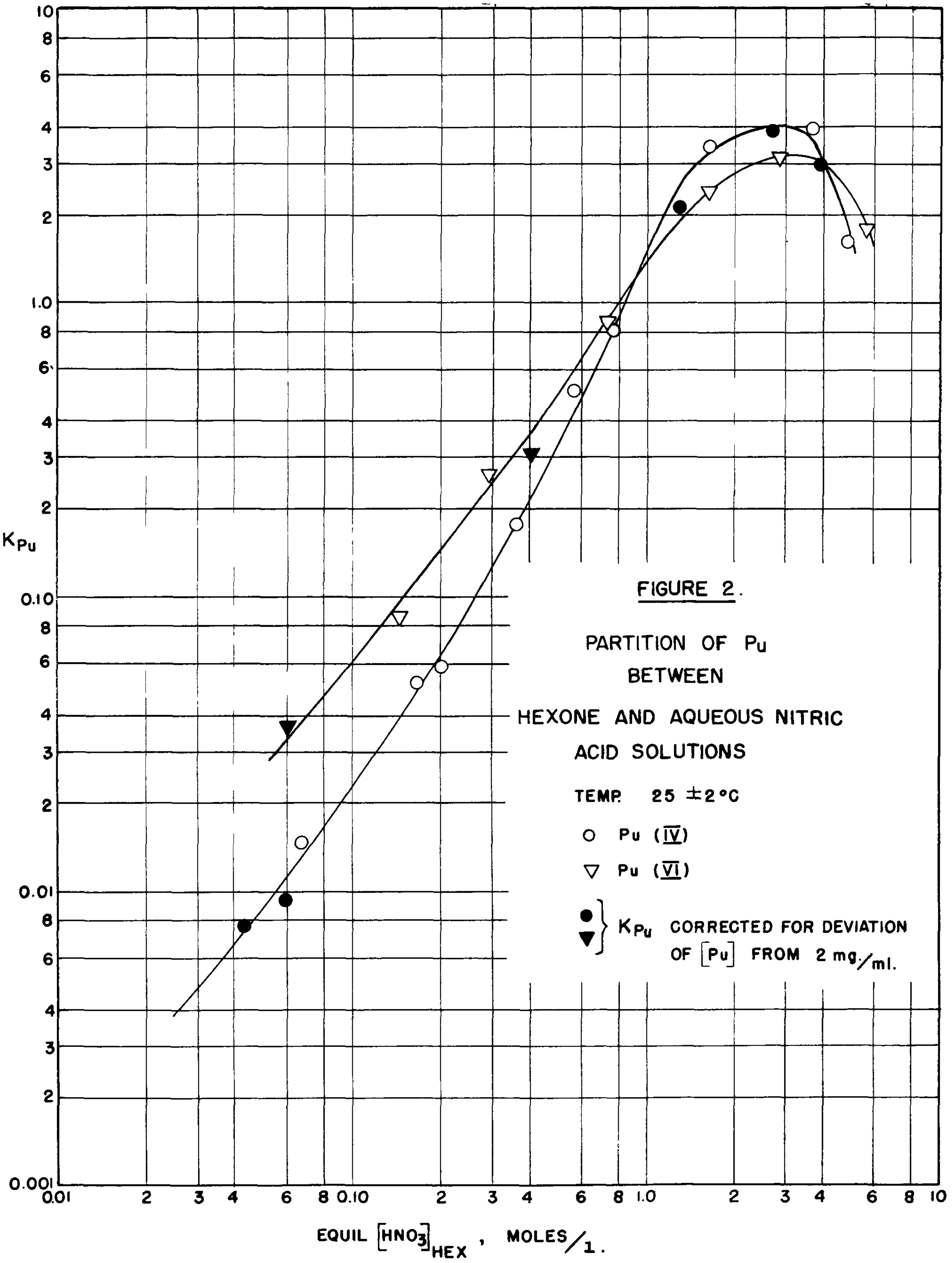

FIGURE 2.

PARTITION OF Pu BETWEEN HEXONE AND AQUEOUS NITRIC ACID SOLUTIONS inappropriate for systems containing salting-out agent. Rather it was felt that aqueous solutions which give the same concentration of nitric acid in the hexone phase after extraction are more comparable from the point of view of acidity than those containing the same concentration initially. No matter which method of expressing acidity is chosen, the overall picture will be the same, but the magnitude of any observed effect will be different for the different methods.

Values of $K_{Pu(IV)}$ and $K_{Pu(VI)}$ are plotted against equil$[HNO_3]_{Hex}$ in Fig. 2. The points shown by the solid circles and triangles are those for which the K_{Pu} values were corrected for plutonium concentration.

The experimental points lie about two slightly curved lines for nitric acid concentrations less than about 1.5 M in the hexone phase, or about 5 M in the original aqueous. These lines cross at a value of equil$[HNO_3]_{Hex}$ of around 0.8 M; above this acidity, Pu(IV) extracts better, below, Pu(VI). The internal consistency is reasonably good. Some of the scatter may be due to the 3 - 4° range of temperature over which the experiments were carried out, but most of it probably arises from the normal errors inherent in micromanipulation during acid determinations and preparation of sources for α-counting.

(ii) Discussion

At a value of equil$[HNO_3]_{Hex}$ of 1.5 - 1.6 M (orig$[HNO_3]_{aq}$ about 5.2 M) a definite change occurs in the trend of the curves from rather steep to gentle slopes. This is the same acidity at which a break occurs in the log-log plot of K_{HNO_3} vs. $[HNO_3]^{(1,11)}$, in the latter case the upper and lower portions of the plot both being straight lines. It is perhaps not surprising that a similar change in the form of the functional relationships should occur at the same nitric acid concentrations in the two cases, although there are no definite breaks and no straight line portions with plutonium as there are with nitric acid alone. This is probably due to the manner in which the degree of complexing of Pu(IV) and Pu(VI) changes with nitric acid concentration, but because of the lack of exact information regarding the nitrate complexes, no definite conclusions can be drawn.

A further change in both $K_{Pu(IV)}$ and $K_{Pu(VI)}$ occurs at a value of equil $[HNO_3]_{Hex}$ between 3 and 4 M. At 4 M nitric acid in the equilibrium hexone phase or 10 M in the original aqueous, the K values have begun to decrease. This decrease appears to be much more rapid for $K_{Pu(IV)}$ than for $K_{Pu(VI)}$, just as the change at 1.5 - 1.6 M was more marked.

It is conceivable that, for each of Pu(IV) and Pu(VI), one or more of the highest nitrate complexes which predominate in the concentrated nitric acid solutions, are less soluble in hexone than are the lower complexes. However, the effect of nitric acid in the hexone phase probably plays a more important role. Thus even if the highest complexes are extracted best by hexone at moderate acidities, at high acidities the solubilities may be considerably decreased due to a salting-out effect of nitric acid in the hexone phase.

An effect of this kind had been observed in the work on extraction properties of hexone for nitric acid(1). It was shown that high concentrations of uranium in the hexone phase had the effect of "salting-back" nitric acid into the aqueous phase, provided the value of K_U (i.e., $[U]_{Hex}/[U]_{aq}$) was sufficiently high. In the case of low concentrations of plutonium, at low acidities when K_{HNO_3} (i.e., $[HNO_3]_{Hex}/[HNO_3]_{aq}$) is low, the nitric acid in the aqueous phase undoubtedly exerts a salting-out effect on the plutonium. However, as the acidity increases, the value of K_{HNO_3} also increases(1). Thus it seems not unlikely that a point of high nitric acid concentration in the hexone phase and high K_{HNO_3} value would be reached where plutonium would begin to be "salted back" from the hexone phase into the aqueous phase. This apparently occurs when the nitric acid concentration in the hexone phase approaches 4 M and $K_{HNO_3} > 0.5$.

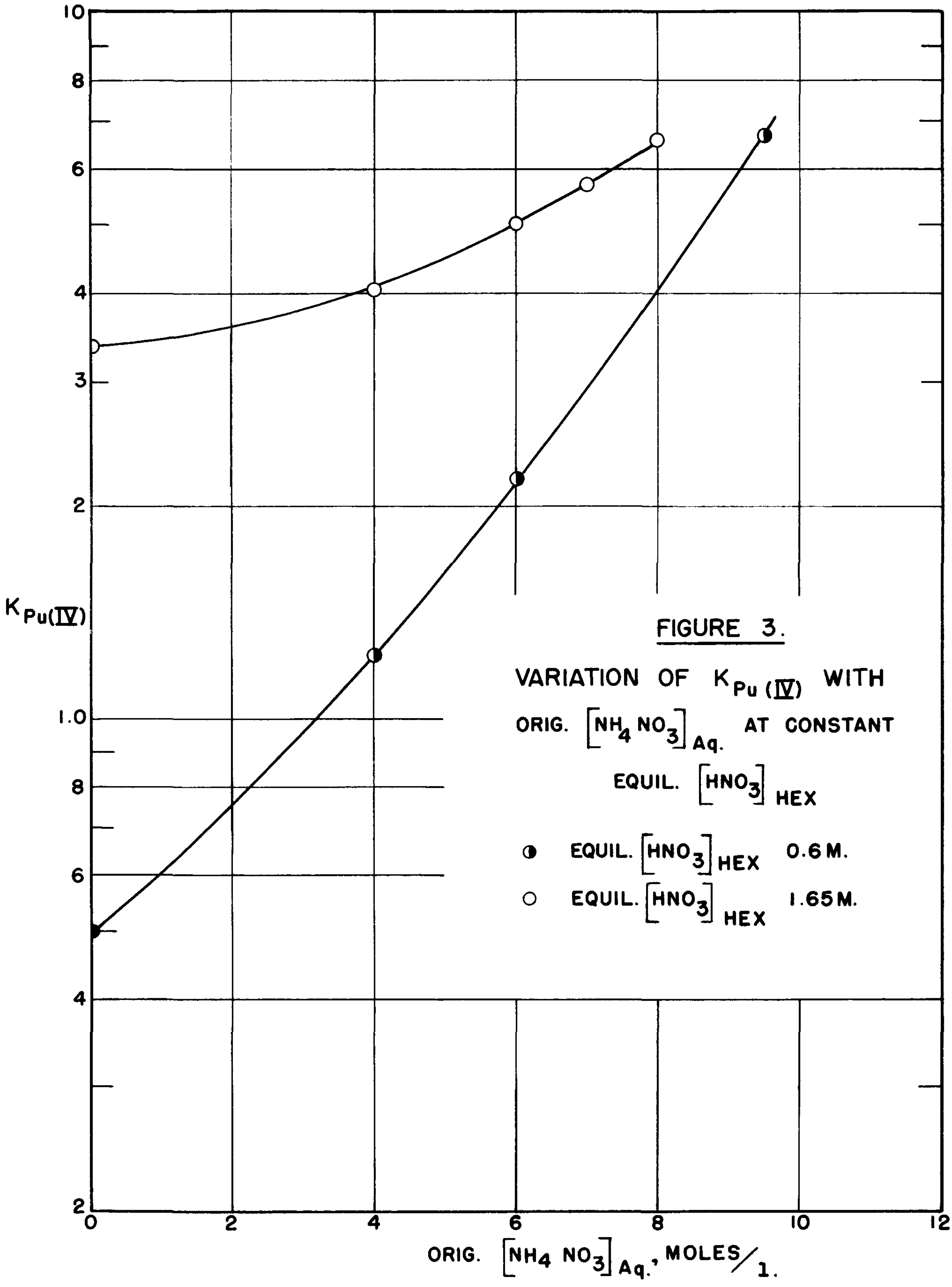

FIGURE 3.

VARIATION OF $K_{Pu(IV)}$ WITH ORIG. $[NH_4NO_3]_{Aq.}$ AT CONSTANT EQUIL. $[HNO_3]_{HEX}$

2. Ammonium Nitrate as Salting-Out Agent

a) Effect of Ammonium Nitrate Concentration on $K_{Pu(IV)}$ at Constant Equil$[HNO_3]_{Hex}$

The change in $K_{Pu(IV)}$ with molarity of ammonium nitrate in the original aqueous phase was investigated at values of equil$[HNO_3]_{Hex}$ of 1.6 and 0.6 M. The initial conditions required to give particular values of equil$[HNO_3]_{Hex}$ were known from the inactive experiments on the extraction of nitric acid by hexone$^{(1)}$. Results of the plutonium experiments are given in Table III, and the values of $K_{Pu(IV)}$ are plotted against initial molarity of ammonium nitrate in Fig. 3.

TABLE III

Variation of K_{Pu} with Orig$[NH_4NO_3]_{aq}$ at Constant Equil$[HNO_3]_{Hex}$

Orig$[NH_4NO_3]_{aq}$ (moles/l)	Orig$[HNO_3]_{aq}$ (moles/l)	Equil$[HNO_3]_{Hex}$ (moles/l)	$K_{Pu(IV)}$
0	5.3	1.64	3.38
4	4.35	1.63	4.06
6	3.8	1.68	5.06
7	3.6	1.61	5.7
8	3.4	1.67	6.6
0	2.80	0.60	0.50
4	1.8	0.64	1.23
6	1.45	0.63	2.20
9.5	1.0	0.57	6.7

$K_{Pu(IV)}$ continuously increases with increase in ammonium nitrate concentration, and hence with ionic strength of the aqueous phase. The rate of increase is much less at higher acidities -- for 1.6 M HNO_3 in the hexone phase, K_{Pu} barely doubles from 0 - 8 M NH_4NO_3, while for 0.6 M HNO_3 the increase is almost ten-fold over the same range of ammonium nitrate concentration. The portions of the graphs above 4 M NH_4NO_3 are very nearly straight lines on the semi-log plot. Below 4 M NH_4NO_3 the graphs become concave to the salt concentration axis. This shows that salting-out of Pu(IV) by low ammonium nitrate concentrations is less efficient in a relative as well as an absolute sense.

b) Effect of Nitric Acid Concentration on K_{Pu} at Near Saturation Concentrations of Ammonium Nitrate

In investigating this effect, conditions of acidity were varied from approximate neutrality to a value of orig$[HNO_3]_{aq}$ of >3 M. The results are given in Table IV, except for experiments in nearly neutral solution. Since both Pu(IV) and Pu(VI) hydrolyze at low acidity, the results of these experiments are not included with the rest, but are given in sections c and d under separate headings.

TABLE IV

Effect of $[HNO_3]$ on the Salting-Out Power of NH_4NO_3 at Near-Saturation Concentrations

	Orig$[HNO_3]_{aq}$ (moles/l)	Orig $[NH_4NO_3]_{aq}$ (moles/l)	Equil$[HNO_3]_{Hex}$ (moles/l)	K_1*	K_2*	K_1/K_2
Pu(IV)	0.19	10.3	0.12	5.5	0.030	183
	0.33	10.2	0.21	6.3	0.080	79
	1.04	9.5	0.57	6.7	0.45	14.9
	3.6	7.0	1.61	5.7	3.10	1.84
Pu(VI)	0.002	10.7	----	2.95	----	----
	0.38	10.4	0.238	12.1	0.175	69.2
	0.59	10.0	0.36	16.0	0.30	53
	1.08	9.5	0.62	17.9	0.67	24.9
	3.1	7.5	1.39	9.1	2.05	4.4
	3.25	8.0	1.57	9.2	2.35	3.9

*K_1 = K_{Pu} for these experiments,

K_2 = K_{Pu} with no NH_4NO_3 and same equil$[HNO_3]_{Hex}$, values taken from smooth curve of Fig. 2.

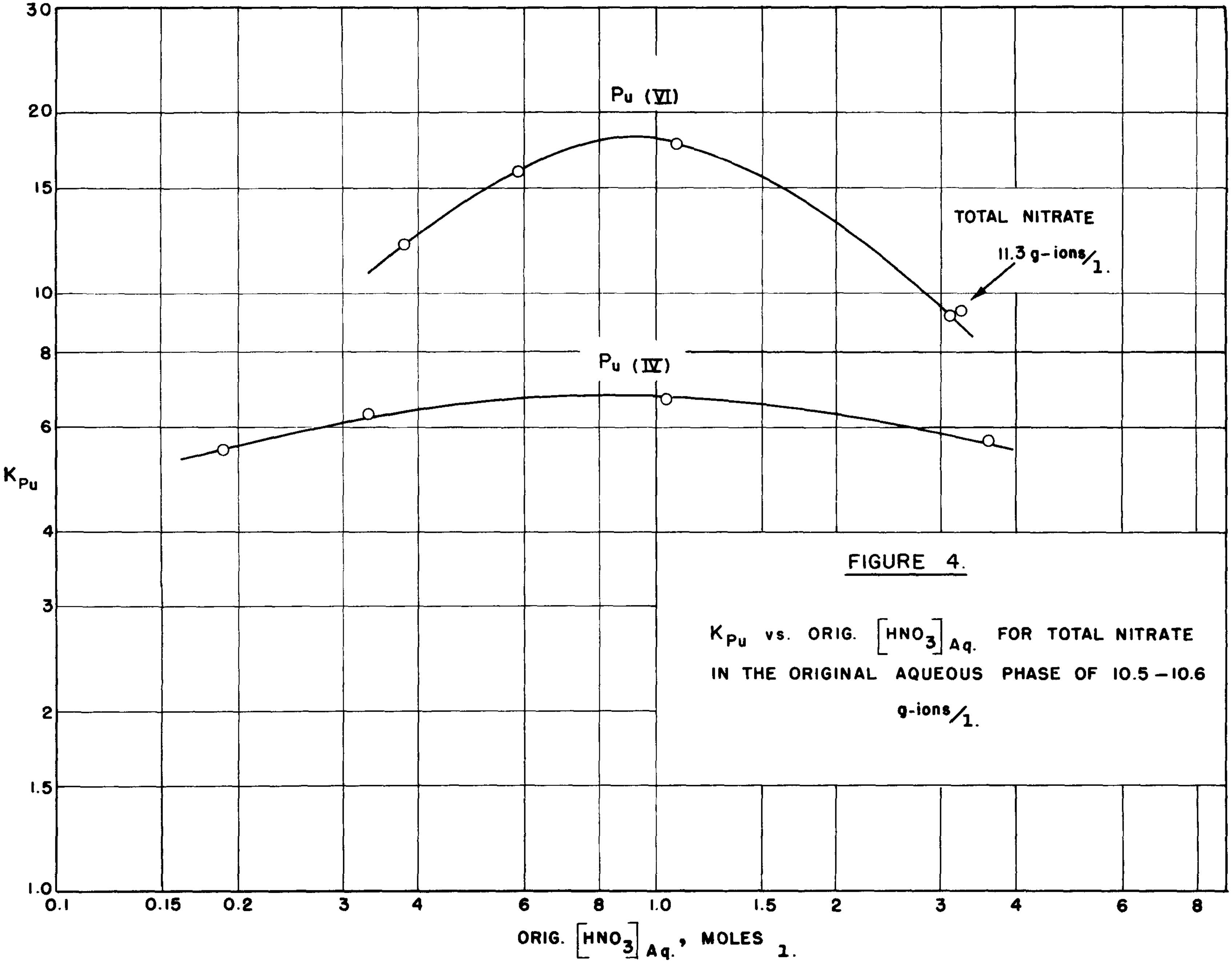

FIGURE 4.

K_{Pu} vs. ORIG. $[HNO_3]_{Aq.}$ FOR TOTAL NITRATE IN THE ORIGINAL AQUEOUS PHASE OF 10.5 – 10.6 g-ions/1.

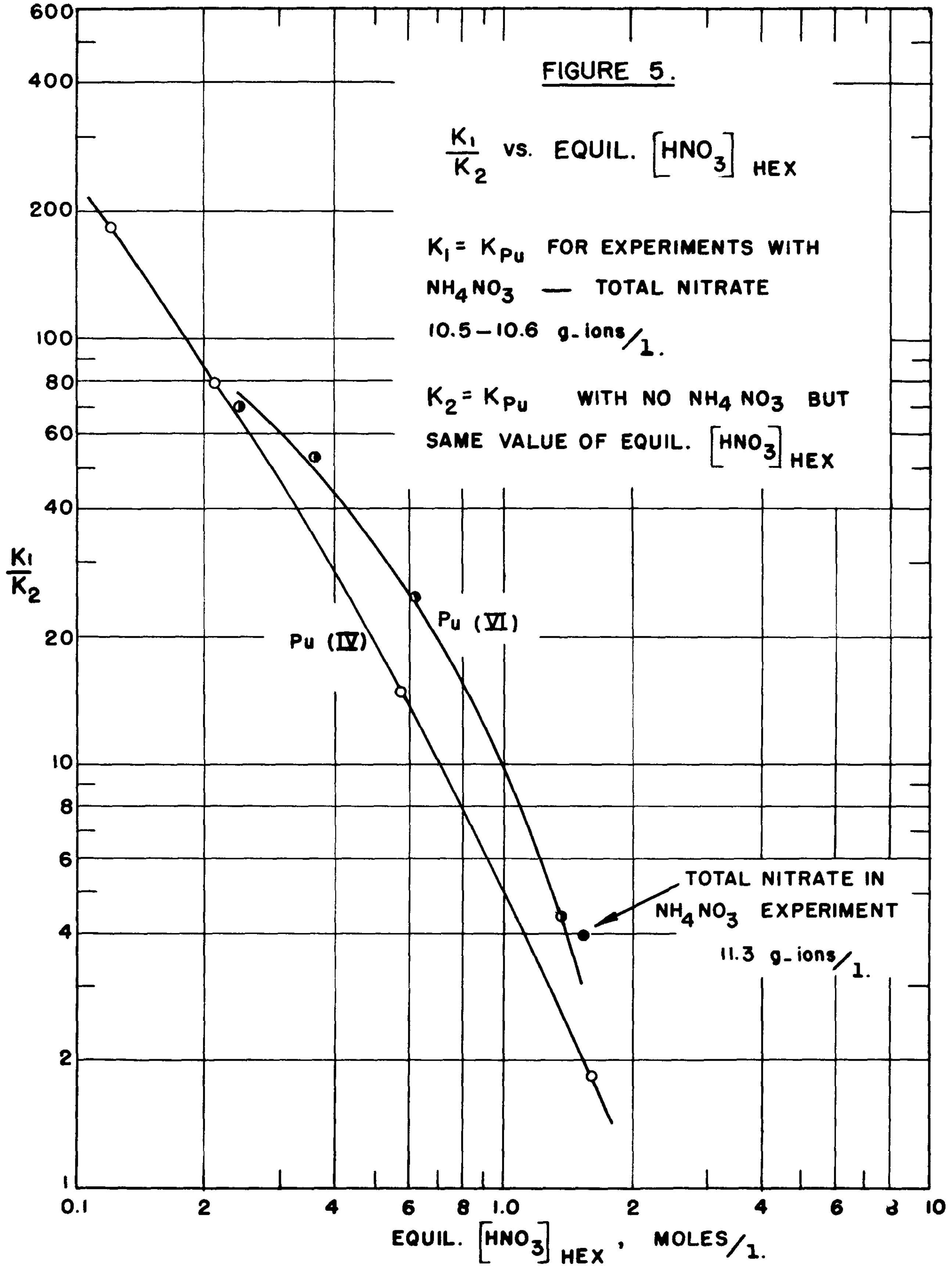
FIGURE 5.
$\frac{K_1}{K_2}$ vs. EQUIL. $[HNO_3]_{HEX}$
$K_1 = K_{Pu}$ FOR EXPERIMENTS WITH NH_4NO_3 — TOTAL NITRATE 10.5–10.6 g-ions/l.
$K_2 = K_{Pu}$ WITH NO NH_4NO_3 BUT SAME VALUE OF EQUIL. $[HNO_3]_{HEX}$
Pu (VI)
Pu (IV)
TOTAL NITRATE IN NH_4NO_3 EXPERIMENT 11.3 g-ions/l.
$\frac{K_1}{K_2}$
600
400
200
100
80
60
40
20
10
8
6
4
2
1
0.1
2
4
6
8
1.0
2
4
6
8
10
EQUIL. $[HNO_3]_{HEX}$, MOLES/l.

Values of K_{Pu} are plotted against orig$[HNO_3]_{aq}$ for constant total nitrate in the initial aqueous phase in Fig. 4. Little change occurs in $K_{Pu(IV)}$ over the range studied, but a definite maximum occurs at aroung 0.9 - 1.0 M HNO_3. Variation of $K_{Pu(VI)}$ is somewhat greater than that of $K_{Pu(IV)}$ with a maximum occurring at approximately the same acidity. In the region of the maximum, $K_{Pu(VI)}$ is roughly three times as great as $K_{Pu(IV)}$, so that Pu(VI) extracts much better under these conditions than does Pu(IV).

The fact that values of K_{Pu} do not change markedly over a considerable range of nitric acid concentration means that ammonium nitrate is much more efficient as a salting-out agent for plutonium at low acidities than at high, since nitric acid alone gives good partitions at the higher acidities. This effect is shown graphically in Fig. 5, where the ratios of K_{Pu} <u>with</u> salting-out agent to K_{Pu} <u>without</u> added salt, but for the same value of equil$[HNO_3]_{Hex}$, are plotted against equil$[HNO_3]_{Hex}$. The values of K_{Pu} with and without ammonium nitrate, and their ratios, are recorded in the last three columns of Table IV. At the higher acidities ($>$ 1.5 M HNO_3 in the hexone) the plutonium partition coefficients with nearly saturated ammonium nitrate solutions are little higher than those without added salt. At 0.2 M HNO_3 in the hexone, however, they are of the order of 100 times higher.

This much greater salting-out efficiency at low acidities is no doubt due to the effect of strong nitrate solutions on complexing of Pu(IV) and Pu(VI). Although the picture of nitrate complex formation is not clear cut(5), it seems certain that at low acidity mainly the lower complexes such as $Pu(NO_3)^{+++}$ are formed and to only a small extent, so that solvent extraction removes little plutonium. However, on making the solution nearly saturated with ammonium nitrate, the very high nitrate ion concentration presumably greatly increases both the degree of complexing and the proportion of higher complexes (such as

$Pu(NO_3)_6^{=}$ and $PuO_2(NO_3)_3^{-}$) formed. Hexone thus extracts plutonium well from this solution, the value of K_{Pu} being around 10 instead of the 10^{-2} to 10^{-1} obtained with no salt.

On the other hand, at moderately high acidities (3 - 4 M) complexing is already extensive, and the proportion of higher complexes quite high(5). Hence addition of ammonium nitrate to give the same total nitrate ion concentration as in the low acid case can not greatly increase the complexing. Thus extraction of plutonium from the strong salt solution is little more efficient than from the salt-free solution at the higher acidities.

It would be expected, though, that K_{Pu} values would increase at least slightly over those obtained at lower acidities, since complexing should be more extensive and could hardly be less. In fact, however, K_{Pu} decreases with increasing acidity (and same total nitrate ion concentration*) above 0.9 - 1.0 M HNO_3 (see Fig. 4). This seems to be due to the relatively high nitric acid concentrations in the hexone phase exerting a "salting-back" effect on the plutonium, in a manner similar to that observed at very high acidities with no salting-out agent. In the latter case (discussed in Section D:1,b) the maximum and subsequent decrease in K_{Pu} did not occur until considerably higher acid concentrations in the hexone phase were reached (roughly 5 - 6 times). However, in the presence of the strong salt solution, the value of K_{HNO_3} at the maximum was about 3 times that in the salt free case. Thus, the extent of "salting-back" appears to depend both on the concentration of "salting-back" agent in the hexone phase and on the ratio of its concentrations in the two phases.

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*Although experimental solutions were made up to have the same total nitrate ion concentration initially, the total nitrate in the equilibrium aqueous phase was also nearly the same throughout. This is a consequence of the increasingly negative ΔV of the aqueous phase on extraction as acidity was increased. Because of it, the loss of acid to the hexone phase was almost compensated for at all acidities by the increase in salt concentration due to the volume decrease.

c) Polymeric Pu(IV)

(i) Formation and Spectrum

On increasing the pH of a Pu(IV) solution nearly saturated with ammonium nitrate to much above 1, the colour deepens and changes to an apple green. Such a solution was prepared by adding concentrated ammonia with stirring to a solution 0.19 M in nitric acid and 10.3 M in ammonium nitrate. A small amount of $Pu(OH)_4$ precipitated locally and did not redissolved. The apple green supernatant which was at pH 2.4 was tested spectrophotometrically and found to be principally Pu(IV) polymer by comparison with Carniglia's spectral data(12) as reproduced by Kasha(10). Pu(IV) monomer was not detectable, nor was Pu(III), but 1.6% Pu(VI) was present, undoubtedly formed from disproportionation of Pu(IV) monomer in the 0.19 M HNO_3 since the latter solution had been prepared several hours before the addition of the ammonia. The high nitrate ion concentration apparently oxidized back to Pu(IV) the Pu(III) formed during disproportionation.

(ii) Extraction with Hexone

The value of K_{Pu} was determined in the usual manner and found to be 0.025 -- i.e., 2.4% of the original plutonium had transferred to the hexone phase. From results obtained with Pu(VI) (Section D:2,b) it is known that most of the 1.6% Pu(VI) originally present would transfer. Thus approximately 1% of some form of Pu(IV) was extracted by the hexone, so that under these conditions* $K_{Pu(IV)} \approx 0.01$.

There is experimental evidence(5) that at pH around 2 in high nitrate solution, unhydrolyzed monomeric Pu(IV), though undetectable, is in equilibrium with the polymer, presumably through several equilibria involving hydrolyzed

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*Since polymeric Pu(IV) is a mixture of high molecular weight hydrolyzed species(5), its properties vary somewhat with the particle structure and particle size distribution, and these in turn with the method of preparation and past history.

monomer. Thus, although it is improbable that the polymeric species are extracted by hexone, the monomer would undoubtedly be extracted until a new equilibrium was attained between monomer in the hexone and aqueous phases, and between monomer and polymer in the aqueous phase. No suggestion of this is made in (5), but it is so similar to the situation obtaining with Pu(III) and Pu(IV) in hexone-aqueous systems containing nitric acid and a holding reductant* that it seems very reasonable.

d) Pu(VI) in Solutions Near Neutrality

Although Pu(IV) is very poorly extracted from ammonium nitrate solutions of pH > 1, Pu(VI) is still extracted reasonably well at pH 3 (see Table IV - $K_{Pu(VI)} = 2.95$ at pH 2.7 in original aqueous solution). When the pH of an aqueous solution (still 10.6 M in ammonium nitrate) is increased to between 3.5 and 4, a deep orange colour appears, indicating a marked change in the species of Pu(VI) predominating in the solution, presumably from the unhydrolyzed to one or more hydrolyzed species. This is undoubtedly the same effect noted by Betts and Harvey(12), who give the spectrum of the orange coloured solution at a somewhat higher pH.

When neutral hexone was shaken with an apparently clear orange "solution" of pH 4.6, a small amount of orange-brown precipitate formed in the aqueous phase. The aqueous supernatant was left yellow instead of orange, and the hexone phase showed the typical colour of Pu(VI) in hexone. The value of K_{Pu} was 0.55, and the pH of the equilibrium aqueous phase about 5. At pH 6, still more precipitate formed, and only 2% of the plutonium went into the hexone phase.

Precipitates formed in solutions of pH > 3.5 that were left standing, the rate being more rapid the higher the pH. Since extraction with neutral

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* See Section IV:C.

hexone increases the pH of the aqueous phase, even though no precipitate was visible before extraction, at/the higher pH resulting from extraction a certain amount of precipitation could easily occur during the time required for the extraction process.

It appears that attainment of equilibrium between the various hydrolyzed Pu(VI) species (of which one or more are insoluble) is a relatively slow process*, the rate varying with pH. Thus even our original aqueous solutions of pH > 3.5 were probably not in true chemical equilibrium. Then extraction with its consequent pH change would presumably alter both the position and rate of attainment of equilibrium. Reaction would be more rapid at the new (higher) pH, but it is not known whether attainment of equilibrium was rapid enough that values obtained for K_{Pu} could be considered true equilibrium values. In any case, those obtained give a good indication of the extent to which Pu(VI) is extracted under these conditions of pH and time of shaking.

Kraus and Nelson(14) have found that "even below pH 7 most of the hydrolysis products of Pu(VI) are polymers of very high molecular weight". It thus seems quite probable that polymer formation occurred in our solutions at pH 3.5 - 4, especially since the sudden change of colour and increased depth of colour suggests a process similar to that occurring in the case of Pu(IV) polymer formation. However, if this is the case, the Pu(VI) polymer in the orange solution is unlike Pu(IV) polymer in two respects:

1) its instability towards formation of insoluble species,

2) its rapid depolymerization on decreasing the pH of the solution.

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*It should be pointed out that the rate of re-formation of unhydrolyzed Pu(VI) on decreasing the pH is very rapid. When the pH of orange solutions with or without precipitate was decreased to 2, any precipitate rapidly dissolved and the solution immediately regained the light amber colour of unhydrolysed Pu(VI).

In any case, extraction properties are very similar in the two cases -- on the acid side of the colour change, plutonium extraction is relatively good, while on the high pH side it is poor.

3. Pu(IV) in Systems with Zinc and Aluminum Nitrates

a) General

Early plutonium extraction studies$^{(2)}$ had shown that for most solvents zinc nitrate was one of the most efficient salting-out agents and that aluminum nitrate in the cases studied had a roughly equal effect. It was of interest, then, to compare the effect of these salts on K_{Pu} with that of ammonium nitrate, expecially since aluminum nitrate is used as the salting-out agent in the U.S. Redox Process.

Rather than make a comprehensive survey as in the case of ammonium nitrate, values of $K_{Pu(IV)}$ were determined for one moderately high acidity and one low.

b) Results and Comparisons with Ammonium Nitrate

Experimental results are recorded in Table V along with K_{Pu} values obtained with ammonium nitrate, and with no added salt. In all experiments of each set the values of equil$[HNO_3]_{Hex}$ were kept approximately the same (1.75 M for the first set, 0.30 M for the second). Values of total nitrate concentration in the original aqueous phase are recorded in Table V. . Although the zinc and aluminum experiments had been designed so that the ionic strengths rather than total nitrate would be the same in each set[✮], values of total nitrate are reasonably close and this property can be taken, along with equil$[HNO_3]_{Hex}$, as the basis for comparison of salting-out efficiencies.

[✮] The salting-out properties of salts whose cations are of different valencies may best be compared, from a thermodynamic viewpoint, using solutions of the same ionic strength. However, there seems to be no advantage in comparing values of empirical properties such as K_{Pu} in this way, and equal values of total nitrate concentration provide an appropriate basis for comparison.

TABLE V

Comparison of Salting-Out Agents at Approximately Constant Values of Equil $[HNO_3]_{Hex}$ and Total Nitrate in the Aqueous Phase

Salting-out agent concentration	Orig $[HNO_3]_{aq}$ (moles/l)	Total nitrate in aqueous phase (gram ions/l)	Equil $[HNO_3]_{Hex}$ (moles/l)	$K_{Pu(IV)}$
none	5.6	----	1.75	3.5*
4 M NH_4NO_3	4.35	8.35	1.63	4.06
1.5 M $Al(NO_3)_3$	2.7	7.2	1.80	37
3.0 M $Zn(NO_3)_2$	2.4	8.4	1.79	55
none	1.75	----	0.30	0.13*
6 M NH_4NO_3	0.75	6.75	0.30	1.3
2 M $Al(NO_3)_3$	0.34	6.34	0.28	13
3.3 M $Zn(NO_3)_2$	0.35	6.95	0.30	12

*Values for K_{Pu} taken from smooth curve of Fig. 2

On this basis, the data of Table V show that zinc and aluminum nitrates are about equally effective in salting-out Pu(IV) from the aqueous phase, and that both are very much better than ammonium nitrate. The same relative effectiveness of these three salts in salting-out nitric acid had been observed in the inactive study(1).

Table V also shows that both zinc and aluminum nitrates, unlike ammonium nitrate, are still very efficient at relatively high acidities. At around 1.7 M HNO_3 in the hexone phase, ammonium nitrate gives a K_{Pu} value little higher than nitric acid alone, whereas both zinc and aluminum nitrates give values over a factor of 10 higher, for the same total nitrate concentration as in the case of the ammonium nitrate.

4. Systems Containing Uranyl Nitrate

a) Nature of Experiments

It had been observed that fairly high concentrations of uranyl nitrate in the equilibrium hexone phase exerted a salting-back effect on nitric acid when $[U]_{Hex}$ was considerably higher than $[U]_{aq}$ (1). Experiments with plutonium present were designed to determine to what extent it was salted out of the hexone phase by uranyl nitrate, and no attempt was made to obtain values of K_{Pu} over a wide range of uranium and nitric acid concentrations.

Difficulty was encountered in analyzing for uranium and nitric acid in the presence of ~ 0.01 M plutonium (both uranium and acid were found in greater amounts after extraction than before). Rather than take up time in developing analytical procedures, initial solutions were made up to contain the same acid, uranium, and salt concentrations as in the inactive experiments with hexone(1). The values for K_{HNO_3}, K_U, etc., obtained in the inactive experiments, were then used for the plutonium experiments, since it was assumed that the low plutonium concentrations employed would exert a negligible effect on the distribution of acid and uranium.

b) Results

(i) No Ammonium Nitrate Present

Two experiments were carried out with no added ammonium nitrate, one with Pu(IV) and one with Pu(VI). In both cases the initial aqueous solutions contained 250 mg. U/ml. and were 1.4 M in nitric acid. Results are recorded in Table VI together with K_{Pu} values for the same acidities (as explained in the footnote to the table) and no uranium.

If the ratio of K_{Pu} with uranium present to K_{Pu} without uranium but at the same acidity is less than 1, the uranium in the hexone phase can be said to salt out some of the plutonium from the hexone back into the aqueous phase. Since the values of K_1/K_2 in Table VI are less than 1, uranium causes "salting-back" of both Pu(IV) and Pu(VI) when the nitric acid concentration in the hexone phase is taken as the measure of acidity.

On the other hand, using the acid concentration in the original aqueous phase as the basis for comparison, K_{Pu} with uranium present (K_1) is higher than K_{Pu} without (K_3). Judged on this basis, the uranyl nitrate in the aqueous phase acts more like a regular salting-out agent, increasing the amount of plutonium transferring to the hexone phase.

TABLE VI

Effect of High Uranyl Nitrate Concentrations on $K_{Pu(IV)}$ and $K_{Pu(VI)}$ in Systems Containing No Other Salt

	Pu(IV)	Pu(VI)
Orig $[HNO_3]_{aq}$ (moles/l)	1.40	1.38
Orig $[U]_{aq}$ (mg/ml)	248	248
Equil $[HNO_3]_{Hex}$ (moles/l)	0.44	0.43
K_U	0.32	0.32
K_1*	0.17	0.28
K_2*	0.26	0.38
K_1/K_2	0.65	0.74
K_3*	0.068	0.14
K_1/K_3	2.5	2.0

*K_1 = K_{Pu} for these experiments
K_2 = K_{Pu} with no uranium and same equil $[HNO_3]_{Hex}$
K_3 = K_{Pu} with no uranium and same orig $[HNO_3]_{aq}$

(ii) With Added Ammonium Nitrate

By adding ammonium nitrate in high concentrations to a hexone-water-nitric acid system containing relatively high concentrations of uranyl nitrate, the values of K_U can easily be increased to considerably > 1. Under these conditions, when $[U]_{Hex}$ is much greater (relative to $[U]_{aq}$) than in the system with no ammonium nitrate, it should be easier to observe any salting-back effect produced by the uranium in the hexone phase.

Experiments were carried out with Pu(IV) only, and it was assumed that the same effect would be observed with Pu(VI). This seems justifiable, since (qualitatively) the same effect was observed for both valence states in the NH_4NO_3-free system (see preceding section, b,i).

Results are given in Table VII, where K_{Pu} values for these experiments (K_1) are compared with K_{Pu} values for the corresponding uranium-free experiments (K_2). Since values of K_1 are considerably less than those of K_2, the uranium exerts a marked salting-back effect on the plutonium.

TABLE VII

Effect of High Uranyl Nitrate Concentration on $K_{Pu(IV)}$ in the Presence of Ammonium Nitrate

	Expt. I	Expt. II
Orig $[HNO_3]_{aq}$ (moles/l)	2.55	2.45
Orig $[NH_4NO_3]_{aq}$ (moles/l)	6	7
Orig $[U]_{aq}$ (mg/ml)	196	196
Equil $[HNO_3]_{Hex}$ (moles/l)	1.125	1.35
K_1*	1.12	1.22
K_2*	3.6	4.4
K_1/K_2	0.31	0.28
K_{HNO_3}/K'_{HNO_3}**	1.04	0.95

*$K_1 = K_{Pu(IV)}$ for these experiments
$K_2 = K_{Pu(IV)}$ with no uranium but otherwise the same conditions of $[NH_4NO_3]$ and $[HNO_3]$.

**K_{HNO_3}/K'_{HNO_3} is the ratio of K_{HNO_3} for these experiments to K_{HNO_3} with no uranium but otherwise the same $[NH_4NO_3]$ and $[HNO_3]$.

c) Discussion

The "corresponding" uranium-free experiments in the case of the system containing ammonium nitrate have very nearly the same acid concentrations as the respective experiments with uranium present, whether judged on the basis of orig$[HNO_3]_{aq}$ or equil$[HNO_3]_{Hex}$. This is because K_{HNO_3} is very nearly the same with these particular concentrations of ammonium nitrate (and nitric acid) whether the uranium is present or not, as is shown by the values of the ratio K_{HNO_3}/K'_{HNO_3} in Table VII.

Thus there is no ambiguity here as to whether K_{Pu} is depressed or increased by adding 200 mg. U/ml. to a given system, depending on how the "acidity" is measured. It is definitely depressed in both experiments, on any basis of expressing the acidity. K_{HNO_3}, on the other hand, is slightly increased in one case.

Thus it is apparent that higher concentrations of uranium in the hexone phase (relative to $[U]_{aq}$) are required to cause salting-back of nitric acid than to cause salting-back of plutonium. It is not surprising that nitric acid distribution responds less readily to fairly high salt concentrations in the organic phase, since it is much less sensitive than $K_{Pu(IV)}$, and especially $K_{Pu(VI)}$, to changes in concentration of salts causing salting-out from the aqueous phase.*

V: CHEMICAL REACTIONS INVOLVING PLUTONIUM AND HEXONE

A: General

During the course of the investigation it was observed that under certain conditions marked changes occurred in hexone solutions containing plutonium and nitric acid. In what follows these changes are referred to as "decomposition" reactions of hexone, since there was evidence that oxidative decomposition to short chain fatty acids did, in fact, occur, although this may not have been the predominant type of reaction. In some cases, also, change of the plutonium valence state was observed without noticeable change in the hexone.

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*For effect of salting-out agents on K_{HNO_3} see CRC-486.

Although a complete explanation of these reactions was beyond the scope of this investigation, a certain amount of information was fairly readily obtained which is of importance in the practical application of hexone extraction to a plutonium separation process.

B: Reactions

1. Pu(III) Oxidation in Aqueous Solutions Saturated with Hexone

Aqueous Pu(III) solutions containing nitric acid are stable as long as a reducing agent such as hydroxylamine is present. However, in the present experiments, when the hydroxylamine solutions had been extracted with, and hence were saturated with, hexone, Pu(IV) formed fairly rapidly after an induction period of several hours.

This behaviour indicates that the hexone caused, either directly or indirectly, oxidation of the hydroxylamine, and that once all the hydroxylamine had been used up, the Pu(III) was oxidized by nitric acid. Evidence has been obtained that Fe(II) slowly reduces hexone to the carbinol(1), so it is quite possible that Pu(III) also reduces hexone, becoming oxidized to Pu(IV) in the process. If this were the case, the Pu(IV) thus formed would be reduced by hydroxylamine as long as any remained, so that the latter would disappear as a result of the hexone being present, whether or not it were oxidized directly by the hexone.

2. Pu(IV) in Hexone Solution

With high enough Pu(IV) concentrations and moderate nitric acid strengths, decomposition occurred to give a yellow solution. This took place quite rapidly in some cases (noticeable decomposition within an hour), and in others not for several months, but the pattern of events seemed always to be the same.

The emerald green colour of the Pu(IV)-hexone solutions changed to a yellow-green, and then a pale brown aqueous phase began to separate out. During this time, effervescence was observed in the hexone when decomposition was rapid enough, and undoubtedly gas was evolved no matter what the rate of decomposition. The gas evolved was probably a mixture similar to that obtained by the U.K. Chemical Research Group(16) from the decomposition of hexone by concentrated nitric acid, i.e., NO_2, NO, CO_2, CO, H_2, etc. A strong rancid odour was noticeable whenever the door on the end compartment of the dry box was opened.

As the volume of aqueous phase increased, its brown colour deepened. During this time the hexone phase became completely yellow, losing all traces of its green colour, as shown by its absorption spectrum in the visible region. This consisted entirely of a broad band beginning in the violet and continuing into the near ultra-violet. No plutonium was therefore detectable spectrophotometrically and the spectrum of the yellow solution was suggestive of a diketone. α-counting at this stage showed that almost all the activity was in the aqueous phase — $[Pu]_{org}/[Pu]_{aq} \approx 10^{-5}$.

Spectrophotometric analysis of the aqueous phase showed that the plutonium was all in the 4-valent state, so that no valence change had occurred during the redistribution. If the aqueous solution was left for a short time longer, almost all the plutonium was thrown out as a brownish-grey to black precipitate. This was soluble in hot concentrated nitric acid to form an emerald green solution of Pu(IV).

The rate of decomposition depends on both the plutonium and the nitric acid concentration. With no plutonium at all, an aqueous phase forms in the case of 5 M nitric acid solution in about a month (at room temperature). At concentrations < 4 M, no aqueous phase appeared in over two months(1). With 0.12 mg. Pu/ml. and 3.9 M HNO_3 it was three weeks before appreciable decomposition was observed, and one week with 4 mg. Pu/ml. and 1.2 M HNO_3. These represent the lower limits of $[Pu]$ and $[HNO_3]$ respectively at which decomposition was observed by means of formation of an aqueous phase in less than a month. Relatively rapid reaction (the most rapid observed) occurred in a solution 3 M in HNO_3 and containing 6.5 mg. Pu/ml. In this case, aqueous phase had begun to separate out within an hour.

3. Pu(VI) Reduction in Hexone

A relatively strong solution of Pu(VI) (100 mg./ml.) in hexone about 1 M in HNO_3 was observed by Aikin(15) to start throwing out an aqueous phase in less than a day. After several more days the process appeared complete, and the aqueous phase contained practically all the plutonium, and all in the 4-valent state. With about one tenth this concentration of Pu(VI) (9 mg./ml.) in a hexone solution 2.8 M in HNO_3, it was observed in the present work that no noticeable hexone decomposition occurred for several weeks. Pu(VI) was slowly reduced to Pu(IV) as evidenced by the typical emerald green colour of Pu(IV) in hexone. At this stage, the Pu(IV) and the nitric acid concentrations were in the appropriate range for decomposition of hexone, and the successive changes associated with this decomposition and outlined in the preceding section occurred over a period of several days.

No other cases of hexone decomposition involving Pu(VI) were observed, since it took such a long time for reduction to Pu(IV) to occur with the plutonium concentrations of 1 - 2 mg./ml. normally used in extraction experiments. Undoubtedly if these solutions had been kept long enough the same sequence of events would have occurred (providing the nitric acid concentration was high enough).

C: Discussion

1. Pu(IV)

The changes occurring in hexone solution of Pu(IV) and nitric acid can not be fully understood until the reaction products and their individual rates of formation under various conditions of plutonium, nitric acid, and possibly water, concentration are known. From the observations made to date, it is possible only to state that a) reactions occur which consume both nitric acid and hexone and leave the Pu unchanged in valence state, b) increase in $[Pu(IV)]$ causes a greater increase in the rate than does a proportionate increase in $[HNO_3]$, and c) increase of rate with $[Pu(IV)]$ is much greater than linear.

The various possible types of reaction occurring have been described for convenience by the single term "decomposition". They probably include a) oxidation of hexone to the diketone, b) oxidative decomposition of hexone or the diketone or both, and possibly c) nitration reactions. (Spence(16), for example, had evidence that nitroparaffins were produced in small amounts by the action of concentrated nitric acid on hexone.)

Whether all the same reactions occur with nitric acid alone can not be stated. Certainly the same general succession of events is observed, but the whole process is very much slower than when Pu(IV) is present. This, together with the fact that the plutonium remains in the 4-valent state throughout, means that Pu(IV) acts as though it were a catalyst for the reaction between hexone and nitric acid. The mechanism may well involve direct reaction between Pu(IV) and hexone, but this would be difficult, if not impossible, to check, since Pu(III) formed by Pu(IV) reduction is unstable in these solutions and would oxidize as fast as formed.

2. Pu(VI)

Since Pu(VI) has a stable reduction product (Pu(IV)) in these solutions, it should be possible to determine whether direct chemical reaction occurs between Pu(VI) and hexone. However, since radiative decomposition of hexone in the presence of nitric acid follows a similar mechanism to the thermal reaction of hexone with nitric acid(16) and, presumably, with Pu(VI) in the presence of nitric acid, it will be very difficult to distinguish between the three. Careful rate studies and accurate analyses of reaction products would be essential, and both were beyond the scope of this work.

Although the method of reduction of Pu(VI) could not be determined, the reaction was observed to be very slow and to produce too small an amount of hexone decomposition products to be easily detectable. However, once a large enough concentration of Pu(IV) had built up, rapid reaction set in leading to relatively large amounts of decomposition products and the usual sequence of changes observed in Pu(IV)-nitric acid-hexone systems.

Plutonium in the hexavalent state has, therefore, small chemical effect on hexone, compared with Pu(IV). When dealing with Pu(VI)-hexone solutions, it is only at very high plutonium concentrations that rapid breakdown of hexone occurs (e.g., the 100 mg./ml. solution prepared by Aikin(15)) and that mainly due to Pu(IV) formed from the "self-reduction" of Pu(VI).

3. Chemical Effects of α-Radiation

At the plutonium concentrations used in the present experiments, the rate of decomposition of hexone by α-radiation could be at most in the range 0.01 - 0.1% per week, assuming negligible contribution from free radical chain reactions. This maximum value considers that the complete α-energy goes into breaking C-C bonds and that breaking only one C-C bond in each hexone molecule constitutes decomposition.

Assuming the mechanism is similar to that involved in decomposition of hexone due to β- and γ-radiation(16), the actual extent of the α-induced decomposition should be considerably lower than the value given above. Thus the observed decomposition in the case of Pu(IV)-hexone solutions -- often causing formation of an aqueous phase in a day or less -- was many times more rapid than can be accounted for by the effect of α-radiation.

VI: CONCLUSIONS

A: Theoretical Point of View

Theoretically, it should be possible to estimate fairly closely the extent of extraction by hexone of the 4- and 6-valent states of plutonium from any given aqueous nitric acid solution from a knowledge of two things:
(i) the extent of nitrate complexing in the particular aqueous solution,
(ii) the relative salting-out power of any added metal nitrate.

If an added salt is soluble in the hexone phase (as is uranyl nitrate) its salting-out power in the organic phase as well as the aqueous must be considered. It is worth noting that nitric acid also must be regarded as a salting-out agent in both phases, since at high nitric acid concentrations in the hexone phase, the values of K_{Pu} begin to decrease noticeably. This indicates that nitric acid exerts a rather large effect in "salting-back" plutonium from the organic phase, despite the presence of relatively high salt concentrations in the aqueous phase.

Measurements of absorption spectra seem not to be capable by themselves of giving quantitative values for the extent of complexing. However, they give good qualitative information, and allow comparison of <u>relative</u> amounts of complexing.

The relative efficiencies of various metal nitrates for salting <u>plutonium</u> out of aqueous nitric acid solution seem to be the same as those for salting out <u>nitric acid</u> itself. Thus the efficiency of a given nitrate for salting out plutonium can be estimated without having to use active material.

B: Practical Considerations

In order to make a decision regarding the use of hexone for a large scale plutonium extraction process, it is necessary to assess many factors not considered here, such as fission product and uranium decontamination, solvent recovery, cost of chemicals, and whether "waste" solutions can be recycled or must be disposed of. In this report the factors considered are the extraction properties of hexone for the various valence states of plutonium (both monomeric and polymeric), and the stability of hexone in the presence of nitric acid and plutonium.

Hexone is well suited to a "redox" process, since values of K_{Pu} under reduced conditions are of the order of 10^{-2} to 10^{-3} while under oxidizing conditions (plutonium in the 6-valent state), K_{Pu} values of 10 or more can easily be achieved at relatively low acidities with ammonium nitrate, and considerably higher with more efficient salting-out agents such as zinc and aluminum nitrates.

Pu(IV) is not extracted quite as well as Pu(VI) under most conditions, and hardly at all from neutral or slightly acid deficient solutions from which Pu(VI) extracts reasonably well.

While the decomposition of hexone under the influence of plutonium and nitric acid is a definite disadvantage, it must be borne in mind that rather high acidities, and also very high plutonium concentrations in the case of the 6-valent state, are required before the rate of decomposition becomes appreciable. Under normal operating conditions, therefore, the decomposition due to plutonium could be kept negligible.

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APPENDIX

METHODS OF ANALYSIS

A: Determination of Plutonium

1. General

Plutonium analysis was carried out entirely by α-counting. A standard procedure for preparation of sources was worked out for each type of experimental solution so that, using known concentrations of plutonium, results could be reproduced within 1% of the true values for most of the solutions. For one or two of the most difficult solutions to handle, a somewhat larger spread in results (usually on the low side of the correct value) had to be accepted. The procedure involved use of the same 2-µl. automatic pipette for all sources prepared during a given experiment. This eliminated constant errors due to possible inaccuracy of calibration. At least two sources were prepared from each solution to be analyzed.

After each source was prepared, the micropipette was cleaned with concentrated nitric acid, rinsed with water, then acetone, and dried, before being used for the next sample. All pipettes, shaking tubes, volumetric flasks and other pieces of apparatus used in the experiments were cleaned in the above manner inside the dry box. This practice avoided spread of α-contamination in the laboratory and also prevented chemical contamination of the glassware by detergents used in the normal laboratory cleaning procedure.

The 2-µl. sample size was chosen because it was the largest amount of hexone solution which could be conveniently laid down on source trays to give accurate analyses. Having chosen the sample size, the standard plutonium concentration for the initial aqueous solution was chosen as 2 mg./ml. 2-µl. samples of higher concentrations gave counting rates with unduly high coincidence corrections in the 50% geometry proportional counter used for this work.

Coincidence corrections were calculated from the experimentally determined resolving time of the counter (14 µsec.).

2. Specific Cases

a) Ammonium Nitrate Solutions

Direct pipetting was employed, and very thin sources could be prepared by decomposing the ammonium nitrate and driving off its volatile decomposition products. Careful heating of the source tray permitted these volatile products to come off with entrainment of negligible amounts of plutonium.

b) Zinc, Aluminum, and Uranyl Nitrate Solutions

Sources prepared by direct pipetting gave slightly low counting rates because of absorption by the uranium and light metal oxides. The extent of this absorption was determined by using a series of sample sizes, and checked by the LaF_3 procedure in the case of the zinc and uranyl nitrate solutions. In the later uranyl nitrate experiments the solutions were diluted five-fold to allow preparation of sources from 2-ul. samples with megligible error due to absorption by uranium. In all the uranium experiments the α-count due to uranium was of the order of 0.1% of the plutonium count and was neglected.

B: Determinations of Acidity

Titrations were carried out with a Gilmont ultramicroburette of 100 ul. capacity using 0.4 N NaOH solution and a suitable indicator. 1-ml. beakers were used for aqueous phase titrations. Hexone phase samples were diluted with distilled water to 2 - 4 ml. in a 5 ml. beaker to ensure a single phase for titration.

A correction had to be applied for the amount of plutonium in solution. For Pu(IV) this correction was taken as 4 moles NaOH per mole Pu regardless of indicator used. For Pu(VI) the correction using methyl red was taken as 2 moles NaOH per mole Pu, and using phenol-phthalein as 3 moles NaOH per mole Pu. These last values were used on the basis of results obtained by Kraus and Dam(17) for titration of Pu(VI) with NaOH. The true values are probably closer to 2.5 and 3.5 respectively, but any error introduced into the acidity by using the integral values would have been small in all cases and negligibly so in most.

Measurement of pH in the aqueous solutions of very low acidity (pH ≥ 2) was carried out with a Beckman pH meter, Model G.