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**THE EXTRACTION MECHANISM OF
PLUTONIUM (IV) TTA CHELATE IN
SEC-BUTYLBENZENE-NITRIC
ACID-URANYL NITRATE MIXTURES**

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July 30, 1952

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ABSTRACT

The rate of extraction of plutonium(IV) in the sec-butylbenzene-thenoyltrifluoroacetone (TTA)-nitric acid system, both with and without uranyl nitrate, has been found to be limited by the rate of transfer of plutonium(IV) across the organic-aqueous boundary layer. The main species of plutonium(IV) which transfer appear to be PuK^{+3} and PuK_2^{++} or these ions complexed with nitrate ions, the neutral molecules $\text{PuK}(\text{NO}_3)_3$ and $\text{PuK}_2(\text{NO}_3)_2$ being the probable transferring species. In these formulas K represents the chelating part of the TTA molecule.

The activation energy, ΔH_g , for the rate of transfer of plutonium(IV) from an aqueous phase consisting of 2.02 M uranyl nitrate and 0.474 M nitric acid into a solution of TTA in sec-butylbenzene is 10,000 calories per mole, while the activation energy for the rate of the reverse transfer, ΔH_h , is 13,000 calories per mole. The heat of extraction, ΔH_e , is roughly -3,000 calories per mole.

The equilibrium extraction coefficients of plutonium(IV), E_m equals total plutonium concentration in the organic phase divided by the total

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plutonium concentration in the aqueous phase, have been measured as a function of TTA, hydrogen ion, and uranyl nitrate concentrations. These data indicate:

1. That at 0.5 M nitrate ion concentration the main species of plutonium(IV) in the aqueous and organic phases are $\text{Pu(IV)(NO}_3)_n^{+(4-n)}$ and PuK_4 , respectively.

and

2. That at 4.9 M nitrate ion concentration partially nitrated species such as PuK_3NO_3 , as well as PuK_4 , exist in appreciable amounts in the organic phase.

The extraction of plutonium chelate from the sec-butylbenzene phase into an aqueous phase in the presence of various reducing agents was also studied.

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INTRODUCTION

Plutonium may be separated from other metal ions by a selective liquid-liquid extraction of the organo-metallic complexes formed from the reaction of thenoyltrifluoroacetone (TTA) and metallic ions. Selective extraction of plutonium from other ions is obtained by varying the TTA and nitric acid concentrations since the equilibrium constants

$$K_M = \frac{[MK_n]_{org} [H^+]_{aq}}{[M^{+n}]_{aq} [HK]_{org}^n} \quad (1)$$

for the metallic chelates in the organic-water two phase system vary over an extremely wide range.¹

In Equation (1), MK_n represents the metallic chelate; M^{+n} , the metallic ion with a charge of $+n$; H^+ , hydrogen ion; and HK , thenoyltrifluoroacetone. Brackets indicate concentration units of moles per liter of benzene or water. Subscripts org and aq indicate that the major portion of the species is in the benzene and aqueous phases, respectively.

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If the metallic ion is complexed by an anion, A^- , in the aqueous phase, K_M will be a function of that anion since the concentration of M^{+n} will be changed by the reaction

where m is the number of anions involved in the reaction.

In studying the mechanism of the extraction of plutonium(IV) from a benzene-TTA solution into 0.5 M nitric acid and also into 0.5 M hydrochloric acid, Thomas and Crandall² observed that under certain conditions the transfer of plutonium from the benzene into the aqueous phase is slow, and they attempted to determine the mechanism of the transfer. If the slow step in the extraction of plutonium is a chemical reaction in either phase, the rate of transfer of plutonium from one phase to the other will be independent of the shaking speed. If the slow step in the extraction is the interphase transfer of plutonium across the benzene-aqueous boundary layer, the rate of this transfer will vary with the shaking speed and the solvent. The term aqueous-benzene boundary layer is used to indicate concentration gradients which may exist near the interface as well as the interface itself.

Using small flasks with motor driven stirrers, Thomas and Crandall found that the rates of extraction of plutonium(IV) in this system were independent of the motor stirring speed although the rates increased a factor of two or three when they changed from glass to stainless steel equipment. They determined the TTA, hydrogen ion, ferrous ion, and plutonium concentration dependences, as well as the volume ratio dependence, of the rate of extraction of plutonium(IV) from benzene into a 0.5 M hydrochloric acid aqueous phase. In these experiments plutonium(IV) was

prevented from extracting back into the benzene phase by reducing it to plutonium(III) as it entered the aqueous phase. The experimental rate law was found to be

$$-\frac{d[P]_{\text{org}}}{dt} = \frac{k_2[P]_{\text{org}}[H^+]_{\text{aq}}^2}{R[HK]_{\text{org}}^2} \quad (3)$$

where $[P]_{\text{org}}$ is the total concentration of plutonium(IV) in the organic phase, $[HK]_{\text{org}}$ is the TTA concentration in the organic phase, $[H^+]_{\text{aq}}$ is the hydrogen ion concentration in the aqueous phase, R is the ratio of the volume of benzene to that of water, and k_2 is the back extraction rate constant with the dimensions of (liters of water)(liters of benzene) $^{-1}(\text{min})^{-1}$. (The terms and definitions used in this report are summarized in the Definition of Terms at the end of the report.)

From this rate law and the fact that they found no change of the reaction rate with the stirring speed, they concluded that the slow step in the extraction of plutonium(IV) is the removal or addition of the second chelate group from the plutonium in the aqueous phase

and that all other steps including the transfer of the plutonium from one phase to the other are fast compared to this step.

The seven experiments which they reported for the system benzene-TTA-0.5 M nitric acid at four different volume ratios and three different TTA concentrations conformed to this rate law so it was concluded that the mechanism was the same in nitric acid as in the hydrochloric acid

system. In the nitric acid system the rate of extraction of plutonium(IV) from the organic to the aqueous phase was increased if either urea or hydroxylamine was added to the reaction mixture to stabilize ferrous ion.²

By combining the equilibrium constant for the extraction of plutonium(IV) at 0.5 M acid with the organic to aqueous extraction rate law, Thomas and Crandall were able to calculate the rate of the aqueous to organic extraction as equilibrium is approached. Their experimental rates agreed with their calculated rates within experimental error for both hydrochloric and nitric acids. This seemed to be further proof that the rate of the extraction of plutonium(IV) in the system benzene-TTA-0.5 M acid is limited by the slow chemical step shown in Equation (4).

Later, Rubin and Hicks³ investigated the system benzene-TTA-nitric acid using equipment similar to that used by Thomas and Crandall and found that the extraction rate varied with the stirring speed. They concluded that the rate limiting step in this extraction is the transfer of some form of PuK_2^{++} across the benzene-water boundary layer, since this process would satisfy the experimental rate law found at a constant stirring speed by Thomas and Crandall, and would also explain the variation of the extraction rate with the stirring speed.

This work was undertaken to clarify the mechanism by which plutonium is extracted in the system benzene-TTA-nitric acid and to determine whether the rate of this process is limited by a slow chemical step in either phase or by the interphase transfer of the plutonium across the benzene-aqueous boundary layer.

For the experiments in this report benzene was replaced by sec-butylbenzene and the 0.5 M nitric acid phase used by previous workers was

replaced in many experiments by an aqueous phase consisting of 0.474 M nitric acid and 2.02 M uranyl nitrate. It was felt that the change in solvents would not change the results significantly since the equilibrium distribution of plutonium is essentially unchanged when sec-butylbenzene is substituted for the benzene (Table V). The addition of uranyl nitrate to the system with the resultant increase in the nitrate ion concentration considerably decreased the K_M value for plutonium(IV) due to the complexing of this ion by nitrate ions in the aqueous phase. The large change in the activity of the solution would also be expected to change K_M .

EXPERIMENTAL PROCEDURE

The experiments were carried out in glass stoppered test tubes which were shaken on a mechanical shaker either in air at room temperature or in a constant temperature bath. The shaker speed was varied by changing the size of the pulley attached to the motor and the shaking speed is specified in the text by the RPM of the wheel attached directly to the shaker. Speeds designated as 450, 790, and 870 RPM were obtained with one shaker and that marked 225 with another having a different length shaker arm so that the latter speed is not one half of the 450 RPM speed. The maximum and minimum room temperatures recorded for each run in air are given with the data for the experiment.

In a typical experiment two milliliters of the organic phase and one milliliter of the aqueous phase were shaken together. When a reducing agent was present, all of the plutonium was initially in the organic phase; otherwise it was in the aqueous phase.

At given time intervals the tubes were removed from the shaker and centrifuged before samples were taken. One hundred microliter samples of the organic phase and fifty microliter samples of the aqueous phase were removed for analysis so as to maintain a constant volume ratio. It was assumed that any reaction taking place when shaking was stopped could be neglected. In one extraction from the organic phase the concentration of the plutonium chelate in that phase changed less than one percent while standing one hour without shaking.

The samples removed from the organic phase were mounted on glass microscope slides and the aqueous samples were similarly mounted if no uranyl nitrate was present. In the presence of uranyl nitrate the amount of plutonium(IV) in the aqueous phase was determined by the Lanthanum Fluoride Technique.⁴ Plutonium was used in trace amounts, about 20,000 c/m/ml of reaction mixture or about 4×10^{-6} M, and was added in the +4 oxidation state from a stock solution. The $\text{Pu}^{239}(\text{NO}_3)_4$ stock was prepared by reducing plutonium nitrate of unknown valence to the +3 oxidation state with hydroxylamine hydrochloride, precipitating the hydroxide, and then dissolving the plutonium(III) in 15.8 M nitric acid. Analysis of the plutonium(IV) stock by extraction with 0.1 M TTA in the presence of 7.4×10^{-5} M potassium dichromate showed that more than 98 percent of the stock extracted as plutonium(IV) chelate into the benzene phase. The potassium dichromate was added to remove trace reducing impurities. Under these conditions neither plutonium(III) nor plutonium(VI) extract since the equilibrium constant,⁵ Equation (1) for plutonium(III) is about 10^{-5} and that for plutonium(VI) is 1.4×10^{-2} .

When no uranyl nitrate was present, the plutonium(IV) was stabilized in the reaction vessel with 10^{-4} M potassium dichromate; with 2.02 M uranyl nitrate, 10^{-3} M potassium dichromate was necessary to stabilize plutonium(IV) in the +4 oxidation state. The sec-butylbenzene used appeared to contain more reducing impurities than benzene since with benzene as the organic solvent, 10^{-4} M potassium dichromate was sufficient to stabilize plutonium(IV) in the presence of 2.02 M uranyl nitrate.

To insure that the conversion of the TTA-enol to the hydrate was not a rate limiting step, the sec-butylbenzene solution of TTA was equilibrated with water before it was used. King and Reas⁶ have shown that the TTA concentration in the aqueous phase reaches 80 percent of its equilibrium value within a minute when a dilute acid phase is equilibrated with a "wet" benzene phase containing TTA. After equilibration for three hours with water, the TTA solutions were standardized with 0.1 M sodium hydroxide.

The concentration of the TTA in the sec-butylbenzene was not corrected for the amount of TTA which extracts into the aqueous phase since the concentration of the TTA in the aqueous phase is small and, moreover, can only be estimated from the data available. It has been shown that the distribution coefficient of TTA, E equals moles of TTA per liter of organic phase divided by moles of TTA per liter of aqueous phase, varies with the ionic strength, the hydrogen ion concentration, and the TTA concentration.⁶⁻⁹ The minimum value of E would be 37 as determined for 1.0 M TTA between 2.0 M perchloric acid and benzene.⁷ It is probably much greater for the conditions used in these experiments.

The TTA used was synthesized by H. R. Lehman and M. W. Davis, Jr., Commercial sec-butylbenzene was redistilled and the fraction boiling at 171-174° C at the prevailing laboratory atmospheric pressure of

approximately 740 mm Hg was used. The sec-butylbenzene discolored when exposed to light for a period of several months. When discolored sec-butylbenzene was used in the extraction experiments, the reproducibility of the rates of extraction of plutonium(IV) decreased considerably.

The distribution coefficients for plutonium(IV), $E_M = [P]_{\text{org}}/[P]_{\text{aq}}$, where $[P]_{\text{org}}$ represents the total plutonium in the organic phase and $[P]_{\text{aq}}$ the total plutonium in the aqueous phase, were determined from the ratio of the plutonium content in equal volumes of the organic and aqueous phases. In the presence of uranyl nitrate the plutonium in the aqueous phase was determined either by the Lanthanum Fluoride technique or from the known material balance. Distribution coefficients calculated by these two methods usually checked within 5 or 10 percent in the range $E_M = 0.2$ to 2.0 . For values of E_M outside of this range the accuracy of the measurement decreases rapidly. When the distribution coefficients calculated from the two methods did not agree, that calculated from the material balance was used.

In general, the experimental rates, except for the rapid extraction rates at high speed, were reproducible within 20 or 30 percent. Occasionally an abnormal rate, either high or low, was obtained. This agreement was considered reasonable, especially for the extraction from the aqueous to the organic phase where the half-times for the reaction are about one minute and the time intervals for measuring the reaction rate were 0.5 minute.

In calculating equilibrium and rate constants no corrections for activities have been used.

RESULTS AND DISCUSSION

Slow Step in the Extraction of Plutonium(IV)

For all systems studied both the rate of the back extraction, the extraction of plutonium chelate from the organic to the aqueous phase in the presence of various reducing agents, and the rate of the forward extraction, the extraction of plutonium(IV) from the aqueous to the organic phase as equilibrium is approached, varied with the shaking speed. This indicates that the slow step in the extraction of plutonium(IV) in a benzene-nitric acid mixture is the transfer of some plutonium(IV) species across the benzene-aqueous boundary layer and is not due to a chemical step in either phase alone.

Back Extraction Rate

The back extraction rate was first order with respect to the concentration of plutonium(IV) in the organic phase in the presence of all reducing agents used and so may be represented by the equations

$$-d[P]_{\text{org}} / dt = h[P]_{\text{org}} / R \quad (5)$$

$$-2.3 \log ([P]_{\text{org}} / [P]_{\text{org } I}) = ht / R \quad (6)$$

In these equations R is the ratio of the volume of organic phase to the volume of aqueous phase, $[P]_{\text{org } I}$ is the initial concentration of plutonium(IV) in the organic phase, and all other symbols have their previously defined meanings. The back extraction rate function, h , is a function of the hydrogen ion, TTA, and nitrate ion concentrations, the particular reducing agent used, and the shaking speed. Its dimensions are (liters of sec-butylbenzene)(liters of water)⁻¹(min)⁻¹. h was

determined from the slope of a plot of $\log ([P]_{org}/[P]_{org I})$ vs time. Several of these plots are shown in Figure 1.

In the system 2.02 M uranyl nitrate-0.474 M nitric acid-TTA-sec-butylbenzene with ferrous sulfamate as the reducing agent sufficient data were obtained to show not only that there is a change in h with the shaking speed at constant TTA and nitric acid concentrations, but also that the TTA dependence of h is unchanged with shaking speed (Table I, Figure 2). Since the TTA dependence of h is constant, it is assumed that the mechanism of the extraction does not change. For the other reducing agents in this system, it was assumed that the TTA dependence did not change with the shaking speed. The dependence of h on the shaking speed in the presence of hydroxylamine hydrochloride is shown by experiments BE 124 and 133 of Table II in which h roughly doubles as the shaking speed is increased from 450 to 730 RPM.

The same dependence of the back extraction rate function on the shaking speed was found for the systems 0.474 M nitric acid-TTA-benzene or sec-butylbenzene as in the uranyl nitrate system (Tables II and III, Figure 3). This is contrary to the observations of Thomas and Crandall who found that the rate of the extraction of plutonium(IV) was independent of the stirring speed. The failure of these workers to observe any stirring speed effects is probably due to the limitations of their stirring equipment which consisted of a small spherical flask and a motor driven paddle. It is possible that as the revolutions per minute of the paddle were increased, the paddle pushed the two liquid phases more rapidly before it around the flask without increasing the interfacial area or the internal mixing in the system. Since the geometry of the stainless steel

FIG. 1: REMOVAL OF Pu(IV) TTA CHELATE FROM SEC-BUTYLBENZENE WITH TIME AT SEVERAL SHAKING SPEEDS

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Shoot same size

Table I

Variation of $\bar{h}$ with TTA Concentration and Shaking Speed

Conditions: sec-butylbenzene
2.02 $\bar{M}$ uranyl nitrate
0.474 $\bar{M}$ nitric acid
0.01 $\bar{M}$ sulfamic acid
0.005 $\bar{M}$ ferrous perchlorate
R = 2

Speed RPM	Ex. No. BEC	T° C Air	TTA $\bar{M}$	$\bar{h}$
450	58	23-4	0.053	0.676
450	46	24-5	0.071	0.278
450	83	22-4	0.101	0.115
450	102	23-4	0.101	0.096
450	50	23-4	0.107	0.089
450	59	23-4	0.107	0.079
450	60	23-4	0.142	0.036
450	48	24-5	0.160	0.026
450	51	23-4	0.160	0.028
450	49	24-5	0.213	0.014
450	67	23	0.213	0.011
450	52	23-4	0.249	0.008
790	39	22-4	0.071	0.576
790	40	22-4	0.107	0.166
790	43	23-5	0.107	0.166
790	41	22-4	0.160	0.052
790	44	23-5	0.160	0.048
790	42	22-4	0.213	0.022
790	45	23-5	0.249	0.017
870	32	21-2	0.071	0.680
870	33	21-2	0.107	0.268
870	36	23-4	0.107	0.280
870	34	21-2	0.160	0.078
870	37	23-4	0.160	0.086
870	38	23-4	0.249	0.023

FIG. 2: THE TTA DEPENDENCE OF h AT SEVERAL SHAKING SPEEDS.

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Table II

Variation of $\underline{h}$ with TTA Concentration and Shaking Speed
No Uranyl Nitrate

Conditions: sec-butylbenzene
0.473 $\underline{M}$ nitric acid
0.01 $\underline{M}$ sulfamic acid
0.005 $\underline{M}$ ferrous perchlorate
R = 2

Speed RPM	Ex. No. BEC	T° C Air	TTA $\underline{M}$	$\underline{h}$
450	17	22-5	0.0260	0.184
450	18	22-5	0.0347	0.087
450	11	22-5	0.0521	0.029
730	31	24-6	0.0336	0.306
730	32	24-6	0.0420	0.236
730	33	24-6	0.0504	0.073
730	34	24-6	0.0672	0.041

Table III

Variation of $\bar{h}$ with TTA Concentration and Shaking Speed in Benzene
No Uranyl Nitrate

Conditions: benzene
0.471 M nitric acid
0.005 M ferrous perchlorate
R = 1
25° C

Speed RPM	Ex. No. BE	TTA <u>M</u>	Urea <u>M</u>	Sulfamic Acid <u>M</u>	$\bar{h}$
225	181	0.0168	0.	0.01	0.079
225	182	0.0252	0.	0.01	0.036
225	183	0.0336	0.	0.01	0.0114
225	184	0.0420	0.	0.01	0.0085
225	188	0.0168	0.014	0.	0.062
225	192	0.0168	0.014	0.	0.070
225	189	0.0252	0.014	0.	0.025
225	193	0.0252	0.014	0	0.029
225	190	0.0336	0.014	0.	0.0187
225	194	0.0336	0.014	0.	0.0127
225	191	0.0420	0.014	0.	0.0073
225	195	0.0420	0.014	0.	0.0091
450	185	0.0168	0.	0.01	0.136
450	186	0.0252	0.	0.01	0.051
450	187	0.0336	0.	0.01	0.021

FIG. 3: THE TTA DEPENDENCE OF h AT SEVERAL SHAKING SPEEDS IN BENZENE AND SEC-BUTYLBENZENE

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mixing equipment they used was different from that of the glass mixer equipment. The difference in mixing obtained from the two pieces of equipment probably explains the difference in extracting rates they obtained when changing from glass to steel containers.

The values of h calculated from the data of Thomas and Crandall are shown by the squares in Figure 3. This latter data was obtained with 0.005 M ferrous chloride as the reducing agent rather than with 0.005 M ferrous perchlorate and 0.01 M sulfamic acid.

With the same shaking speed, the extraction is several times faster in sec-butylbenzene than in benzene which is further indication that the interphase transfer is not limited by aqueous reaction kinetics.

There is some question as to the relation of the rates of the back extraction of plutonium(IV) from the organic to the aqueous phase in the presence and in the absence of a reducing agent. However, the variation of the rate of the back extraction of plutonium(IV) with the shaking speed shows that the transfer of plutonium across the organic and aqueous boundary layer is a slow step. A chemical slow step alone in either phase cannot explain the slow rate of extraction of plutonium(IV) in this system.

Forward Extraction Rate

The extraction of plutonium(IV) from the aqueous to the sec-butylbenzene phase as equilibrium is approached was also studied. The generalized rate equation for the forward extraction as equilibrium is approached may be represented as

$$d[P]_{org}/dt = (g/R)[P]_{aq} - (h/R)[P]_{org} \quad (7)$$

where $[P]_{org}$, $[P]_{aq}$, and R have their previously defined meanings, $(g/R)[P]_{aq}$ expresses the rate of transfer of plutonium from the aqueous to the organic phase, and $(h/R)[P]_{org}$ the rate of the reverse transfer. g and h are functions of TTA, hydrogen ion and nitrate ion concentrations, and, as it will be shown, of the shaking speed. g has the dimension $(\text{min})^{-1}$ while h has dimensions of $(\text{liters of sec-butylbenzene})(\text{liters of water})^{-1}(\text{min})^{-1}$. Equation (7) is valid if the rate of extraction is limited either by a slow chemical step or by the transfer of plutonium(IV) across the benzene-aqueous boundary layer. If the slow step is a chemical one, g and h will be independent of the shaking speed. From Equation (7) it is seen that when equilibrium is reached

$$[P]_{org}/[P]_{aq} = E_M = g/h \quad (8)$$

With the use of the relation

$$C = [P]_{aq} + R[P]_{org} \quad (9)$$

where C is the initial concentration of plutonium(IV) in the aqueous phase, Equation (7) becomes

$$d[P]_{org}/dt + (g + h/R)[P]_{org} = gC/R \quad (10)$$

where $(g + h/R)$ is the forward equilibrium extraction rate function.

The solution of Equation (10) is

$$2.3 \log (1 - [P]_{org}/[P]_{org e}) = -(g + h/R)t \quad (11)$$

where $[P]_{org e}$ is the concentration of plutonium(IV) in the organic phase at equilibrium. The slope of a plot of $\log (1 - [P]_{org}/[P]_{org e})$ vs time is a constant for a given experiment and has the value

$$\text{slope} = -(g + h/R)2.3 \quad (12)$$

Figure 4 shows such a plot at 0.05 M TTA for two shaking speeds.

In order to demonstrate that g and h are functions of the shaking speed, these functions must be compared for different shaking speeds when the TTA, hydrogen ion, and nitrate ion concentrations are constant. This is done in Figure 5 from the data of Table IV for the system 2.02 M uranyl nitrate-0.474 M nitric acid-0.05 M TTA-sec-butylbenzene where at a given E_M on the abscissa all conditions but the shaking speed are maintained constant. The values of $(g + h/R)$ for the two shaking speeds shown vary by a factor of more than two.

The dependence of the forward equilibrium extraction rate function of plutonium(IV) on the shaking speed indicates that with the agitation used the extraction is at least partially limited by the rate of transfer of plutonium(IV) across the boundary layer. The first order disappearance of plutonium with respect to itself indicates a single slow step in the extraction. Within the experimental error of the measurements, it is possible that a slow chemical step in either phase, whose rate is of the same order of magnitude as the rate of the transfer of plutonium(IV) from one phase to the other, may determine the rate of the extraction to some extent. However, no direct evidence of a slow chemical reaction in either phase has been found to this date.

Mechanism of the Interphase Transfer

Although the data indicate that the rate of the extraction is controlled by the interphase transfer of plutonium(IV) it is possible that a slow chemical step may determine which plutonium species will diffuse across the benzene-aqueous boundary layer by blocking some of the

FIG. 4: THE EXTRACTION OF Pu(IV) FROM THE AQUEOUS TO THE ORGANIC PHASE AS A FUNCTION OF TIME AT TWO SHAKING SPEEDS

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FIG.5: THE VARIATION OF $(g + \frac{h}{R})$ WITH TTA CONCENTRATION AT TWO SHAKING SPEEDS.

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Table IV

Variation of g , h , and E_M with TTA Concentration and Shaking Speed

Conditions: sec-butylbenzene
2.02 M uranyl nitrate
0.474 M nitric acid
0.0013 M potassium dichromate
 $R = 2$

Speed RPM	Ex. No. E	T° C	TTA M	E_M	Method	K_M	($g + h/R$)	g	h
450	66	22-3	0.0336	0.205	LaF ₃	8130	0.92	0.27	1.20
450	67	22-3	0.0386	0.313	LaF ₃	7120	0.85	0.33	1.04
450	68	22-3	0.0454	0.567	LaF ₃	6740	0.82	0.44	0.76
450	69	22-3	0.0504	0.756	LaF ₃	5910	0.73	0.44	0.58
450	70	22-3	0.0504	0.796	LaF ₃	6230	0.68	0.42	0.52
450	71	22-3	0.0672	2.15	LaF ₃	5320	0.76	0.62	0.28
450	72	22-3	0.101	-	-	-	1.02	-	-
450	73	22-3	0.134	-	-	-	1.19	-	-
960	78	25-6	0.0336	0.202	MB	-	2.4	0.70	3.4
960	79	25-6	0.0504	0.702	LaF ₃	-	1.8	1.1	1.4
960	80	25-6	0.0672	2.28	MB	-	3.2	2.6	1.2
960	81	25-6	0.134	-	-	-	3.6	-	-

possible transfer paths. If the plutonium chelate system is represented as

with the subscript org indicating species which are in the organic phase and subscript aq those in the aqueous phase, and with the understanding that these species may exist either partially or completely nitrated as well as shown here, it is evident that there are five possible paths for plutonium to transfer from one phase to the other. The path which predominates will be determined by the product of the interphase transfer rate constant for each path and the concentration of the particular transferring species. Thus a slow chemical step in either phase might determine the path of the interphase transfer by limiting the concentration of a particular species.

The transfer of a solute from an aqueous to an organic phase has generally been found to be a slow process.^{10,11} J. T. Davies¹⁰ has investigated the diffusion of ions from water into nitrobenzene and found that the diffusion of potassium iodide from the aqueous to the organic phase is many orders of magnitude slower than the intraphase diffusion of the ions in either water or nitrobenzene alone. He, therefore, concludes that the rate of transfer of potassium iodide from the aqueous to the organic phase is determined by the rate of the progressive solvation-desolvation of the ions at the interface or in the boundary layer as well as the rate of diffusion across the concentration gradients in the boundary

layer. It is probable that both of these processes contribute to the slow rate of extraction of plutonium(IV) observed in the benzene-TTA-uranyl nitrate-nitric acid systems. A low concentration of the extracting plutonium chelate species with respect to the total plutonium(IV) present may also be a determining factor.

Equilibrium Extraction Coefficient of Plutonium(IV)

Relation of the TTA Dependence and the Species in Solution

The relation between the TTA dependence of the equilibrium extraction coefficient of plutonium(IV) and the species of plutonium present in the organic and aqueous phases has been shown by Connick and Reas.⁷ In this section their treatment is applied to the plutonium(IV)-sec-butylbenzene-nitric acid-uranyl nitrate-TTA system to show that at high nitrate concentrations, the deviation of the TTA and hydrogen ion dependences of E_M from +4 and -4, respectively, is caused by the extraction of species such as PuK_3NO_3 , as well as by PuK_4 , into the organic phase.

The equilibrium extraction coefficient of plutonium(IV) in the sec-butylbenzene-TTA-nitric acid-uranyl nitrate system has been defined as

$$E_M = \frac{[P]_{org}}{[P]_{aq}} = \frac{\sum_p [PuK_p(NO_3)_{4-p}]_{org}}{\sum_m \sum_n [PuK_m(NO_3)_n]_{aq}^{+4-m-n}} \quad (13)$$

$$p = 0, 1, 2, 3, 4$$

$$m = 0, 1, 2, 3, 4$$

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

$[PuK_p(NO_3)_{4-p}]_{org}$ represents the concentration in the benzene phase of the plutonium(IV) species containing 4-p nitrate groups and p chelate

groups. All species of plutonium(IV) in the benzene phase are considered to be uncharged. $[\text{PuK}_m(\text{NO}_3)^{+4-m-n}]_{\text{aq}}$ is the concentration in the aqueous phase of the plutonium(IV) species having n nitrate groups, m chelate groups and a charge of $+(4-n-m)$. m and p may vary from 0 to 4 since the coordination number of plutonium(IV) is eight and each chelate group occupies two coordination positions. At equilibrium all species of plutonium(IV) in the aqueous and organic phases can be related to the concentration of PuK_4 in the organic phase by the following equations if activity effects are neglected.

$$K_{1p} = \frac{[\text{PuK}_4]_{\text{org}} [\text{H}^+]_{\text{aq}}^{4-p} [\text{NO}_3^-]_{\text{aq}}^{4-p}}{[\text{PuK}_p(\text{NO}_3)_{4-p}]_{\text{org}} [\text{HK}]_{\text{org}}^{4-p}} \quad p = 0, 1, 2, 3, 4 \quad (15)$$

$$K_{2mn} = \frac{[\text{PuK}_4]_{\text{org}} [\text{H}^+]_{\text{aq}}^{4-m} [\text{NO}_3^-]_{\text{aq}}^n}{[\text{PuK}_m(\text{NO}_3)_n]^{+(4-m-n)}_{\text{aq}} [\text{HK}]_{\text{org}}^{4-m}} \quad \begin{matrix} m = 0, 1, 2, 3, 4 \\ n = 0, 1, 2, \dots, n \end{matrix} \quad (17)$$

By substituting Equations (15) and (17) in Equation (13) and canceling the concentration of PuK_4 one obtains E_M as a function of TTA, hydrogen ion, and nitrate ion concentrations.

$$E_M = \frac{\sum_p \frac{[H^+]_{aq}^{4-p} [NO_3^-]_{aq}^{4-p}}{K_{1p} [HK]_{org}^{4-p}}}{\sum_m \sum_n \frac{[H^+]_{aq}^{4-m} [NO_3^-]_{aq}^n}{K_{2mn} [HK]_{org}^{4-m}}} \quad \begin{array}{l} p = 0,1,2,3,4 \\ m = 0,1,2,3,4 \\ n = 0,1,2,\dots,n \end{array} \quad (18)$$

The TTA dependence of E_M can be related to the species of plutonium in the aqueous and organic phases by differentiating $\log E_M$ partially with respect to $\log [HK]_{org}$ and making substitutions from Equations (15) and (17).

$$\frac{\partial \log E_M}{\partial \log [HK]_{org}} = 4f_0 - 3f_1 - 2f_2 - f_3 - 0f_4 + 4f'_0 + 3f'_1 + 2f'_2 + f'_3 + 0f'_4 \quad (19)$$

In Equation (19) f_p is the fraction of plutonium(IV) in the organic phase containing p chelate groups, and f'_m is the fraction of plutonium(IV) in the aqueous phase containing m chelate groups. In this differentiation it is assumed that the activity coefficients of the solvents and of all species involved in the equilibria are constant. In the experimental work the ionic strength was maintained constant and the TTA concentration was varied from 0.01 to 0.07 M. When a benzene solution of TTA is in equilibrium with 0.1 M hydrochloric acid, the activity coefficients of TTA have been found to change from 1.0 to 0.96 as the TTA concentration increases from 0.1 to 0.07 M.⁶ For this change in TTA concentration the activity coefficients of PuK_4 , which are assumed to be the same as those of UK_4 , vary from 1.0 to 0.95.⁷

Equation (19) shows the relation between the TTA dependence of E_M and the fraction of each plutonium(IV) species present in each phase. As has been pointed out by Connick and Reas,⁷ if the TTA dependence is +4, the unique solution to Equation (19) requires that all values of f_p and f'_m be zero but f'_o and f_4 which are unity. For any value of the TTA dependence less than +4 many combinations of f'_m and f_p are possible.

TTA Dependence in the 0.5 M Nitric Acid-TTA-Sec-Butylbenzene System

In the system 0.5 M nitric acid-benzene-TTA, the TTA dependence of E_M was found to be +4 by Thomas and Crandall.² The TTA dependence in this system was redetermined from a plot of $\log E_M$ vs $\log [HK]_{org}$ for the data of Table V. The points are fairly well represented by the line of slope +4.0 as shown in Figure 6 although a line of slope +3.9 would fit the data as well. A plot of $\log E_M$ vs $\log [HK]_{org}$ for the system 0.474 M nitric acid-sec-butylbenzene-TTA is also shown in Figure 6 from the data of Table V. Although the line drawn through the points in Figure 6 has a slope of +4.0, these points are as well represented by a line of slope +3.6. This lower value of the slope is believed to be due to experimental error since the solutions of TTA in sec-butylbenzene for these experiments were prepared by diluting 30 to microliters of a concentrated TTA stock solution to one milliliter.

Thus, the TTA dependences of E_M in the system benzene or sec-butylbenzene-TTA-0.5 M nitric acid appear to be very close to +4.0. This would correspond to the case for Equation (19) in which all of the f values are zero but f_4 and f'_o , which are unity. The equation for the extraction of plutonium(IV) in this system is then from Equation (16)

Table V

Variation of g , h , and E_M with TTA Concentration
No Uranyl Nitrate

Conditions: 0.471 M nitric acid
R = 1
225 RPM
25° C

Solvent = Sec-Butylbenzene						
Ex. No. EC	TTA M	E_M	$K_M \times 10^{-6}$	$g + h/R$	g	h
36	0.0105	0.39	1.60	0.82	0.23	0.59
40	0.0106	0.54	2.18	0.88	0.31	0.57
37	0.0123	0.87	2.15	0.64	0.30	0.34
38	0.0140	1.34	1.72	0.54	0.31	0.23
39	0.0175	2.96	1.55	0.68	0.51	0.17
Average			1.84			

Solvent = Benzene

Ex. No. EC	TTA M	E_M	$K_M \times 10^{-6}$
41	0.0086	0.285	2.59
42	0.0107	0.564	2.12
43	0.0129	1.08	1.93
44	0.0150	2.39	2.32
35	0.015	2.26	2.20
45	0.0172	3.59	2.04
Average			2.20

FIG. 6: THE TTA DEPENDENCE OF E_M FOR Pu(IV) - NO URANYL NITRATE

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$$K_M = \frac{[\text{PuK}_4]_{\text{org}}}{[\text{Pu}(\text{NO}_3)_n^{4-n}]_{\text{aq}}} \times \frac{[\text{H}^+]_{\text{aq}}^4}{[\text{HK}]_{\text{org}}^4} \quad (21)$$

Equation (20) represents a group of reactions of TTA with the various plutonium(IV) nitrate species. K_M is the equilibrium constant for the sum of these reactions, and is, therefore, a complex function of the nitrate ion concentration.

The values of K_M determined in this laboratory for the system TTA-0.474 M HNO_3^- solvent are 2.2×10^6 in benzene and 1.8×10^6 in sec-butylbenzene (Column 4, Table V). The constant determined in benzene is somewhat higher than that of 1.39×10^6 determined by Thomas and Crandall. The TTA solution in benzene used in this laboratory was prepared by dissolving a weighed amount of TTA in benzene and diluting to a known volume. Unlike the solutions in sec-butylbenzene, this solution was not standardized. However, when solutions of TTA in sec-butylbenzene were standardized, the concentration of the solutions calculated from the weight of the TTA always agreed with the concentration determined by titrating the solution with 0.1 M sodium hydroxide within one or two percent.

TTA Dependence in 2.02 M Uranyl Nitrate-0.474 M Nitric Acid-TTA-Sec-Butylbenzene System

For the system containing 2.0 M uranyl nitrate as well as 0.474 M nitric acid the TTA dependence of E_M was found to be closer to +3.5 than 4.0 with very little scatter in the data (Figure 7, Tables IV and XII).

The column headed Method in these tables indicates whether the plutonium(IV) concentration in the aqueous phase was measured by the Lanthanum Fluoride Technique (LaF_3) or calculated from the material balance (MB).

There are several possible explanations for the deviation of the TTA dependence of E_M from +4 in this system:

1. Uranyl ion may extract into the sec-butylbenzene as the dichelate reducing the free TTA concentration.
2. The activity coefficients of the species involved may be changing with the TTA concentration.
3. Nonextractable plutonium in the +3 or +6 oxidation state may be present in the extraction mixture.
4. The TTA may be complexing the plutonium(IV) in the aqueous phase.
5. Chelated plutonium(IV) molecules containing less than four chelate groups per molecule may be extracting into the organic phase.

Uranyl Ion Extraction.--Measurements made by the method of Orr¹² showed that at a TTA concentration greater than any used in determining the equilibrium extraction coefficients of plutonium(IV), namely 0.09 M TTA, the concentration of UO_2K_2 in the sec-butylbenzene was only 0.0002 M (Table VI, Column 8). Since the extraction of 0.0002 M UO_2K_2 into the organic phase would not change appreciably the TTA concentration in the sec-butylbenzene, the deviation of the TTA dependence of the equilibrium extraction coefficient of plutonium(IV) from +4.0

FIG. 7: THE TTA DEPENDENCE OF E_M FOR $\text{Pu(IV)}-2.02 \text{ M}$
URANYL NITRATE

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Table VI

Extraction of Uranium(VI) into Sec-Butylbenzene-TTA Solutions

Conditions: sec-butylbenzene
 2.02 M uranyl nitrate
 0.474 M nitric acid
 25° C

Initial TTA in the Organic Phase M	λ_0 A	Dilution	OD	OD _{TTA}	OD _{UO₂K₂}	ϵ	UO ₂ K ₂ Organic Phase M x 10 ⁵
0.035	4000	10	0.458	0.381	0.077	16200	4.8
0.035	4040	10	0.205	0.147	0.058	13050	4.4
0.035	4100	10	0.071	0.034	0.037	8250	4.8
						Average	4.6
0.053	4000	10	0.728	0.590	0.138	16200	8.5
0.053	4040	10	0.334	0.225	0.109	13050	8.4
0.053	4100	10	0.125	0.052	0.073	8250	8.9
						Average	8.6
0.087	4000	10	1.30	0.944	0.354	16200	22
0.087	4040	10	0.655	0.358	0.297	13050	23
0.087	4100	10	0.282	0.081	0.201	8250	24
						Average	23

cannot be due to the extraction of UO_2K_2 into the sec-butylbenzene.

In these measurements solutions of TTA in sec-butylbenzene were equilibrated for three hours with equal volumes of 2.02 M uranyl nitrate solution containing 0.474 M added nitric acid. The organic layer was then diluted by a factor of ten with thiophene-free benzene and its optical density measured with the Beckman Spectrophotometer (Table VI, Column 4). The blank for the absorption of TTA (Table VI, Column 5) was determined by equilibrating sec-butylbenzene solutions of TTA with 2.0 M calcium nitrate solutions containing 0.474 M added nitric acid and then measuring the absorption of the diluted organic phase. Since the pH of the 2.0 M calcium nitrate solution was 5 as compared to 0.38 for 2.02 M uranyl nitrate the distribution of TTA in these two cases may vary somewhat, although from the work of Tong,⁹ the variation of the TTA distribution coefficient with acid at these acidities is small. The concentration of UO_2K_2 in the sec-butylbenzene phase was then calculated using the extinction coefficients measured by Orr (Table VI, Column 7). Corrections for the presence of small amounts of $\text{UO}_2\text{K}_2 \cdot \text{HK}$ were not made but these were not large enough to change the results significantly.

Activity Coefficients.--It is also unlikely that the deviation of the TTA dependence of E_M is due to activity coefficient changes alone. In these experiments the aqueous phase concentrations are maintained constant while the only change in the butylbenzene phase is the variation of the TTA concentration from 0.03 M to 0.07 M . Under these conditions the activity coefficients of TTA and PuK_4 vary less than 5 percent,^{6,7} and it is probable that the activity coefficients of any other plutonium(IV)

species present in the organic phase vary in a similar manner.

Plutonium Oxidation State.—If a fixed percentage of plutonium(III) or plutonium(VI) were present in each extraction the TTA dependence of E_M would be lowered since the +3 or +6 oxidation state does not extract under the conditions used. However, to lower the TTA dependence from +4 to +3.5 between 10 and 20 percent of the total plutonium would have to be in a nonextractable oxidation state. Since 98 percent of the total plutonium was found to extract into a TTA solution in benzene at a TTA concentration low enough to prevent the extraction of plutonium(III) or plutonium(VI), the presence of large amounts of nonextractable plutonium is not likely to be the explanation for the observed +3.5 TTA dependence of E_M in the presence of a high nitrate ion concentration.

Aqueous TTA Complexing.—The concentration of plutonium(IV) containing one chelate group per molecule in the aqueous phase can be estimated roughly as follows: in 1.0 M hydrochloric acid Zebroski¹³ has reported the equilibrium constant for the complexing of plutonium(IV) with TTA in the aqueous phase as

$$\frac{[\text{PuK}^{+3}][\text{H}^+]}{[\text{Pu(IV)}]_{\text{total}}[\text{HK}]} = \sim 75 \quad (23)$$

where $\text{Pu(IV)}_{\text{total}}$ is the total concentration of plutonium(IV) in the aqueous phase including the species Pu^{+4} and PuCl^{+3} . To apply the

constant in Equation (23) to the 2.0 M uranyl nitrate system it must be corrected for the chloride complexing of plutonium(IV) in the 1.0 M hydrochloric acid system.

Various workers^{14,15} have estimated that from 40 to 60 percent of plutonium(IV) is complexed by chloride ion in 1 M hydrochloric acid that

$$\frac{[\text{PuK}^{+3}] [\text{H}^+]}{[\text{Pu}^{+4}] [\text{HK}]} = \sim 130 \text{ to } 200 \quad \mu = 1 \quad (24)$$

The concentration of Pu^{+4} in the system must then be determined from the fraction of plutonium(IV) that is present as nitrate complexes in 0.5 and 4.5 M nitrate in solutions. At an ionic strength of 6.1 in a mixture of sodium perchlorate and sodium nitrate Zebroski and Heumann¹⁶ have reported the complexing constants for the first and second nitrate complexes of plutonium(IV) in water as

$$\frac{[\text{Pu}(\text{NO}_3)^{+3}]}{[\text{Pu}^{+4}] [\text{NO}_3^-]} = 5 \quad (26)$$

$$\frac{[\text{Pu}(\text{NO}_3)_2^{+2}]}{[\text{Pu}^{+4}] [\text{NO}_3^-]^2} = 10 \quad (28)$$

With these equations and the distribution coefficient of TTA between benzene and 1.0 M perchloric acid,⁷

$$[\text{TTA}]_{\text{org}} / [\text{TTA}]_{\text{aq}} = 37$$

which would give the largest possible concentration of TTA in the aqueous phase, it was estimated that a maximum of 1 to 2 percent of the plutonium in the aqueous phase exists as $\text{PuK}(\text{NO}_3)_n^{+(3-n)}$ in the 0.5 M nitric acid-TTA-sec-butylbenzene system under conditions where the equilibrium extraction coefficient is unity. Since the values of the constants have been determined at different ionic strengths these values are rough estimates only. As has been previously pointed out the experimental data obtained at 0.5 M nitric acid indicate that $\text{Pu}(\text{NO}_3)_n^{+(4-n)}$ is the major species of plutonium(IV) in the aqueous phase, although the presence of as much as 10 percent $\text{Pu}(\text{NO}_3)_n\text{K}_m^{+(4-n-m)}$ is within the experimental error.

From Equations (24), (26), and (28) it can be seen that as the nitrate ion concentration is increased, the fractions of the total plutonium(IV) in the aqueous phase that exists as $\text{PuK}(\text{NO}_3)_n^{+(3-n)}$ decreases. Thus, in the system 2.0 M uranyl nitrate-0.474 M nitric acid-TTA-sec-butylbenzene one would predict that but 0.1 to 0.2 percent of the plutonium in the aqueous phase would be complexed with TTA. This calculation neglects all but the first two nitrate complexes of plutonium(IV). Similar conclusions are reached if the nitrate complexing constant of plutonium(IV) determined by Hindman¹⁷ or Rabideau and Lemons¹⁵ is used.

Organic Nitrated Complexes.—Therefore, it appears that the deviation of the slope of a plot of $\log E_M$ vs $\log [\text{HK}]_{\text{org}}$ from +4 for the system 2.02 M uranyl nitrate-TTA-0.474 M nitric acid-sec-butylbenzene is due not to the presence of large amounts of $\text{PuK}(\text{NO}_3)_n^{+(3-n)}$ in the aqueous phase, but to species of plutonium(IV) in the organic phase containing less than four chelate groups per molecule and one or more nitrate groups.

Equation (19) then becomes

$$\frac{\partial \log E_M}{\partial \log [HK]_{org}} = -4f_0 - 3f_1 - 2f_2 - f_3 - 0f_4 + 4 = \sim 3.5 \quad (29)$$

where as before f_p indicates the fraction of all the plutonium in the organic phase that exists as $PuK_p(NO_3)_{4-p}$, and the concentrations of any plutonium(IV) species in the aqueous phase complexed with TTA are considered to be negligible. 3.5 is the experimental value of $\partial \log E_M / \partial \log [HK]_{org}$. Many combinations of values of f_0, f_1, f_2, f_3 , and f_4 will give 3.5 in Equation (29). For instance, $f_4 = 0.70$, $f_3 = 0.15$, $f_2 = 0.10$, $f_1 = 0.04$, $f_0 = 0.01$ to give an idea of the possible magnitude of the fractions of plutonium species containing 4,3,2,1, and 0 chelate species, respectively, which might exist in the organic phase at equilibrium under these conditions. However, if one assumes the only species present are PuK_4 and PuK_3NO_3 , then the plutonium chelate is divided equally between these two species.

Hydrogen Ion Dependence in High Nitrate Ion Concentrations

The hydrogen ion dependence of E_M at 4.9 M nitrate ion concentration in the absence of uranyl nitrate was also measured with benzene as the organic solvent (Table VII, Figure 8). The dependence of -3.1 when analyzed by the above methods is further evidence that plutonium(IV) species such as PuK_3NO_3 as well as PuK_4 are present in the organic phase.

Table VII

Variation of E_M of Plutonium(IV) with Hydrogen Ion Concentration

Conditions: benzene
 4.9 M NO_3^-
 0.19 M TTA
 R = 1
 25° C

Ex. No. EC	HNO_3 M	LiNO_3 M	E_M	K_M
50	1.56	3.50	1.54	7,200
51	1.95	3.00	0.787	8,700
52	2.18	2.75	0.545	9,400
53	2.57	2.35	0.332	11,100
54	2.96	1.98	0.210	12,400
55	3.35	1.58	0.141	13,600
56	4.13	0.80	0.074	16,500
57	4.91	0.00	0.041	17,800

FIG. 8 : THE HYDROGEN ION DEPENDENCE FOR Pu(IV) IN THE PRESENCE OF 4.9 M NITRATE ION

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Variation of K_M

Values of K_M shown in Tables IV, V, VII, VIII, and XII vary with:

1. TTA and hydrogen ion concentrations because the extraction of partially nitrated species of plutonium(IV) into the organic phase at high nitrate ion concentrations is neglected,
2. nitrate ion concentration because of the complexing of plutonium(IV) by nitrate ion in the aqueous phase, and
3. the uranyl ion concentration because of the hydrolysis of uranyl ion.

The drop in the value of K_M with the uranyl nitrate concentration is shown in Table VIII and Figure 9. Here the change in the value of K_M is due to all of the above mentioned effects.

Forward Extraction

If the number of chelate groups per molecule determines a species, then five plutonium(IV) species may exist in either the aqueous or organic phases. Each species may contain a variable number of nitrate groups but at constant nitrate concentration the proportions of the same species containing different numbers of nitrate groups should be more or less constant since the TTA concentration is not varied over a wide range. In this section the forward equilibrium extraction rate data is analyzed to determine if possible which of the five species of plutonium(IV) transfers across the benzene and aqueous boundary layer.

If the thesis expressed in the first part of the discussion section of this report—that the rate of the extraction of plutonium(IV) is limited principally by the rate of transfer of the plutonium species from

Table VIII

Variation of E_M with Uranyl Nitrate Concentrations

Conditions: sec-butylbenzene
0.0265 $\underline{M}$ TTA
0.471 $\underline{M}$ nitric acid
 $R = 1$
25° C

Ex. No. E	UNH $\underline{M}$	NO_3^- $\underline{M}$	$K_M \times 10^{-6}$
Calc.	0.000	0.47	1.8
132	0.475	1.42	0.24
133	0.950	2.37	0.065
134	1.430	3.33	0.020
From Table XII	2.02	4.51	0.008

FIG. 9: THE VARIATION OF K_M WITH THE NITRATE ION CONCENTRATION IN URANYL NITRATE SOLUTION

one phase to the other—is accepted, the equation for the extraction of the k th plutonium species, the species containing k chelate groups per plutonium ion in the aqueous phase, may be represented as follows:

where the nitrate ion function is incorporated into the equilibrium constants K_p' and K_{1p} since the nitrate ion concentration is kept constant in each experiment. f_p is the specific rate constant for the transfer of $\text{PuK}_p^{+(4-p)}$ from the aqueous to the organic phase, and b_p is the specific rate constant for the reverse transfer. These constants are functions of temperature, shaking speed, and the nitrate ion concentration. The plutonium species in the benzene phase are considered to be uncharged so that any value of $4-p$ differing from zero for the charge on the plutonium species in the benzene phase represents the number of nitrate groups associated with that molecule. Nitrate groups in the aqueous phase are not shown although plutonium(IV) is highly complexed in water.

Reaction 30a involves the slow conversion of the TTA enol to the hydrate. As has already been mentioned, the TTA hydrate-enol equilibrium in the organic phase was reached before the plutonium(IV) extraction was started by equilibrating the sec-butylbenzene solution of TTA with water. The transfer of TTA from one phase to another appears to be rapid.⁶

If $\text{PuK}_p^{+(4-p)}$ were the only species of plutonium(IV) transferring from one phase to the other, the observed rate law for the extraction of plutonium(IV) from the aqueous to the benzene phase as equilibrium is approached by the mechanism expressed in Equation (30) would be

$$\frac{d[\text{P}]_{\text{org}}}{dt} = (f_p / R) [\text{Pu}_p^{+(4-p)}]_{\text{aq}} - (b_p / R) [\text{PuK}_p^{+(4-p)}]_{\text{org}} \quad (31)$$

In this equation $(f_p / R) [\text{PuK}_p^{+(4-p)}]_{\text{aq}}$ expresses the rate of transfer of the $\text{Pu}_p^{+(4-p)}$ species from the aqueous to the benzene phase and $(b_p / R) [\text{PuK}_p^{+(4-p)}]_{\text{org}}$ expresses the reverse rate. However, since the observed rate of the extraction of plutonium(IV) is determined by the rate of transfer across the benzene and aqueous boundary layer of all the $\text{PuK}_p^{+(4-p)}$ species, where p varies from 0 to 4, the general rate law for the extraction of plutonium(IV) from the aqueous to the benzene phase as equilibrium is approached is

$$\frac{d[\text{P}]_{\text{org}}}{dt} = \frac{1}{R} \sum_p f_p [\text{PuK}_p^{+(4-p)}]_{\text{aq}} - \frac{1}{R} \sum_p b_p [\text{PuK}_p^{+(4-p)}]_{\text{org}} \quad (32)$$

$$p = 0, 1, 2, 3, 4$$

Equilibrium between all species in the sec-butylbenzene phase and between all species in the aqueous phase, respectively, is assumed so

that the concentration of the pth species may be related to PuK_4org and $\text{Pu(IV)}_{\text{aq}}$ concentrations by the equations

$$[\text{PuK}_p^{+(4-p)}]_{\text{org}} = K_{1p}' \frac{[\text{H}^+]_{\text{aq}}^{4-p}}{[\text{HK}]_{\text{org}}^{4-p}} [\text{PuK}_4]_{\text{org}} \quad (15)$$

$$p = 0, 1, 2, 3, 4$$

and

$$[\text{PuK}_p^{+(4-p)}]_{\text{aq}} = K_p' \frac{[\text{HK}]_{\text{org}}^p}{[\text{H}^+]_{\text{aq}}^p} [\text{Pu(IV)}]_{\text{aq}} \quad (33)$$

$$p = 0, 1, 2, 3, 4$$

K_{1p}' and K_p' are equilibrium constants dependent on the nitrate concentration and the temperature.

With the use of Equations (15) and (33), Equation (32) is transformed to

$$\frac{d[\text{P}]_{\text{org}}}{dt} = \frac{[\text{Pu(IV)}]_{\text{aq}}}{R} \sum_p f_p K_p' \frac{[\text{HK}]_{\text{org}}^p}{[\text{H}^+]_{\text{aq}}^p} - \frac{[\text{PuK}_4]_{\text{org}}}{R} \sum_p f_p K_{1p}' \frac{[\text{H}^+]_{\text{aq}}^{4-p}}{[\text{HK}]_{\text{org}}^{4-p}} \quad (34)$$

$$p = 0, 1, 2, 3, 4$$

In order to compare Equation (34) with Equation (7) the relation between the concentrations of uncomplexed plutonium(IV) in the aqueous phase and the total plutonium(IV) concentration in the aqueous phase as well as the relation between the PuK_4 concentration in the benzene phase and the total plutonium concentration in the benzene phase must be derived.

The fraction of the total plutonium(IV) in the organic phase that exists as the PuK_4 may be expressed as a function of TTA, H^+ , and NO_3^- concentrations with the use of Equation (15).

$$\frac{[\text{PuK}_4]_{\text{org}}}{[\text{P}]_{\text{org}}} = K_5 \frac{[\text{PuK}_4]_{\text{org}}}{\sum_p [\text{PuK}_p(\text{NO}_3)_{4-p}]_{\text{org}}} = \frac{1}{\sum_p \frac{[\text{H}^+]_{\text{aq}}^{4-p} [\text{NO}_3^-]_{\text{aq}}^{4-p}}{K_{1p} [\text{HK}]_{\text{org}}^{4-p}}} \quad (35)$$

$$p = 0, 1, 2, 3, 4$$

The fraction of the total plutonium(IV) in the aqueous phase that is uncomplexed by TTA can be expressed as

$$\frac{[\text{Pu}^{+4}]_{\text{aq}}}{[\text{P}]_{\text{aq}}} = K_6 = \frac{[\text{Pu}^{+4}]_{\text{aq}}}{\sum_n \sum_m [\text{PuK}_m (\text{NO}_3)_n^{+4-m-n}]_{\text{aq}}} \quad (36)$$

$$m = 0, 1, 2, 3, 4$$

$$n = 0, 1, 2, 3, n$$

K_6 is essentially independent of the TTA concentration since only a small fraction of plutonium(IV) is complexed by TTA in an aqueous phase containing nitrate ion.

With substitutions from Equations (9), (35), and (36), Equation (34) becomes identical in form with Equation (7). g and h can now be expressed as functions of the TTA and H^+ concentrations.

$$g = K_6 \sum_p f_p K_p' \frac{[\text{HK}]_{\text{org}}^p}{[\text{H}^+]_{\text{aq}}^p} \quad (37)$$

$$p = 0, 1, 2, 3, 4$$

$$h = K_5 \sum_p f_p K_{1p} \frac{[H^+]_{aq}^{4-p}}{[HK]_{org}^{4-p}} \quad (38)$$

$$p = 0, 1, 2, 3, 4$$

The TTA dependence of g can be related to the species of plutonium(IV) which extract from the aqueous to the organic phase by differentiating $\log g$ partially with respect to $\log [HK]_{org}$ and making substitutions from Equations (15) and (33).

$$\frac{\partial \log g}{\partial \log [HK]_{org}} = \frac{\sum_p P_{fp} [PuK_p^{+(4-p)}]_{aq}}{\sum_p f_p [PuK_p^{+(4-p)}]_{aq}} = 0G_0 + G_1 + 2G_2 + 3G_3 + 4G_4 \quad (39)$$

G_0, G_1 , etc. are the fractions of the total plutonium(IV) concentration transferring per minute from the aqueous to the organic phase which contain 0, 1, etc. chelate groups per molecule of plutonium. In taking the partial derivative it was assumed that the activity coefficients were constant although this is known to be only an approximation. Equation (39) is valid only for constant nitrate, hydrogen, and uranyl ion concentrations.

The solution to Equation (7) has already been shown to be

$$2.3 \log (1 - [P]_{org} / [P]_{org} e) = -(g + h/R)t \quad (11)$$

From the function $(g + h/R)$, Equation (12), and the relation $E_M = g/h$, g and h are calculated. They are recorded in Tables IV and XII, columns 9 and 10, and Table V, columns 6 and 7.

The values of $\log g$ are plotted vs $\log [HK]_{org}$ for both the sec-butylbenzene-TTA-uranyl nitrate system and the

sec-butylbenzene-TTA-nitric acid system in Figure 10 from the data of Tables IV and V. The points are somewhat scattered but the slope of the best line through these points lies between +1 and +2. Therefore, from Equation (39) it appears that the average plutonium(IV) molecule transferring from the aqueous to the organic phase contains from one to two chelate groups. Similar conclusions are reached from the analysis of the variation of $\log h$ with $\log [HK]_{\text{org}}$ since these functions are not calculated independently.

Back Extraction

0.5 M Nitric Acid-TTA-Solvent System

Experimentally, the rate of the extraction of plutonium chelate from sec-butylbenzene or benzene into an aqueous phase containing a reducing agent and nitric acid has been found to satisfy the relation

$$2.3 \log ([P]_{\text{org}} / [P]_{\text{org } I}) = - \frac{ht}{R} \quad (5)$$

where all symbols have their previously defined meanings and h is a function of the shaking speed, TTA and nitric acid concentrations, the particular reducing agent used, and the nitrate concentration. Plutonium(IV) is prevented from returning to the organic phase by reducing it to nonextractable plutonium(III) as it enters the aqueous phase.

The rate function, h , for the extraction of plutonium(IV) from benzene or sec-butylbenzene into 0.5 M nitric acid has the same TTA dependence and shows the same variation with the shaking speed in the presence of all reducing combinations tried within the experimental error. Furthermore, the data of Thomas and Crandall measured at a constant volume ratio

FIG. 10: THE TTA DEPENDENCE OF g AND h FOR Pu(IV)

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in the 0.5 M nitric acid system give a TTA dependence similar to those measured in benzene in this report although slightly lower.

The TTA dependence of $\underline{h}$ in benzene with 0.014 M urea and 0.005 M ferrous perchlorate is -2.3 at 225 RPM; with 0.01 M sulfamic acid and 0.005 M ferrous perchlorate it is -2.6 at 225 RPM and -2.7 at 450 RPM. The TTA dependence of $\underline{h}$ found by Thomas and Crandall with 0.005 M ferrous perchlorate and with their mixing conditions is -2.3. These data are shown in Table III and Figure 3. In the sec-butylbenzene-0.5 M nitric acid system the TTA dependences measured were -2.6 at 450 RPM and -2.8 at 130 RPM (Table II, Figure 3) in the presence of 0.01 M sulfamic acid and 0.005 M ferrous perchlorate. The back extraction rate function, $\underline{h}$, in sec-butylbenzene is about three times greater than the corresponding function in benzene at the same shaking speeds.

Since the back extraction rate functions in the system 0.47 M nitric acid-TTA-solvent vary with the shaking speed while the TTA dependence of $\underline{h}$ remains constant within the experimental error, it appears that the rate limiting step that was measured was the interphase transfer of plutonium(IV) from the organic to the aqueous phase. The three fold increase in the rate of extraction when sec-butylbenzene replaces benzene is further indication that the slow step is not in the aqueous phase. If the slow step is the interphase transfer of plutonium(IV), the slope of a plot of $\log \underline{h}$ vs $\log [\text{HK}]_{\text{org}}$ indicates the average plutonium species which transfer across the benzene-water boundary layer.

Partial differentiation of $\underline{h}$ by methods analogous to those used previously described gives, for the case where PuK_4 is the principal species of plutonium(IV) in the organic phase at equilibrium,

$$\frac{\partial \log h}{\partial \log [HK]_{org}} = -4H_0 - 3H_1 - 2H_2 - H_3 - OH_4 \quad (40)$$

H_p is the fraction of the total plutonium(IV) in the organic phase transferring per minute from the organic to the aqueous phase which contain p chelate groups per molecule of plutonium(IV).

From Equation (40) the slopes lying between -2 and -3 of the plots of $\log h$ vs $\log [HK]_{org}$ for the systems sec-butylbenzene or benzene-TTA and 0.474 M nitric acid (Figure 3) indicate that a mixture of the plutonium(IV) species containing on the average between one and two chelate groups per molecule is transferring from the benzene to the aqueous phase.

The hydrogen ion dependence for the sec-butylbenzene-TTA-nitric acid system at constant nitrate ion concentration has also been determined (Table IX, Figure 11). The slope of +2.5 may be compared to -2.6 to -2.8 for the corresponding TTA dependence. The difference between these values lies within the experimental error.

It is not certain that the back extraction rate function measured in the presence of ferrous sulfamate or ferrous ion and urea are a measure of the rate of transfer of plutonium(IV) from the organic to the aqueous phase without added complications from the reducing agent. Data is not available in this system to permit the comparison of the actual magnitudes of h and $\underline{h}$ measured under the various conditions. However, in the absence of uranyl nitrate, the TTA dependence of the back extraction rate function measured in the presence and absence of a reducing agent are the same within the experimental error (compare Figures 10 and 3).

Table IX

Variation of $\underline{h}$ with Hydrogen Ion Concentration

Conditions: sec-butylbenzene
0.052 $\underline{M}$ TTA
0.01 $\underline{M}$ sulfamic acid
0.005 $\underline{M}$ ferrous perchlorate
R = 2
450 RPM

Ex. No. BEC	Temp. °C	HNO ₃ $\underline{M}$	LiNO ₃ $\underline{M}$	$\underline{h}$
20	22-6	0.630	-	0.068
24	21-5	0.474	0.154	0.037
23	21-5	0.394	0.237	0.022

Conditions: sec-butylbenzene
0.16 $\underline{M}$ TTA
2.02 $\underline{M}$ uranyl nitrate
0.01 $\underline{M}$ sulfamic acid
0.005 $\underline{M}$ ferrous perchlorate
R = 2

Ex. No. BEC	Temp. °C	HNO ₃ $\underline{M}$	NaNO ₃ $\underline{M}$	$\underline{h}$
48	24-5	0.474	0.	0.0258
51	23-4	0.474	0.	0.0276
66	23	0.395	0.071	0.0133
65	23	0.316	0.151	0.0071

FIG. 11: THE HYDROGEN ION DEPENDENCE OF h

MU3990

2.0 M Uranyl Nitrate-0.5 M Nitric Acid-TTA-Sec-Butylbenzene System

The absolute magnitude as well as the TTA dependence of $\bar{h}$ in the 2.0 M uranyl nitrate-0.5 M nitric acid-TTA-sec-butylbenzene system varies with the particular reducing agents used (Tables I and X). In each case at constant TTA and nitric acid concentrations the back extraction rate is independent of the concentration of the particular reducing combination in the narrow region tested, but dependent on the particular combination used. The TTA dependences of $\bar{h}$ for the ferrous sulfamate, ferric sulfamate, and sulfamic acid systems alone are -2.9, -2.4, and -2.2, respectively (Figure 12). The first slope is considerably more reliable than the second two since it is based on many more points. It has been shown by spectrophotometric measurements in this laboratory that a 2.0 M uranyl nitrate aqueous solution containing sulfamic acid does not reduce plutonium(IV) to plutonium(III).²⁰ The function of the sulfamic acid in these solutions is to react with nitrous acid which, if present, would reoxidize plutonium(III) to plutonium(IV) as it is formed. The reducing agent for plutonium(IV) in the absence of added ferrous ion or hydroxylamine hydrochloride must be either an impurity in the solvent or possibly uranium(IV) formed by the photo-reduction of uranyl ion as found by workers at Knolls Atomic Power Laboratory.²¹

The presence of ferric or ferrous iron in solution at high TTA and uranyl nitrate concentrations seems to inhibit the rate of the extraction (Figure 12). The rate of extraction of plutonium(IV) from the benzene to

Table X

Variation of $\underline{h}$ with Reducing Agent and TTA Concentration

Conditions: *sec*-butylbenzene
 2.02 $\underline{M}$ uranyl nitrate
 0.474 $\underline{M}$ nitric acid
 R = 2
 450 RPM

0.01 $\underline{M}$ Sulfamic Acid + Ferric Nitrate

Ex. No. BE	Temp. °C	TTA $\underline{M}$	Fe(NO ₃) ₃ $\underline{M}$	$\underline{h}$
143	20-3	0.104	0.005	0.045
145	22-3	0.104	0.001	0.051
143A	20-3	0.104	0.010	0.045
146	22-3	0.139	0.005	0.022

Sulfamic Acid

Ex. No. BE	Temp. °C	TTA $\underline{M}$	NH ₂ SO ₃ H $\underline{M}$	$\underline{h}$
134	25-6	0.052	0.01	0.576
130	22-4	0.104	0.01	0.124
131	22-4	0.104	0.03	0.124
136A	25-6	0.139	0.01	0.067

Hydroxylamine Hydrochloride

Ex. No. BE	Temp. °C	TTA $\underline{M}$	NH ₂ OH·HCl $\underline{M}$	$\underline{h}$
134	24	0.0504	0.015	0.280
124	24	0.101	0.015	0.086
133*	22-3	0.104	0.015	0.168
125	24	0.151	0.015	0.031

*Speed = 730 RPM.

FIG. 12: THE TTA DEPENDENCE OF h WITH VARIOUS REDUCING AGENTS

MU3991

the aqueous phase is slower in the presence of hydroxylamine hydrochloride than with sulfamic acid alone (Table X). The transfer of plutonium chelate from the organic to the aqueous phase occurs in the absence of sulfamic acid or any added reducing agent. In this case the plot of $\log [P]_{\text{org}}$ vs time is not linear, probably due to the partial reoxidation of plutonium(III) to plutonium(IV) by nitrous acid followed by the extraction of the plutonium(IV) into the organic phase.

The variation of $\log h$ with $\log [HNO_3]_{\text{aq}}$ in the system containing ferrous sulfamate was measured and is plotted in curve B, Figure 11 from the data of Table IX. The ionic strength in this series varied from 6.4 to 6.6. The slope of this plot is +3.1 corresponding roughly to the slope of -2.8 to -2.9 for the TTA dependence in this system.

In Table XI, values of h and $\bar{h}$ measured at 0.0504 and 0.0672 M TTA in the forward equilibrium extraction, the back extraction in the presence of ferrous perchlorate and sulfamic acid, and in the presence of sulfamic acid alone are compared. All of the values shown agree within the experimental error. However, they are measured in a region where the sulfamic acid and ferrous sulfamate curves are essentially the same (Figure 12).

The variation of $\bar{h}$ as well as the TTA dependence of $\bar{h}$ with the reducing combinations seems to indicate that the extraction of plutonium(IV) from the organic to the aqueous phase is not the only reaction being studied in this system. Possibly some of the plutonium in the aqueous phase remains in the +4 valence state and is transferred back into the organic phase, thereby reducing the extraction rate and the TTA dependence. The aqueous-organic re-extraction could take place to some extent without being detectable as a curve in the plot of $\log [P]_{\text{org}} / [P]_{\text{org}}$ I

Table XII

Variation of g , h , and E_M with TTA Concentration and Temperature

Conditions: sec-butylbenzene
 2.02 $\underline{M}$ uranyl nitrate
 0.474 $\underline{M}$ nitric acid
 225 RPM

Temp. °C	Ex.No. E	R	TTA $\underline{M}$	E_M	Method	K_M	($g + h/R$)	g	h
25.	121	1	0.0211	0.033	LaF ₃	8400			
25.	123	1	0.030	0.126	LaF ₃	7800			
25.	117	1	0.044	0.561	MB	7750	0.54	0.20	0.35
25.	112	2	0.053	1.02	LaF ₃	6520			
25.	118	1	0.053	0.994	MB	6360	0.39	0.20	0.19
25.	116	2	0.106	~8	MB		0.85	0.80	0.10
35.2	94	1	0.044	0.523	LaF ₃		0.97	0.33	0.64
35.2	95	1	0.053	0.962	LaF ₃		0.82	0.40	0.42
35.2	96	1	0.062	1.77	LaF ₃				
35.2	97	1	0.071	2.70	LaF ₃		0.96	0.70	0.26
44.6	110	1	0.044	0.397	LaF ₃				
44.6	119	1	0.044	0.385	MB		1.92	0.53	1.39
44.6	109	1	0.053	0.936	MB				
44.6	120	1	0.053	0.792	MB		1.44	0.64	0.80

vs time. It is possible that the reaction with sulfamic acid and no added iron represents the back extraction rate since it proceeds most rapidly.

Temperature Effects

The equilibrium extraction coefficient of plutonium(IV) in the system 2.02 M uranyl nitrate-0.474 M nitric acid-TTA-sec-butylbenzene was measured at 25, 35, and 45° C (Table XII). The scattering in the data in these experiments is believed to be due to the decomposition of sec-butylbenzene which had become slightly discolored with standing. To determine the heat of extraction, ΔH_e , $\log E_M$, measured at constant TTA and hydrogen ion concentrations, was plotted against the reciprocal of the absolute temperature. From the relation

$$\frac{\partial \log E_M}{\partial K} = - \frac{\Delta H_e}{4.6} \quad (41)$$

and an average of the slopes measured at 0.053 and 0.044 M TTA the heat of extraction was found to be about -3000 ± 1000 calories.

The forward extraction rate functions, $(g + h/R)$, was also measured at 25, 35, and 45° C (Table XII). This function was separated into the forward and backward rate functions, and g and h were plotted vs TTA on log paper for each temperature (Figures 13 and 14).

From the slope of a plot of $\log g$ and h , taken at 0.05 M TTA and constant nitrate and hydrogen ion concentrations, vs the reciprocal of the absolute temperature, the apparent activation energies for the

Table XII

Variation of g , h , and E_M with TTA Concentration and Temperature

Conditions: sec-butylbenzene
 2.02 M uranyl nitrate
 0.474 M nitric acid
 225 RPM

Temp. °C	Ex.No. E	R	TTA M	E_M	Method	K_M	($g + h/R$)	g	h
25.	121	1	0.0211	0.033	LaF ₃	8400			
25.	123	1	0.030	0.126	LaF ₃	7800			
25.	117	1	0.044	0.561	MB	7750	0.54	0.20	0.35
25.	112	2	0.053	1.02	LaF ₃	6520			
25.	118	1	0.053	0.994	MB	6360	0.39	0.20	0.19
25.	116	2	0.106	~8	MB		0.85	0.80	0.10
35.2	94	1	0.044	0.523	LaF ₃		0.97	0.33	0.64
35.2	95	1	0.053	0.962	LaF ₃		0.82	0.40	0.42
35.2	96	1	0.062	1.77	LaF ₃				
35.2	97	1	0.071	2.70	LaF ₃		0.96	0.70	0.26
44.6	110	1	0.044	0.397	LaF ₃				
44.6	119	1	0.044	0.385	MB		1.92	0.53	1.39
44.6	109	1	0.053	0.936	MB				
44.6	120	1	0.053	0.792	MB		1.44	0.64	0.80

extraction of plutonium(IV) from the aqueous to the organic phase and for the reverse extractions were calculated. They are $\Delta H_f = 10,000$ calories and $\Delta H_p = 13,000$ calories, respectively, with an error of about ± 3000 calories.

These activation energies are apparent only since the variations of g and h with temperature are due to the changes in the equilibria of the various species present as well as the change in the rate of transfer of each plutonium species.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

FIG. 13: THE TTA DEPENDENCE OF g AT SEVERAL TEMPERATURES

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FIG. 14: THE TTA DEPENDENCE OF h AT SEVERAL TEMP.

MU3993

APPENDIX

Definition of Terms

1. HK represents thenoyltrifluoroacetone (TTA), where H^+ is the removable proton and K^- is the chelating part of the molecule.
2. Subscripts org and aq indicate concentrations in the organic and aqueous phases, respectively.
3. λ = microliters.
4. R is the ratio of the volume of the organic phase to that of the aqueous phase.
5. $[P]_{org}$ is the total concentration in moles per liter of all species of plutonium(IV) in the organic phase at any time. $[P]_{org\ i}$ represents the initial value and $[P]_{org\ e}$ the equilibrium value of $[P]_{org}$.
6. $[P]_{aq}$ is the total concentration of all species of plutonium(IV) in the aqueous phase.
7. C is the initial concentration of plutonium(IV) in the aqueous phase $[P]_{org} = 0$.
8. E_M , the equilibrium extraction coefficient of plutonium(IV), is the ratio of the plutonium in the organic phase to that in the aqueous phase at equilibrium.
9. The back extraction is the extraction of plutonium chelate from the organic to the aqueous phase.
10. The forward extraction is the extraction of plutonium from the aqueous to the organic phase.
11. k_2 is the specific rate constants for the extraction of plutonium(IV) from the organic phase used by Thomas and Crandall.

12. h is the back extraction rate function with the dimensions (liters of benzene)(liters of water)⁻¹(min)⁻¹. h is a function of the NO_3^- , H^+ , and TTA concentrations and of the stirring speed.
13. $\underline{h}$ is the back extraction rate function measured in the presence of a reducing agent.
14. g is the forward extraction rate function with the dimensions (min)⁻¹. It is a function of the NO_3^- , H^+ , and TTA concentrations and of the stirring speed.
15. The forward equilibrium extraction is the extraction of plutonium(IV) from the aqueous to the organic phase as equilibrium is approached. Both the forward and back extractions are taking place.
16. The forward extraction rate function, $(g + h/R)$, is 2.3 times the slope of a plot of $\log (1 - [\text{P}]_{\text{org}} / [\text{P}_0]_{\text{org}})$ vs time.
17. The TTA dependence of any function is the slope of a plot of $\log (\text{function})$ vs $\log [\text{HK}]_{\text{org}}$.
18.
$$K_M = E_M \frac{[\text{H}^+]_{\text{aq}}^4}{[\text{HK}]_{\text{org}}^4}$$
19. f_p and b_p are the specific rate constants for the transfer of the plutonium(IV) species containing k chelate groups per molecule from the aqueous to the organic phase and the organic to the aqueous phase, respectively.
20. K_5 is the fraction of the plutonium(IV) in the organic phase which exists as PuK_4 .
21. K_6 is the fraction of the plutonium(IV) in the aqueous phase which exists as uncomplexed Pu(IV) .

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