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IONIC EQUILIBRIA AND REACTION KINETICS OF PLUTONIUM
IN HYDROCHLORIC ACID SOLUTIONS

by

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By M. Kasha and G. E. Sheline

ABSTRACT

The reaction $3\text{Pu(IV)} = 2\text{Pu(III)} + \text{Pu(VI)}$ has been studied in solutions of hydrochloric acid varying from 0.183M to 1.545M. In the case of the forward reaction (disproportionation), the studies have been carried out at temperatures from 25°C to 70°C, whereas the back reaction (reproportionation), has been investigated at 25°C only. Measurements of both rates of reaction and equilibrium concentrations have been made. At 25°C the disproportionation constant $K = [\text{Pu(III)}]^2 [\text{Pu(VI)}] / [\text{Pu(IV)}]^3$ ranged from $\sim 1 \times 10^{-4}$ in 1.545M hydrochloric acid to 6.9 in 0.183M hydrochloric acid. Raising the temperature to 70°C increased this constant by a factor of 300 to 4000 depending upon the acidity. Without making corrections for ionic strength and chloride complexing effects, K was found to vary inversely as about the fifth power of the hydrochloric acid concentration.

The rate of disproportionation at 25°C is inversely proportional to about the second or third power of the Pu(IV) concentration. The rate of reproportionation is greater at higher acidities and at higher concentrations of Pu(III) and Pu(VI). Thermodynamic calculations give the following data for the disproportionation at 25°C: $\Delta H^\circ = 41,000$ cal/mole, $\Delta F^\circ = 3,300$ cal/mole, $\Delta S^\circ = 127$ E.U. The entropy of Pu(IV) is approximately -83 E.U.

An attempt has been made to interpret the rate data for the disproportionation of Pu(IV) in terms of a reaction mechanism. Of the rate laws tested, only those which involved the concentration of Pu(IV) to the second or third power seemed to fit the data. The evidence favors the rate law in which the Pu(IV) concentration appears to the second power but it is not possible at present to make a clear-cut distinction between the validity of this second power rate law and that of the third power rate law. A possible complex rate law involving both powers is discussed.

By mixing solutions of Pu(III) and Pu(VI) at low acidities (0.1081M and 0.0615M hydrochloric acid) it was found possible to study plutonium equilibria without causing the formation of colloidal Pu(IV). In these experiments, Pu(III), Pu(IV), Pu(V), and Pu(VI) were present in stable equilibrium in aqueous solution at 25°C, the Pu(V) representing 19 and 35% of the total plutonium in the 0.1081M and 0.0615M hydrochloric acid experiments, respectively. This is the first time that large amounts of Pu(V) were prepared in a stable form in aqueous solution. The concentration of Pu(IV) was very low in these experiments, making the analysis for this species relatively uncertain. An equilibrium constant involving Pu(V) but not Pu(IV) was therefore calculated, $K_s = [\text{Pu(III)}] [\text{Pu(VI)}]^2 / [\text{Pu(V)}]^3$, giving values of 8.1 and 0.59 for the 0.1081M and 0.0615M hydrochloric acid solutions, respectively.

Solutions of disproportionated Pu(IV) in 0.183 to 1.545M hydrochloric acid were heated at 70°C for varying lengths of time and measurements made of the formation of colloidal Pu(IV). In a solution of 0.183M hydrochloric acid and 4.29×10^{-3} M plutonium about 70% of the plutonium was converted to colloidal Pu(IV) in 42 hours. In 0.244M hydrochloric acid and 1.35×10^{-3} M plutonium, little or no formation of colloidal Pu(IV) was observed in 116 hours at 70°C. Similarly, no colloidal Pu(IV) was found in solutions of higher acidity.

The rate of reduction of Pu(VI) resulting from products produced in solution by alpha particles was measured. It was found to correspond to a diminution in average oxidation number of 0.003 to 0.01 per day, in the range of hydrochloric acid concentration of 1M to 0.06M, the rate increasing with decreasing hydrochloric acid concentration. The rate was proportional to the total amount of plutonium but bore no relationship to the concentration of Pu(VI) present. The rate of reduction at 70°C corresponded to a diminution of the average oxidation number of approximately 0.02 per day, but this rate may be partially due to reduction by Cl^- .

In the Appendix, discussions of the absorption spectra and the method of calculation used for determining the concentrations of the various states of plutonium are presented. The absorption spectrum of Pu(V) in a 0.5M hydrochloric acid solution is shown. Data indicating the existence of a chloride complex of Pu(IV) in 0.183 to 1.545M hydrochloric acid, which is stabilized at higher temperatures, are given.

* * * * *

INTRODUCTION

When the Pu(III)–Pu(IV) potential first became known, it was pointed out by W. M. Latimer that this potential was probably close enough to the Pu(IV)–Pu(VI) potential so that appreciable concentrations of Pu(III), Pu(IV), and Pu(VI) could exist in equilibrium in the same solution. This was quickly verified by visual observation of the absorption spectrum of Pu(IV) solutions in nitric acid and hydrochloric acid.¹ These initial observations were of only a qualitative nature but were sufficient to demonstrate that the disproportionation of Pu(IV) is significant and that it is very sensitive to temperature changes.^{1,2}

Since the time these preliminary results were reported, much work has been done at Chicago and Berkeley in studying this equilibrium between Pu(III), Pu(IV), and Pu(VI). The studies presented here represent a quantitative and more complete investigation of this important reaction under various conditions of acidity, temperature, and plutonium concentration. Rates and equilibria were studied and an attempt was made to interpret the data in terms of reaction mechanisms. All reactions were carried out in hydrochloric acid solutions since it was desirable to work in a solution which would not directly oxidize or reduce any of the oxidation states of plutonium and which would not form strong complexes with plutonium.

It is recognized that chloride ion forms a weak complex with Pu(VI), but compared to the effect of H^+ on the disproportionation equilibrium, this complex exerts relatively little influence. By mixing solutions of Pu(III) and Pu(VI) at low acidities, it was found possible for the first time to stabilize appreciable amounts of Pu(V) in equilibrium with the other oxidation states of plutonium, in aqueous solution at 25°C.

The analysis for plutonium in the four oxidation states occurring in aqueous solution was carried out by means of spectrophotometric measurements. The absorption spectra of the various plutonium ions are discussed in the Appendix, and the limitations of the spectrophotometric method of analysis are indicated. In order to control the temperature of the absorption cells as the reaction proceeded, a special thermostat chamber for use in the Beckman spectrophotometer³ was used; this maintained the temperature to within $\pm 0.5^\circ\text{C}$.

1. THE DISPROPORTIONATION OF Pu(IV) IN HYDROCHLORIC ACID SOLUTIONS

The reaction of Pu(IV) referred to as the "disproportionation reaction" may be defined as:



The term disproportionation will be used to refer to the forward reaction in the equation as written, while the back reaction will be called reproporationation. The influence of temperature and of the concentrations of Pu(IV), and hydrochloric acid on the equilibrium and on the rates of disproportionation and reproporationation has been studied. The concentration equilibrium constant, K, is defined as

$$K = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3} \quad (2)$$

where brackets indicate concentrations in moles per liter. The values of K obtained under various conditions are given in this section. The qualitative aspects of the rate data are also presented here. Attempts to treat the rate data quantitatively and to determine the rate law are discussed in Section 2.

In each experiment the solution of Pu(IV) was prepared by dissolving a hydroxide precipitate of pure Pu(IV) in a small volume of strong hydrochloric acid. The amount of hydrochloric acid used was determined by the final acidity desired in the experiment. The solution was heated at approximately 70°C for a few minutes to insure the absence of colloidal Pu(IV) and then slowly cooled to 25°C (under these conditions the disproportionation of Pu(IV) is slight). The experiment was begun by dilution of the hydrochloric acid solution to the desired acidity with water, at 25°C. The solution was stirred and transferred rapidly to the thermostated absorption cell³ and absorption measurements made with a Beckman spectrophotometer.

Because of some uncertainties in these analyses, the columns giving "Total Pu" are slightly inconsistent. These deviations are probably of an experimental nature and give some indication of the accuracy of this method of measurement of plutonium concentrations. The acidity of the solutions was determined at the conclusion of the experiment by titration of an aliquot with dilute sodium hydroxide to the end point of phenolphthalein. A small correction for plutonium was applied, assuming that Pu(III) and Pu(IV) precipitate as hydroxides, and that Pu(VI) is converted to the diplutonate during the titration.

a) Disproportionation at 25°C

In 1.545M hydrochloric acid ($1.50 \times 10^{-3}\text{M Pu}$), equilibrium was not reached even after 1000 hours (Table 1 and Figures 1 and 2). Decreasing the acidity to 0.950M resulted in an increase in the rate of disproportionation but in 750 hours equilibrium was not attained (Table 2 and Figures 1 and 2). It is probable that in both of these experiments sufficient time was actually allowed to permit the attainment of equilibrium, if disproportionation were the only reaction involved, which, however, was not the case. As seen in Figure 1, the Pu(VI) concentration in each experiment falls well below the level it should have, if one Pu(VI) molecule were formed coincident with the formation of every pair of Pu(III) molecules. These low values for Pu(VI) are attributable to the reduction of Pu(VI) by ion pairs produced by the alpha radiation. This effect was previously described⁴ and will be discussed more fully in Section 5. The reduction of Pu(VI) is sufficiently rapid, so that in these higher acidities Pu(VI) is reduced at a rate somewhat less than that at which it is formed by disproportionation.

The net results are (1) the maintenance of very low concentration levels of Pu(VI), (2) continuation of the disproportionation, and (3) an overall reduction of Pu(IV) to Pu(III). The low concentrations of Pu(VI) made the analyses for this constituent difficult and, consequently, these values of the equilibrium constant K are inaccurate. Since the rates of reduction of Pu(VI) and of the disproportionation of Pu(IV)

Table 1. Disproportionation of Pu(IV) in 1.545M HCl at 25°C 1.50 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)				K = $\frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu	
8.6	0.7	97.9	0.6	99.2	
20.0	0.8	97.5	0.8	99.1	
56.0	1.2	94.8	1.0	97.0	
103.	2.2	93.2	1.3	96.7	
139.	3.2	91.5	1.4	96.1	1.9 x 10 ⁻⁵
188.	4.2	90.9	1.5	96.6	3.5 x 10 ⁻⁵
260.	5.4	89.4	1.6	96.4	6.5 x 10 ⁻⁵
332.	6.4	88.5	1.6	96.5	9.5 x 10 ⁻⁵
436.	7.8	87.5	1.3	96.6	9.1 x 10 ⁻⁵
649.	10.2	85.4	0.6	96.2	10 x 10 ⁻⁵
717.	10.9	85.0	0.5	96.4	9.7 x 10 ⁻⁵
1005.	14.6	80.3	(0.1?)	95.3	

* No Pu(V) or colloidal Pu(IV) was found.

Table 2. Disproportionation of Pu(IV) in 0.950M HCl at 25°C 1.60 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)				K = $\frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu	
0.4	4.2	102	1.4	107.6	
1.9	4.2	99.2	1.2	104.6	
3.0	4.7	98.8	1.2	104.7	
5.9	4.8	97.7	1.2	103.7	
8.5	5.0	96.2	1.2	102.4	
22.6	5.7	94.6	1.6	101.9	0.06 x 10 ⁻³
71.	8.9	89.8	2.6	101.3	0.25 x 10 ⁻³
102.	10.4	86.6	4.4	101.4	0.63 x 10 ⁻³
287.	15.3	80.0	5.2	100.5	1.9 x 10 ⁻³
365.	16.4	80.0	4.9	101.3	2.1 x 10 ⁻³
606.	18.5	77.6	3.3	99.4	1.9 x 10 ⁻³
750.	20.0	76.8	2.9	99.7	2.0 x 10 ⁻³

* No Pu(V) or colloidal Pu(IV) was found.

are of the same order of magnitude, the disproportionation equilibrium may not have been reached in these reactions at higher hydrochloric acid concentrations. Instead, a steady state may have been set up. In this case the equilibrium constant for these long term experiments (500-1000 hours) would represent a lower limit. However, rough calculations have shown that the error due to this cause is less than 20%. The experimentally determined values of K are 1×10^{-4} and 2×10^{-3} for 1.545M and 0.950M hydrochloric acid, respectively.

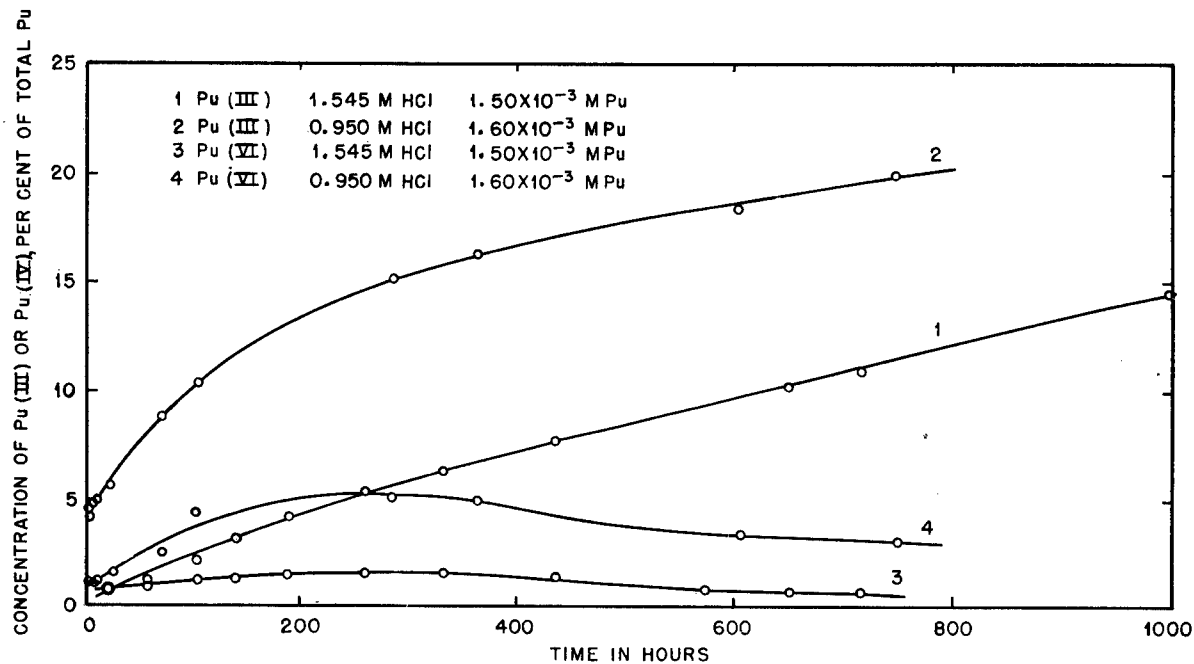


Figure 1. Disproportionation of Pu(IV) at 25°C.

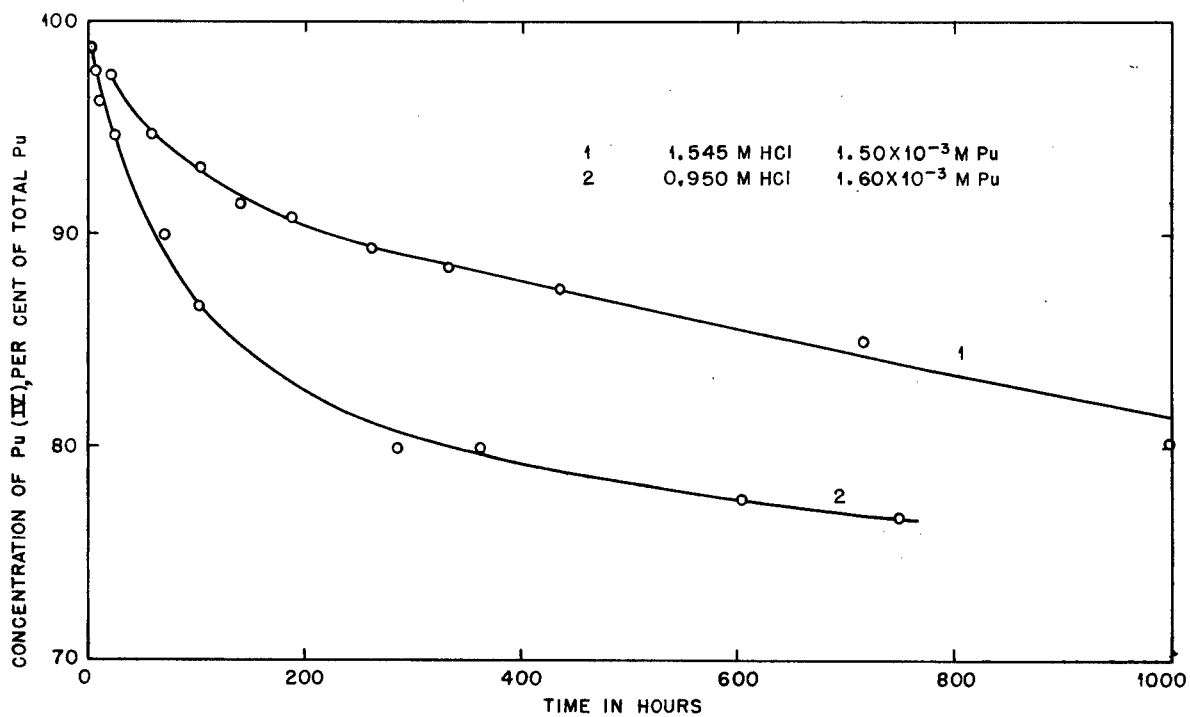


Figure 2. Disproportionation of Pu(IV) at 25°C.

Table 3. Disproportionation of Pu(IV) in 0.5M HCl at 25°C 1.93×10^{-3} M plutonium.

Time (hr)	Composition of solution* (%)				$K = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu	
1.0	2.0	97.0	1.0	100.0	
4.9	4.2	92.7	2.3	99.2	
8.1	6.0	90.3	3.2	99.5	
12.8	8.2	86.8	4.4	99.4	
25.1	13.2	78.2	7.2	98.6	
32.0	15.5	74.4	8.3	98.2	0.005
50.0	20.6	68.5	10.3	99.4	0.014
72.6	24.5	63.2	12.5	100.2	0.030
121.	27.3	58.2	13.7	99.2	0.052
152.	27.7	57.6	13.5	98.8	0.054
216.	28.4	57.7	13.2	99.3	0.056

* No Pu(V) or colloidal Pu(IV) was found.

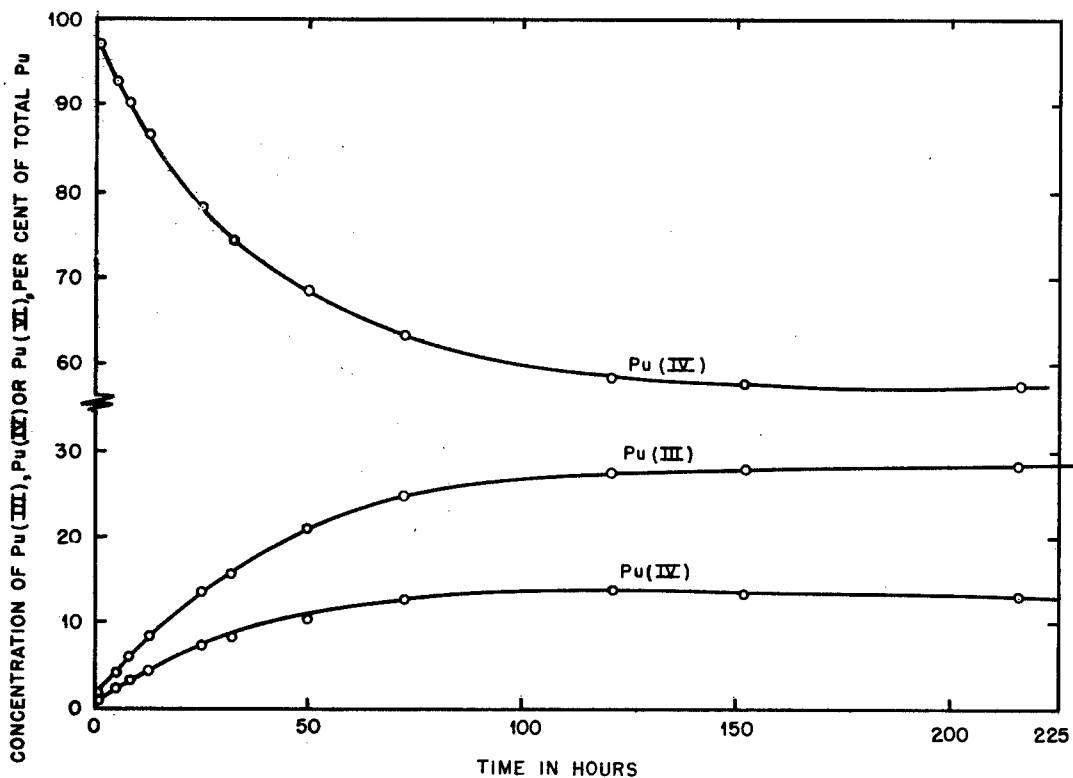


Figure 3. Disproportionation of Pu(IV) at 25°C, 0.5M HCl, 1.93×10^{-3} M Pu.

Table 3 and Figure 3 show the disproportionation in ~0.5M hydrochloric acid and 1.93×10^{-3} M plutonium. Equilibrium was reached in approximately 150 hours at which time $K = 0.055$. The effect of alpha radiation on the Pu(VI) concentration begins to be discernable at about 150 hours.

The data for the disproportionation in 0.474M, 0.244M, and 0.183M hydrochloric acid are given in Tables 4, 5, and 6. The equilibrium constants are 0.063, 2.4, and 6.9, respectively. The rate of disproportionation is increased both by lowering the acidity and by increasing the Pu(IV) concentration (Figure 4). As will be noted in Section 2, the hydrogen ion dependence of the disproportionation rate is inversely proportional to about the third power of the hydrogen ion concentration and directly proportional to between the second and third power of the Pu(IV) concentration. Table 7 gives the approximate times required for each of these Pu(IV) solutions to proceed halfway to equilibrium. In 0.183M hydrochloric acid a small concentration of Pu(V) was found, thus indicating the presence of this state is favored in solutions of low acidity. The constant K_1 , where

$$K_1 = \frac{[\text{Pu(III)}][\text{Pu(VI)}]}{[\text{Pu(IV)}][\text{Pu(V)}]} \quad (3)$$

was found to be approximately 14.

Table 4. Disproportionation of Pu(IV) in 0.474M HCl at 25°C 4.25×10^{-3} M plutonium.

Time (hr)	Composition of solution* (%)				$K = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu	
0.7	3.3	93.2	3.2	99.7	
1.2	4.3	91.4	4.0	99.7	
1.6	5.2	89.7	4.5	99.4	
2.0	6.5	88.6	5.0	100.1	
2.8	8.1	85.8	6.0	99.9	
3.2	9.6	84.3	6.6	100.5	
4.4	11.6	80.5	7.7	99.8	
5.1	13.2	78.3	8.3	99.8	
6.1	14.7	76.2	9.3	100.2	
7.4	16.3	73.3	10.4	100.0	
8.1	17.4	72.1	10.9	100.4	
9.3	18.9	69.7	11.4	100.0	
10.4	19.9	67.9	11.9	99.7	
12.3	21.2	66.2	12.6	100.0	
14.2	22.5	63.7	13.5	99.7	
16.0	23.9	62.0	14.1	100.0	
17.8	24.5	60.5	14.7	99.7	
18.1	25.2	60.3	14.8	100.3	
21.8	26.1	58.8	15.1	100.0	
24.0	26.2	58.4	15.3	99.9	
25.7	26.4	57.3	15.3	99.0	0.057
29.5	27.1	57.0	15.8	99.9	0.063
32.2	27.3	56.7	15.7	99.7	0.064
49.0	27.0	56.1	15.3	98.4	0.063
56.0	26.9	56.6	15.3	98.8	0.061
72.1	27.3	56.0	15.5	98.8	0.066

* No Pu(V) or colloidal Pu(IV) was found.

Table 5. Disproportionation of Pu(IV) in 0.244M HCl at 25°C 1.38×10^{-3} M plutonium.

Time (hr)	Composition of solution* (%)				$K = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu	
0.3	4.2	93.0	2.3	99.5	
0.6	6.3	90.0	3.4	99.7	
0.9	7.7	87.9	4.2	99.8	
1.2	9.5	86.0	5.2	100.7	
1.7	11.0	83.5	6.0	100.5	
2.1	12.9	81.3	6.6	100.8	
2.6	14.3	78.5	7.4	100.2	
3.2	16.2	75.5	8.1	99.8	
3.7	17.2	73.4	8.5	99.1	
4.5	19.3	70.8	9.6	99.7	
5.3	21.0	68.1	11.1	100.2	
6.5	23.3	64.7	11.9	99.9	
7.5	24.8	62.2	13.1	100.1	
8.4	26.2	60.6	14.2	101.0	
9.5	27.4	58.2	14.6	100.2	
10.9	29.0	55.8	15.3	100.1	
12.5	30.8	53.8	16.2	100.8	
14.5	32.2	50.7	17.1	100.0	
16.2	33.8	48.2	17.5	99.5	
17.8	35.0	46.2	17.8	99.0	
19.4	35.9	45.1	18.2	99.2	
21.4	37.0	43.6	19.0	99.6	
24.6	38.4	40.8	19.4	98.6	
27.7	39.9	38.7	20.6	99.2	
30.6	41.3	37.6	21.0	99.9	0.67
33.5	42.1	36.7	21.1	99.9	0.76
37.3	42.8	34.9	21.0	98.7	0.91
49.0	44.5	32.4	21.7	98.6	1.26
76.0	46.6	28.9	22.0	97.5	1.99
170.	48.3	28.0	22.1	98.4	2.34

* No Pu(V) or colloidal Pu(IV) was found.

b) Disproportionation at 40°C to 70°C

The six solutions in which the disproportionation was measured at 25°C (Tables 1 to 6) were heated to 70°C and after sufficient time had elapsed for the new equilibrium to be attained, determination of the concentrations of the various plutonium ions was made (Tables 8 to 13). That equilibrium had been reached was assured by repeating the measurement of the absorption spectrum until the values were constant. In all cases the rate of disproportionation at 70°C was too rapid to measure.

The absorption spectra for Pu(IV) and Pu(V) at 70°C were not accurately known. Accordingly, the equilibrium concentrations of the various plutonium ions at 70°C might be determined by first cooling the solution rapidly to 25°C and measuring the concentration of the various ions during the repropor-tionation.

Table 6. Disproportionation of Pu(IV) in 0.183M HCl at 25°C 4.38 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)					K = $\frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$	K = $\frac{[\text{Pu(III)}][\text{Pu(VI)}]}{[\text{Pu(IV)}][\text{Pu(V)}]}$
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)	Total†Pu		
0.3	15.8	77.1	~0	11.2	104.1		
0.5	20.7	69.3	~0	14.4	104.4		
0.6	24.1	63.2		16.2	103.5		
0.8	26.8	59.1		17.8	103.7		
0.9	29.3	55.0	~0	19.2	103.5		
1.1	31.4	51.7		19.8	102.9		
1.3	33.5	48.1		21.4	103.0		
1.5	35.1	44.9		22.0	102.0		
1.7	36.8	43.0		22.8	102.6		
1.8	38.2	40.8	~0	23.8	102.8		
2.0	39.1	38.9		24.1	102.1		
2.2	40.0	37.2		24.7	101.9		
2.4	41.1	35.5		25.1	101.7		
2.8	42.3	33.4		25.5	101.2		
3.1	43.6	31.2	~1	25.8	100.6		
3.6	45.0	29.4		26.4	100.8		
4.2	45.7	27.7		27.0	100.4		
5.0	46.3	26.0		27.4	99.7		
5.5	46.8	25.2		27.5	99.5		
5.7	47.0	25.0	~4	27.4	99.4		~13
7.4	48.0	23.5		27.8	99.3	4.8	
9.3	48.3	22.5		27.8	98.6	5.7	
21.5	48.4	21.1		27.3	96.8	6.8	
23.6	49.0	21.2		27.4	97.3	6.9	
29.6	49.0	21.1	~5	27.3	97.4	7.0	~13
46.0	48.9	21.1	~4	26.9	96.9	6.9	~16

* No colloidal Pu(IV) was found. † "Total" does not include Pu(V).

Table 7. Half-times for the disproportionation of Pu(IV) at 25.0°C.

Initial Pu(IV) concentration (M x 10 ³)	HCl concentration (M)	Time for half disproportionation (hr)
1.50	1.545	~400
1.60	0.950	~90
1.93	~0.5	25
4.25	0.474	5
1.38	0.244	7
4.38	0.183	1

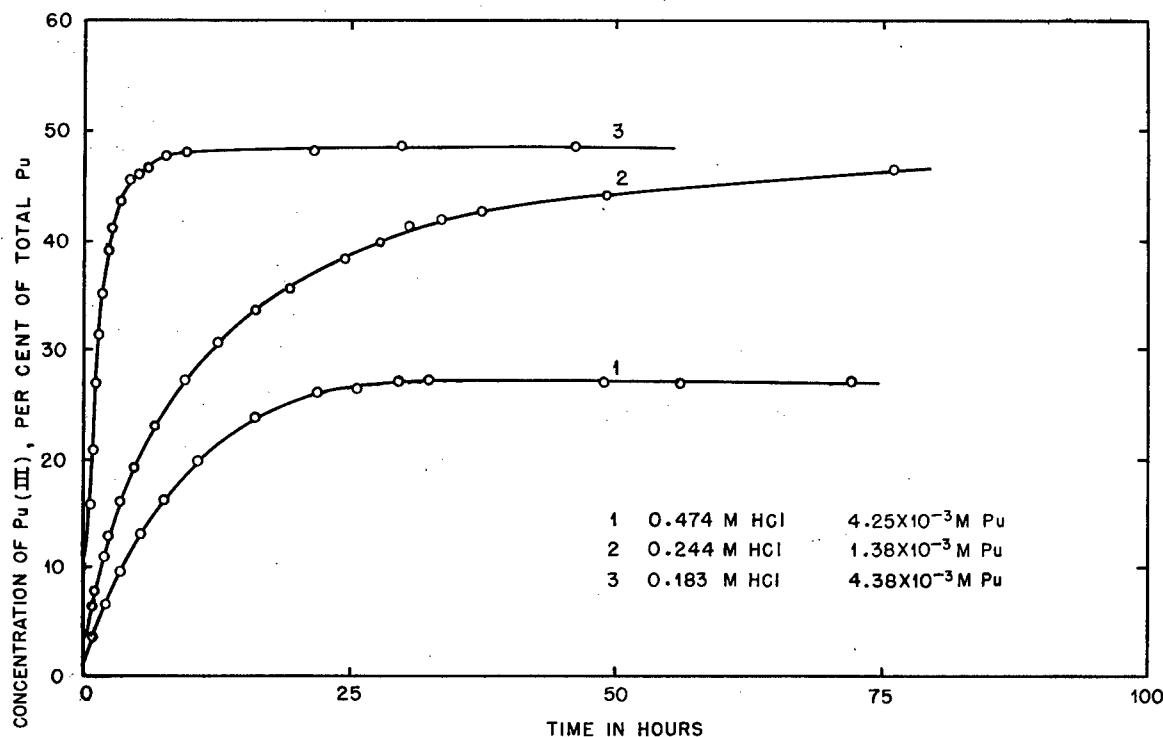


Figure 4. Disproportionation of Pu (IV) at 25°C (all data are not plotted; see Tables 4, 5, and 6.)

An extrapolation back to zero time would then give the concentration of the ions at 70°C. If during the cooling period, the reproporationation was more rapid than at 25°C, more Pu(IV) would be indicated as present at zero time than if the reproporationation rate were uniform, so that the value of the equilibrium constant so obtained would represent but a lower limit. However, if Pu(V) were present in the equilibrium mixture at 70°C, cooling to 25° would immediately establish the Pu(III)-Pu(IV)-Pu(V)-Pu(VI) equilibrium for 25°C, with the result that Pu(V) and Pu(IV) would react to produce more Pu(III) and Pu(VI) than expected by the reproporationation reaction. This would cause the value of K to have too high values when calculated by the extrapolation method. Therefore, the extrapolation method of calculating the concentrations of plutonium ions is a rather uncertain process, and at present the concentrations obtained by analysis at 70°C have to be used, despite the fact that the absorption spectra are not known accurately at this temperature (see Appendix).

In 1.545M hydrochloric acid, K at 70°C had increased from its 25°C value of 1×10^{-4} to 0.25 (Table 8). This represents an increase of approximately 2500 fold. The value for K for the 0.950M hydrochloric acid solution at 70°C increased to 8 or by about a factor of 4000 (Table 9). In the ~0.5M hydrochloric acid solution, the K for 70°C is 100, an increase of 1800 times over the 25°C value. The values of K at the intermediate temperatures 40°C and 55°C were found to be ~1.3 and ~15, respectively (Table 10). Table 11 presents the data from a solution 0.474M in hydrochloric acid. The average value of K is 19, representing an increase by a factor of 300 over the 25°C value. The value of K for the 0.244M hydrochloric acid solution at 70°C is of the order of 5000 (Table 12), which is about 2000 times the 25°C value of K, but the value could not be accurately determined because of uncertainties in the Pu(IV) analysis. As explained in the footnotes to Table 13, the value found for K (1300) in the 0.183M hydrochloric acid solution at 70°C is believed to be high.

Table 8. Disproportionation of Pu(IV) in 1.545M HCl at 70°C 1.47 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)				$K^\dagger = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu [‡]	
0	10.9	85.0	0.5	96.4	1 x 10 ⁻⁴
0.7	36.	51.	11.	98.	0.11
2.8	39.	44.	14.	97.	0.25
4.3	39.	45.	13.	97.	0.22
5.9	39.	45.	13.	97.	0.22
23.0	41.	43.	12.	96.	0.25

* Colloidal Pu(IV) was <2%.

† The values obtained by the extrapolation method for this solution are: Pu(III) = 44.6%, Pu(IV) = 42.0%, Pu(V) = ~4%, Pu(VI) = 10.1%, and K = 0.27.

‡ In the column giving values of "Total Pu," the per cent present as Pu(V) has been disregarded because of analytical uncertainties in the value of the latter at 70°C. The discrepancies between 100% and the quoted values of total Pu may be accounted for, at least in part, by this neglect of Pu(V).

Table 9. Disproportionation of Pu(IV) in 0.950M HCl at 70°C 1.57 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)				$K^\dagger = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu [‡]	
0.	20.0	76.8	2.9	99.7	
0.4	50.4	26.4	20.6	93.3	2.9
1.7	53.9	19.8	22.6	93.1	8.5
2.4	54.3	20.6	22.7	92.6	7.7

* Colloidal Pu(IV) was <1%.

† Values at 70°C obtained by the extrapolation method are: Pu(III) = 55.3%, Pu(IV) = 23.5%, Pu(V) = ~3%, Pu(VI) = 17.2%, and K = 4.1.

‡ See footnote (‡), Table 8.

Table 10. Disproportionation equilibria of Pu(IV) in ~0.5M HCl at 25.0°, 40.0°, 55.0°, 70.0°C, 1.93 x 10⁻³M plutonium.

Temperature (°C)	Composition of solution* (%)				$K^\dagger = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu	
25.0 ± 0.5	28.4	57.7	13.2	99.3	0.056
25.0 ± 0.5	31.7	57.9	11.1	100.7	0.057
40.0 ± 0.5	44.6	32.2	21.9	98.7	1.3
55.0 ± 0.5	52.7	17.1	27.1	96.9	15.
70.0 ± 0.5	54.7	9.7	30.4	94.8	100.

* No colloidal Pu(IV) was found. No determination of Pu(V) was made.

† Values at 70°C obtained by the extrapolation method are: Pu(III) = 56.0%, Pu(IV) = 14.5%, Pu(VI) = 23.3%, and K = 24.

c) Reproportionation at 25°C

Each of the solutions (except the one in 0.183M hydrochloric acid) which had been heated to 70°C was cooled rapidly to 25°C and a series of measurements were taken as the solution returned to the 25°C equilibrium concentrations. In 1.545 and 0.950M hydrochloric acid these experiments were continued long enough to obtain an estimate of the reproportionation rate but not long enough for equilibrium to be reached. Hence in these cases, only an upper limit for K was obtained. The data for these measurements are given in Tables 14 through 18. The values for K and K_1 , calculated from the reproportionation data together with those presented in subsections (a) and (b) are summarized in Table 19. In Figure 5 the rates of reproportionation are shown. The right-hand column of Figure 5 gives the approximate half period for the reproportionation. On the basis of these values for the half periods, it is seen that the reproportionation rate is markedly increased at the higher acidities and higher concentrations of Pu(III) and Pu(IV).

Table 11. Disproportionation of Pu(IV) in 0.474M HCl at 70°C 4.16×10^{-3} M plutonium.

Time (hr)	Composition of solution* (%)				$K \ddagger = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu †	
0.	27.3	56.0	15.5	98.8	
0.4	52.2	15.5	24.9	92.6	18
1.0	52.0	15.7	24.7	92.4	17
1.9	52.5	14.8	24.7	92.0	21

* Colloidal Pu(IV) was <1%.

† Values at 70°C obtained by the extrapolation method are: Pu(III) = 57%, Pu(IV) = 12%, Pu(VI) = 26%, and $K = 49$.

‡ See footnote (‡), Table 8.

Table 12. Disproportionation of Pu(IV) in 0.244M HCl at 70°C 1.35×10^{-3} M plutonium.

Time (hr)	Composition of solution* (%)				$K \ddagger = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)†	Pu(VI)	Total Pu §	
0.	48.3	28.0	22.1	98.4	
0.4	56.1	3.5	25.6	85.2	(1900)
0.8	56.3	2.4	23.7	82.4	(5400)
1.1	56.4	2.1	23.7	82.2	(8100)

* Colloidal Pu(IV) was <1%.

† Values of Pu(IV) may be very much in error since in this experiment calculation of Pu(IV) was based on small differences between large and somewhat uncertain numbers (See Appendix). Thus, K calculated from these data may be considerably in error.

‡ Values at 70°C obtained by the extrapolation method are: Pu(III) = 59.0%, Pu(IV) = 6.3%, Pu(V) = 13.2%, Pu(VI) = 21.0%, and $K = 290(?)$.

§ See footnote (‡), Table 8.

Table 13. Disproportionation of Pu(IV) in 0.183M HCl at 70°C 4.29 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)				K _‡ = $\frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV) [‡]	Pu(VI)	Total Pu [§]	
0.	48.9	21.1	26.9	92.9	
0.5	51.9	4.3	26.5	82.7	(900)
1.0	53.0	5.0	27.7	85.7	(620)
1.8	52.6	4.0	27.6	84.2	(1200)
5.0	51.0	3.8	26.8	81.6	(1300)

* See Table 26 for colloidal Pu(IV).

[†] Formation of colloidal Pu(IV) set in very rapidly when the solution was heated. Lack of information about the absorption spectrum of colloidal Pu(IV) formed under these conditions interfered with the measurement of the other species present and prevented the later following of reproporationation at 25°C.

[‡] Inconsistencies in Pu(IV) values are probably of an experimental nature.

[§] See footnote (‡), Table 8.

d) Summary and Discussion

The data already presented and collected in Table 19 show that the disproportionation constant, K, is inversely related to the hydrogen ion concentration. Increasing the temperature from 25°C to 70°C increases K by a factor of about ~300 to 4000. The rate of disproportionation is markedly increased at 70°C as compared with 25°C and is likewise increased by raising the concentration of Pu(IV) (varies as [Pu(IV)]ⁿ, where n = 2 to 3), or lowering the acidity (varies as 1/(H⁺)ⁿ, where n = ~3). On the other

Table 14. Reproportionation of Pu(IV) in 1.545M HCl at 25°C, 1.50 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)					K _‡ = $\frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$	K ₁ = $\frac{[\text{Pu(III)}][\text{Pu(VI)}]}{[\text{Pu(IV)}][\text{Pu(V)}]}$
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)	Total Pu		
0 [†]	44.6	42.0	~ 4	10.1	100.7		~ 2.7
0.8	42.3	45.7	~ 2.3	8.7	99.0		~ 3.5
1.3	40.9	48.0	~ 1.6	8.3	98.8		~ 4.4
2.2	38.9	51.1	§	7.0	97.0	0.080	
3.3	36.8	54.1	§	5.9	96.8	0.050	
5.0	34.6	57.1	§	4.9	96.6	0.032	
7.0	33.3	60.1	§	4.0	97.4	0.020	
10.0	31.3	62.8	§	2.9	97.0	0.012	
21.5	27.7	67.5	§	1.2	96.4	0.0030	
52.0	24.9	69.8	§	~ 0	94.7		
74.0	24.7	70.0	§	~ 0	94.7		

* Colloidal Pu(IV) was <2%. [†] These values were determined by extrapolation.

[‡] Measurements were not continued long enough for equilibrium to be reached.

[§] Undetectable.

Table 15. Reproportionation of Pu(IV) in 0.950M HCl at 25°C 1.60 x 10⁻³M plutonium.

Time (hr)	Composition of solution* (%)					$K_{\ddagger} = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$	$K_1 = \frac{[\text{Pu(III)}][\text{Pu(VI)}]}{[\text{Pu(IV)}][\text{Pu(V)}]}$
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)	Total Pu		
0.†	55.3	23.5	~ 3	17.2	99.0		~ 14
0.4	54.1	26.1	~ 2.2	16.7	99.1		~ 16
1.1	52.5	30.4	~ 1.3	15.8	99.9		~ 21
2.1	50.0	34.2	~ 0.5	14.7	99.4		
3.2	48.1	37.7	§	13.9	99.7		
4.3	46.3	40.6	§	13.0	98.8		
6.1	44.2	44.0	§	11.7	98.6		
7.8	42.1	46.5	§	11.0	99.2		
10.5	40.4	50.2	§	10.2	100.8		
15.3	37.3	54.8	§	8.4	100.5		
20.7	35.0	56.9	§	6.7	98.6	0.045	
27.0	33.4	60.3	§	6.1	99.8	0.031	
33.7	32.1	62.6	§	5.5	100.2	0.023	
44.3	30.5	65.1	§	5.0	100.6	0.017	
92.3	27.4	68.8	§	3.7	99.9	0.009	

* Colloidal Pu(IV) was <1%. † These values were determined by extrapolation.

‡ Measurements not continued long enough for equilibrium to be reached.

§ Undetectable.

hand, the rate of reproportionation is greater at higher acidities and higher concentrations of Pu(III) and Pu(VI). This information is of value in predicting the composition of a solution of plutonium, and should aid considerably in understanding the reaction of plutonium ions. It may also be of value in studying such reactions as the oxidation of Pu(IV) which may go via the disproportionation mechanism.

The disproportionation constant K , as used, was defined in such a manner that the hydrogen ion concentration was not included. Evaluation of K for several acidities, however, permits the calculation of the dependence of the constant upon the concentration of hydrogen ion. The derivation of this relationship is:

$$K[\text{H}^+]^X = \text{a constant} = K' \quad (4)$$

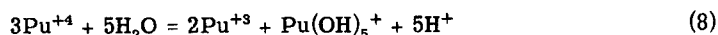
$$\log K = -X \log [\text{H}^+] + \log K' \quad (5)$$

$$\frac{d \log K}{d \log [\text{H}^+]} = -X \quad (6)$$

In Figure 6, $\log [\text{H}^+]$ is plotted against $\log K$ (see columns 1 and 2, respectively, of Table 19); thus the negative slope of the curve is equal to the power of the hydrogen ion dependence of K . The slope is 5.1. The new constant, K' , takes into consideration the effect of $[\text{H}^+]$ on the disproportionation and may be defined:

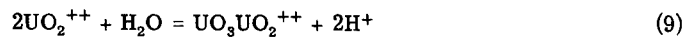
$$K' = \frac{[\text{Pu(III)}]^2 [\text{Pu(VI)}] [\text{H}^+]^5}{[\text{Pu(IV)}]^3} \quad (7)$$

If this expression is used in an attempt to determine the state of the plutonium ions in solution, an equation such as equation 8 would result.



It must be remembered, however, that the effects of chloride complexing and hydrolysis of the various ions and of ionic strength have been neglected. The chloride complexing would probably act to increase the stability of Pu(VI) with respect to Pu(IV), since in dilute hydrochloric acid solutions at room temperature the Pu(VI) is known to form a complex with chloride ion, whereas in similar solutions the chloride complex of Pu(IV), if it exists, is very weak. Thus, the chloride complexing would make the hydrogen ion dependence appear smaller than it actually is. Hydrolysis of either Pu(IV) or Pu(VI) may occur and change the apparent dependence of the reaction on hydrogen ion concentration. From the chemistry of the uranyl ion it seems unlikely that Pu(VI) would hydrolyze under such conditions.

In CCA-380, Best, Taub, and Longworth⁵ have found equations 9 and 10 to apply for the uranyl system in dilute acid solution:



$$K = \frac{[\text{UO}_3\text{UO}_2^{++}][\text{H}^+]^2}{[\text{UO}_2^{++}]^2} = 1.35 \times 10^{-6} \quad (10)$$

In a solution 0.183M in hydrogen ion and $1 \times 10^{-3}\text{M}$ in plutonyl (Table 6), assuming the same equations are applicable to plutonyl solutions, the ratio $[\text{PuO}_3\text{PuO}_2^{++}]/[\text{PuO}_2^{++}]$ would be $\sim 4 \times 10^{-4}$.

There is evidence, however, that Pu(IV) may hydrolyze to some extent in the 0.18M hydrochloric acid solution.⁶ Such a hydrolysis would also cause the H^+ dependence to appear too small. The slope of the curve in Figure 6 does show some indication of breaking over to a lower value of hydrogen ion dependence in the more dilute solutions of hydrochloric acid.

Table 16. Reproportionation of Pu(IV) in 0.5M HCl at 25°C $1.93 \times 10^{-3}\text{M}$ plutonium.

Time (hr)	Composition of solution* (%)				$K = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$
	Pu(III)	Pu(IV)	Pu(VI)	Total Pu	
0.†	56.0	14.5	23.3	93.8	
0.2	55.4	15.3	23.0	93.7	
0.4	55.4	16.5	23.0	94.9	
1.1	54.3	19.1	22.8	96.2	
2.1	51.2	21.2	21.9	94.3	
3.6	50.0	25.2	21.6	96.8	
18.5	39.5	41.4	16.0	96.9	
24.	37.7	46.0	15.4	99.1	
43.	33.7	51.4	13.6	98.7	0.114
51.	33.0	53.2	13.3	99.5	0.096
69.	31.8	55.7	11.4	98.9	0.076
75.	31.5	56.4	12.3	100.2	0.068
90.	31.2	57.7	11.3	100.2	0.057
192.	31.7	57.9	11.1	100.7	0.057

* No colloidal Pu(IV) was found. The low values for total Pu probably indicate the presence of Pu(V); however, no direct analysis for Pu(V) was made.

† These values were determined by extrapolation.

Table 17. Reproportionation of Pu(IV) in 0.474M HCl at 25°C 4.25 x 10⁻³ M plutonium.

Time (hr)	Composition of solution* (%)					K = $\frac{[\text{Pu(III)}]^2 [\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$	K ₁ = $\frac{[\text{Pu(III)}] [\text{Pu(VI)}]}{[\text{Pu(IV)}] [\text{Pu(V)}]}$
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)	Total Pu		
0†	57.0	12.0		26.0	95.0		
1.5	47.1	25.5	~1.5	23.9	98.0		~29
2.0	44.5	29.5	~1.8	23.3	98.1		~19
3.0	41.6	33.2	~1.3	22.7	98.8		~22
4.0	39.8	36.5	‡	21.5	97.8		
5.1	38.0	39.4	‡	20.6	98.0		
7.0	35.7	43.7	‡	19.4	98.8		
8.8	34.3	46.5	‡	18.4	99.2		
10.5	32.8	48.4	‡	18.0	99.2		
12.0	31.8	49.8	‡	17.5	99.1		
14.4	30.9	51.7	‡	17.1	99.7	0.118	
21.4	28.8	54.3	‡	15.6	98.7	0.081	
25.4	28.7	54.9	‡	15.3	98.9	0.077	
29.3	28.6	55.5	‡	15.5	99.6	0.074	
47.8	27.7	55.4	‡	15.2	98.3	0.068	

* Colloidal Pu(IV) was <1%. †These data were determined by extrapolation.

‡ Undetectable.

Table 18. Reproportionation of Pu(IV) in 0.244M HCl at 25°C 1.38 x 10⁻³ M plutonium.

Time (hr)	Composition of solution* (%)					K = $\frac{[\text{Pu(III)}]^2 [\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$	K ₁ = $\frac{[\text{Pu(VI)}] [\text{Pu(III)}]}{[\text{Pu(IV)}] [\text{Pu(V)}]}$
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)	Total Pu		
0†	59.0	6.3	13.2	21.0	100.0		15
0.5	58.8	7.0	12.5	20.4	98.7		14
0.9	58.5	7.4	10.8	20.3	97.0		15
1.1	58.3	9.1	11.3	20.4	99.1		12
4.2	58.1	10.6	8.4	21.4	98.5	61	14
6.9	57.2	12.5	8.1	21.5	99.3	36	12
20.2	54.1	19.2	2.4	21.4	97.1	8.9	
49.5	50.1	25.9	1.1	20.4	97.5	3.0	
68.0	49.1	25.5	~0.	20.1	94.7	2.9	

* Colloidal Pu(IV) was <1%. †These values were obtained by extrapolation.

The effect of ionic strength is unknown since the activity coefficients of the various ions have never been measured. However, it does not seem unreasonable that the effect of ionic strength could be in the direction and of the order of magnitude necessary to correct the hydrogen ion dependence to fourth power. Moreover, the majority of the chemical evidence indicates Pu(VI) is probably PuO₂⁺⁺ (or Pu(OH)₄⁺⁺), or in hydrochloric acid solutions, some chloride complex of this ion.

Table 19. Summary of equilibrium constants, K and K_1 .

HCl (M)	$K = \frac{[\text{Pu(III)}]^2 [\text{Pu(VI)}]}{[\text{Pu(IV)}]^3}$						$K_1 = \frac{[\text{Pu(III)}] [\text{Pu(VI)}]}{[\text{Pu(IV)}] [\text{Pu(V)}]}$	
	25°C		40°C	55°C	70°C		25°C	
	D	R	D	D	D	R*	D	R
1.545	1×10^{-4}	$\ll 3 \times 10^{-3}$			0.25	0.27		~ 4
0.950	2×10^{-3}	$< 9 \times 10^{-3}$			8.1	4.1		~ 17
0.5	0.055	0.057	1.3	15	100	24		
~0.474	0.063	0.068			19	49		~ 23
0.244	2.4	2.9			(5000?)†	(290?)†		14
0.183	6.9				(1300?)†		~ 14	

D = Data were taken from a disproportionation experiment in which equilibrium was reached from the Pu(IV) side.

R = Data were taken from a reproporationation experiment in which equilibrium was reached from the Pu(III)-Pu(VI) side

* In these cases the measurements were made at 25°C and an extrapolation made to a time corresponding to the 70°C equilibrium. See text.

† ? = Denotes a very doubtful value.

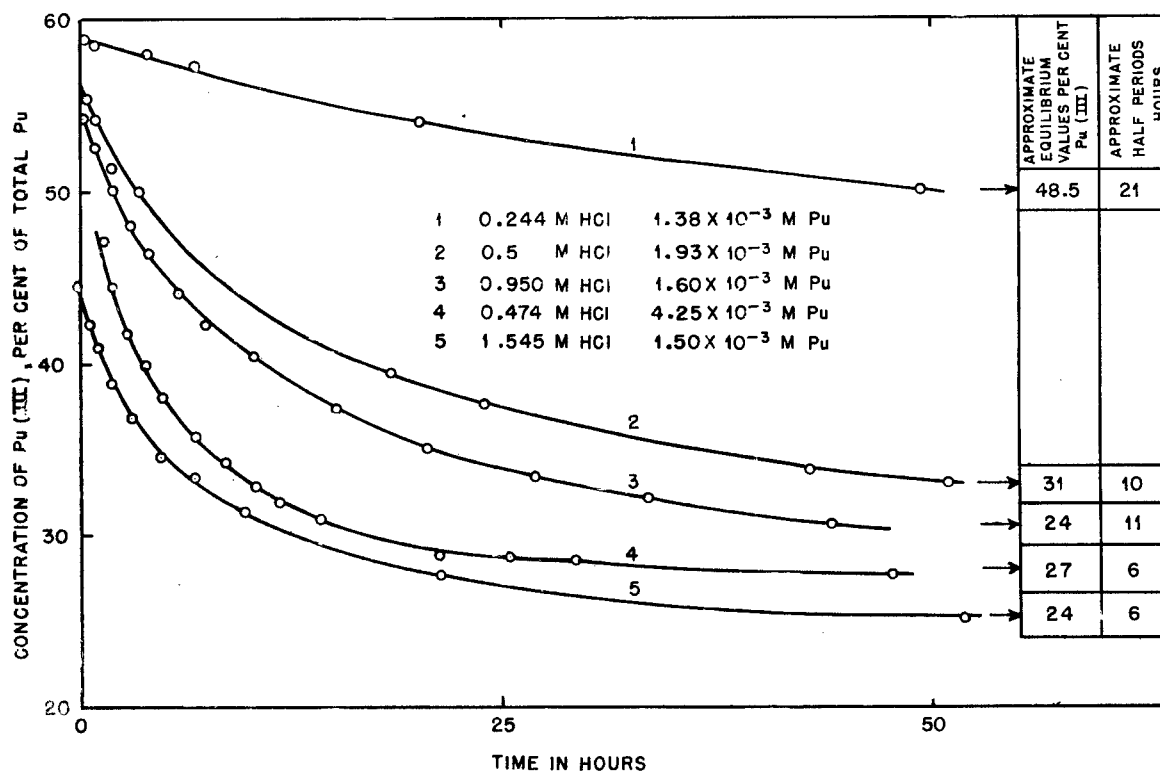


Figure 5. Reproportionation of Pu(IV) at 25°C.

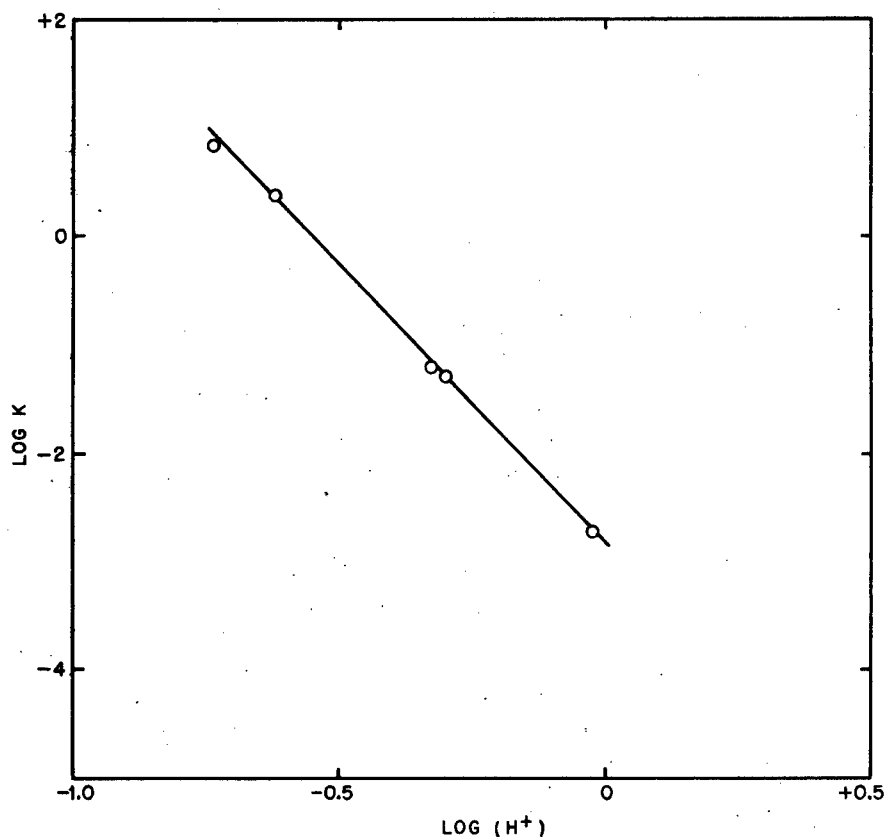
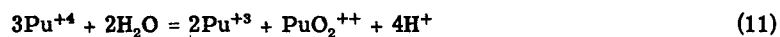


Figure 6. H^+ dependence of the disproportionation constant K in HCl solutions.

From the relation of the disproportionation constant to the temperature of the solution, it is possible to make several interesting thermodynamic calculations. For this purpose the equilibrium constant will be defined somewhat differently from either K or K' and for convenience will be referred to as K'' .



$$K'' = \frac{[Pu^{+3}]^2 [PuO_2^{++}] [H^+]^4}{[Pu^{+4}]^3} \quad (12)$$

The fourth power of the hydrogen ion concentration is used since other evidence strongly favors PuO_2^{++} (or $Pu(OH)_4^{++}$) rather than $Pu(OH)_5^{+}$ for the formula of Pu(VI). The calculations given here are based on the $\sim 0.5M$ hydrochloric acid solution. The values for the concentrations of the various ions were taken from Table 10. First, $R \ln K''$ was plotted against $1/T$ and the slope of the curve at $298^\circ C$ was used to evaluate ΔH in equation 11 (Figure 7).

$$\Delta H_{298}^\circ = \frac{-d(R \ln K'')}{d(1/T)} = 41,000 \text{ cal./mole} \quad (13)$$

$$\Delta F_{298}^{\circ} = -298 R \ln K'' = 3,300 \text{ cal./mole} \quad (14)$$

$$\Delta S_{298}^{\circ} = \frac{\Delta H^{\circ} - \Delta F^{\circ}}{T} = 1.27 \text{ E.U.} \quad (15)$$

From the value of ΔS_{298} for equation 11 it now becomes possible to calculate the entropy of the +4 plutonium ion. This is the first time the entropy of a +4 ion in aqueous solution has been determined. In order to make this calculation, it is first necessary to make certain assumptions regarding the entropies of Pu(III) and Pu(VI). The values of the aqueous entropies of Pu(III) and Pu(VI) are taken respectively as being approximately the same as those of Gd^{+++} and UO_2^{++} . This choice is based on the similarities of the charges and the ionic radii for the analogous pairs. In the case of the Gd^{+++} - Pu(III) pair the mass of the plutonium ion is considerably larger than that of its model, so that a correction was applied according to the formula:⁷

$$S_{Pu(III)} - S_{Gd^{+++}} = \frac{3}{2} R \ln \frac{M_{Pu}}{M_{Gd}} = 1.6 \text{ E.U.} \quad (16)$$

The difference in the contribution to the ionic entropy due to differences in the electronic structures of each pair (i.e., UO_2^{++} - PuO_2^{++} and Gd^{+++} and Pu^{+++}) is probably small. However, one difference that will be present is the difference in the magnetic entropy. Thus, to the entropy of UO_2^{++} must be added an amount which corresponds to the magnetic entropy of PuO_2^{++} (presumably UO_2^{++} itself will have

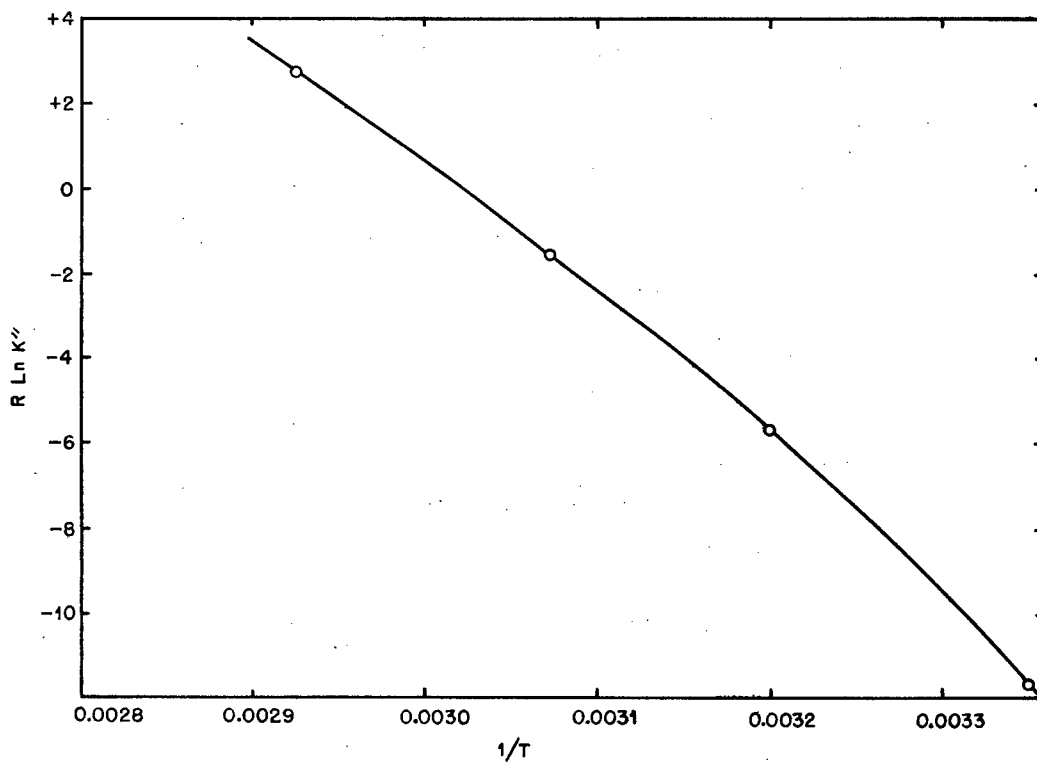


Figure 7. Temperature dependence of the disproportionation constant K'' in $\sim 0.5M$ HCl.

zero magnetic entropy); the entropy of Gd^{+++} must first be decreased by $R \ln 8 = 4.2$ corresponding to its magnetic entropy and then increased by an amount corresponding to the magnetic entropy of Pu^{+++} . Unfortunately, the magnetic entropies of Pu^{+++} and PuO_2^{++} are not known and cannot be reliably estimated; therefore, no correction could be made for their magnetic entropies. This means that the final value of $S(Pu(IV))$ will be too negative, by an amount corresponding to the sum of $2/3$ the Pu^{+++} magnetic entropy and $1/3$ the PuO_2^{++} magnetic entropy. This correction might be of the order of 5 E.U. This correction probably introduces less uncertainty in the final result than do the possible errors in the determination of ΔH° of the disproportionation equilibrium. Making these corrections for $S(Gd^{+++})$ one obtains:

$$S_{Pu(III)} = S_{Gd^{+3}} + 1.6 - 4.2 = -35.1 \text{ E.U.}^* \quad (17)$$

$$S_{Pu(VI)} = S_{UO_2^{++}} = -17 \text{ E.U.}^9 \quad (18)$$

$$S_{H_2O} = 16.8 \text{ E.U.}^7 \quad (19)$$

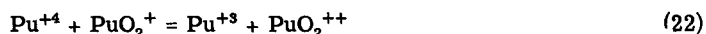
Then the entropy of $Pu(IV)$ is calculated:

$$\Delta S^\circ = 2S_{Pu(III)} + S_{Pu(VI)} + 4S_{H^+} - 2S_{H_2O} - 3S_{Pu(IV)} \quad (20)$$

$$\text{and } S_{Pu(IV)} = -83 \text{ E.U.} \quad (21)$$

It was difficult to measure values of $K_1 = [Pu(III)][Pu(VI)]/[Pu(IV)][Pu(V)]$ at room temperature because of the low concentration of $Pu(V)$. This difficulty could be partially overcome by heating the solution to $70^\circ C$, then rapidly cooling to $25^\circ C$ and measuring the concentrations of $Pu(III)$, $Pu(IV)$, $Pu(V)$, and $Pu(VI)$. The concentration of $Pu(V)$ was always higher at $70^\circ C$ than at $25^\circ C$ due to greater disproportionation of $Pu(IV)$. The rapid cooling prevented the re-establishment of the $25^\circ C$ disproportionation equilibrium. However, the equilibrium represented by K_1 was presumably re-established rapidly and the values of K_1 measured are believed to apply to the equilibrium at $25^\circ C$.

The measurement of $Pu(V)$ concentration at $70^\circ C$ was attempted; however, due to the uncertainties in the $Pu(IV)$ and $Pu(V)$ absorption curves at $70^\circ C$, the values thus obtained are not reliable and are therefore not reported. With the exception of the value in 1.545M hydrochloric acid ($25^\circ C$) the constancy of K_1 at $25^\circ C$ is better than one would expect from experimental variations (Table 19). In 1.545M hydrochloric acid ($25^\circ C$) the value is ~ 4 , whereas the remaining values range from 14 to 23, while a value of 8.5 has been previously reported at room temperature.¹⁰ Thus, there is no large dependence of K_1 upon the hydrochloric acid concentration. If $Pu(V)$ may be represented as PuO_2^+ and the equilibrium as



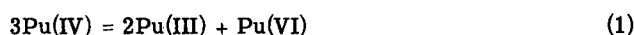
then no hydrogen ion dependence would be expected. The effect of chloride complexing and ionic strength on K_1 are unknown. If equation 22 is correct, the reason $Pu(V)$ appears to be more stable in low acid and at high temperatures is because these conditions favor the increase of the ratio $[Pu(III)][Pu(VI)]/[Pu(IV)]$ through disproportionation of $Pu(IV)$. Further support for the suggestion that $Pu(V)$ is PuO_2^+ is found in the fact that the $Pu(V) - Pu(VI)$ couple is probably reversible whereas the $Pu(IV) - Pu(V)$ couple is probably irreversible.¹⁰ In Section 3, experiments on the $Pu(III) - Pu(V) - Pu(VI)$ equilibrium at low acidities are presented.

* The entropy of Gd^{+++} has been determined to be -32.5 E.U.^8

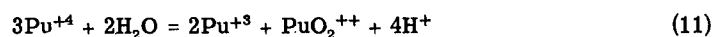
2. MECHANISM OF THE DISPROPORTIONATION OF Pu(IV)*

In Section 1, data relating to the effect of acidity and temperature upon both the disproportionation constant and the rate of disproportionation of Pu(IV) are given. The effect of the concentration of Pu(IV) upon the rate of disproportionation is also shown. In the present section an attempt will be made to interpret the effects of Pu(IV) and hydrogen ion concentrations on the rate of disproportionation in terms of the reaction mechanism. From such measurements only the rate determining step can actually be studied. However, this is the most important step of the reaction and such knowledge would be useful in extrapolating values for the rate of disproportionation to other conditions of acidity and Pu(IV) concentration.

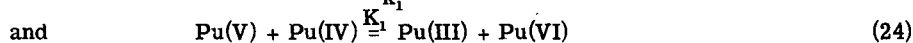
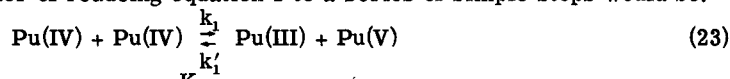
The net reaction involved in the disproportionation of Pu(IV) may be written:



or with assumptions regarding the ionic formulas:



Probably the most apparent manner of reducing equation 1 to a series of simple steps would be:



The first of the steps, equation 23, probably involves the oxygenation of one of the plutonium ions and the second a simple transfer of an electron; it is likely that the first would be a much slower step than the second. In CN-1912, evidence is given that reaction 24 is rapid.¹⁰ Since CN-1912 was published, Connick has made further calculations from the data on the disproportionation of Pu(V) which indicate that reaction 23 is actually a slow step.¹¹ The rate law for the mechanism represented by equations 23 and 24 when the concentration of Pu(V) is small relative to the total plutonium concentration is:

$$-\frac{d[\text{Pu(IV)}]}{dt} = k_1[\text{Pu(IV)}]^2 - k_2 \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]} \quad (25)$$

$$\text{where} \quad k_2 = \frac{K_1'}{K_1}$$

The first term of equation 25 represents the rate of the forward reaction (disproportionation) while the second term corrects for the back reaction (reproportionation). In making the calculations it was always necessary to take full account of the back reaction since it introduces an appreciable correction in even the early part of the disproportionation.

From the data of Section 1, the concentrations of Pu(III), Pu(IV), and Pu(VI) as a function of time were known. The two constants k_1 and k_2 are related ($K = k_1/k_2$, where K is the disproportionation constant) and the rate law expressed in equation 25 may be rewritten to include only one unknown, k_1 . If this law is correct, k_1 will have a constant value as long as the hydrochloric acid concentration remains unchanged. The evaluation of k_1 from the experimental data for this and several other mechanisms is given in Table 20. Before discussing the results, a brief description of the method used for determining $d[\text{Pu(IV)}]/dt$ will be given; all other phases of the calculations were straightforward.

* The authors wish to acknowledge the guidance of Dr. R. E. Connick in the development of the theory of this section.

In evaluating $d[\text{Pu(IV)}]/dt$ the concentration of Pu(IV) was plotted as a function of time. With the aid of a straightedge placed tangent to the curve, the slope of the curve was determined at a number of points, usually 12 to 15. Since $-d[\text{Pu(IV)}]/dt = 3/2 d[\text{Pu(III)}]/dt$, evaluation of $3/2 d[\text{Pu(III)}]/dt$ afforded a separate check on the values for the slope of the Pu(IV) curve. On a third graph the values for $-d[\text{Pu(IV)}]/dt$ and $3/2 d[\text{Pu(III)}]/dt$ were plotted as a function of time. The actual values of $d[\text{Pu(IV)}]/dt$ used in all calculations were selected from a curve drawn through the points obtained from both the Pu(IV) and the Pu(III) curves. In this way the errors involved in plotting the data and subsequently reading slopes were minimized. In Figure 8 a typical curve showing the plot of both $-d[\text{Pu(IV)}]/dt$ and $3/2 d[\text{Pu(III)}]/dt$ against time is given. The two sets of data are in excellent agreement and fall on a smooth curve.

In addition to the rate law described, four others were investigated (Table 20):

$$-\frac{d[\text{Pu(IV)}]}{dt} = k_1[\text{Pu(IV)}] - k_2 \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(IV)}]^2} \quad (26)$$

$$-\frac{d[\text{Pu(IV)}]}{dt} = k_1[\text{Pu(IV)}]^3 - k_2[\text{Pu(III)}]^2[\text{Pu(VI)}] \quad (27)$$

$$-\frac{d[\text{Pu(IV)}]}{dt} = k_1 \frac{[\text{Pu(IV)}]^2}{[\text{Pu(III)}]} - k_2 \frac{[\text{Pu(III)}][\text{Pu(VI)}]}{[\text{Pu(IV)}]} \quad (28)$$

$$-\frac{d[\text{Pu(IV)}]}{dt} = k_1 \frac{[\text{Pu(IV)}]^3}{[\text{Pu(III)}]} - k_2[\text{Pu(III)}][\text{Pu(VI)}] \quad (29)$$

For each rate law the constant k_1 was calculated at 10 to 12 different times in every experiment. If a rate law were correct, the values calculated for k_1 would, of course, be constant for any experiment. This constancy, or lack thereof, was used as the criterion for the correctness of a given rate law. The values obtained for k_1 , in solutions of different acidity cannot be directly compared since no account has been taken of the hydrogen ion dependence. Of these possible rate laws only the ones in which the forward reaction is proportional to $[\text{Pu(IV)}]^2$ or $[\text{Pu(IV)}]^3$ gave promise of fitting the data as shown in Table 20. These will be referred to as the square and the cube rate laws, respectively.

The data of Table 20 which have to do with the square and cube rate laws are briefly summarized in Table 21. The constancy of the values of k_1 for each set of conditions is somewhat better for the square law than for the cube law. Furthermore, it should be pointed out that the values of k_2 calculated on the basis of the cube law show a consistent tendency to increase during the course of the experiment. Any such trend is much less apparent in the values of k_1 based on the square law.

On the basis of the values of k_1 in 0.183 and 0.474M hydrochloric acid the hydrogen ion dependence of k_1 was found to be the 2.81 power for the square rate law and the 3.51 power for the cube law. Using these powers and calculating k_1 for 0.244M hydrochloric acid a value of 65 is found for the square law and 3.4×10^4 for the cube law. These compare about equally well with the values 40 and 5.6×10^4 found experimentally. It should be emphasized that the initial concentrations of Pu(IV) in these experiments varied from $1.38 \times 10^{-3}\text{M}$ (0.244M hydrochloric acid) to $4.38 \times 10^{-3}\text{M}$ (0.183M hydrochloric acid). In the case of the experiment in 0.244M hydrochloric acid the final concentration of Pu(IV) had decreased to $0.4 \times 10^{-3}\text{M}$ (Table 5). The range of Pu(IV) concentrations studied was thus sufficient so that a distinction between the square and cube rate laws seemed possible; however, from the present data a clear-cut distinction cannot be made.

It is difficult to write a rate mechanism in which the rate of the forward reaction of the rate determining step is proportional to the third power of the Pu(IV) concentration. As described, a mechanism for the square rate law can be easily written and there is independent information (given earlier) which

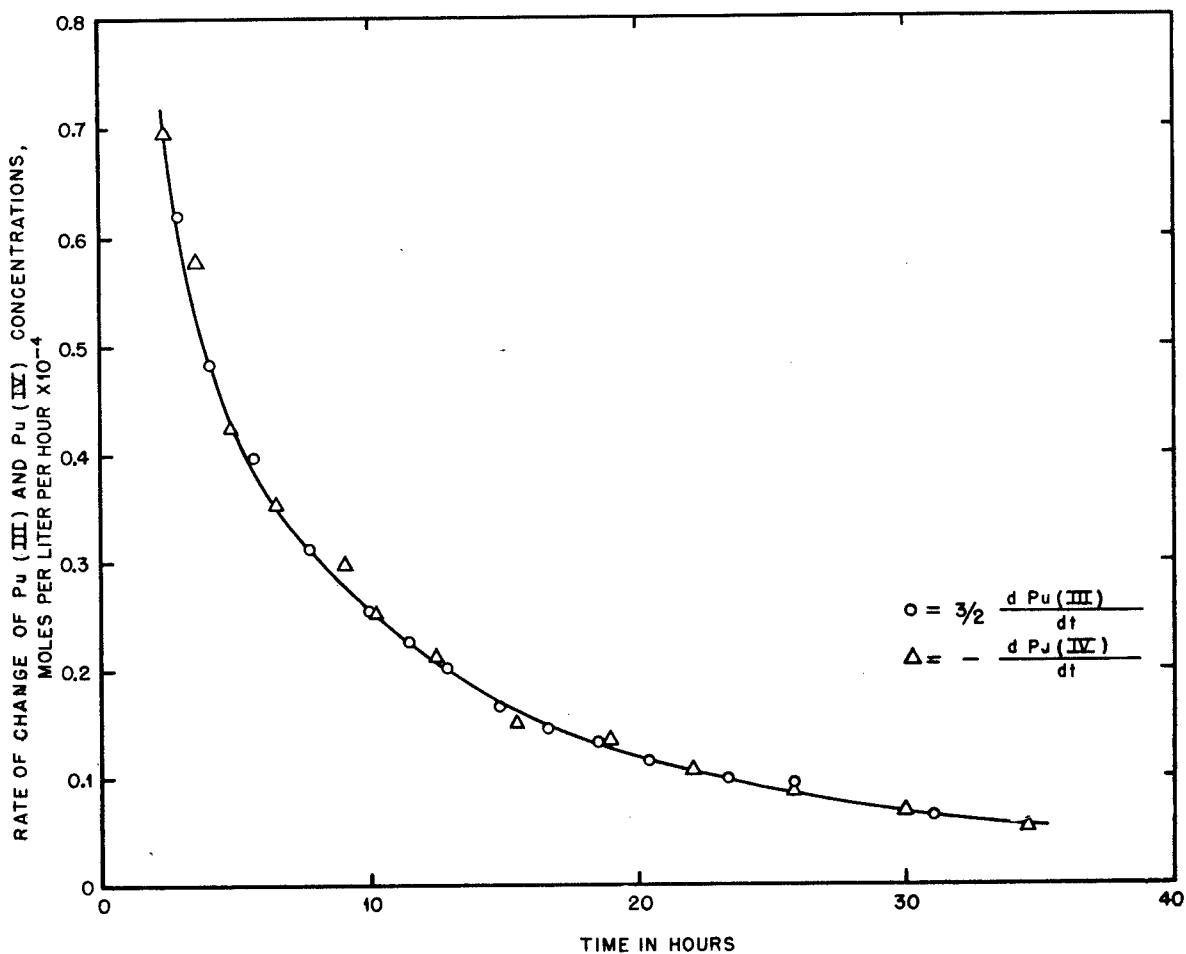
Table 20. Rate constants for the disproportionation of Pu(IV) in HCl solutions at 25°C.

Experiment	Time, Hours	Acidity	Total Plutonium	Pu(IV), M x 10 ⁴	k ₁ ^a , Assuming the Rate Laws Here Given				
					$-\frac{d[\text{Pu(IV)}]}{dt} = k_1 \frac{[\text{Pu(IV)}]}{[\text{Pu(IV)}]^2}$	$-\frac{d[\text{Pu(IV)}]}{dt} = k_1 \frac{[\text{Pu(IV)}]^2}{[\text{Pu(IV)}]}$	$-\frac{d[\text{Pu(IV)}]}{dt} = k_1 \frac{[\text{Pu(IV)}]^3}{[\text{Pu(IV)}]}$	$-\frac{d[\text{Pu(IV)}]}{dt} = k_1 \frac{[\text{Pu(IV)}]^2}{[\text{Pu(IV)}]}$	
1	4	0.244M	1.38 x 10 ⁻³ M	9.95	0.049	49	5.0 x 10 ⁴	0.012	12.
	6			9.12	0.041	45	4.9 x 10 ⁴	0.014	15.
	8			8.43	0.037	44	5.2 x 10 ⁴	0.016	19.
	10			7.89	0.033	42	5.4 x 10 ⁴	0.016	21.
	12			7.43	0.030	41	5.5 x 10 ⁴	0.017	23.
	14			7.02	0.027	39	5.5 x 10 ⁴	0.017	24.
	16			6.69	0.025	38	5.6 x 10 ⁴	0.017	26.
	18			6.38	0.023	37	5.7 x 10 ⁴	0.018	28.
	20			6.10	0.022	36	6.0 x 10 ⁴	0.018	30.
	22			5.69	0.021	36	6.2 x 10 ⁴	0.019	32.
24	5.69	0.020	36	6.3 x 10 ⁴	0.019	33.			
28	5.35	0.019	35	6.5 x 10 ⁴	0.019	36.			
2	0.8	0.183M	4.38 x 10 ⁻³ M	25.7	0.41	159	6.2 x 10 ⁴	0.19	72.
	1.2			21.7	0.34	157	7.2 x 10 ⁴	0.22	102.
	1.6			19.1	0.29	154	8.1 x 10 ⁴	0.24	128.
	2.0			17.2	0.26	151	8.8 x 10 ⁴	0.26	149.
	2.4			15.7	0.23	149	9.5 x 10 ⁴	0.27	170.
	2.8			14.5	0.21	145	10.0 x 10 ⁴	0.27	186.
	3.2			13.6	0.20	145	10.7 x 10 ⁴	0.28	205.
	3.6			12.9	0.18	138	10.7 x 10 ⁴	0.27	209.
	4.0			12.3	0.17	134	10.9 x 10 ⁴	0.27	216.
	4.4			11.9	0.15	124	10.4 x 10 ⁴	0.25	209.
3	10	0.5M	1.98 x 10 ⁻³ M	17.0	86 x 10 ⁻⁴	5.1	0.30 x 10 ⁴	6.6 x 10 ⁻⁴	0.39
	15			16.2	80 x 10 ⁻⁴	5.0	0.31 x 10 ⁴	8.6 x 10 ⁻⁴	0.53
	20			15.6	76 x 10 ⁻⁴	4.8	0.31 x 10 ⁴	10.3 x 10 ⁻⁴	0.66
	25			15.0	73 x 10 ⁻⁴	4.8	0.32 x 10 ⁴	12.2 x 10 ⁻⁴	0.81
	30			14.5	70 x 10 ⁻⁴	4.8	0.33 x 10 ⁴	13.7 x 10 ⁻⁴	0.95
	35			14.0	68 x 10 ⁻⁴	4.8	0.35 x 10 ⁴	15.2 x 10 ⁻⁴	1.09
	40			13.7	66 x 10 ⁻⁴	4.8	0.35 x 10 ⁴	16.5 x 10 ⁻⁴	1.20
	45			13.3	65 x 10 ⁻⁴	4.9	0.37 x 10 ⁴	18.1 x 10 ⁻⁴	1.36
	50			13.1	62 x 10 ⁻⁴	4.9	0.36 x 10 ⁴	18.7 x 10 ⁻⁴	1.43
55	12.8	63 x 10 ⁻⁴	4.9	0.38 x 10 ⁴	20.3 x 10 ⁻⁴	1.59			
4	2	0.474M	4.25 x 10 ⁻³ M	37.5	42 x 10 ⁻³	11.2	0.30 x 10 ⁴	29 x 10 ⁻⁴	0.8
	4			34.7	38 x 10 ⁻³	10.9	0.32 x 10 ⁴	50 x 10 ⁻⁴	1.5
	5			33.4	36 x 10 ⁻³	10.8	0.32 x 10 ⁴	59 x 10 ⁻⁴	1.8
	6			32.4	34 x 10 ⁻³	10.5	0.33 x 10 ⁴	65 x 10 ⁻⁴	2.0
	7			31.4	32 x 10 ⁻³	10.3	0.33 x 10 ⁴	70 x 10 ⁻⁴	2.2
	8			30.6	30 x 10 ⁻³	9.9	0.32 x 10 ⁴	73 x 10 ⁻⁴	2.4
	9			29.8	29 x 10 ⁻³	9.6	0.32 x 10 ⁴	75 x 10 ⁻⁴	2.5
	10			29.2	27 x 10 ⁻³	9.2	0.31 x 10 ⁴	76 x 10 ⁻⁴	2.6
	11			28.6	26 x 10 ⁻³	9.2	0.32 x 10 ⁴	79 x 10 ⁻⁴	2.8
	12			28.1	26 x 10 ⁻³	9.2	0.33 x 10 ⁴	83 x 10 ⁻⁴	2.9
14	27.2	26 x 10 ⁻³	9.7	0.36 x 10 ⁴	94 x 10 ⁻⁴	3.4			
16	26.4	28 x 10 ⁻³	10.6	0.40 x 10 ⁴	107 x 10 ⁻⁴	4.1			

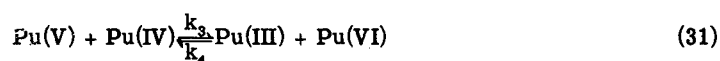
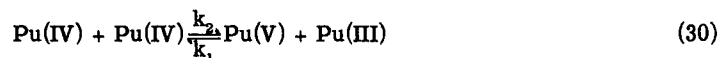
* Dimensions of k₁ as used in this table are in moles, liters, and hours. In all rate laws k₂ = k₁/K, where K is the disproportionation constant.

Table 21. Comparison of the rate constant for the square and cube rate laws.

HCl (M)	Square law				Cube law				
	0.183	0.244	~0.5	0.474	0.183	0.244	~0.5	0.474	
Total Pu (M x 10 ³)	4.38	1.38	1.93	4.25	4.38	1.38	1.93	4.25	
k ₁	Average	146	40	4.9	10.1	9.3 x 10 ⁴	5.6 x 10 ⁴	0.34 x 10 ⁴	0.33 x 10 ⁴
	Average	8.4	3.7	0.1	0.6	1.3 x 10 ⁴	0.4 x 10 ⁴	0.02 x 10 ⁴	0.02 x 10 ⁴
	Deviation	5.8%	9.2%	1.6%	6.1%	14.2%	7.2%	7.1%	5.1%

Figure 8. Disproportionation of Pu(IV) (Experiment 1), 0.244M HCl, 1.38 x 10⁻³M Pu, 25.0 ± 0.5°C.

is in accord with the proposed steps of this mechanism. Since the data suggest that the true rate law lies somewhere between the square and the cube rate laws, a mechanism was suggested by Dr. R. E. Connick in which the disproportionation rate would be proportional to between the second and third powers of the Pu(IV) concentration. This mechanism involves two steps, the rates of which are chosen to be so nearly the same that either may control the rate, depending upon the stage of the disproportionation. During the intermediate periods the overall rate would be a combination of the rates of the two steps. The mechanism and derivation of the rate law are given. It was assumed that the concentration of Pu(V) is always small relative to the total plutonium concentration and that $d[\text{Pu(V)}]/dt$ is therefore negligible with respect to $d[\text{Pu(IV)}]/dt$.



$$-\frac{d[\text{Pu(IV)}]}{dt} = 2k_2[\text{Pu(IV)}]^2 + k_3[\text{Pu(V)}][\text{Pu(IV)}] - 2k_1[\text{Pu(V)}][\text{Pu(III)}] - k_4[\text{Pu(III)}][\text{Pu(VI)}] \quad (32)$$

$$+\frac{d[\text{Pu(V)}]}{dt} = k_2[\text{Pu(IV)}]^2 + k_4[\text{Pu(III)}][\text{Pu(VI)}] - k_1[\text{Pu(V)}][\text{Pu(III)}] - k_3[\text{Pu(IV)}][\text{Pu(V)}] \quad (33)$$

Combining equations 32 and 33 gives

$$-\frac{d[\text{Pu(IV)}]}{dt} = 3k_2[\text{Pu(IV)}]^2 - 3k_1[\text{Pu(V)}][\text{Pu(III)}] - \frac{d[\text{Pu(V)}]}{dt} \quad (34)$$

Assuming $d[\text{Pu(V)}]/dt$ is negligible and evaluating $[\text{Pu(V)}]$ from equation 33 one obtains

$$-\frac{d[\text{Pu(IV)}]}{dt} = 3 \left[\frac{K[\text{Pu(IV)}]^3 - [\text{Pu(III)}]^2[\text{Pu(VI)}]}{[\text{Pu(III)}] + K[\text{Pu(IV)}]} \right] \quad (35)$$

where $K = k_2k_3/k_1k_4$ is the disproportionation constant.

Since the final expression contains two unknowns, k_2 and k_4 , it was necessary to set up pairs of simultaneous equations in solving for the constants. In testing the fit of this rate law, at least three pairs of equations were solved for each experiment and the values of k_2 and k_4 thus obtained were averaged. The actual test used for the correctness of this rate law was not the constancy of the values for k_2 and k_4 but the ability to accurately calculate $-d[\text{Pu(IV)}]/dt$ by the use of these values.

In Table 22 the calculated values for $-d[\text{Pu(IV)}]/dt$ are compared with those found experimentally and are in very good agreement. This rate law is based on the premise that reactions 30 and 31 are both measurably slow. As described, there is independent evidence that the equilibrium shown in reaction 31 is rapidly established. It is quite possible that the apparent fit of this two-step rate determining mechanism with the data is merely a result of introducing a sufficient number of constants. To compare values of k_2 between the different experiments it is necessary to know the hydrogen ion dependence. As before, this was calculated from the experiments in 0.474M hydrochloric acid and 0.183M hydrochloric acid, assuming that the hydrogen ion concentration enters into k_2 at a constant power over this range of acidity. Thus, one obtains the following expression for k_2 :

$$k_2 = k(\text{H}^+)^{-2.8}$$

Using this equation, the value of k_2 for the 0.244M hydrochloric acid experiment was calculated to be 0.042 which is to be compared with the experimental value of 0.056. The agreement is about the same

Table 22. Rate constants for the disproportionation of Pu(IV) in HCl solutions at 25°C assuming the following rate law:

$$-\frac{d[\text{Pu(IV)}]}{dt} = 3 \left[\frac{K[\text{Pu(IV)}]^3 - [\text{Pu(III)}]^2[\text{Pu(VI)}]^*}{[\text{Pu(III)}] + K[\text{Pu(IV)}]} \right] \frac{1}{k_2}$$

Experiment 1				Experiment 2			
0.244M HCl 1.38 x 10 ⁻³ M total Pu 1/k ₄ = 0.077; 1/k ₂ = 0.056				0.183M HCl 4.38 x 10 ⁻³ M total Pu 1/k ₄ = 0.021; 1/k ₂ = 0.017			
Time (hr)	Pu(IV) (M x 10 ⁴)	-d[Pu(IV)] dt		Time (hr)	Pu(IV) (M x 10 ⁴)	-d[Pu(IV)] dt	
		Experi- mental x 10 ⁵	Calcu- lated x 10 ⁵			Experi- mental x 10 ⁵	Calcu- lated x 10 ⁵
4	9.95	48.7	46.1	0.8	25.7	104.	106.
6	9.12	37.0	37.1	1.2	21.7	71.6	71.7
8	8.43	30.5	30.2	1.6	19.1	53.3	53.0
10	7.89	25.6	25.3	2.0	17.2	40.8	40.8
12	7.43	21.5	21.6	2.4	15.7	31.9	31.3
14	7.02	18.1	19.0	2.8	14.5	25.2	26.3
16	6.69	15.6	16.0	3.2	13.6	20.3	19.7
18	6.38	13.5	13.9	3.6	12.9	16.2	16.2
20	6.10	12.0	12.1	4.0	12.3	13.0	13.2
22	5.89	10.8	10.6	4.4	11.9	10.4	11.4
24	5.69	9.6	9.4				
28	5.35	7.7	7.5				

Experiment 3				Experiment 4			
0.5M HCl 1.93 x 10 ⁻³ M total Pu 1/k ₄ = 0.003; 1/k ₂ = 0.609				0.474M HCl 4.25 x 10 ⁻³ M total Pu 1/k ₄ = 0.005; 1/k ₂ = 0.281			
Time (hr)	Pu(IV) (M x 10 ⁴)	-d[Pu(IV)] dt		Time (hr)	Pu(IV) (M x 10 ⁴)	-d[Pu(IV)] dt	
		Experi- mental x 10 ⁵	Calcu- lated x 10 ⁵			Experi- mental x 10 ⁵	Calcu- lated x 10 ⁵
10	17.0	1.45	1.41	2	37.5	15.8	14.5
15	16.2	1.28	1.27	4	34.7	12.8	12.1
20	15.6	1.15	1.16	5	33.4	11.5	11.3
25	15.0	1.04	1.04	6	32.4	10.3	10.1
30	14.5	0.94	0.95	7	31.4	9.1	9.4
35	14.0	0.85	0.85	8	30.6	8.0	8.3
40	13.7	0.77	0.77	9	29.8	7.0	7.8
45	13.3	0.69	0.68	10	29.2	6.1	6.9
50	13.1	0.61	0.62	11	28.6	5.5	6.4
55	12.8	0.55	0.54	12	28.1	5.0	5.6
				14	27.2	4.2	4.5
				16	26.4	3.5	3.4

*See text for derivation. K is the disproportionation constant (Section 1). The dimensions of k₂ and k₄ are moles, liters, and hours.

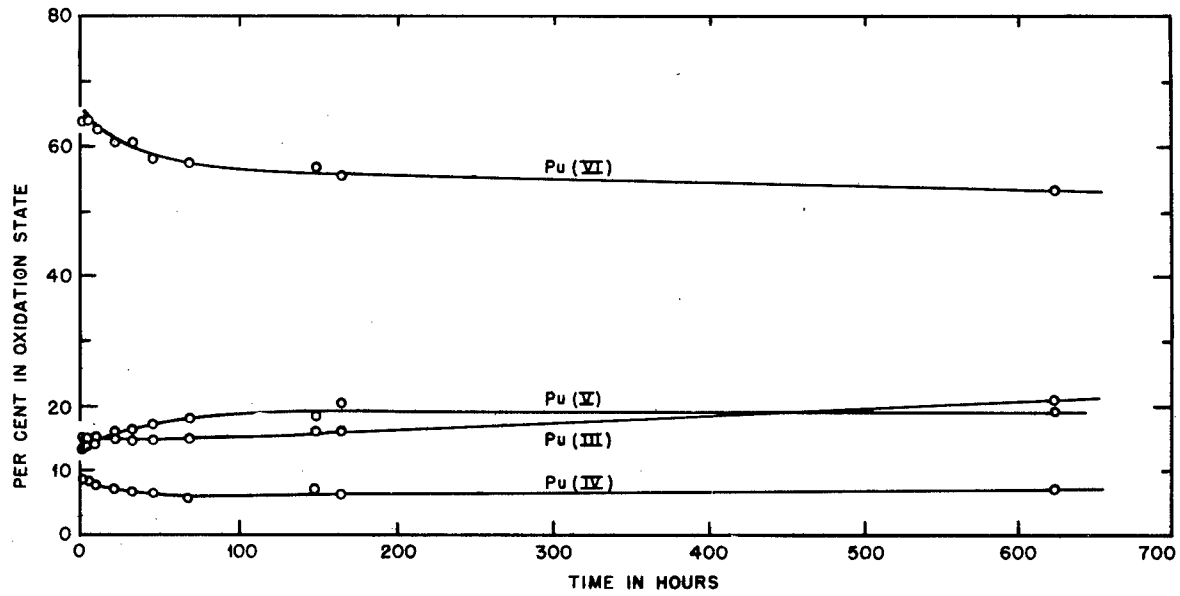


Figure 9. Reaction between plutonium ions in 0.1081M HCl at 25°C, $1.74 \times 10^{-3}M$ Pu.

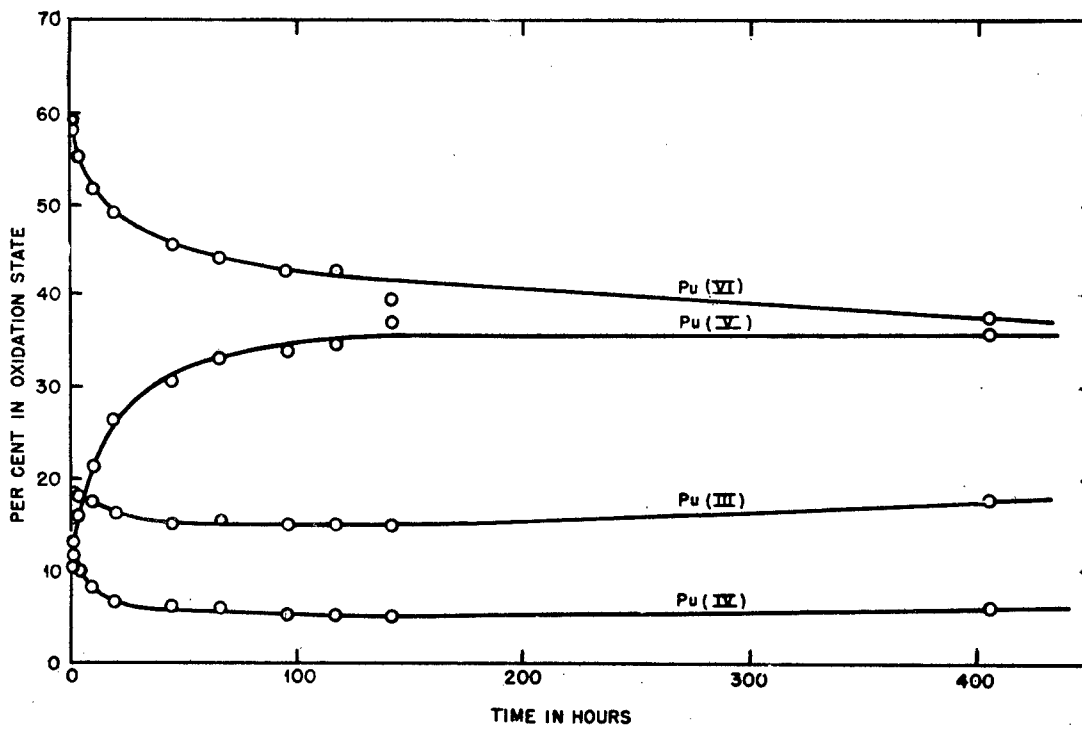


Figure 10. Reaction between plutonium ions in 0.0615M HCl at 25°C, $1.82 \times 10^{-3}M$ Pu.

as was previously obtained for the square and cube law mechanisms, and thus does not particularly argue for this mechanism.

In summary, it may be stated that the rate of disproportionation appears to be proportional to between the second and third power of the Pu(IV) concentration and inversely proportional to about the third power of the hydrogen ion concentration. No rate law has been found that will satisfactorily fit the experimental data. The square law is favored over other rate laws as there is additional evidence from other sources that the mechanism giving rise to this rate law is correct. Additional measurements must necessarily be made before a definite conclusion as to the mechanism can be reached.

3. THE EQUILIBRIUM BETWEEN PLUTONIUM IONS IN HYDROCHLORIC ACID SOLUTIONS OF LOW ACIDITY

The equilibrium between Pu(III), Pu(IV), and Pu(VI) was studied in the preceding part of this paper by causing the disproportionation of Pu(IV) to occur upon dilution of Pu(IV) solutions, containing a high concentration of hydrochloric acid; the final acid concentration varied from 1.545M to 0.183M. Attempts to study plutonium equilibria at still lower acid concentrations by this same technique result in the rapid formation of colloidal Pu(IV).

Consequently, in order to extend the experiments to 0.1M and 0.05M hydrochloric acid solutions, Pu(III) and Pu(VI) were used in starting the experiments with the intention of approaching equilibrium from the other direction in order to avoid a large concentration of Pu(IV) at any time. Larger ratios of Pu(VI)/Pu(III) were chosen to start the reactions than are required by the stoichiometry of the disproportionation reaction, since by making use of the equilibrium constants given earlier, calculation indicated that the relative amount of Pu(IV) would be decreased by such ratios, thus reducing the hazard of forming colloidal Pu(IV). In addition the calculations indicated that Pu(V) makes its appearance at low acidities, in stable equilibrium with the other oxidation states of plutonium.

The reactions were started by mixing thermostated solutions of Pu(III) and Pu(VI), each previously adjusted to the desired acidity, transferring to optical absorption cells contained in the special thermostat chamber, and the reaction followed by making absorption readings in the spectrophotometer at the desired wavelengths. When the reactions had come to equilibrium, aliquots were removed and titrated with standard sodium hydroxide solution to the phenolphthalein end point, to determine the acidity. A correction was applied for the plutonium precipitated by means of the plutonium analysis data at equilibrium.

Two experiments were performed in 0.1081M and 0.0615M hydrochloric acids, respectively. From the spectrophotometric data the per cents of Pu(III), Pu(IV), Pu(V), and Pu(VI) were calculated at each time point. Rate curves for the reactions, obtained by drawing a smooth curve through the analytical data plotted against time, are given in Figures 9 and 10. By reading values of per cent of plutonium in a given oxidation state at convenient time intervals from the rate curves, smoothed analyses versus time data were obtained and are given in Tables 23 and 24. It will be observed that in 0.1081M hydrochloric acid at 25° as much as 19 per cent of the plutonium appears as Pu(V) in stable equilibrium with Pu(III), Pu(IV), and Pu(VI); while in 0.0615M hydrochloric acid at 25°C, 35 per cent of the plutonium is stabilized in the form of Pu(V).

The last columns of Tables 23 and 24 contain values of the apparent equilibrium constants K and K_1 , as defined by equations 2 and 3. The values of K_1 should be constant at all times during the experiments, since the Pu(III)-Pu(IV)-Pu(V)-Pu(VI) equilibrium involves merely the transfer of an electron between two plutonium ions and is thus expected to be rapidly reversible, as has been shown by other experimental work.¹⁰ The mean values of K_1 , obtained by averaging the starred values of Tables 23 and 24, are 7.8 and 3.6 for 0.1081M and 0.0615M hydrochloric acid, respectively. In the case of the more dilute acid solution, the first few values were more divergent, probably due to analytical uncertainties, and were not included.

Table 23. Data for the reaction between plutonium ions in 0.1081M HCl at 25°C,
 1.74×10^{-3} M plutonium.

Time (hr)	Pu(III) (%)	Pu(IV) (%)	Pu(V) (%)	Pu(VI) (%)	Σ	Apparent equilibrium constant		
						K_1	K	K_5
0	15.0	8.5	13.5	64.9	101.9	8.5*	23.8	25.7
10	15.0	7.7	14.7	63.0	100.4	8.4*	31.0	18.7
20	15.0	7.2	15.5	61.5	99.2	8.3*	37.1	15.2
40	15.0	6.5	17.0	59.2	97.7	8.1*	48.5	10.7
60	15.0	6.3	17.9	58.0	97.2	7.7*	52.2	8.80
80	15.1	6.3	18.5	57.3	97.2	7.4*	52.2	7.83
100	15.3	6.4	18.8	56.8	97.3	7.2*	50.7	7.42
120	15.5	6.5	19.0	56.5	97.5	7.1*	49.5	7.21
140	15.6	6.5	19.2	56.4	97.7	7.1*	50.0	7.01
200	16.3	6.5	19.3	56.0	98.1	7.3*	54.2	7.11
300	17.5	6.5	19.2	55.5	98.7	7.6*	62.0*	7.62*
400	18.5	6.7	19.2	55.1	99.5	7.9*	62.7*	7.94*
500	19.5	6.9	19.2	54.7	100.3	8.1*	63.5*	8.24*
600	20.5	6.9	19.2	54.3	100.9	8.4*	69.5*	8.54*

* Used for obtaining average values of the equilibrium constant.

Table 24. Data for the reaction between plutonium ions in 0.0615M HCl at 25°C,
 1.82×10^{-3} M plutonium.

Time (hr)	Pu(III) (%)	Pu(IV) (%)	Pu(V) (%)	Pu(VI) (%)	Σ	Apparent equilibrium constant		
						K_1	K	K_5
10	17.0	7.5	21.8	51.6	97.9	5.37	35.4	4.37
20	16.2	6.3	26.4	49.0	97.9	4.76	51.3	2.11
30	15.5	5.9	29.0	47.3	97.7	4.28	55.3	1.42
40	15.2	5.6	30.6	46.0	97.4	4.08*	60.5	1.123
50	15.0	5.5	31.8	45.1	97.4	3.87*	61.0	0.948
60	14.9	5.4	32.7	44.5	97.5	3.76*	62.7	0.845
70	14.9	5.3	33.5	43.8	97.5	3.67*	65.3	0.760
80	14.9	5.2	34.0	43.2	97.3	3.64*	68.4*	0.707
100	15.0	5.1	34.8	42.5	97.4	3.60*	72.3*	0.643*
120	15.0	5.0	35.2	41.9	97.1	3.57*	75.5*	0.604*
140	15.0	5.0	35.4	41.5	96.9	3.52*	75.6*	0.582*
160	15.1	5.1	35.4	41.2	96.8	3.45*	70.8*	0.577*
200	15.4	5.2	35.4	40.5	96.5	3.39*	68.2*	0.569*
400	17.6	5.6	35.5	37.5	96.5	3.34*	66.1*	0.553*

* Used for obtaining average values of the equilibrium constant.

One indication of analytical uncertainties is in the fact that the analytical sums do not total 100 per cent. In the 0.1081M acid experiment, there is a wide divergence for the data in the middle of the table, and the corresponding values of K_1 show a similar trend. The accuracy of the analysis for Pu(IV) is poor when the relative amount of Pu(IV) is low, and since the Pu(IV) concentration was kept low intentionally to prevent colloid formation, the values of the equilibrium constants suffer in accuracy.

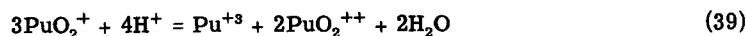
In calculating K , defined by equation 2, the concentration of Pu(IV) is raised to the third power. Because of the nature of the analysis for Pu(IV), the average values of K , 64 and 71 for the 0.1081M and 0.0615M hydrochloric acid solutions, respectively, must be regarded as approximate. More accurate absorption data should, of course, lead to an improvement in the accuracy for the analyses. On the basis of these considerations, it is highly desirable to calculate an equilibrium constant which does not involve the concentration of Pu(IV). Such an equilibrium is represented by the reaction



with the equilibrium constant

$$K_5 = \frac{[\text{Pu(III)}][\text{Pu(VI)}]^2}{[\text{Pu(V)}]^3} \quad (38)$$

The average values of K_5 obtained for the 0.1081M and 0.0615M hydrochloric acid experiments are 8.1 and 0.59, respectively. When the reaction is written with the accepted formula of the ions,



it is apparent that an inverse fourth power dependence is to be expected for the Pu(III)–Pu(V)–Pu(VI) equilibrium constant

$$K_5'' = \frac{K_5}{(\text{H}^+)^4} \quad (40)$$

Using the values of K_5 for the 0.1081M and 0.0615M hydrochloric acids, an inverse 4.7 power dependence on hydrochloric acid concentration is found. This is similar to the 5.1 power dependence of the Pu(III)–Pu(IV)–Pu(VI) equilibrium constant found for solutions of 0.183 to 1.545M acid, and the deviation from the fourth power is probably to be explained on the basis of chloride complexing and ionic strength effects.

Testing the acidity dependence of the Pu(III)–Pu(IV)–Pu(VI) equilibrium constant, K , for the 0.1081M and 0.0615M hydrochloric acid experiments reveals that only a 0.18 power dependence on hydrochloric acid concentration is required to correct for the acidity effect, as compared with the 5.1 power dependence obtained over an acid range of 0.183 to 1.545M. This small dependence is undoubtedly to be attributed to the large errors occurring in the analysis for small amounts of Pu(IV). It should be pointed out that this small acidity dependence at low acid concentrations is not to be explained by hydrolysis of the Pu(IV), if the hydrolyzed form has the absorption spectrum reported by Kraus.⁶

The analysis for Pu(IV) was based on the absorption spectrum for normal Pu(IV) as obtained at higher acid concentrations. If, as Kraus assumes,⁶ the hydrolyzed ion has an absorption spectrum different from that of normal Pu(IV) and with relatively little absorption in the region of the main absorption peak of normal Pu(IV), then the analysis as carried out here gives only the concentrations of unhydrolyzed plutonium ions. Therefore, the fourth power dependence expected theoretically should still exist at the low acidities.

4. RATE OF FORMATION OF COLLOIDAL Pu(IV)

The existence of a colloidal form of Pu(IV) has been recognized for some time. Absorption spectra of colloidal Pu(IV) have been reported for both nitric and hydrochloric acid systems.^{12,13} According to Kraus, this hydrolyzed form may be prepared by heating solutions of Pu(IV) in either nitric or hydrochloric acid for 1 hour, if the acidity is less than 0.3M. Upon standing at room temperature in 1M nitric acid, the colloidal Pu(IV) will become partially reconverted to the normal Pu(IV) over a period of several days.¹² The reversion of colloidal Pu(IV) to normal Pu(IV) has been described as being nearly complete upon standing in 0.5M hydrochloric acid for 48 hours at room temperature.⁴ In the present studies on the disproportionation of Pu(IV), we have obtained some additional information which we wish to add to the general picture regarding the limits of stability of colloidal Pu(IV).

The experiments consisted of heating the solutions used for the experiments of Sections 1 and 2 at $70.0 \pm 0.5^\circ\text{C}$, and periodically measuring portions of the absorption spectrum. The concentrations of Pu(III), Pu(IV), colloidal Pu(IV), Pu(V), and Pu(VI) were calculated from these measurements. At 70°C the spectrophotometric measurements become somewhat inaccurate but are sufficiently good for the qualitative determination of the species present (Appendix). In Table 25 the formation of colloidal Pu(IV) in a solution of disproportionated Pu(IV) ($1.35 \times 10^{-3}\text{M}$ in Pu) in 0.244M hydrochloric acid is shown. This solution was heated at 70°C for 116 hours.

At this acidity a small amount of colloidal Pu(IV) seems to have formed. If these amounts are real, the data would indicate that the reactions involved proceed rapidly and soon reach equilibrium values with 2 to 3% of the plutonium in the form of colloidal Pu(IV). However, it is known that spectrophotometric analyses for these species at 70°C are not too reliable, especially when small amounts of one form are analyzed for in the presence of large quantities of other forms. The variability of the analyses for colloidal Pu(IV) coupled with the low values for "Total Pu" suggest that the appearance of colloidal Pu(IV) in this experiment may well be an artifact of the calculations. In solutions of higher acidity no evidence of colloidal Pu(IV) formation was found.

Reducing the acidity to 0.183M resulted in extensive colloidal formation at 70°C . (Table 26 and Figure 11). This solution was $4.29 \times 10^{-3}\text{M}$ in Pu. The formation of colloidal Pu(IV) was relatively slow and the rate could be followed easily. Thus, in 25 hours approximately 38% of the plutonium present was converted to colloidal Pu(IV), while 71% was present as colloidal Pu(IV) in 42 hours. The reaction seems to have reached equilibrium with about 90% of the plutonium in the colloidal Pu(IV) form.

Table 25. Data on formation of colloidal Pu(IV) in 0.244M HCl at 70°C , $1.35 \times 10^{-3}\text{M}$ plutonium.

Time (hr)	Composition of solution (%)					Total Pu
	Pu(III)	Pu(IV)	Colloidal Pu(IV)	Pu(V)	Pu(VI)	
1.3	59.6	2.9	0.9	7.0	23.2	93.6
21.0	60.5	4.0	3.4	7.9	20.9	96.7
25.3	60.7	2.3	3.2	7.7	21.1	95.0
45.5	61.7	1.7	2.6	8.7	20.1	94.8
69.5	62.5	1.6	1.8	6.3	20.0	92.2
96.	63.9	3.7	2.1	7.9	19.4	97.0
116.	63.8	2.8	1.7	6.9	18.2	93.4

Table 26. Data on formation of colloidal Pu(IV) in 0.183M HCl at 70°C, 4.29×10^{-3} M plutonium.

Time (hr)	Composition of solution (%)					Total Pu
	Pu(III)	Pu(IV)	Colloidal Pu(IV)	Pu(V)	Pu(VI)	
0	48.9	21.1	0	4.0	26.9	100.9
0.5	51.9	4.3	0	11.7	26.5	94.4
1.0	53.0	5.0	0	12.5	27.7	98.2
1.8	52.6	4.0	0.6	12.3	27.6	97.1
5.0	51.0	3.8	2.4	12.2	26.8	96.2
18.0	41.2	*	22.9	8.5	21.1	93.7
24.7	34.4	*	38.2	8.4	17.5	98.5
31.3	27.0	*	52.6	8.4	13.8	101.8
42.3	20.6	*	70.9	7.2	11.9	110.6
66.1	10.4	*	86.1	5.1	6.8	108.4
70.3	8.1	*	88.2	4.7	6.4	107.4
73.5	8.2	*	87.4	4.7	6.2	106.5
90.1	8.0	*	89.1	4.4	5.2	106.7

* Not measurable.

The effect of the higher concentration of plutonium upon the colloid formation was probably to increase the rate. The curve representing the formation of colloidal Pu(IV) as a function of time has an interesting shape (Figure 11). The first part of the reaction is autocatalytic as shown by the increase in rate near the start of the experiment. This might be interpreted as a slow initial formation of colloidal centers followed by a more rapid growth of these colloidal centers. The percentages of Pu(IV) were calculated on the assumption that the extinction coefficient at 4380 Å for colloidal Pu(IV) is not affected by particle size, which is contrary to the behavior of the colloidal Pu(IV) spectrum as reported by Kraus.⁶ In addition to not knowing how much the spectrum is affected by particle size, it is also not known at which stage in the change, from the simple Pu(IV) ion to the formation of the colloid, the new absorption spectrum appears. Therefore, such an interpretation of the rate curve is very uncertain.

5. REDUCTION OF PLUTONIUM BY PRODUCTS OF ITS OWN ALPHA RADIATION

It was previously reported that a solution of pure Pu(VI) in hydrochloric acid undergoes reduction spontaneously with the appearance of mainly Pu(IV).⁴ The reduction is believed to be caused by products produced in the solution by alpha particles. During our study of the disproportionation reaction, additional data on the alpha reduction of plutonium have been accumulated, and although these do not represent a systematic series of experiments, some interesting results were obtained.

In Figure 12, the spontaneous appearance and growth of the 4700 Å absorption peak, characteristic of Pu(IV), in a solution initially containing pure Pu(VI) is shown. The experiment was carried out in ~0.5M hydrochloric acid at room temperature (~20°C). As the Pu(IV) is produced, it in turn disproportionates into Pu(VI) and Pu(III). The rate of reduction as calculated from the change in average oxidation number over the long time interval corresponds to a diminution in the average oxidation number of 0.0040 per day for the experiment in 0.5M hydrochloric acid at room temperature (~25°C). This is equivalent to a reduction of 0.20 per cent of the total plutonium from Pu(VI) to Pu(IV) per day. In these and the following calculations, the average oxidation numbers were normalized by correcting all analyses to 100%.

This spontaneous reduction of Pu(VI) to Pu(IV) must, of course, be taken into account when dealing with the chemistry of plutonium. Indeed, in our experiments on the disproportionation of Pu(IV) in solutions of higher hydrochloric acid concentrations (1M and 1.5M), where the rate of disproportionation was very slow, the reduction of Pu(VI) became a major factor in the reaction. The rates of reduction of plutonium in the 1.545M and the 0.950M hydrochloric acid solutions were calculated from the change in average oxidation number as before and are recorded in Table 27. Also included in the table are the rates calculated from the change in average oxidation number for the plutonium solutions at lower hydrochloric acid concentrations.

The calculations of change in average oxidation number for the 0.0615M, 0.1081M, 0.950M, and 1.545M hydrochloric acid solutions were made for time intervals of 400, 600, 750, and 1005 hours, respectively, and are fairly reliable because the change in oxidation number was appreciable for such time intervals. The calculations for the experiments in 0.244M, and ~0.5M (at 25°C) hydrochloric acid are for time intervals of 170 and 211 hours, respectively; thus, since the change in average oxidation number is relatively small, it is susceptible to large errors due to analytical uncertainties.

Using the most favorable data, as indicated, gives a rate of reduction in the average oxidation number of plutonium of about 0.004 per day in the experiments in from 0.5 to 2M hydrochloric acid, while the rate of reduction in the average oxidation number calculates to be about 0.008 per day in the very dilute acids (0.1 to 0.06M hydrochloric acid), with a definite trend of greater rate of reduction in the more dilute acid. For perchloric acid solutions of plutonium, a rate of reduction in the average oxidation number of 0.012 per day is obtained,¹⁴ and is independent of acidity over an acid range of 0.1 to 2M. It is thus apparent that chloride ion is involved in the reaction in hydrochloric acid in such a way as to reduce the rate of reduction due to alpha-radiation products.

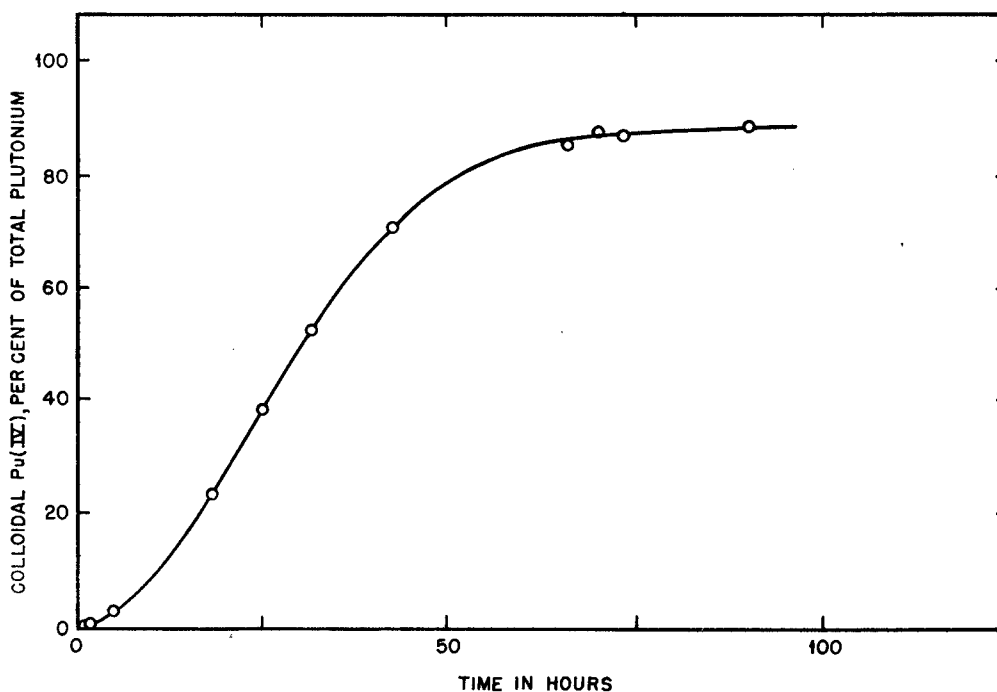


Figure 11. Formation of colloidal Pu(IV) at 70°C in 0.183M HCl, 4.29×10^{-3} M Pu.

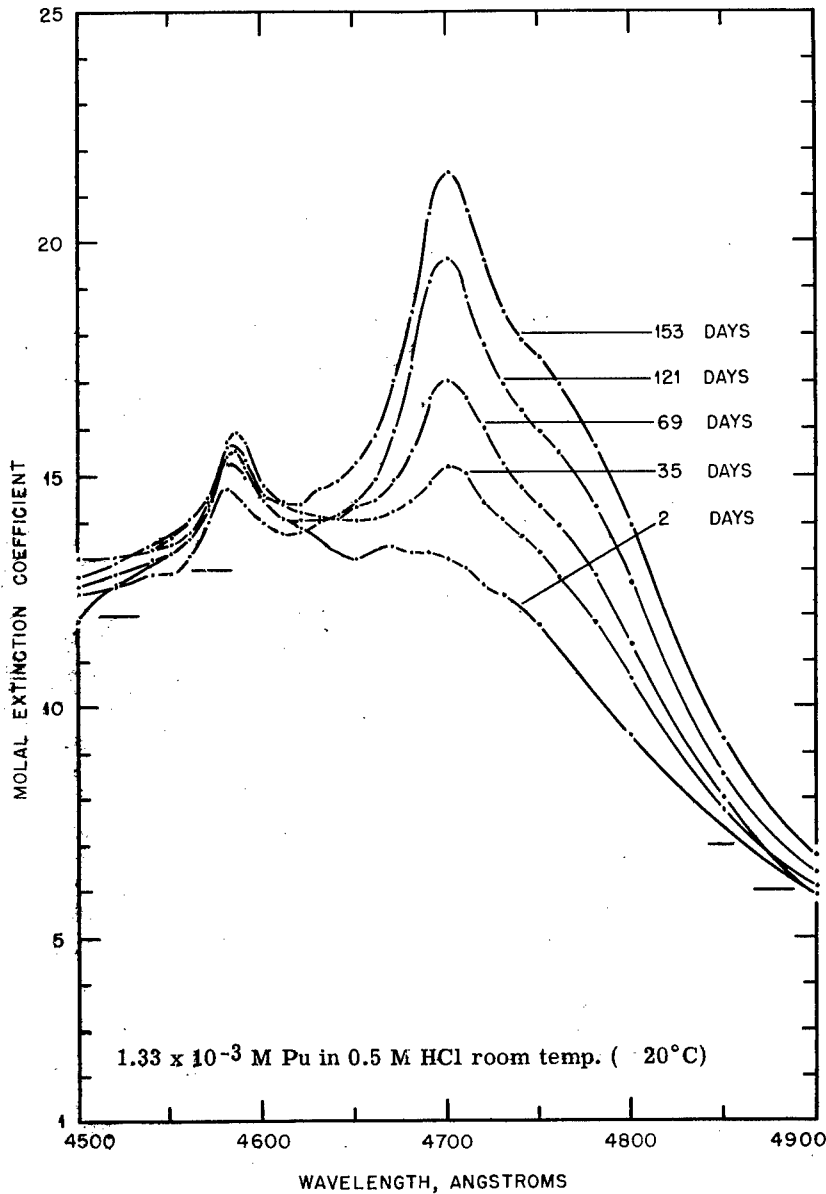


Figure 12. Growth of Pu(IV) peak at 4700 Å, resulting from self-reduction of Pu(VI) by α -radiation products.

By comparison of the reduction rate in the mixed solutions, with the rate of reduction in solutions containing chiefly Pu(VI), it is seen that the rate of reduction in the mixed solutions is the same as the rate of reduction when the plutonium is all Pu(VI). Therefore, the rate of reduction is seen to be dependent upon the total Pu present (i.e., on the total alpha-radiation produced) and not to be dependent on the amount of Pu(VI) in the solution. Thus, the rate of reduction of plutonium appears to be of zero order with respect to the Pu(VI) concentration, but first order with respect to the total plutonium concentration.

Table 27. Rate of reduction of plutonium in hydrochloric acid solutions due to products of its own alpha radiation.

Concentration of HCl	Principal species in solution	Temperature	Diminution in average oxidation number per day
0.0615M	Pu(VI), Pu(V), Pu(III)	25°C	0.0096
0.1081M	Pu(VI), Pu(V), Pu(III)	25°C	0.0079
0.244M	Pu(IV), Pu(III)	25°C	0.0066
0.474M	Pu(IV), Pu(III)	25°C	Not detectable in 72 hours
~0.5M	Pu(VI)	~20°C	0.0040
~0.5M	Pu(IV)	25°C	0.0030
0.950M	Pu(IV)	25°C	0.0038
1.545M	Pu(IV)	25°C	0.0046

From an experiment in which a solution of disproportionated Pu(IV) in 0.244M hydrochloric acid was kept at 70°C for 116 hours, we have a rough measure of the rate of reduction of Pu(VI) at 70°C. A calculation shows that the reduction in the average oxidation number was equivalent to approximately 0.02 per day at 70°C. Although the reduction of Pu(VI) in the solutions at 25°C does not seem to be caused by⁴ Cl⁻, it may be that the increased rate of reduction at 70°C is due largely to this ion.

APPENDIX

Calculation of the Concentration of Plutonium in its Various Oxidation States by Spectrophotometric Methods

a) Absorption Spectra

In order to calculate the concentrations of Pu(III), Pu(IV), Pu(V), and Pu(VI) from the absorption spectrum of a mixed solution, it is necessary to know the absorption spectrum for each ion under the conditions of the particular experiment. The spectra used are discussed here.

Pu(III): The spectrum of Pu(III) in 1.5M hydrochloric acid was measured at 25°C and was found to agree closely with that previously found for Pu(III) in 0.5M hydrochloric acid.⁴ Since the Pu(III) spectrum was evidently unaffected by the hydrochloric acid concentration, the extinction coefficients selected for the experiments in 0.2M hydrochloric acid and 1.0M hydrochloric acid were the averages of the values found in 0.5 and 1.5M hydrochloric acid. A small change in the spectrum occurred upon heating a 0.5M hydrochloric acid solution of Pu(III) to 60°C.⁴ No correction was made for this change since errors from this source were negligible compared with those arising from uncertainties in the Pu(IV) and Pu(VI) spectra at 70°C and from the operational characteristics of the spectrophotometer when warmed due to the presence of the thermostat chamber at 70°C.

Pu(IV): The absorption spectrum for Pu(IV) in 0.5M hydrochloric acid has been reported⁴ but was again measured, since the Pu(IV) solution previously used had disproportionated to a considerable extent at the time of the measurements and large corrections for the absorption by Pu(III) and Pu(VI) were necessary. The new spectrum was taken on a solution which contained only about 2% Pu(III) and 1% Pu(VI). In the main it is in good agreement with the previously measured spectrum. The Pu(IV) absorption in 1.5M hydrochloric acid was measured and found to be only slightly changed from that in 0.5M hydrochloric acid.

Attempts to measure the absorption spectrum of Pu(IV) in 0.2M hydrochloric acid or at temperatures above 25°C were unsuccessful due to the rapid disproportionation under these conditions. The values for the extinction coefficient, ϵ , of Pu(IV) in 0.2M hydrochloric acid used for the measurements at 25°C were assumed to be the same as for 0.5M hydrochloric acid. It is recognized that chloride complexes of Pu(IV) exist in both strong hydrochloric acid solutions at 25°C,¹⁵ and in dilute hydrochloric acid solutions at 70°C as is shown later. However, it is believed that at 25°C in the solutions used here the errors so introduced into the calculations are small. An average of the 0.5 and 1.5M hydrochloric acid spectra was used for the 1.0M hydrochloric acid solutions.

Large changes of the absorption spectrum would not be expected to occur upon changing the temperature from 25 to 70°C unless, of course, there was some temperature sensitive equilibrium involving Pu(IV) occurring in the solution or if the Pu(IV) was converted to colloidal Pu(IV); formation of colloidal Pu(IV) was never observed when the hydrochloric acid concentration was 0.24M or greater (Section 4).

Thus, it was thought unlikely that major changes in the Pu(IV) absorption spectrum would take place on raising the temperature to 70°C. Since at this temperature and in these concentrations of hydrochloric acid, the disproportionation is very rapid and the equilibrium is displaced far toward the Pu(III)–Pu(VI) side, it is impossible to determine directly the absorption spectrum of Pu(IV) under these conditions. Thus, the initial calculations were based upon the tacit assumption that the absorption spectrum of Pu(IV) is not materially changed at 70°C. However, the values obtained for the concentration of Pu(IV) varied greatly depending upon the wavelength selected for the calculation. Thus, at 7000 Å the Pu(IV) concentration was calculated to be much higher than when the wavelength 4700 Å was used. While these variations were large, they were also regular indicating that the absorption spectrum of Pu(IV) at 70°C is different from its spectrum at 25°C. The change is probably due to a chloride complex of Pu(IV) which is much more stable at 25°C.

Hindman and Ames have shown recently that at least two chloride complexes of Pu(IV) occur in solutions of hydrochloric acid at room temperature.¹⁵ Since at 70°C in the present work it is not known how the Pu(IV) absorption spectrum changes due to chloride complexing, the calculations for Pu(IV) are arbitrarily based on the extinction coefficient for Pu(IV) at 25°C. The calculations for Pu(IV) concentrations at 70°C are probably correct within a factor of 2 and become increasingly more accurate as the temperature is decreased from 70 to 25°C. The accuracy, of course, becomes greater when the Pu(IV) concentration is high.

Colloidal Pu(IV): The absorption spectrum of colloidal Pu(IV), was measured in 0.15M hydrochloric acid.¹³ This spectrum will probably vary with the method used in preparing the colloid; being dependent upon particle size, etc.⁶ Hence, the values for the concentration of colloidal Pu(IV) are considered to be approximate.

Pu(V): The absorption spectrum of Pu(V) in 0.5M hydrochloric acid was described in CN-1912.¹⁰ The measurements were not repeated at other acidities and the concentrations of Pu(V) reported here are approximate.

Pu(VI): Absorption curves of Pu(VI) were run in 0.2M, 0.5M, and 1.5M hydrochloric acid at 25°C. Because of the chloride complex of Pu(VI) there was considerable variation between the several spectra. A portion of each of these solutions was diluted⁴ with hydrochloric acid of the corresponding concentration and the extinction coefficients of the diluted solutions were measured at 25°C and 70°C over the range 8050 Å to 8550 Å. The extinction coefficients for 1.0M hydrochloric acid solutions are interpolated from the data in 0.2M, 0.5M, and 1.5M hydrochloric acid.

b) Calculations

The first step in the calculation was to select the most suitable absorption bands for each of the oxidation states of plutonium and from the corresponding extinction coefficients make a preliminary

estimate of the concentration of plutonium in each oxidation state, including colloidal Pu(IV). The concentrations could then be calculated more exactly by applying corrections for the interfering ions at each of the selected wavelengths. If the second values did not agree well with the initial approximations, the calculation was repeated using the second set of values in making the corrections. Usually more than one wavelength was used in calculating each state. In these cases the average value is reported. The wavelengths selected for the calculations and some deviations from the general method of calculation are discussed. By restricting the measurements to the absorption bands described, it was possible to obtain the spectrophotometric data for the five plutonium species in about 12 minutes.

Pu(III): Absorption bands at 5600, 6000, and 6030 Å were used for the measurement of the Pu(III) concentration. Agreement between the values obtained was quite good with the exception of the 5600 Å band which gave slightly low results when the Pu(III) concentration was low compared to the Pu(IV) concentration. Under the latter conditions the correction for Pu(IV) absorption is very large. In such a case the 5600 Å value was discarded.

Pu(IV): The bands selected were 4700, 6550, 7000, 7300, and 8150 Å. At 25°C the values were generally in good agreement. The 4700 Å band is very narrow and occasionally gave erratic results because of difficulty in setting the spectrophotometer to the exact maximum. As described, formation of Pu(IV)-chloride complexes interfered with the calculations at 70°C. Thus, calculations for solutions at higher temperatures gave values which sometimes varied by as much as a factor of 2. There is evidence which suggests that the true concentration of Pu(IV) in these solutions is between the two extremes. Thus, the average is probably close to the correct value and may be taken as a qualitative indication, and with reservations, as a quantitative measure of the Pu(IV) concentration.

Colloidal Pu(IV): This constituent was determined by its absorption at 4380 Å. The uncertain nature of its absorption spectrum makes the values only qualitative. Colloidal Pu(IV) appeared in appreciable amounts only in 0.18M hydrochloric acid which had been maintained at 70°C for several hours. For this reason its presence rarely interfered with the calculations for Pu(III), normal Pu(IV), Pu(V), and Pu(VI).

Pu(V): The only strong absorption band of Pu(V) lies at 5690 Å. At this wavelength there is considerable interference from both Pu(III) and Pu(IV). Since in these experiments the concentration of Pu(V) was appreciable only when the Pu(III) concentration was high and the temperature elevated (with all the described errors which arise from increasing the temperature) the determination of the Pu(V) concentration was exceedingly difficult.

In the hope that some of the errors might thereby cancel out, another method was adopted for these calculations. In this method the concentrations of all other states including colloidal Pu(IV) were first calculated, this could be accomplished without knowing the Pu(V) concentration since the Pu(V) absorption is generally weak and the corrections for its presence are, therefore, negligible. Knowing the concentrations of Pu(III), Pu(IV), colloidal Pu(IV), and Pu(VI), the total absorption at 5600 Å and 5690 Å arising from these constituents was calculated. The experimentally obtained extinction coefficient at 5690 Å was subtracted from the experimental value for 5600 Å. This difference was then subtracted from the difference between the calculated values for Pu(III), Pu(IV), colloidal Pu(IV), and Pu(VI) at the corresponding wavelengths. This final difference represents the amount of Pu(V) absorption at 5690 Å less that due to Pu(V) at 5600 Å. To obtain the concentration of Pu(V) the latter value was divided by the difference between the absorption coefficients of pure Pu(V) at 5600 Å and 5690 Å.

Pu(VI): Absorption bands at 8310 Å and 9530 Å were selected for the determination of Pu(VI). In cases of disagreement the value for 9530 Å was used since the 8310 Å band is very narrow and consequently difficult to measure reproducibly. Measurements made at 8310 Å band were corrected for the nonlinearity⁴ of its molal extinction coefficient with $\log I_0/I$.

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