THE CHEMISTRY OF

PLUTONIUM

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CHAPTER 2

OXIDATION STATES IN SOLUTION

2.1 DISSOLUTION OF PLUTONIUM METAL

SINCE VIRTUALLY ALL plutonium is currently produced in a metallic state, initial solution preparation involves dissolution of the metal. Moreover, even for laboratory studies it is common practice to store plutonium metal and dissolve it as needed to prepare required solutions. For these reasons, it is logical that any discussion of solution chemistry begin with a consideration of metal dissolution.

Because of its highly electropositive nature, plutonium metal is soluble in a number of mineral acids. The effect of various solutions on the metal is shown in Table 2.1. While a number of dilute acids will attack the metal, frequently a residue is left which is probably polymeric plutonium hydroxide[5]. Using a microcalorimeter, Fuger and Cunningham[6] found the heat of solution of alpha plutonium metal to be -138.65 ± 0.7 kcal/mole in $1.5 M$ HCl and -138.90 ± 0.9 kcal/mole in $6 M$ HCl. By combining their value for the heat of formation of $PuCl_3$ (see Chapter 10) with the heat of solution data obtained by Westrum and Robinson[7], they obtained a value of -138.6 ± 0.7 kcal/mole for the standard heat of formation of $Pu^{3+}_{(aq.)}$ at 298°K. This value has been questioned by Akhachinski[8], who found the heat of solution to be -141.5 ± 0.4 kcal/mole and recommended a value of -141.6 ± 0.5 kcal/mole for the standard heat of formation of $Pu^{3+}_{(aq.)}$ at 298°K. On the other hand, Hinchey[9] found the heat of solution to be -139.2 ± 0.8 kcal/mole in $2.0 M$ HCl and -139.4 ± 0.8 kcal/mole in $6.03 M$ HCl—values in good agreement with those of Fuger and Cunningham[6]. From data on the heat of solution and the solubility of $PuCl_3$ along with estimates of activity coefficients, the entropy of $Pu^{3+}_{(aq.)}$ was calculated to be -47 ± 3 cal/mole-deg. at 298°K[9].

Plutonium ions in solution commonly exist in the (III), (IV), (V), and (VI) oxidation states, as Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_2^{2+}, respectively. Because of the relationships between the equilibria, and the kinetics of converting from one state to another, it is possible for all four of these oxidation states to co-exist in appreciable concentrations in the same solution, as will be explained in section 2.4.

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Table 2.1   Reactivity of plutonium in various solutions[1]

Solution	Reactivity
Water	Reacts very slowly at room temperature, slightly faster at the boiling point.
HNO_3	No attack at any concentration because of passivation; in the presence of $0.005M$ HF, the boiling concentrated acid will dissolve plutonium fairly rapidly.
HCl, HBr	Very rapid dissolution by concentrated and moderately dilute acids.
HF	Very slowly attacked. Briquets made by pressing plutonium metal turnings will often dissolve rapidly and completely, forming insoluble PuF_3[2].
72% $HClO_4$	Rapid dissolution.
H_2SO_4	Concentrated acid forms protective coating on the metal which causes initially slow reaction to stop. Moderately dilute acid (5N) attacks the metal slowly: occasionally impure samples of the metal may be dissolved completely in 5N acid.
85% H_3PO_4	Attacked fairly rapidly.
Acetic Acid	Unattacked by glacial acid, even when hot; slow attack by dilute acid.
Trichloroacetic Acid	Rapid dissolution by concentrated acid; slower attack by dilute acid.
Trifluoroacetic Acid	Slow dissolution by concentrated acid; frequently leaves residue of undissolved oxide[3].
Sulfamic Acid	Fairly rapid dissolution in $1.7M$ acid; temperature must be below 40°C to prevent decomposition of the acid. Small amount of potentially pyrophoric sludge remains; if HNO_3 is also present in the solution, the amount of sludge is greater[4].

Recently a new oxidation state of plutonium—the heptavalent state—has been prepared by the ozonation of Pu(VI) in alkaline solution[10]. The species is unstable in alkaline media and apparently does not exist in acidic solution. Although its composition has not been determined, the Pu(VII) species is almost certainly oxygenated; the compound $Co(NH_3)_6NpO_5$ has been precipitated from analogous solutions of Np(VII)[11], and it would therefore seem reasonable to assume the presence of a species such as PuO_5^{3-} in Pu(VII) solutions. The existence of this new oxidation state was unexpected, but in retrospect it is not really surprising considering that the plutonium atom has eight electrons above the filled shell of radon, and because of this, it does not seem unreasonable to expect the eventual preparation of Pu(VIII).

Solutions of Pu(III) are blue when viewed by reflected light; when seen by transmitted light they are blue with a pronounced green tinge. Tetravalent

plutonium forms brown solutions in dilute acids; in more concentrated acids the color often changes because of formation of colored complexes. For example, Pu(IV) in concentrated (above about $6N$) HNO_3 yields a spinach-green
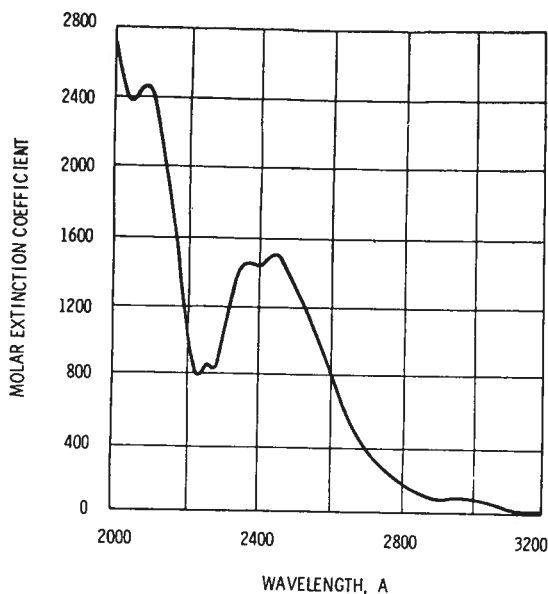

Figure 2.1 Ultraviolet absorption spectrum of Pu(III) in $1M$ $HClO_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 212 (1961)

solution, while H_3PO_4 solutions are pink. Plutonyl(V) is colorless in solution, while Pu(VI) forms a solution whose color can vary from yellow to pink-orange depending on conditions.

The oxidation state produced by dissolution of plutonium metal depends on the acid employed. Thus HCl, HBr, H_3PO_4, and $HClO_4$ in any concentration produce a blue solution containing essentially only the trivalent ion, while HNO_3–HF dissolution forms mainly Pu(IV) and produces a green solution.

2.2   SPECTRA

Absorption spectra of Pu(III), (IV), (V), (VI), and (VII) ions are given in Figs. 2.1 through 2.13. The sharp absorption bands are characteristic of ions containing f electrons, as explained in Chapter 1. The lack of sharp absorption bands in the Pu(VII) spectrum may indicate the absence of $5f$ electrons in this

species. The bands in the visible and near-infrared regions are due to internal 5f transitions, while the ultraviolet bands are the result of allowed transitions to other electron levels. A detailed interpretation of the Pu(VI) spectrum has been made by Eisenstein and Pryce[12].

Since there is little or no complexing in HClO$_4$ solutions, these spectra are of the aquo ions of plutonium, containing only water molecules in the co-ordination sphere. In solutions containing more strongly complexing anions the spectra [except those of Pu(III)] are generally different, and for this reason spectrophotometry is a useful tool for determining the presence and identity of plutonium complexes.

2.3 OXIDATION POTENTIALS

The formal potential diagrams of plutonium in a number of different solutions at 25°C are reproduced in Table 2.2. In all cases the convention with respect to sign is that used by Latimer[19]. These values indicate that Pu(IV) and Pu(V),
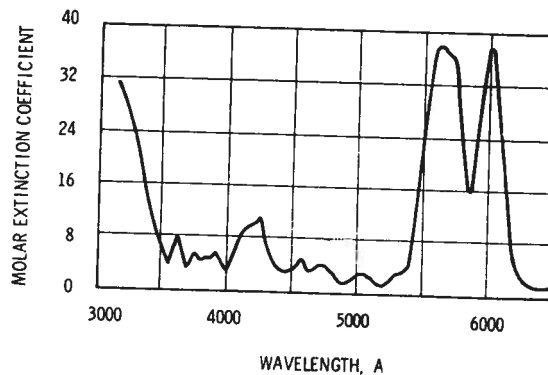
Figure 2.2 Visible absorption spectrum of Pu(III) in 1M HClO$_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 213 (1961)

particularly the latter, are unstable toward self oxidation–reduction (dispro-portionation), a phenomenon that will be discussed below.

It should be noted that the stability of the Pu(IV) ion is increased if HClO$_4$ is replaced by HCl, HNO$_3$, or H$_2$SO$_4$, being greatest for the last. This effect is due to the enhanced complex-forming tendency of the tetravalent ion in the presence of strongly complexing anions, such as sulfate, and, to a lesser extent, nitrate and chloride ions. Furthermore, the potential of the Pu(III)–Pu(IV) couple in HClO$_4$ becomes more negative by about 9 mv if the acid concentra-

Figure 2.3 Near infrared absorption spectrum of Pu(III) in $1M$ $HClO_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 213 (1961)

tion is increased from 1 to $2M$[20], presumably because of the effect of the ionic strength on the ratio of the activity coefficients of Pu(IV) and Pu(III).[21] In HCl, on the other hand, the potential becomes more positive by about 12 mv as the acid molarity is increased from 1 to 2 as a result of the formation of chloro complexes of Pu(IV)[20, 21].

Figure 2.4 Ultraviolet absorption spectrum of Pu(IV) in $1M$ $HClO_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 213 (1961)

Figure 2.5   Visible absorption spectrum of Pu(IV) in $1M$ HClO$_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 214 (1961)
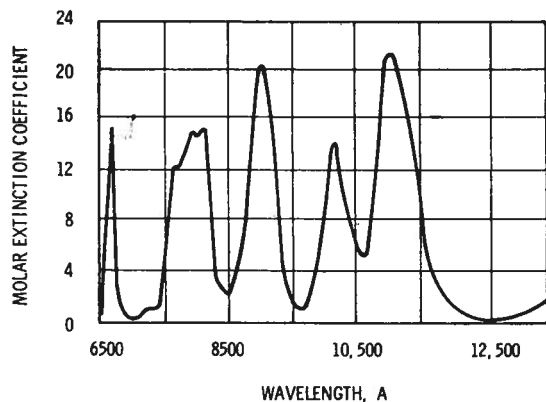

Figure 2.6   Near-infrared absorption spectrum of Pu(IV) in $1M$ HClO$_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 214 (1961)

Figure 2.7 Ultraviolet absorption spectrum of Pu(V) in $0.2M$ $HClO_4$ at 10°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 215 (1961)
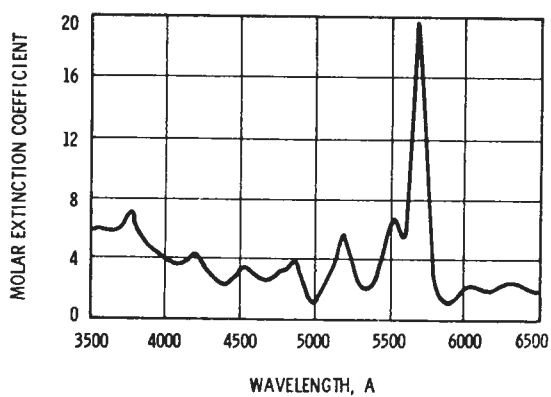
Figure 2.8 Visible absorption spectrum of Pu(V) in $0.2M$ $HClO_4$ at 10°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 215 (1961)

Figure 2.9 Near-infrared absorption spectrum of Pu(V) in $0.2M$ HClO$_4$ at 10°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 216 (1961)
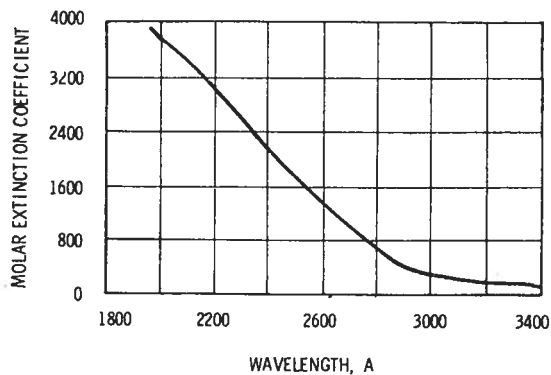

Figure 2.10 Ultraviolet absorption spectrum of Pu(VI) in $1M$ HClO$_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 216 (1961)
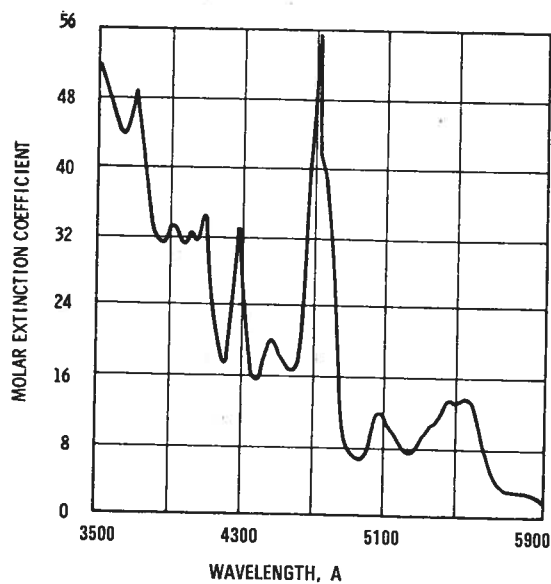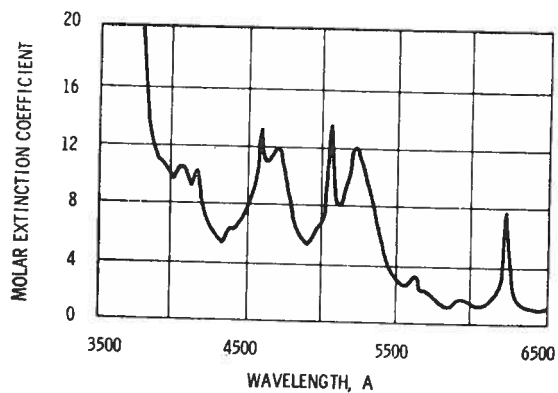
Figure 2.11   Visible absorption spectrum of Pu(VI) in $1M$ HClO$_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 217 (1961)
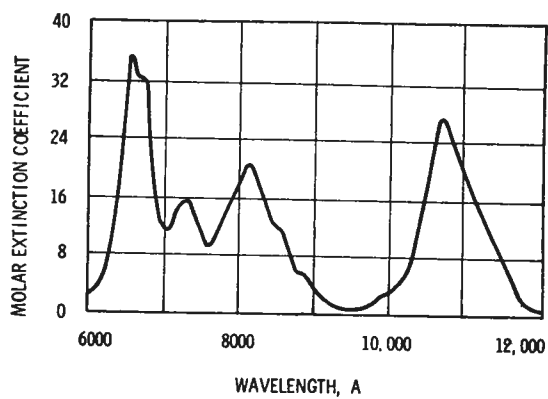

Figure 2.12   Near-infrared absorption spectrum of Pu(VI) in $1M$ HClO$_4$ at 25°C. From D. Cohen, *J. Inorg. Nucl. Chem.*, **18**: 217 (1961)
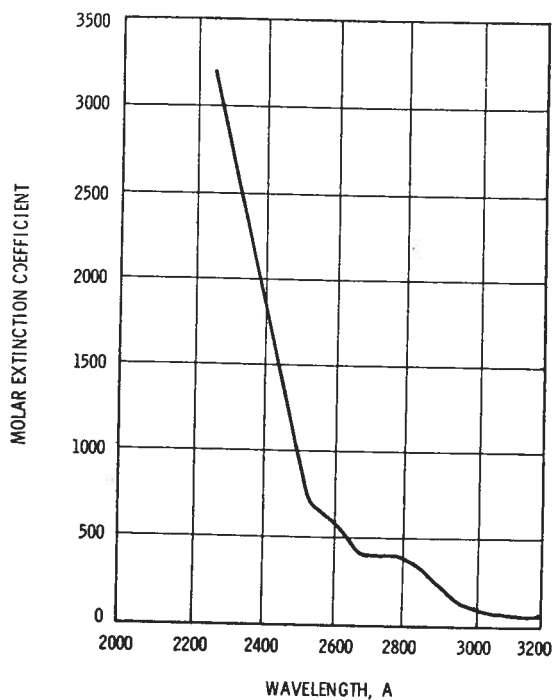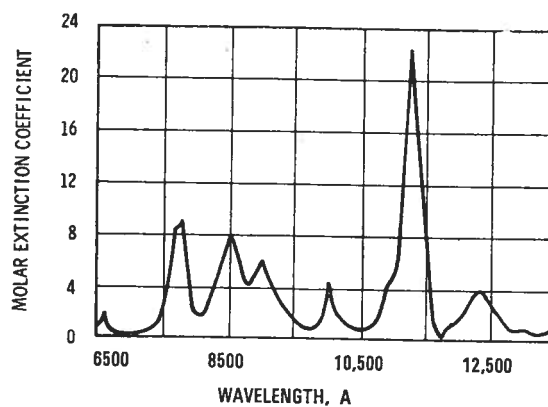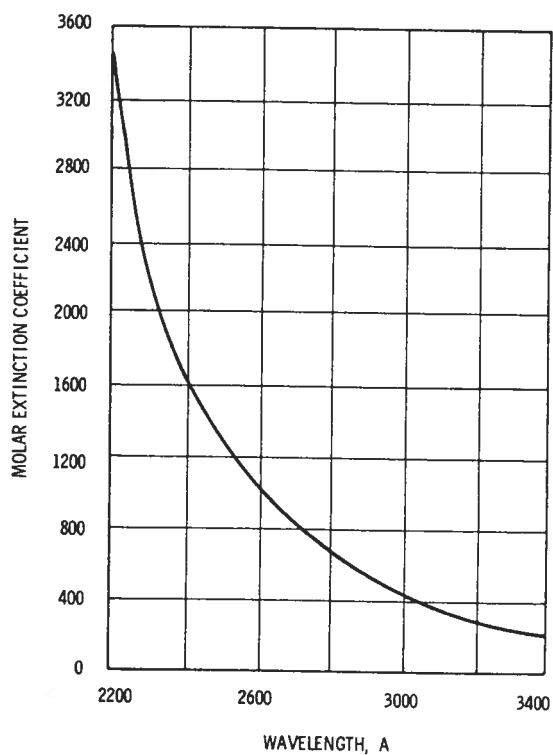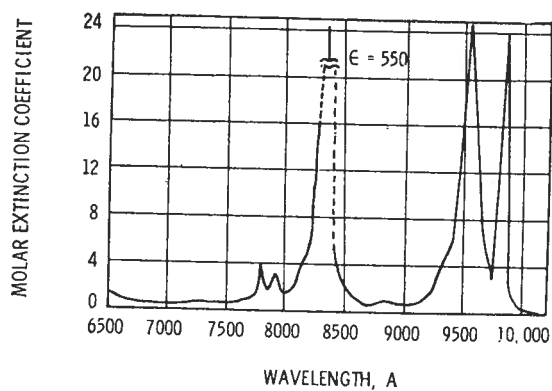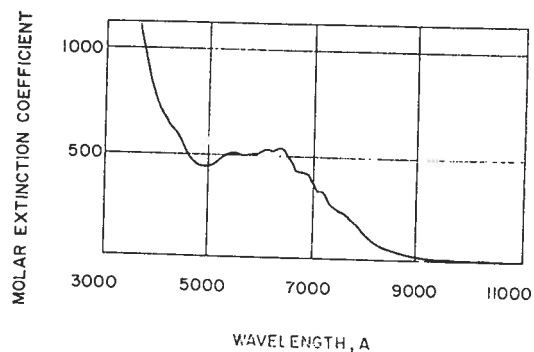

Figure 2.13   Absorption spectrum of Pu(VII) in $0.5M$ NaOH at 25°C From N. N. Krot and A. D. Gel'man, *Dokl. Akad. Nauk SSSR*, **177**: 124 (1967)

Table 2.2   Formal potentials of plutonium couples in volts at 25°C

In $1M$ $HClO_4$:[13,14,17]

$$Pu^0 \xrightarrow{2.03} Pu^{3+} \xrightarrow{-0.9819} Pu^{4+} \xrightarrow{-1.1702} PuO_2^+ \xrightarrow{-0.9164} PuO_2^{2+}$$

with -1.0433 (Pu^{4+} to PuO_2^{2+}) and -1.0228 (Pu^{3+} to PuO_2^+)

In $1M$ HCl:[14-17]

$$Pu^0 \xrightarrow{2.03} Pu^{3+} \xrightarrow{-0.97019} Pu^{4+} \xrightarrow{-1.1895} PuO_2^+ \xrightarrow{-0.9122} PuO_2^{2+}$$

with -1.0508 (Pu^{4+} to PuO_2^{2+}) and -1.0238 (Pu^{3+} to PuO_2^+)

In $1M$ HNO_3:[18]

$$Pu^{3+} \xrightarrow{-0.914} Pu^{4+} \longrightarrow PuO_2^+ \xrightarrow{-0.920*} PuO_2^{2+}$$

*In $0.1M$ HNO_3

with -1.054 (Pu^{4+} to PuO_2^{2+}) and -1.006 (Pu^{3+} to PuO_2^{2+})

In $1M$ H_2SO_4:[16]

$$Pu^{3+} \xrightarrow{0.75} Pu^{4+} \xrightarrow{\sim(-1.2 \text{ to } -1.4)} PuO_2^{2+}$$

In neutral solution (pH = 7):[15]

$$Pu^{3+} \xrightarrow{0.63} Pu(OH)_4 \cdot yH_2O_{(s)} \xrightarrow{-1.11} PuO_2^+ \xrightarrow{-0.77} PuO_2(OH)_{2(aq.)}$$

with -0.94 ($Pu(OH)_4 \cdot yH_2O_{(s)}$ to $PuO_2(OH)_{2(aq.)}$)

In $1M$ OH^-:[17]

$$Pu(OH)_3 \cdot xH_2O \xrightarrow{0.95} Pu(OH)_4 \cdot yH_2O \xrightarrow{-0.76} PuO_2(OH)_{(aq.)} \xrightarrow{-0.26} PuO_2(OH)_3^-{}_{(aq.)}$$

with ~ -0.4 ($Pu(OH)_4 \cdot yH_2O$ to $PuO_2(OH)_3^-{}_{(aq.)}$)

Even more pronounced is the effect of HNO_3 concentration on the potentials, as shown in Table 2.3.

Table 2.3   Effect of HNO_3 concentration on plutonium couples at 25°C [18]

[HNO₃], M	Pu(III)–Pu(IV)	Potential, V Pu(IV)–Pu(VI)	Pu(III)–Pu(VI)
0.1	− 0.952	− 0.925	− 0.934
0.2	− 0.939	− 0.949	− 0.946
0.3	− 0.935	− 0.973	− 0.961
0.4	− 0.927	− 0.993	− 0.972
1.0	− 0.914	− 1.054	− 1.006

The temperature dependences of the Pu(III)–Pu(IV) potential and the Pu(III)–Pu(VI) potential in $1M$ HCl have been determined and the results are given in Table 2.4. As can be seen, the potential of the Pu(III)–Pu(IV) couple becomes more negative with increasing temperature, while that of the Pu(III)–Pu(VI) couple becomes slightly less negative. Thermodynamic values for some of the half-cell reactions of plutonium ions are summarized in Table 2.5.

Table 2.4 Effect of temperature on plutonium formal potentials in $1M$ HCl [15]

Pu(III)–Pu(IV)		Pu(III)–Pu(VI)	
Temperature, °C	E^0, v	Temperature, °C	E^0, v
6.31	-0.94815	6.43	-1.0301
25.00	-0.97019	25.00	-1.0238
35.24	-0.98208	35.24	-1.0202
45.10	-0.99356	45.16	-1.0150

Table 2.5 Thermodynamic values for plutonium couples at 25°C

Cell reaction	ΔG, kcal/mole	ΔH, kcal/mole	ΔS, cal/mole-deg	Reference*
In $1M$ HClO$_4$:				
$Pu^0 + 3H^+ \rightarrow Pu^{3+} + \frac{3}{2}H_2$	-139.9	-141.8	-6	16
$Pu^{3+} + H^+ \rightarrow Pu^{4+} + \frac{1}{2}H_2$	22.64	13.63	-30.2	14
$Pu^0 + 4H^+ \rightarrow Pu^{4+} + 2H_2$	-117.2	-128.3	-37	16
$Pu^{3+} + 2H_2O \rightarrow PuO_2^{2+} + H^+ + \frac{3}{2}H_2$	70.8	78†	24†	14
$PuO_2^+ + H^+ \rightarrow PuO_2^{2+} + \frac{1}{2}H_2$	21.13	22.9	5.9	14
In $1M$ HCl:				
$Pu^0 + 3H^+ \rightarrow Pu^{3+} + \frac{3}{2}H_2$	~ -142.7	-141.9	—	22
$Pu^{3+} + H^+ \rightarrow Pu^{4+} + \frac{1}{2}H_2$	22.37	14.32	-27.0	14
$Pu^0 + 4H^+ \rightarrow Pu^{4+} + 2H_2$	-120.6	-129.0	—	22
$Pu^{3+} + 2H_2O \rightarrow PuO_2^{2+} + H^+ + \frac{3}{2}H_2$	70.8	78.4	25.4	14
$PuO_2^+ + H^+ \rightarrow PuO_2^{2+} + \frac{1}{2}H_2$	21.04	23†	6†	14

* Values taken from References 16 and 22 are based on potentials that in some cases are slightly uncertain; these values, therefore, should be regarded as only approximate.
† Estimated.

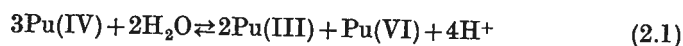## 2.4 EQUILIBRIA BETWEEN Pu(III), (IV), (V), AND (VI) IN SOLUTION

As mentioned above, it is possible for finite concentrations of the four common oxidation states of plutonium to co-exist in the same solution. Such behavior, unique for plutonium among all the elements of the periodic table, is due to the

interplay of two phenomena: (1) the tendency of Pu(IV) and Pu(V) ions to disproportionate and (2) the slow rate of reactions involving formation or rupture of plutonium–oxygen bonds (such as exist in PuO_2^+ and PuO_2^{2+}), as compared to the much faster reactions involving only electron transfer.
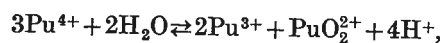
Much research has been done on the equilibria, kinetics, and mechanisms of these reactions; the results, which are discussed in this section, have gone a long way toward elucidating plutonium solution chemistry.

a) The disproportionation of Pu(IV)

Plutonium(IV) disproportionates according to the net equation:

$$3Pu(IV) + 2H_2O \rightleftarrows 2Pu(III) + Pu(VI) + 4H^+ \tag{2.1}$$

or

$$3Pu^{4+} + 2H_2O \rightleftarrows 2Pu^{3+} + PuO_2^{2+} + 4H^+,$$

for which the equilibrium constant expression is

$$K' = \frac{[Pu(III)]^2[Pu(VI)]}{[Pu(IV)]^3} \tag{2.2}$$

omitting for the moment the hydrogen ion concentration. The equilibrium constant for this reaction in $HClO_4$ has been determined by Rabideau[23], who, unlike earlier workers[24, 25], corrected for reduction by alpha particles as well as for hydrolysis at low acidities. The equilibrium constant was determined at the time at which the rate of disappearance of Pu(IV), $-d[Pu(IV)]/dt$, equaled the rate of alpha reduction.

The hydrolysis of Pu(IV) proceeds according to the equation

$$Pu^{4+} + H_2O \rightleftarrows Pu(OH)^{3+} + H^+. \tag{2.3}$$
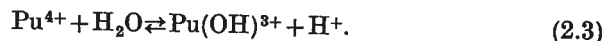
The hydrolysis constant for Pu(IV) in perchlorate solutions of unit ionic strength is 0.031[26]; thus the unhydrolyzed species is related to the total Pu(IV) concentration by

$$Pu^{4+} = \Sigma Pu(IV) \times \frac{[H^+]}{[H^+] + 0.031}. \tag{2.4}$$

From the equilibrium expression

$$K'' = K'[Pu(IV)]^3/[Pu^{4+}]^3 \tag{2.5}$$

where [Pu(IV)] is the total tetravalent plutonium concentration and [Pu^{4+}] is the concentration of the unhydrolyzed species, it is possible to determine the hydrogen ion dependence of the disproportionation reaction; K'' was found experimentally, over a fivefold range of acidity, to be proportional to the

fourth power of the hydrogen ion concentration, as is predicted by equation (2.1). The true equilibrium constant K may be obtained by multiplying K'' by $[H^+]^4$, so that the equilibrium expression becomes

$$K = \frac{[Pu(III)]^2[Pu(VI)]\,[H^+]^4}{[Pu^{4+}]^3} \qquad (2.6)$$

in accordance with the disproportionation equation (2.1).

Rabideau's equilibrium data for the disproportionation of Pu(IV) are reproduced in Table 2.6. A weighted average value, $K = 0.0089$ was obtained from these data, more weight being given to the values in 1.0 and $0.5M$ $HClO_4$ because of the decreased correction for hydrolysis in these cases.

Table 2.6 Disproportionation equilibrium constants for Pu(IV) in $HClO_4$ solutions of unit ionic strength at 25°C [14,23]

$[H^+]$, M	$NaClO_4$, M	K''	$K(=K''[H^+]^4)$
1.000	0.000	0.0084	0.0084
0.500	0.500	0.135	0.0084
0.200	0.800	6.80	0.0109

Rabideau and Cowan[15] have studied the disproportionation of Pu(IV) in HCl and found the hydrogen ion dependence, and therefore, presumably, the mechanism, to be the same as that for perchlorate media. The principal difference between the two was that in HCl solutions the correction for alpha reduction could be omitted, since in HCl solutions of unit ionic strength it was found that this effect was essentially absent. This observation, which contradicts that of Kasha and Sheline[25], is discussed in detail in section 2.5.

The disproportionation equilibrium constants in HCl solution are reproduced in Table 2.7. These values compare quite well with those determined earlier by Connick and McVey[27].

A $0.002M$ solution of Pu(IV) in $0.5M$ HCl at 25°C was found to disproportionate to give approximately 26.3% Pu(III), 62.7% Pu(IV), an estimated

Table 2.7 Disproportionation equilibrium constants for Pu(IV) in HCl solutions of unit ionic strength at 25°C [14,15]

$[H^+]$, M	$NaCl$, M	K''	$K(=K''[H^+]^4)$
1.000	0.000	$(1.75 \pm 0.2) \times 10^{-3}$	0.00192
0.500	0.500	$(2.40 \pm 0.04) \times 10^{-2}$	0.00180
0.200	0.800	$(7.7 \pm 0.1) \times 10^{-1}$	0.00190

0.5% of the pentavalent ion, and 10.5% Pu(VI), and required about 200 hr to reach equilibrium[28]. Likewise, a 2-g/liter Pu(IV) solution in 0.344M HNO$_3$ was found to reach equilibrium in 17 hr, at which time it contained 12% Pu(III), 66% Pu(IV), and 22% Pu(VI)[29]. The smaller degrees of disproportionation observed in HCl and HNO$_3$ are due to stabilization of Pu(IV) ions by complexing.

The temperature dependence of the disproportionation equilibrium constant in HCl, as determined by Rabideau and Cowan[15], is shown in Table 2.8. It is apparent that disproportionation is very temperature-dependent; raising the temperature from 25 to 45°C increases the equilibrium constant by a factor of about 70.

Table 2.8 Variation of Pu(IV) disproportionation equilibrium constant with temperature in 1M HCl [15]

Temperature, °C	K
6.43	3.76×10^{-5}
25.00	1.42×10^{-3}
35.24	1.35×10^{-2}
45.16	9.67×10^{-2}

Artyukhin and coworkers[30] found that the disproportionation of Pu(IV) in HNO$_3$ takes place by the same mechanism as that in HClO$_4$. The disproportionation equilibrium constant as a function of HNO$_3$ concentration is shown in Table 2.9. These results indicate that the equilibrium constant is inversely proportional to the 5.3 power of the hydrogen ion concentration rather than the fourth power. In view of the fact that this work was done in

Table 2.9 Disproportionation equilibrium constants for Pu(IV) in HNO$_3$ at 25°C [30]

[H$^+$], M	K'
0.40	0.0045
0.30	0.049
0.20	0.41
0.10	7.8

solutions of varying ionic strength and no correction was made for alpha reduction, hydrolysis, and nitrate complexing, the discrepancy is not surprising. As would be expected, there is essentially no disproportionation of Pu(IV) in strongly acidic solutions.

Although the net reaction for Pu(IV) disproportionation is

$$3Pu^{4+} + 2H_2O \rightleftharpoons 2Pu^{3+} + PuO_2^{2+} + 4H^+, \qquad (2.1)$$
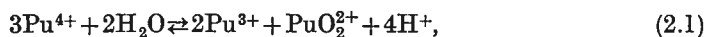
Connick[31] has shown that the overall reaction consists of two separate reactions, one slow and one fast:

$$Pu(IV) + Pu(IV) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pu(III) + Pu(V) \quad \text{(slow)} \qquad (2.7)$$

and

$$Pu(V) + Pu(IV) \rightleftharpoons Pu(III) + Pu(VI) \quad \text{(fast)}. \qquad (2.8)$$

The rate of reaction (2.7) is slow because of the formation of a plutonium–oxygen bond.

After corrections have been made for alpha reduction, the rate law for the disproportionation of Pu(IV) is[14]
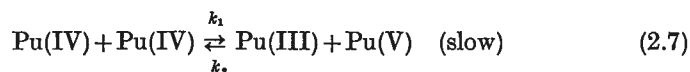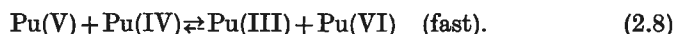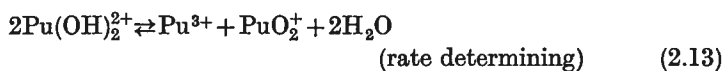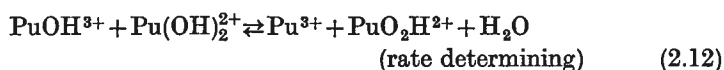
$$-d[Pu(IV)]/3dt = [Pu^{4+}]^2 \{k_1[H^+]^{-3} + k_1'[H^+]^{-4}\}$$
$$- [Pu^{3+}][PuO_2^+] \{k_2[H^+] + k_2'\} \qquad (2.9)$$

where $[Pu(IV)]$ is the total tetravalent plutonium concentration and $[Pu^{4+}]$ is the concentration of the unhydrolyzed ion. In $1M$ perchlorate solution, k_1 was found to be 2.56×10^{-5} mole^2/liter^2-sec and k_1' to be 3.9×10^{-6} mole^3/liter^3-sec.

A consistent reaction sequence for the disproportionation is as follows[15]:

$$Pu^{4+} + H_2O \rightleftharpoons PuOH^{3+} + H^+ \qquad \text{(fast)} \qquad (2.10)$$

$$Pu^{4+} + 2H_2O \rightleftharpoons Pu(OH)_2^{2+} + 2H^+ \qquad \text{(fast)} \qquad (2.11)$$

$$PuOH^{3+} + Pu(OH)_2^{2+} \rightleftharpoons Pu^{3+} + PuO_2H^{2+} + H_2O$$
$$\text{(rate determining)} \qquad (2.12)$$

$$2Pu(OH)_2^{2+} \rightleftharpoons Pu^{3+} + PuO_2^+ + 2H_2O$$
$$\text{(rate determining)} \qquad (2.13)$$

$$PuO_2H^{2+} \rightleftharpoons PuO_2^+ + H^+ \qquad \text{(fast)} \qquad (2.14)$$

$$PuO_2^+ + Pu^{4+} \rightleftharpoons PuO_2^{2+} + Pu^{3+} \qquad \text{(fast)}. \qquad (2.15)$$
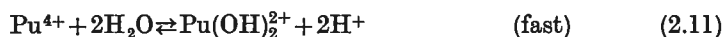
The rate of disproportionation of Pu(IV) in HCl is approximately 5.5 times that in $HClO_4$ of the same acidity[15]. As in $HClO_4$, the rate is approximately inversely proportional to the third power of the hydrogen ion concentration. It is of interest to note at this point that while the equilibrium constant for the disproportionation is about 4.5 times greater in $HClO_4$ than in HCl, the *rate* of disproportionation is greater in the latter. This distinction is a good illustration of the fact that there is frequently no relation between the degree of completion of a reaction and the rate of the reaction.

The rate constant for the disproportionation in HCl has been found to increase by a factor of about 2000 as the temperature is raised from 6° to 45°C [15]. From these data the heat and entropy of activation of the disproportionation reaction were calculated to be 39 kcal/mole and 53 cal/mole-deg, respectively.

The rate of disproportionation in mixed $HClO_4$–HCl is in accordance with the equation[14]

$$-d[Pu(IV)]/dt = [Pu^{4+}]^2 \{0.298 + 2.50 \, [Cl^-] \\ + 10.9 \, [Cl^-]^2\} \times 10^{-4} \text{ mole/liter-sec.} \qquad (2.16)$$

Artyukhin et al.[30] found the rate of disproportionation in HNO_3 to be approximately the same as that in $HClO_4$; they explain this surprising behavior as being due to the participation of $Pu(NO_3)^{3+}$ ions, as well as Pu^{4+} ions, in the reaction. Since they did not make corrections for alpha reduction, however, their data should be considered as only approximate.

b) The disproportionation of Pu(V)

In moderately acidic solutions Pu(V) is unstable toward disproportionation according to the overall reaction

$$3PuO_2^+ + 4H^+ \rightleftarrows Pu^{3+} + 2PuO_2^{2+} + 2H_2O. \qquad (2.17)$$
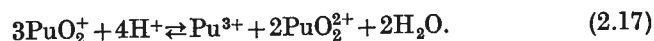
The actual route taken is dependent on other plutonium ionic species present.[31] Normally the reaction proceeds primarily according to the equations

$$Pu(V) + Pu(III) \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2Pu(IV) \quad \text{(slow)} \qquad (2.18)$$

or

$$PuO_2^+ + Pu^{3+} + 4H^+ \rightleftarrows 2Pu^{4+} + 2H_2O$$

and

$$Pu(V) + Pu(IV) \underset{k_4}{\overset{k_3}{\rightleftarrows}} Pu(III) + Pu(VI) \quad \text{(fast).} \qquad (2.8)$$
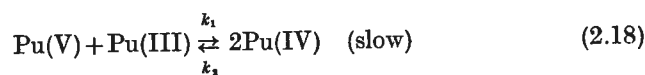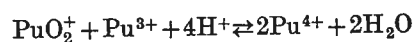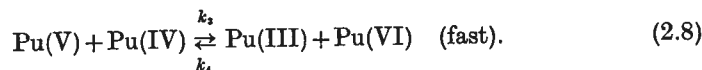
If Pu(V) is the only ionic species present, the reaction follows the much slower route

$$Pu(V) + Pu(V) \rightleftarrows Pu(IV) + Pu(VI) \quad \text{(slow)} \qquad (2.19)$$

or

$$PuO_2^+ + PuO_2^+ + 4H^+ \rightleftarrows Pu^{4+} + PuO_2^{2+} + 2H_2O.$$
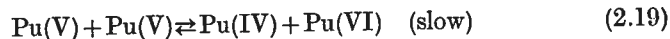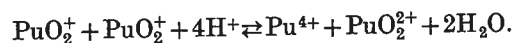
It will be noted that equation (2.8) describes the equilibrium between all four oxidation states of plutonium. This reaction will be discussed in detail in section 2.4(c).

In the presence of Pu(III), the disproportionation takes place according to equations (2.18) and (2.8), and the rate law is

$$-d[Pu(V)]/dt = 3k_1[Pu(V)][Pu(III)]$$
$$-3k_2[Pu(IV)]^2 - d[Pu(VI)]/dt. \qquad (2.20)$$

The value of k_1 in $0.50M$ HCl at room temperature was found to be 3.5 liter/mole-min.

To study the rate and mechanism of the Pu(V)–Pu(V) reaction (2.19), Rabideau[32] prepared a Pu(V) solution essentially free of Pu(III) by the reduction of Pu(VI) ion with iodide ion. The Pu(V) disproportionates as follows:

$$Pu(V) + Pu(V) \rightarrow Pu(VI) + Pu(IV). \qquad (2.19)$$

As soon as Pu(IV) is formed by this reaction, however, it will react rapidly with Pu(V) according to the equation

$$Pu(IV) + Pu(V) \rightarrow Pu(III) + Pu(VI). \qquad (2.8)$$

After correcting for reaction (2.8), the rate law for the Pu(V)–Pu(V) reaction (2.19) was found to be[13]

$$-d[PuO_2^+]/dt = 3k[PuO_2^+]^2[H]^+ \qquad (2.21)$$

which is consistent with the following reaction mechanism:

$$PuO_2^+ + H^+ \rightarrow PuO_2H^{2+} \qquad \text{(fast)} \qquad (2.22)$$

$$PuO_2^+ + PuO_2H^{2+} \rightarrow PuO_2^{2+} + PuO\,OH^+ \quad \text{(rate determining)} \qquad (2.23)$$

$$PuO\,OH^+ + 3H^+ \rightarrow Pu^{4+} + 2H_2O \qquad \text{(fast)} \qquad (2.24)$$

$$Pu^{4+} + PuO_2^+ \rightarrow Pu^{3+} + PuO_2^{2+} \qquad \text{(fast)}. \qquad (2.8)$$
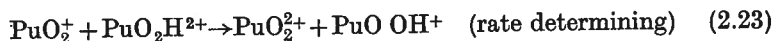
The rate constant, k, was found to be 3.6×10^{-3} liter^2/mole^2-sec in HClO$_4$ solutions of unit ionic strength at 25°C; under the same 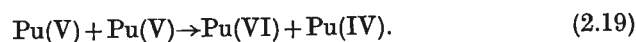conditions, but with deuterium oxide instead of water as solvent, k increased by a factor of 1.17, to 4.3×10^{-3} liter^2/mole^2-sec. The increase in rate in deuterium oxide would appear to rule out a hydrogen atom transfer mechanism for the disproportionation of Pu(V)[32].

Raising the temperature of the solution from 10° to 35°C increased the rate of the disproportionation reaction by a factor of about 12. From these data the activation energy, heat of activation, and entropy of activation for reaction (2.19) were calculated to be 19.6 kcal/mole, 19.0 kcal/mole, and −5.8 cal/mole-deg, respectively.

Artyukhin et al.[30] studied the rate of disproportionation of Pu(V) in HNO$_3$

and found the mechanism to be the same as in $HClO_4$. As the HNO_3 concentration was increased from $0.10M$ to $0.30M$, the rate of reaction (2.19) increased from 0.73 liter/mole-hr to 3.4 liter/mole-hr. Although the rate is not quite directly proportional to the hydrogen ion concentration, as Rabideau found, the discrepancy probably is due to the variable ionic strengths of the HNO_3 solutions. As was noted in $HClO_4$, the rate of disproportionation becomes increasingly rapid as Pu(III) is formed and reacts with Pu(V) by the faster reaction (2.18).

Disproportionation of Pu(V) in oxalate solutions produces only Pu(IV) and Pu(VI) and is irreversible because of the stabilization of the products by complex formation[33]. The rate is second-order in [Pu(V)] and first-order in [H$^+$] and at pH > 3.5 is independent of oxalate concentration in the 0.025–0.25M range. Although the mechanism of disproportionation in oxalate solution is the same as that described above, the rate is greater because complex formation weakens the Pu—O bonds, thus facilitating reaction (2.23).

Since the rate of disproportionation of Pu(V) is quite low in weakly acid solutions in the absence of other oxidation states, it is possible to prepare solutions of this species and keep them for reasonable periods of time. The use of iodide ion to reduce Pu(VI) to Pu(V) was mentioned above. The reaction

$$Pu(III) + Pu(VI) \rightarrow Pu(IV) + Pu(V) \qquad (2.8)$$
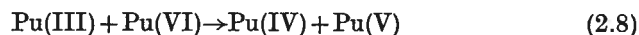
to be discussed in section 2.4(c), was used by Markin and McKay[34] to prepare a solution containing only Pu(V). They stirred equimolar quantities of Pu(III), prepared by reduction of Pu(IV) with SO_2, and Pu(VI) [electrolytically oxidized Pu(IV)] in $0.2M$ HNO_3 in the presence of a 0.1% solution of dibutyl phosphate in benzene. As Pu(IV) was formed, it was extracted into the organic phase, thus driving the reaction to the right and producing an aqueous solution of Pu(V) whose absorption spectrum showed it to contain no other plutonium oxidation states. Gel'man and Zaitseva[35] have prepared Pu(V) in concentrations as high as 5 g/liter in HNO_3 solutions by reduction of Pu(VI) with H_2O_2 at pH 3–4. Since Pu(VI) precipitates as $PuO_2(OH)_2$ at pH $\geqslant$ 4, it is best to begin at pH 3–3.5 and increase the pH to 4 as the reduction proceeds.

As suggested by equation (2.19), the equilibrium constant for the disproportionation of Pu(V) is proportional to the fourth power of the hydrogen ion concentration. It is thus not surprising that significant concentrations of the pentavalent species exist only in solutions of low acidity.

Gevantman and Kraus[36] have studied the stability of Pu(V) solutions in $HClO_4$ as a function of acidity, concentration, and temperature. They found that the optimum range of stability of Pu(V) is from pH 1.5 to pH 5; rapid disproportionation occurs below pH 1.5 and above pH 7. A solution of 0.1 g

Pu(V) per liter at pH 3.5, and containing up to $10M$ nitrate and $8M$ chloride ion, was quite stable at room temperature; after 6 days there was negligible disproportionation. At constant pH the stability of Pu(V) decreases appreciably as the concentration is raised. In one case at pH 3.5, there was essentially no disproportionation in a 0.5-g/liter solution after 10 days, while in a similar solution containing 5 g of Pu(V) per liter there was approximately 10% disproportionation in the same time. Increasing the temperature also decreases the stability, especially for the higher concentrations; at pH 3.5, 99% of the Pu(V) in a 5-g/liter solution had disproportionated after 30 min at 95°C, while in a similar solution containing 0.112 g of Pu(V) per liter, only 2% disproportionated with this treatment.

In HNO_3 solutions, Pu(V) is most stable at pH 3.5–4.5 [37]. Solutions with 2.5 g Pu(V)/liter or less at pH 4 still contained at least 80% of their plutonium in the pentavalent state after storage for 13 days. At higher Pu(V) concentrations and at other pH values, lower percentages of this oxidation state remained. Thus for solutions initially containing 3.4–5 g Pu(V)/liter, the approximate percentages of plutonium remaining in this oxidation state after 13 days at various pH values were as follows: pH 2, [Pu(V)] = 3.4 g/l, 40%, pH 3, [Pu(V)] = 3.72 g/l, 50%; pH 4, [Pu(V)] = 5 g/l, 60%; pH 5, Pu(V) = 5 g/l, 55%. The lower stability of Pu(V) as its concentration was increased was attributed to oxidation or reduction by products of alpha-radiolysis of the solution (see section 2.5).

c) The Pu(III), (IV), (V), (VI) equilibrium

The reaction

$$Pu^{4+} + PuO_2^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pu^{3+} + PuO_2^{2+}, \qquad (2.8)$$
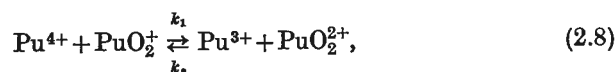
which describes the equilibrium between all four oxidation states of plutonium, has been used in the previous two sections to help explain the disproportionation of Pu(IV) and Pu(V). Because of its importance, this reaction is worthy of further discussion.

The equilibrium constant

$$K = \frac{[Pu^{3+}][PuO_2^{2+}]}{[Pu^{4+}][PuO_2^+]} \qquad (2.25)$$

for the reaction has been determined in various media. It was found to be 8.5 in $0.5M$ HCl at room temperature[13], and 3.2 in $0.1M$ HNO_3 at 25°C [30], both values apparently being uncorrected for hydrolysis of Pu(IV). Rabideau and Kline[38] determined the equilibrium constant in perchlorate solutions of unit

ionic strength but varying acidity; their value, corrected for hydrolysis of
Pu(IV), is 13.1 ± 0.08, and is independent of hydrogen ion concentration in the
0.1 to $1M$ range. The corresponding value at 25°C in deuterium oxide solvent
(also corrected for hydrolysis) is 40.6 ± 1.0, and is also independent of hydrogen
ion concentration. In water, the value for K (not corrected for hydrolysis)
varies from 4.3 at 3°C to 23.5 at 35°C; in deuterium oxide, from 16 at 5°C to 39
at 25°C.

Rabideau and Kline also studied the kinetics of the reaction and found it to
be first order in each of the reactants:

$$-d[Pu^{4+}]/dt = -d[PuO_2^+]/dt = k_1[Pu^{4+}][PuO_2^+] - k_2[Pu^{3+}][PuO_2^{2+}]. \quad (2.26)$$

Values for k_1 and k_2 obtained in perchlorate solutions of unit ionic strength in
both water and deuterium oxide solvents at 25°C are given in Table 2.10.

Table 2.10 Effect of hydrogen ion concentration on rate of Pu(IV)–Pu(V)
reaction in perchlorate solutions of unit ionic strength at 25°C [38]

[H+], M	Water solvent		Deuterium oxide solvent	
	k_1, liter/mole-sec	k_2, liter/mole-sec	k_1, liter/mole-sec	k_2, liter/mole-sec
1.000	37.1	2.63	57.3	1.49
1.000	37.5	2.73	55.8	1.47
0.500	29.3	2.57	47.5	1.38
0.500	30.5	2.58	45.6	1.37
0.100	26.1	2.82	34.9	1.62
0.100	27.7	2.77	33.7	1.62
0.100	26.0	2.50		Mean $= 1.49 \pm 0.09$
		Mean $= 2.66 \pm 0.09$		

It will be noted that the rate of the forward reaction appears to depend
slightly on hydrogen ion concentration, while the rate of the back reaction is
independent of this concentration. The rate of the forward reaction is greater
in deuterium oxide than in water, while the opposite is true for the back re-
action. Thus the use of deuterium oxide solvent results in higher concentrations
of Pu(III) and Pu(VI) than those found in water, and vice versa.

The data indicate that a hydrogen-atom transfer process is not involved in
the reaction; also, since the reaction was found not to be influenced by the
addition of chloride ion, it appears that chloride is not involved as a bridging
group in the activated complex.

The effect of temperature on reaction rates both in water and in deuterium
oxides was determined. In water, the rate of the forward reaction increased by

a factor of about 16, and that of the reverse reaction by a factor of approximately 3, as the temperature was raised from 3° to 35°C. In deuterium oxide the forward rate increased by a factor of about 5 and the reverse rate by a factor of around 2 as the temperature was increased from 5° to 25°C. These results have been used to calculate the thermodynamic quantities of activation quoted in Table 2.11. The free energies, heats, and entropies of the reactions have been determined both by kinetic and by potentiometric methods, and are given in Table 2.12.

Table 2.11   Thermodynamic quantities of activation for
Pu(IV)–Pu(V) reactions[38]

	$\Delta G\ddagger$ kcal/mole	$\Delta H\ddagger$ kcal/mole	$\Delta S\ddagger$ cal/mole-deg
Water solvent:			
Forward reaction	15.3 ± 0.04	13.6 ± 0.4	$-\ 5.7 \pm 1$
Reverse reaction	16.86 ± 0.02	4.82 ± 0.01	-40.4 ± 0.1
Deuterium oxide solvent:			
Forward reaction	15.1 ± 2	11.8 ± 1	$-11\ \pm 5$
Reverse reaction	17.2 ± 1	4.5 ± 0.6	-42.6 ± 2

Table 2.12   Thermodynamic values for the Pu(IV)–Pu(V) reaction in
$1M$ HClO$_4$ of unit ionic strength at 25°C [38]

	$\Delta G,$ kcal/mole	$\Delta H,$ kcal/mole	$\Delta S,$ cal/mole-deg
Water solvent:			
Kinetic data	-1.6 ± 0.1	8.7 ± 0.3	$35\ \pm 1$
Potentiometric data	-1.51 ± 0.01	9.3 ± 1.0	36.1 ± 0.5
Deuterium oxide solvent:			
Kinetic data	$-2.1\ \pm 0.1$	7.2 ± 1.6	31.2 ± 4

The discussion above was concerned with HClO$_4$ solutions; in complexing acids such as HNO$_3$ and HCl, the equilibrium would be expected to shift so as to favor a relatively higher concentration of tetravalent plutonium, with Pu(V) disproportionating by the mechanisms discussed in the previous section.

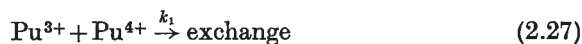### d) Isotopic exchange reactions

Although isotopic exchange reactions do not produce any changes in the oxidation states present in solution, their study can result in useful information

on factors affecting rates of oxidation and reduction, such as reaction mechanisms and the type and stability of the bonds in the ionic species present. Two exchange reactions have been investigated, one involving electron transfer and the other proceeding by oxygen transfer.
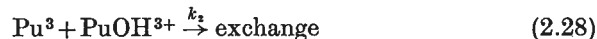
1) *The Pu(III)–Pu(IV) exchange*

A study of the isotopic exchange reaction between Pu(III) and (IV) in $HClO_4$ solutions has been made by Keenan[39] using Pu^{238} ($t_{1/2} = 86.4$ years). Because the reaction is so rapid it was necessary to work with solutions in the range of 10^{-6} to $10^{-5} F$ in plutonium; even in a solution $5 \times 10^{-6} F$ in both Pu(III) and (IV) in $1 F$ $HClO_4$ at 25°C, the half-time for the exchange reaction is 0.68 min. Due to these difficulties, there is considerable uncertainty in the experimental results.

In solutions of ionic strength $2.00 M$, the rate of exchange was found to vary inversely with the hydrogen ion concentration at 0°C, 12.5°C, and 25°C, suggesting that there are two competing reactions:

$$Pu^{3+} + Pu^{4+} \xrightarrow{k_1} \text{exchange} \qquad (2.27)$$

and

$$Pu^3 + PuOH^{3+} \xrightarrow{k_2} \text{exchange} \qquad (2.28)$$

with the latter route being favored at low hydrogen ion concentrations because of the reaction

$$Pu^{4+} + H_2O \rightleftharpoons PuOH^{3+} + H^+. \qquad (2.29)$$
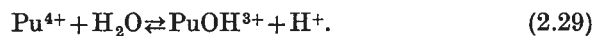
Hydrolysis of Pu(III) does not take place to a significant extent under these conditions.

The rate expression for the exchange is

$$\text{Rate} = k_1[Pu^{3+}][Pu^{4+}] + k_2[Pu^{3+}][PuOH^{3+}], \qquad (2.30)$$

and values for k_1 and k_2 are reproduced in Table 2.13.

Table 2.13 Rate constants for the Pu(III)–Pu(IV) exchange reaction[39]

Temperature, °C	k_1, liter/mole-min	k_2, liter/mole-min
25	$(0.13 \pm 0.53) \times 10^4$	$(1.2 \pm 0.1) \times 10^6$
12.5	$(2.3 \pm 0.5) \times 10^4$	$(0.70 \pm 0.18) \times 10^6$
0	$(1.1 \pm 0.4) \times 10^4$	$(0.80 \pm 0.14) \times 10^6$

Thus the rate expression may be written

$$\text{Rate (mole/liter-min} = 1.8 \times 10^{10} [\text{Pu}^{3+}] [\text{Pu}^{4+}] \exp(-7700/RT)$$
$$+ 1.3 \times 10^{8} [\text{Pu}^{3+}] [\text{Pu(OH)}^{3+}] \exp(-2800/RT). \quad (2.31)$$

From these results and Rabideau's[40] data on the hydrolysis of Pu(IV), the thermodynamic quantities of activation have been calculated[39, 41]:

$$\Delta H\ddagger = 9.5 \text{ kcal/mole}$$
$$\Delta G\ddagger = 13.3 \text{ kcal/mole}$$
$$\Delta S\ddagger = -13 \pm 4.7 \text{ cal/mole-deg.}$$

The mechanism for the more rapid exchange path involving Pu(OH)^{3+} may involve OH group transfer, which should proceed at a faster rate than direct electron transfer.

2) The Pu(VI)–solvent water oxygen exchange

Using water enriched in O^{18}, Masters and Rabideau[42] have measured the rate of exchange of oxygen between PuO_2^{2+} and water in dilute HClO_4 solution. Since it was observed that the rate of exchange was greatly accelerated by the presence of lower-valent species of plutonium (formed by alpha reduction), all studies were conducted in a chlorine atmosphere to ensure that Pu(VI) was the only plutonium species present.

The rate of exchange was found to be very slow. Thus, at 23°C in $1M$ HClO_4 solution containing $0.15M$ PuO_2^{2+} and having an ionic strength of $1.45M$, the half-time for exchange was found to be 4.55×10^4 hr. The rate was observed to be increased by increasing temperature and acidity; at 83°C in solutions of ionic strength $1.45M$ and containing $0.15M$ PuO_2^{2+}, the half-time for exchange was 1.16×10^4 hr in $0.21M$ HClO_4 and 4.39×10^3 hr in $1M$ acid. However, since the solubility of chlorine is decreased by increasing acidity and temperature, it is possible that the increased rates observed were due to the presence of plutonium ions in lower valence states which had not been oxidized by chlorine.

The rates cited above are actually the sum of the rates of two different reaction paths: the intrinsic PuO_2^{2+}–H_2O^* exchange reaction and exchange induced by rupture of plutonium–oxygen bonds by alpha radiation. The exchange rate was found to be much greater in solutions of Pu^{238} because of its greater alpha activity, and extrapolation of these values to the flux conditions of the Pu^{239} solutions indicated that the half-time for radiation-induced exchange was of the order of 10^4 hr, approximately equal to the observed exchange rate. It therefore appears that in $0.15M$ Pu(VI) solutions the major contribution to the exchange is made by the radiation-induced reaction and

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that the rate of the intrinsic exchange reaction must be very slow. Attempts to measure the rate of exchange in more dilute ($1.33 \times 10^{-3}M$) Pu(VI) solutions, where the contribution of the radiation-induced reaction would be small, failed to yield meaningful results because of uncertainties in the experimental technique. In summary, therefore, it appears that the reported exchange rates are primarily caused by the radiation-induced reaction; the half-time for the intrinsic exchange has a lower limit of about 10^4 hr but is probably much longer.

The rate of oxygen exchange in the absence of chlorine appears to be auto-catalytic because of the presence of lower oxidation states of plutonium; thus in one experiment in $0.235M$ HClO$_4$ at 23°C, the exchange was 45% complete after only 215 hr[43]. To determine which species were responsible for this catalytic effect, rate studies were conducted in Pu(VI) solutions containing each ionic species separately. The half-time of exchange in a $1M$ HClO$_4$ solution at 23°C containing $0.1158M$ Pu(VI) and $3.86 \times 10^{-3}M$ Pu(III) was found to be 1737 ± 90 hr. On the other hand, a solution containing $0.121M$ Pu(VI) and $5.29 \times 10^{-3}M$ Pu(IV) in $1.03M$ HClO$_4$ exhibited no measurable exchange, leading to the conclusion that Pu(IV) does not catalyze the exchange. This conclusion may have been somewhat hasty, however, since even in the Pu(III) solution, where a definite catalytic effect was observed, exchange was considerably less than 1% complete after 30 hr. It would appear, therefore, that the Pu(IV) solution should have been investigated for a longer period of time.

Plutonyl(V) was observed to have a much greater catalytic effect on oxygen exchange than Pu(III); exchange in a $0.457M$ HClO$_4$ solution at 23°C containing $0.106M$ PuO$_2^{2+}$ and $5.28 \times 10^{-3}M$ PuO$_2^+$ was 50% complete after approximately 100 hr. While other reactions may also contribute, it has been concluded from these results and from rate data for other plutonium reactions that the PuO$_2^+$–H$_2$O* exchange is the major contributor to the observed PuO$_2^{2+}$–H$_2$O* exchange. The PuO$_2^+$–PuO*$_2^{2+}$ reaction was assumed to be very rapid and, therefore, not the rate-determining step.

Fluoride ion was found to cause an even greater labilization of the Pu(VI) oxygen atoms. Thus, the exchange half-time in a $6.5M$ HF solution at 23°C containing $0.111M$ Pu(VI) was approximately 17 hr. This acceleration was interpreted by considering the hydrated Pu(VI) ion to be PuO$_2$(H$_2$O)$_6^{2+}$, in which the six oxygen atoms form a puckered ring about the equator of the linear O—Pu—O^{2+} group. Fluoride ions would replace these equatorial atoms during complex formation, and they would interact electrostatically with the axial oxygen atoms, resulting in a decrease in the ionic contribution to the axial bonding and a consequent labilization of the axial oxygen atoms.

Oxygen exchange was also measured in Pu(VI) solutions that were made

alkaline with sodium, ammonium, and barium hydroxides and subsequently reacidified with $2.7M$ $HClO_4$. There was no exchange in those cases where sodium and ammonium hydroxides were used, indicating that the axial oxygen atoms retain their identity. In the precipitates formed with barium hydroxide, however, there was a partial oxygen exchange, varying from 18 to 50%, suggesting a structure in which the axial and equatorial oxygen atoms were more nearly equivalent.

The Pu(VI) used in these exchange studies was made by the ozonation of Pu(III), and the use of labeled oxygen yielded interesting information on the mechanism of this reaction. It was found that in the oxidation of Pu(III) with ozone, one of the Pu(VI) oxygen atoms is supplied by the ozone and the other by the water, suggesting that the reaction involves formation of an activated complex in which an oxygen atom of the ozone is bonded directly to the plutonium ion instead of a simple electron transfer through the hydration sphere of the metal ion. The rate of ozonation of Pu(III) appears to depend inversely on the hydrogen ion concentration.

2.5   EFFECT OF RADIATION ON THE OXIDATION STATE OF PLUTONIUM IN SOLUTION

Apart from the disproportionation reactions discussed previously, the oxidation state of plutonium ions in solution is affected by radiation, either its own alpha radiation or external gamma or X rays, and all of these can be significant in the processing and storage of plutonium solutions.

a) Alpha radiation effects

Plutonium-239, with a half-life of 24,360 years, emits alpha particles, most with an energy of 5.15 mev, at a rate of approximately $137,000/min/\mu g$. Thus the energy released in a $0.001M$ (0.24 g/liter) plutonium solution is of the order of 1.8×10^{14} ev/min; with this rate of energy dissipation it is not surprising that the oxidation state of plutonium solutions is altered by alpha radiation. Although under some conditions oxidation has been observed, the most common effect is a decrease in the average oxidation number, which is defined as

$$\overline{Ox} = \frac{3[Pu^{3+}]+4[Pu^{4+}]+5[PuO_2^+]+6[PuO_2^{2+}]}{\Sigma[Pu]}. \qquad (2.32)$$

Kasha[12] found the mean change in average oxidation number in 0.5 to $2M$ $HClO_4$ to be 0.018 per day, corresponding to a G value of 3.2 equivalents/100

ev. Pagés[44] has subsequently confirmed this value in studies on the rate of alpha reduction of Pu(VI) solutions, and has found that the course of the reduction varies depending on the total dose. By the addition of small quantities of Po^{210} ($t_{1/2}$ = 139 days), a much more active alpha emitter, to the Pu(VI) solutions, it was possible to attain high irradiation doses in relatively short periods of time. For very weak doses it was observed that Pu(V) was the only reduction product. Plutonium (IV) was the main product of doses greater than 20×10^{18} ev/cm^3, while for doses greater than 70×10^{18} ev/cm^3, the reduction was found to proceed all the way to Pu(III). Identical results were obtained in both the presence and absence of air.

Rabideau[32] observed that in perchlorate solutions of unit ionic strength Pu(VI) is reduced by its own alpha radiation to Pu(V) at a rate of about 1.5% per day. Initially the Pu(V) concentration increases at a rate equal to that of Pu(VI) reduction; with increasing concentration, however, the rate of Pu(V) disproportionation to Pu(IV) and Pu(VI) becomes greater, being proportional to the square of the Pu(V) concentration. The Pu(IV) thus formed can react with Pu(V) to produce Pu(III) and Pu(VI). It therefore appears that Pu(V) is the usual product of alpha reduction, with lower oxidation states being formed primarily by disproportionation of this species.

In solutions approximately 0.01M in plutonium ($\overline{Ox}$ = 4.0) and 1M in $HClO_4$ at 25°C, Rabideau and collaborators[45] found that the mean oxidation number decreased 0.014 per day until a steady-state oxidation number of 3.02 to 3.05 was reached. This rate was observed to be remarkably constant, and insensitive to a number of variables.

The presence of dissolved oxygen in the solution did not change the rate of reduction appreciably compared to that for a solution saturated with argon. It was further noted that the rate of alpha reduction was not altered by the presence of Cr(III). The rate was found to be independent of the average oxidation number of the solution, provided it was above the steady state value; thus a Pu(VI) solution is reduced at the same rate as a solution of Pu(IV). Likewise, variation of the acidity from 1 to 3M, the plutonium concentration from 0.01 to 0.04M, and the temperature from 5° to 45°C had no significant effect on the rate of reduction.

The alpha reduction of plutonium ions in dilute acid solution appears to be due primarily to H_2O_2 formed by radiolysis of water[44], and the induction periods generally observed are due to the slowness of reduction by H_2O_2. Other radiolysis products also participate; atomic hydrogen and HO_2 radicals function as other reducing agents, while hydroxide radicals tend to reoxidize the Pu(V) reduction product to Pu(VI) [equation (2.37)]. The observation by Rabideau et al.[45] that the concentration of H_2O_2 in such solutions is greatly dependent on temperature and to a lesser extent, acidity—two factors that

did not appear to affect the reduction rate—does not necessarily contradict this mechanism, since their solutions had anion concentrations high enough to permit appreciable radiolysis into products that could participate in the reduction along with the H_2O_2.

Collection and analysis of the gases evolved from a solution of trivalent plutonium revealed them to be approximately 60% oxygen and 40% hydrogen. Significant amounts of chloride ion were detected in the solution. These observations have been explained in terms of the following reaction of alpha particles on perchlorate solution:

$$ClO_4^- + \alpha \rightarrow Cl^- + 2O_2. \tag{2.33}$$

A similar effect was noted with the action of gamma radiation on such solutions.

In HCl solutions the situation was observed to be remarkably different. In $1M$ HCl solutions containing approximately $0.01M$ plutonium there was no observable change in oxidation number over periods as long as 75 days, regardless of the average oxidation number. Pagés[46] likewise found no evidence of reduction of Pu(VI) in HCl. These results are in contrast to those of Kasha and Sheline[25], who found the reduction rate in HCl to be approximately 40% of that in $HClO_4$. Chlorine was detected in the HCl solutions; in $3M$ acid, the G_{Cl_2} value (molecules $Cl_2/100$ ev) was found to be 0.24 [45].

In various mixtures of HCl and $HClO_4$ containing $0.015M$ plutonium with an average oxidation number of 3.95, the results given in Table 2.14 were obtained. The presence of chlorine was also detected in these mixed acid solutions. In mixed $HClO_4$—HCl solutions of constant chloride ion concentration, the rate of alpha reduction was relatively independent of acidity up to about $2M$, above which it decreased considerably.

Table 2.14   Alpha reduction rates in $HClO_4$–HCl
mixtures at 25°C [45]

[$HClO_4$], M	[HCl], M	$-d[Ox]/dt$, day^{-1}
1.00	0.00	0.0140
0.90	0.10	0.0084
0.80	0.20	0.0070
0.60	0.40	0.0040
0.20	0.80	0.0015
0.00	1.00	0.000

In mixed acids with the acidity held constant at $3M$ and the chloride ion concentration varied from 0.1 to $0.8M$, an interesting effect was observed; at

chloride ion concentrations of $0.2M$ and above, alpha reduction was supplanted by alpha oxidation, with the rate of oxidation becoming greater at higher chloride concentrations. This behavior was explained on the basis of an oxidation (by HClO present in the solution) of the chloride to chlorine, which destroys H_2O_2 according to the equation

$$H_2O_2 + Cl_2 \rightarrow O_2 + 2H^+ + 2Cl^-. \tag{2.34}$$
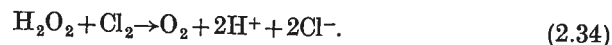
It was verified experimentally that the concentration of H_2O_2 is markedly decreased in the presence of chloride ions, thus suggesting that in mixed $HClO_4$—HCl solutions the alpha reduction mechanism does indeed involve H_2O_2.

In $1M$ $HClO_4$ solutions containing $0.1M$ bromide ion, alpha oxidation was again observed. At 25°C, the average oxidation number increased 0.0079 per day; at 5°C, it increased at a rate of 0.015 per day.

Artyukhin and coworkers[47] found that the rate of alpha reduction of Pu(VI) in HNO_3 solutions increased with increasing nitrate ion concentration and decreased with increasing hydrogen ion concentration. In the 0.1 to $5.0N$ nitrate concentration range at pH 3, the initial rate of change of the average oxidation number was found to obey the following expression:

$$\bar{A}\,\frac{\mathrm{d}\overline{Ox}}{\mathrm{d}t} = 1.6 \times 10^{-2} + 0.57 \times 10^{-2}\,[NO_3^-]^{\frac{1}{4}}\;\text{days}^{-1}. \tag{2.35}$$
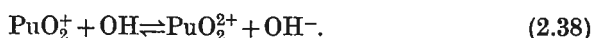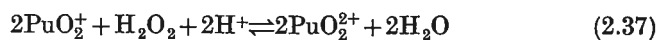
The rate of reduction was constant for 15 to 25 days, and Pu(V) was the only product. After longer periods of reduction the rate decreased; furthermore, colloidal Pu(IV) began to appear. The Pu(V) concentration reached a maximum and then decreased. The effect of nitrate ion apparently is due to the formation of nitrite, which participates in the reduction along with H_2O_2.

The decrease in rate with increasing acidity, which was also observed in HCl solutions, may be caused by the increased rate of reaction of hydrogen ions with Pu(V) and molecular oxygen to form Pu(VI) and H_2O_2. This decrease was also observed by Nikol'skii et al.[48], who concluded that partially-hydrolyzed Pu(VI) was the species being reduced:

$$PuO_2OH^+ + H \rightleftharpoons PuO_2^+ + H_2O. \tag{2.36}$$
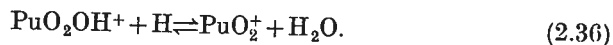
Hence the reduction would be retarded at low pH values because of the lower concentration of the hydrolyzed species. It was further suggested that radiolytic reduction of the other oxidation states of plutonium also involved hydrolyzed species. Gel'man and Zaitseva[37] found that solutions of Pu(V) in HNO_3 stored for 50 days experienced a decrease in pH if the initial pH was > 3.5, whereas if the initial pH was < 3.5 there was no change, or in some cases, a slight increase in pH during the same period. It was also observed that the

solutions of low pH had a higher Pu(VI) content than those of high pH. The authors concluded that at pH values > 3.5, the Pu(V) was reduced by H, HO_2, H_2, and H_2O_2 to Pu(IV) which precipitated as $Pu(OH)_4$; since all of these possible reactions liberate H^+ ions, the pH of the solution decreases. On the other hand, at pH values < 3.5, radiolysis products such as OH and H_2O_2 tend to oxidize Pu(V):

$$2PuO_2^+ + H_2O_2 + 2H^+ \rightleftharpoons 2PuO_2^{2+} + 2H_2O \qquad (2.37)$$

$$PuO_2^+ + OH \rightleftharpoons PuO_2^{2+} + OH^-. \qquad (2.38)$$

Both of these reactions cause an increase in pH, and the fact that a greater increase was not observed was rather vaguely explained as indicating that other reactions were also occurring.

After a certain irradiation dose, the autoreduction of Pu(VI) becomes rapid, possibly due to the slow accumulation of Pu(IV), which is readily reduced to Pu(III), the latter then reacting with Pu(VI). Pagés[44], on the other hand, has found no evidence for the alpha reduction of Pu(VI) in $0.6N$ HNO_3 solutions, even at doses as high as 62×10^{18} ev/cm³. More work is necessary to reconcile this contradiction. Plutonium (III) in HNO_3 solution is oxidized to the tetravalent state by alpha radiation.

Opposite trends in reduction rate were noted in H_2SO_4 solutions containing approximately 0.001 to $0.01M$ Pu(VI)[49]. In the presence of a constant concentration of sulfate ions the rate of alpha reduction increased by a factor of about 2.5 as the acidity was varied from 0.2 to $1N$, but the results were not very reproducible. Increasing the sulfate ion concentration from 0.1 to $0.9M$ at a constant acidity of $0.2N$ caused the reduction rate to decrease by a factor of 20. Thus the net effect of increasing H_2SO_4 concentration was to cause a marked decrease in the alpha reduction rate. These results are in contrast to those obtained in HNO_3 solutions, and, to a lesser extent, to the results in mixed HCl–$HClO_4$. Since the data obtained in H_2SO_4 were not reproducible, and the rate of reduction of Pu(VI) was interpreted on the basis of formation of Pu(IV) only, it would seem advisable to regard these results with skepticism until further confirmation is available.

b) Gamma and X-radiation effects

The mechanism of gamma-reduction appears to be similar to that of reduction by X rays. Pagés[44] has conducted a thorough study of the gamma reduction of plutonium, using acid solutions dilute enough that the effect of radiation on the anion was negligible. The results indicated that the reduction is actually effected by radiolysis products of water, just as was observed in the case of

alpha reduction; H_2O_2 and atomic hydrogen function as reducing agents, while hydroxide radicals tend to reoxidize the products of reduction. Because of the slow rate of reduction by H_2O_2, there is frequently an induction period, and the reaction is of long duration, reduction continuing several days after irradiation has ceased[50].

As in the case of alpha reduction, the primary product of gamma reduction of Pu(VI) in $HClO_4$ appears to be Pu(V), which then disproportionates to produce Pu(IV) and Pu(VI)[44]. Thus in the gamma irradiation of a $0.0043M$ Pu(VI) solution in $0.2N$ $HClO_4$, the disappearance of Pu(VI) was followed spectrophotometrically, but immediately after the irradiation there was no evidence of the formation of Pu(IV) or (III). The G value (0.8 ions/100 ev) was therefore apparently for the net reduction of Pu(VI) to Pu(V) by atomic hydrogen minus the oxidizing effect of the hydroxide radicals. Twenty-four hours after the irradiation, the H_2O_2 had begun to reduce plutonyl and the G value was 2.3; after 4 days the presence of Pu(IV) was detected, its rate of appearance being related to the rate of disappearance of Pu(VI). The decreased yield ($G = 1.7$) for the Pu(VI) reduction after 4 days was due to its reformation as a disproportionation product of Pu(V). After 10 days the G value had fallen to 1.2 (for weak doses) and the formation of Pu(IV) was equivalent to the disappearance of Pu(VI). For strong doses, the G value decreased, and the formation of Pu(III) was also observed. Similar results were obtained from the gamma irradiation of a solution $5.4 \times 10^{-3}M$ in Pu(VI), the only difference being the lack of an induction period; the G value was 2.3 rather than 0.8 immediately after irradiation. In $0.5N$ $HClO_4$ the results were also similar, although there were some changes in the G values. Identical results were obtained in both the presence and the absence of air.

Spectrophotometric studies of the gamma reduction of Pu(IV) in 0.2 and $0.5N$ $HClO_4$ indicated that the reaction proceeds through formation of a peroxide complex [see Chapter 5]. This complex slowly decomposes, liberating H_2O_2, which partially reduces the Pu(IV) to Pu(III). It is also possible that such a peroxide complex, rather than H_2O_2 itself, is responsible for the reduction of Pu(VI); although the final product would be the same in either case, the rate of reduction of Pu(VI) by the complex could be different from that of H_2O_2.

Plutonium (III) in 0.2 and $0.5N$ $HClO_4$ solutions was not affected by gamma irradiation.

The results of gamma irradiation of H_2SO_4 solutions were somewhat different, largely because of the stabilization of Pu(IV) by the formation of sulfate complexes. As in $HClO_4$ solution, the initial reaction involves reduction of Pu(VI) to Pu(V) ($G = 0.75$). The long-range effects, namely reduction by H_2O_2 and disproportionation of Pu(V) to Pu(IV) and Pu(VI), occur simul-

taneously, with the result that the yield for Pu(VI) reduction ($G = 1.18$) is equal to that for formation of Pu(IV). Whereas in $HClO_4$ solutions Pu(III) is the ultimate product of reduction, the reaction does not proceed beyond Pu(IV) in H_2SO_4 solution. Results were identical in an air-free system.

In H_2SO_4 solutions of normality 0.5 and above, the results were more complex and not subject to simple interpretation. Thus when the Pu(VI) concentration of a $0.5N$ H_2SO_4 solution was increased from 0.00002 to 0.009M, G for gamma reduction increased from 0.05 to 1.7 [49]. This concentration dependence was ascribed to a dilution effect, but such a simple interpretation seems unlikely, since a 300-fold increase in concentration produced only about a 3.4-fold change in the reduction yield.

The stabilization of Pu(IV) is also apparent from the results of gamma irradiation of plutonium in the lower oxidation states. In $0.5N$ H_2SO_4 Pu(III) is oxidized to the tetravalent state, while under similar conditions Pu(IV) is unaffected by gamma irradiation[46].

In $0.8N$ H_2SO_4 Pu(III) (at an initial concentration of $0.001M$) was oxidized to Pu(IV) by gamma irradiation, the initial G value for Pu(IV) production being 7.2 ± 0.5 in an air atmosphere and 4.5 ± 0.2 in an argon atmosphere.[51] The higher yield in an air atmosphere suggested that dissolved oxygen may be involved in the oxidation, and this supposition was supported by the observation in an air atmosphere the yield decreased at high radiation doses, presumably because of depletion of oxygen in the solution. It was concluded that the principal oxidants were OH radicals and H^+ ions (in the presence of HO_2 groups, which react to produce the H_2O_2 also observed in the irradiated solutions). Irradiation of Pu(IV) solutions in $0.8N$ H_2SO_4 up to doses of 1.43×10^{19} ev/ml failed to produce any Pu(III) or Pu(VI).

The gamma reduction of plutonium in H_2SO_4 solution is inhibited by the presence of HCl [44]. Thus the G value for formation of Pu(IV) in $0.1N$ H_2SO_4 is decreased to approximately one-third upon addition of $0.1N$ HCl. In a $0.4N$ HCl–$0.1N$ H_2SO_4 solution a much greater dose (150×10^{18} ev/cm^3) is necessary before Pu(IV) is first detected. This inhibition has been ascribed to the reaction of chloride ions with hydroxide radicals:

$$Cl^- + OH \rightarrow Cl + OH^-. \tag{2.39}$$

This reaction competes with that for the formation of hydrogen peroxide

$$OH + OH \rightarrow H_2O_2, \tag{2.40}$$
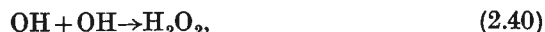
thus resulting in a lower yield of H_2O_2 and a consequent decrease in reduction yield. Furthermore, the atomic chlorine produced may inhibit the reduction by reacting with H_2O_2 or by reoxidizing some of the reduced plutonium.

In HCl solution alone the irradiation of Pu(VI) once again results in the

formation of Pu(V) and its subsequent disproportionation but the G value is lower (less than 1). Irradiation of a $0.00386M$ Pu(VI) solution in $0.2N$ HCl to a dose of 1.8×10^{20} ev/cm^3 resulted in a 43% reduction of the Pu(VI) to Pu(V).

Irradiation of solutions of Pu(III) in $0.5M$ HCl in the presence of air resulted in its oxidation to the tetravalent state; the Pu(IV) produced, however, was reported to be not the simple hydrated ion but a mixture of a peroxide complex and polymeric forms of Pu(IV). The reaction possibly proceeds by the oxidation of Pu(III) by atomic chlorine produced by direct radiolysis of chloride ions followed by complexing of the resulting Pu(IV) by H_2O_2. The only effect of gamma irradiation of a Pu(IV) solution was the apparent formation of a peroxide complex, which subsequently was converted to polymeric Pu(IV). In the irradiation of Pu(III) in more concentrated HCl solutions, no H_2O_2 was detected, and the oxidation apparently is effected by atomic chlorine[52]. This conclusion resulted from the observation that the G value for the oxidation of Pu(III) to Pu(IV) in an argon atmosphere varies with the HCl concentration according to the expression

$$G = 0.35 \times [\text{HCl}, M] \qquad (2.41)$$

in the 1 to $8M$ HCl concentration range. Furthermore, although chlorine has been detected in the irradiation of Pu(III)-free HCl solutions, none was detected in plutonium-containing solutions until most of the Pu(III) had been oxidized, apparently because reaction of atomic chlorine with Pu(III) is more favorable than reaction to form molecular chlorine. The G value does not depend on the concentration of Pu(III) or on the total dose absorbed, and it is possible to oxidize Pu(III) completely to Pu(IV). No Pu(VI) was detected after irradiation under these conditions.

In HCl solutions of Pu(III) irradiated in the presence of air, the initial G value was observed to be approximately 4 times that obtained in argon, but decreased with increasing dose. In $6.0M$ HCl the initial G value was 8.2, but at a total dose of 10^{19} ev/ml, G had decreased to 1.9, thereafter remaining essentially constant for the remainder of the irradiation. Apparently, in the presence of oxygen the oxidation of Pu(III) to Pu(IV) is accomplished both by atomic chlorine and by HO_2 (produced by the reaction of atomic hydrogen with oxygen). The decrease in G value with dose was attributed to depletion of oxygen in the solution, thus diminishing the importance of HO_2 in the oxidation.

Plutonyl (VI) and mixtures of this species and Pu(IV) in 0.5 and $1.5N$ HNO$_3$ solution are not affected by gamma irradiation at doses up to 1.8×10^{20} ev/cm^3. Plutonium (III) in HNO$_3$ solution, however, is rapidly oxidized to the tetravalent state, probably because NO and NO_2^-, formed by radiolysis of nitrates, catalyze the oxidation by the nitrate ion.

The effect of X-rays on the valence state of plutonium in $HClO_4$ and HNO_3 has been investigated by Popov and coworkers[53, 54]. In their studies, the plutonium solutions were characterized not by the exact state, but only as "reduced" [Pu(III) and (IV)] and "oxidized" [Pu(V) and (VI)]. In $0.3M$ $HClO_4$ it was found that under irradiation $10^{-4}M$ plutonium solutions tend to establish a steady-state ratio of oxidized-to-reduced forms, and the net effect of the irradiation could be either oxidation or reduction of the plutonium, depending upon whether the initial oxidized/reduced ratio was below or above the steady-state ratio[53]. Likewise, there was no appreciable change in oxidation state when the initial ratio was equal to the steady-state ratio. Similar results were obtained in $0.3M$ $HClO_4$ in the presence of $2M$ $NaClO_4$, suggesting that in this range the reaction does not involve radiolysis products of the perchlorate ion. In both cases, the steady-state ratio corresponded to just under 50% of the oxidized form.

In the presence of $UO_2(ClO_4)_2$, the plutonium also tended to establish a steady-state ratio, but the ratio varied depending upon the direction from which it was approached. The degree of reduction increased with increasing U(VI) concentration; the steady-state oxidized/reduced ratio decreased from 1.0 to 0.02 as the $UO_2(ClO_4)_2$ concentration was raised from $0.001M$ to $0.1M$, and at concentrations of $UO_2(ClO_4)_2$ of $0.3M$ and above essentially all the plutonium was in the reduced form. As in HNO_3 solutions, it was concluded that reduction involved U(V), as shown in equation (2.43).

It was found that plutonium in the reduced state in $0.3M$ HNO_3 is oxidized by X-radiation, but the yield is low ($G = 0.05$) and the oxidation very soon reaches a steady state[54]. The oxidation yield decreases with increasing hydrogen ion or nitrate ion concentrations, the latter effect undoubtedly being due to stabilization of the reduced plutonium by nitrate formation. The mechanism for the oxidation was believed to involve the hydroxide radical

$$Pu^{4+} + OH + H_2O \rightarrow PuO_2^+ + 3H^+ \qquad (2.42)$$
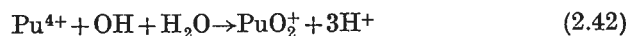
with a possible contribution from the higher oxides of nitrogen.

The radiation stability of Pu(VI) in $0.3M$ HNO_3 solutions containing uranyl nitrate was reported to depend on the concentration of the latter. At $UO_2(NO_3)_2$ concentrations up to $0.3M$, oxidation of the plutonium occurred; above this concentration the plutonium was reduced by X-radiation. The G value for reduction in the presence of $0.88M$ $UO_2(NO_3)_2$ was found to be 0.17 ion/100 ev. In general the reduction did not proceed to completion, particularly in the 0.30 to $0.60M$ $UO_2(NO_3)_2$ concentration range. X-ray reduction of plutonium in this concentration range was found to commence only after absorption of a certain quantity of radiation. These effects have been explained in terms of two competing reactions. At low $UO_2(NO_3)_2$ concentrations (below

$0.3M$), oxidation takes place according to the hydroxide radical mechanism, equation (2.42), while at higher $UO_2(NO_3)_2$ concentrations some of the U(VI) is reduced by X rays to U(V), which then reduces plutonium by the reaction

$$PuO_2^+ + UO_2^+ + 4H^+ \rightarrow Pu^{4+} + UO_2^{2+} + 2H_2O. \qquad (2.43)$$

Addition of $K_2Cr_2O_7$ to these solutions caused X-ray induced oxidation to take place regardless of the $UO_2(NO_3)_2$ concentration, probably because of the oxidation of UO_2^+, thus preventing the reduction reaction (2.43). [A correction was made for the chemical oxidation of Pu(IV) by the dichromate.] As soon as all the $K_2Cr_2O_7$ had been reduced, however, the behavior of the solution was similar to that of solutions that contained no $K_2Cr_2O_7$.

In $1.5M$ HNO_3 solutions containing both $UO_2(NO_3)_2$ and $K_2Cr_2O_7$, reduction of plutonium was observed to occur, probably because of stabilization of the tetravalent ion by nitrate complex formation in the more concentrated HNO_3 solution.

The radiation chemistry of plutonium in HNO_3 solutions is of particular interest because of its process importance, and has been reviewed by Miner and Seed[55].

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