# RADIATION CHEMISTRY OF PLUTONIUM NITRATE SOLUTIONS

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*Received September 16, 1966*

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## I. INTRODUCTION

In the near future, large quantities of plutonium will become available as the result of the expanding use of atomic reactors for the generation of electric power (89). Plutonium is produced in thermal power reactors as a by-product and is recovered in the fuel reprocessing operations. Nitric acid or nitrate salts are used in most of the aqueous reprocessing methods now in use (9, 15) producing plutonium nitrate solutions. As a result, nitrate solutions are involved in the processing, handling, storing, and shipping of plutonium. The chemistry of plutonium in these solutions is closely related to the radiolysis of the solutions with plutonium being the source of the radiation. This review is concerned specifically with the effect of this radiolysis on the chemistry of plutonium in nitrate solutions.

The effect of radiation on the aqueous chemistry of plutonium has received attention since the element was first prepared. The primary chemical effect of $\alpha$ irradiation is a decrease in the mean oxidation state of plutonium in solution with time. Such a decrease was first observed in 1944 in a hydrochloric acid solution (43). The decrease could be explained only by the presence of reducing agents generated in the solution by the $\alpha$ irradiation. At the time, the nature of the reducing agents was unknown. Later, the same phenomenon was observed in perchloric acid (71). More recently, Pagés in France (64, 65) and several workers in Russia (7, 61, 68) have investigated the effect of radiation on plutonium in several mineral acids. The source of radiation was either $\alpha$ radiation from contained plutonium or added polonium (64) or externally applied X-ray or $\gamma$ radiation (64, 68).

Most of the investigations of radiolysis have been carried out in hydrochloric or perchloric acids. Only recently have there been any extensive investigations in nitric acid. This lack of work in nitric acid is probably due, as Pagés indicates (64), to difficulties encountered in interpreting results because of the complex radiolysis behavior of aqueous nitrate solutions.

There are 15 known isotopes of plutonium all of which are radioactive. They range from $^{232}$Pu to $^{246}$Pu (45). Of these, $^{239}$Pu is the most common and, in fact, is the only one available in quantity. Data on the half-lives and the primary modes and energies of decay for the more common isotopes are given in Table I.

TABLE I
ISOTOPES OF PLUTONIUM[a]

| Isotope | Half-life, years | Primary mode and energy of decay[b] |
|---|---|---|
| $^{238}$Pu | 87.5 | $\alpha$ (5.495, 5.452, 5.352) |
| $^{239}$Pu | 24,181 | $\alpha$ (5.147, 5.134, 5.096) |
| $^{240}$Pu | 6,600 | $\alpha$ (5.159, 5.115, 5.014) |
| $^{241}$Pu | 13.24 | $\beta^-$ (>99%, 0.0205)<br>$\alpha$ (*ca.* $10^{-3}$ %, 4.91) |
| $^{242}$Pu | $3.8 \times 10^5$ | $\alpha$ (4.898, 4.854) |

[a] Adapted from Katz and Seaborg (45) with more recent half-life values from Oetting (62). [b] Energy of radiation in million electron volts.

The radiolysis products of water and of nitrate play an important role in determining the chemistry of plutonium in nitrate solutions. For this reason, the radiolysis chemistry of aqueous nitrate solutions is considered first in this review. Since the majority of the stable isotopes of plutonium are $\alpha$ emitters, the discussion is primarily directed at an understanding of $\alpha$-induced reactions of water and the nitrate ion. General aspects of the radiation chemistry of water and aqueous solutions are not discussed. They are covered in a number of reviews, the most recent of which is a book by Allen (2).

Radiation affects the chemistry of plutonium in aqueous nitrate solutions primarily by the production of oxidizing and reducing agents which subsequently react with plutonium. Mechanisms of the oxidation–reduction reactions of plutonium in nitric acid solutions, as well as the influence of solution parameters on these reactions, are discussed in the second part of this review. The review covers the literature on the radiolysis of plutonium nitrate solutions through February 1966.

## II. AQUEOUS NITRATE SYSTEMS

### A. RADIOLYSIS OF WATER

The radiolysis of water is the most studied subject in the field of radiation chemistry and should probably be ranked today among the better understood topics in chemical kinetics (3). Excellent reviews on the subject have appeared in *Annual Review of Physical Chemistry* for the past 10 years as well as in the annual *Advances in Inorganic Chemistry and Radiochemistry.*

The observation that water is rapidly decomposed by $\alpha$ radiation goes back to the days when radioactivity was first studied. The early workers observed that the number of water molecules decomposing to hydrogen and oxygen was numerically equal to the number of ions produced in air by $\alpha$ radiation (17).

In 1913, Duane and Scheuer published a study of the $\alpha$-induced decomposition of water in its three phases of ice, liquid, and steam (26).

In 1914 Debierne suggested that free radicals were responsible for the effects observed when aqueous systems were irradiated (25). Similar suggestions were later made by Risse (79). In 1944 Weiss advanced the free-radical theory for the radiolysis of water (90). In the last few years a great deal of work has been published about the primary active species and basic mechanisms in the radiation chemistry of aqueous media (2, 33, 34, 37, 39).

Water is decomposed by radiolysis into free-radical and molecular products, as indicated by

$$H_2O \rightsquigarrow H\cdot,\ \cdot OH,\ HO_2\cdot,\ H_2,\ H_2O_2 \qquad \text{(Eq 1)}$$

This expression is an oversimplification. The radical products shown may result from reactions involving various energetic intermediates, *e.g.*, solvated electrons or activated water molecules. The free radicals can combine with themselves to produce molecular hydrogen and hydrogen peroxide or they can react with the molecular products

$$H\cdot + H\cdot \rightarrow H_2 \qquad \text{(Eq 2)}$$

$$HO\cdot + HO\cdot \rightarrow H_2O_2 \qquad \text{(Eq 3)}$$

$$HO\cdot + H_2 \rightarrow H\cdot + H_2O \qquad \text{(Eq 4)}$$

$$HO\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O \qquad \text{(Eq 5)}$$

$$H\cdot + H_2O_2 \rightarrow HO\cdot + H_2O \qquad \text{(Eq 6)}$$

If oxygen is present, the following reaction is also possible

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad \text{(Eq 7)}$$

The relative amounts of the various radiolysis products that are produced during irradiation are governed, to a certain extent, by the type of radiation used (36). The yields of free-radical products are highest for $\gamma$ and X-ray irradiations, while the yields of molecular products are highest for $\alpha$ and other heavy-particle irradiations. Molecular products would be favored in plutonium solutions because of $\alpha$ irradiation from the plutonium.

Specific reactions that occur in solutions as a result of radiolysis depend both on the particular solutes present and their concentration. Thus the action of radiation on an aqueous solution can be described in terms of the amount of molecular and free-radical products formed, together with descriptions of the subsequent reactions undergone by these products with the solutes in the particular solution. The reactions when the solute is nitrate are described in the following section.

### B. RADIOLYSIS OF NITRATE SOLUTIONS

As far back as 1907, various chemical changes were observed when a solution of potassium nitrate was exposed to the radiation of a quartz–mercury arc lamp (86). Since then, many other investigations involving radiation have been conducted with nitrate solutions. Light, neutrons, $\gamma$ radiation, and pile radiation have been used. This earlier work was reviewed by Mahlman in 1956 (53). From all of this work, there is general agreement that the major products of the radiolysis of aqueous nitrate solutions are nitrite and oxygen.

Although there is general agreement on the major products of radiolysis, there is not complete agreement on the mechanism which produces these products. Several mechanisms have been proposed. One is an "indirect" mechanism involving reduction of the nitrate by atomic hydrogen produced in the radiolysis of water (14, 39, 41, 54, 55, 66).

$$NO_3^- + H\cdot \rightarrow NO_2 + OH^- \qquad \text{(Eq 8)}$$

$$2NO_2 + H_2O \rightarrow 2H^+ + NO_3^- + NO_2^- \qquad \text{(Eq 9)}$$

While most recent workers agree with this mechanism for solutions of low nitrate concentration, they do not agree that it is the mechanism for solutions of high nitrate concentration. For these solutions a second mechanism is proposed. It is a "direct-effect" mechanism and involves a direct transfer of energy from the radiation to the nitrate ion. Although the specific mechanism involved in the transfer is unknown, it can be represented as

$$NO_3^- \rightsquigarrow NO_2^- + 0.5O_2 \qquad \text{(Eq 10)}$$

Recent work involving irradiation of concentrated salt solutions by Hayon and Moreau (39) and by Hyder (41) supports a direct-effect type of radiolysis mechanism. Specifically, Hyder found that nitrate was produced at higher concentrations than would be expected from an indirect mechanism such as the reactions in Eq 8 and 9 (41).

Work at high nitrate concentrations carried out by Proskurnin and Kolotyrkin (69) has not, however, been interpreted by the authors to support a direct-effect mechanism. In basic solutions Proskurnin and Kolotyrkin found that the radiolytic yield of nitrite increased as a function of the nitrate concentration up to 10 *M* nitrate. But at higher nitrate concentrations, such as a melt of calcium nitrate, the yield dropped dramatically. This drop in yield is contrary to what would be expected from a direct-effect mechanism of radiolysis. In fact, the authors state that in general the direct effect of radiation does not play an important role in the sense of increasing the yields.

It is interesting to notice Allen's interpretation (4) of Proskurnin and Kolotyrkin's work (69). According to Allen, the observed increase in nitrite yield obtained by Proskurnin and Kolotyrkin at high nitrate concentrations is probably due to a direct effect which becomes important when the percentage of nitrate in the solution becomes large. This interpretation by Allen appears to contradict the conclusions of Proskurnin and Kolotyrkin.

Bakh, Medvedouskii, Revina, and Bityukov (10) and Kabakchi, Erokhin, and Gramolin (42) have also studied the radiolysis of aqueous nitrate solutions of relatively high nitrate content. Results of the latter group of workers (42) indicate more nitrite is produced than can reasonably be accounted for by an indirect radiolysis mechanism. A direct-effect mechanism is suggested, although the authors indicate there are other processes, such as reactions involving excited water molecules, that might play a role in this increase in nitrite yield. (Hyder, in a subsequent report (41), seems to rule out any excited water mechanism, however.) Bakh, Medvedouskii, Revina, and Bityukov (10) indicate that with data available from their work with solutions of high nitrate concentration, it is not yet possible to distinguish between direct or indirect mechanisms.

Additional processes that may occur during radiolysis of nitrate solutions have been proposed. These include (a) the excited water theories of Proskurnin and Sharpatyi (70, 82), (b) the theory of Bednář and Lukáč which involves a combination of excited water theories and primary excitation of the solute ions (13), and (c) reactions between the nitrate ion and the hydroxyl radical to produce a hydrated form of the $NO_3$ radical (4). These processes, as they apply to nitrate solutions, have been recently reviewed and evaluated (41).

It is apparent that there is disagreement as to the mechanism by which nitrite is produced by radiolysis of nitrate solutions. It is agreed, however, that nitrite is a major product of the radiolysis of nitrate solutions. In plutonium nitrate solutions it is this nitrite which is important because of its ability to enter into oxidation–reduction reactions with plutonium.

Another major product of nitrate solution radiolysis is oxygen. Oxygen is important in plutonium nitrate solution chemistry not only because it can react with some plutonium ions itself (48, 60) but also because of what it indicates about the presence and the concentration of its primary precursor, hydrogen peroxide. Hydrogen peroxide is important because in solutions it can react both as an oxidizing agent and a reducing agent with plutonium (58).

In the mechanisms proposed to explain the radiolysis of nitrate, only a direct-effect mechanism, such as expressed in Eq 10, could yield oxygen along with nitrite as a major product. Since oxygen is produced in solutions in which the nitrate concentration is too low for a direct-action mechanism to be significant, there must be another radiolytic source of oxygen. This source is believed to be hydrogen peroxide which is produced by the radiolysis of water. Hydrogen peroxide can react with other radiolysis products (Eq 5 and 6), but it can also decompose, producing oxygen (Eq 11). The amount

$$H_2O_2 \rightarrow 0.5O_2 + H_2O \qquad \text{(Eq 11)}$$

of oxygen produced can serve as a measure of the amount of hydrogen peroxide formed in solution.

The results of a study of the effect of nitrate concentration on the radiolytic yield of hydrogen peroxide are described in a recent review (88). The work was done by Anta (5) who found that by increasing the concentration of nitrate from 0.003 to 0.4 *M*, the yield of hydrogen peroxide was lowered from a $G$ value of 1.15 (1.15 molecules of hydrogen peroxide produced per 100 ev of radiation energy absorbed) to a $G$ value of zero. To explain these results, Anta ascribed reducing properties to the hydroxyl radical, *i.e.*, $\cdot OH + NO_3^- \rightarrow NO_2^- + HO_2\cdot$. This reaction would replace the conventional hydroxyl radical combination reaction which produces hydrogen peroxide (Eq 3).

Further investigations of the reactions proposed by Anta seem warranted because the hydroxyl radical usually acts as an oxidizing rather than a reducing agent (38). It has recently been proposed, however, that in basic media, $\cdot OH$ can ionize to $O^-$ which is a reducing agent (41).

The effect of the nitrate concentration on hydrogen peroxide production, as observed by Anta, is contrary to the effect observed more recently by Bakh, Medvedouskii, Revina, and Bityukov (10). In this work the hydrogen peroxide yield remained constant, instead of decreasing as the nitrate concentration was increased. Data showing this are summarized in Table II. Note that although the observed hydrogen peroxide yield remained relatively constant as the nitrate concentration increased, the molecular hydrogen yield decreased and the molecular oxygen yield increased. The authors (10) attributed the decrease in the molecular hydrogen yield to the capture of atomic hydrogen by nitrate (Eq 8). Thus, as the nitrate concentration increased, there was less possibility for atomic hydrogen radicals to combine to produce molecular hydrogen (Eq 2). Solutes that have been found to react with ("scavenge") atomic hydrogen radicals include oxygen (12, 32), hydrogen peroxide (32), and ferric ion (81) as well as the nitrate ion (1, 10, 14, 49, 54, 55, 69). In the reaction of nitrate and atomic hydrogen, the end product is nitrite (Eq 8 and 9).

TABLE II

RELATIONSHIP BETWEEN NITRATE CONCENTRATION AND YIELD OF RADIOLYSIS PRODUCTS[a]

| $NO_3^-$ concn, *M* | *G* value[b] | | |
|---|---|---|---|
| | $H_2O_2$ | $O_2$ | $H_2$ |
| 0.1 | 1.60 | 0.07 | 0.5 |
| 1.0 | 1.77 | 0.47 | 0.18 |
| 5.0 | 1.66 | 1.45 | 0.05 |

[a] Adapted from Bakh, Medvedouskii, Revina, and Bityukov (10). [b] The *G* value is the number of molecules formed per 100 ev of radiation energy absorbed.

Data in Table II show that the molecular oxygen yield increased with an increase in the nitrate concentration while the hydrogen peroxide yield remained relatively constant. Although no explanation is given for this (10), if one were to assume that the hydrogen peroxide concentration reported was a steady-state concentration, any hydrogen peroxide generated in excess could decompose, producing the oxygen. (A steady-state concentration of radiolysis-produced peroxide has not been reported in nitric acid, but it has been shown to exist in a perchloric acid solution of plutonium (76).)

Several radiolysis reactions in aqueous solutions lead to the formation of hydrogen peroxide. These reactions can be influenced by nitrate in such a way as to favor the formation of hydrogen peroxide. For example, hydroxyl radicals, which combine to form hydrogen peroxide (Eq 3), can be destroyed by molecular hydrogen (Eq 4). But since nitrate is a scavenger for atomic hydrogen, the precursor of molecular hydrogen, the formation of molecular hydrogen is reduced or even eliminated as the nitrate concentration is increased (10). The end result is that the hydroxyl radicals are free to combine, producing hydrogen peroxide.

If present, atomic hydrogen can react with hydrogen peroxide, destroying it (Eq 6). But again, nitrate will scavenge the atomic hydrogen, thereby protecting the hydrogen peroxide. Likewise, by scavenging atomic hydrogen, nitrate will prevent the destruction of hydroxyl radicals by recombination with atomic hydrogen to produce water.

In their investigation of the radiolysis of nitrate solutions, Bakh, Medvedouskii, Revina, and Bityukov indicate that hydrogen peroxide is formed by the combination of hydroxyl radicals (10). Allen questions this mechanism in nitrate solutions (4) and points out that it is unlikely that these radicals could live long enough to undergo combination in the presence of the nitrite formed as a reaction product. Besides, the yield of hydrogen peroxide is too high to be formed in this way. Instead, the formation of some unstable peroxidic compound is proposed which subsequently decomposes to produce hydrogen peroxide.

Further experimental work on the radiation chemistry of aqueous nitrate solutions will be necessary before the various mechanisms suggested for the formation of hydrogen peroxide can be reconciled.

The status of present knowledge on the radiolysis of aqueous nitrate solutions can be summarized as follows. The major products of radiolysis are nitrite and oxygen. There is general agreement on the mechanism for nitrite production at low nitrate ion concentrations (Eq 8 and 9). At higher nitrate ion concentrations, there appears to be other radiolysis mechanisms involving some sort of direct transfer of energy from the radiation to the nitrate ion. There is not general agreement on either the mechanisms for this direct effect or on the relative contribution of this effect to the total radiolysis reaction.

## III. AQUEOUS PLUTONIUM NITRATE SYSTEMS

The aqueous chemistry of plutonium has been reviewed several times (44, 56, 87), the most recent being by Cleveland (18). Aspects of this chemistry, which are important in an understanding of the radiolytic-induced reactions of plutonium in nitrate solutions, are mentioned here.

Plutonium possesses four oxidation states, in aqueous solutions: III, IV, V, and VI. In a situation rare in chemistry, all four of these oxidation states can exist simultaneously in solution in equilibrium with each other in finite concentrations. This creates a complicated system. A study of the equilibria involved and the kinetics and the mechanisms of the oxidation-reduction reactions which these plutonium ions undergo has resulted in a great deal of research, yet much remains to be done.

Plutonium ions exist in aqueous solutions in the following forms: Pu(III) as $Pu^{3+}$, Pu(IV) as $Pu^{4+}$, Pu(V) as $PuO_2^+$, and Pu(VI) as $PuO_2^{2+}$ (46). A large number of complex ions are formed. Information about these complexes was summarized in 1961 by Gel'man, Moskvin, Zaitsev, and Mefod'eva (29).

The tendency for plutonium ions to form complexes decreases in the following order (29): $Pu^{4+} > Pu^{3+} > PuO_2^{2+} > PuO_2^+$ although the position of $Pu^{3+}$ and $PuO_2^{2+}$ is sometimes reversed (56). Nitrate complexes have been identified for three of these ions: $Pu^{4+}$, $Pu^{3+}$, and $PuO_2^{2+}$. Pertinent data on these complexes are given in Table III.

TABLE III
NITRATE COMPLEXES FORMED BY PLUTONIUM IONS

| Pu ion | Complex | Selected values of stability constant[a] | $HNO_3$ concn, *M*, at which complex exists | Ref |
|---|---|---|---|---|
| $Pu^{3+}$ | $PuNO_3^{2+}$ | 6 | 1 | 83 |
| | $Pu(NO_3)_2^+$ | 14 | 1 | 83 |
| | $Pu(NO_3)_3$ | 14 | 1 | 83 |
| $Pu^{4+}$ | $PuNO_3^{3+}$ | 5 | 1–4 | 35 |
| | $Pu(NO_3)_2^{2+}$ | 24 | 1–4 | 35 |
| | $Pu(NO_3)_3^+$ | 15 | 1–4 | 35 |
| | $Pu(NO_3)_4$ | | 1–4 | 15 |
| | $Pu(NO_3)_5^-$ | Predominate species | 4–11 | 15 |
| | $Pu(NO_3)_6^{2-}$ | | >11 | 15 |
| $PuO_2^{2+}$ | $PuO_2NO_3^+$ | 72[b] | >4 | 51 |
| | $PuO_2(NO_3)_2$ | 36[b] | >4 | 51 |
| | $PuO_2(NO_3)_3^-$ | | >4 | 52 |

[a] These stability constants are cumulative except those for $PuO_2^{2+}$ which are consecutive (84). [b] These values questioned by Sillén and Martell (84).

Oxidation potentials for the plutonium ions in nitric acid solutions are summarized in Table IV. It is apparent that the potentials are quite sensitive to the nitric acid concentrations. The potentials of the Pu(III)–Pu(IV) couple (and presumably the Pu(V)–Pu(VI) couple, if the data were available) decrease with increasing acid concentration while the reverse is true for the Pu(IV)–Pu(VI) and Pu(III)–Pu(VI) couples. This follows, in part at least, from the relative strengths of the nitrate complexes of these ions as discussed above.

TABLE IV
OXIDATION POTENTIALS OF PLUTONIUM IN NITRIC ACID[a]

| $HNO_3$ concn, *M* | Oxidation potentials, v | | | |
|---|---|---|---|---|
| | (III)–(IV) | (IV)–(VI) | (III)–(VI) | (V)–(VI) |
| 1.0 | −0.914 | −1.054 | −1.006 | −0.92 |
| 0.4 | −0.927 | −0.993 | −0.972 | |
| 0.3 | −0.935 | −0.973 | −0.961 | |
| 0.2 | −0.939 | −0.949 | −0.946 | |
| 0.1 | −0.952 | −0.925 | −0.934 | |

[a] Data from Artyukhin, Gel'man, and Medvedouskii (6).

## A. MECHANISMS FOR OXIDATION AND REDUCTION OF PLUTONIUM IN NITRIC ACID SOLUTIONS

### 1. *Reactions Involving Radiolysis Products of Nitric Acid*

Much of the chemistry of plutonium is relatively independent of the radioactivity of the element except when isotopes of very short half-lives ($^{238}Pu$, $^{240}Pu$, and $^{241}Pu$, for example) are involved. The most common and most important isotope of plutonium is $^{239}Pu$. It has a half-life of 24,181 years. While this half-life is long enough to permit chemical studies, it is still short enough so that its radiation ($1.4 \times 10^8$ $\alpha$ particles per minute per milligram of plutonium (47)) can affect solutions containing it. This effect is manifested by the formation of various radiolysis products in solution and by accompanying changes in the relative concentration of the various oxidation states of the plutonium ions. These changes usually involve reduction of plutonium (47) although oxidation has been observed (64, 68). The particular reaction that takes place is determined by the products of radiolysis, and these products are dependent on the specific ions present in the solution (64).

Nitrate solutions form various products under $\alpha$ irradiation as indicated in section II of this review. These include products expected from the radiolysis of water, *viz.*, $H\cdot$, $\cdot OH$, $\cdot HO_2$, $H_2O_2$, and $H_2$, as well as $HNO_2$ and nitrogen oxides (31, 68) which result from the radiolysis of nitrate. The chemical reactions that take place in solution as a result of radiolysis occur through the interaction of these products, either ditectly or indirectly, with plutonium.

Of the radiolysis products, $H_2$, $\cdot H$, $H_2O_2$, $HNO_2$, and perhaps some of the nitrogen oxides usually function as reducing agents. The first two of these have little significant effect on the reduction of plutonium. Molecular hydrogen will not reduce plutonium in the absence of a catalyst such as platinum (68). Atomic hydrogen is a strong reducing agent and would be capable of reducing any of the higher oxidation states of plutonium, but in the presence of the nitrate ion it is destroyed by the reaction $NO_3^- + \cdot H \rightarrow NO_2 + OH^-$ (68).

Hydrogen peroxide, an important radiolysis product of water, can reduce plutonium to Pu(IV) or Pu(III) (58, 68). Nitrous acid will reduce plutonium to similar oxidation states (19). The particular species of nitrogen oxides that are formed during radiolysis is not clear, nor is their exact behavior as reductants. It has been suggested that the stable oxides, NO, $NO_2$, and $N_2O_4$, are the ones formed (64, 68). These particular oxides are known to form an equilibrium mixture with nitrous acid (21) in which nitric oxide acts as a reducing agent, depending on the solutes present, and nitrogen di- or tetroxide act as oxidizing agents.

The remaining radiolysis products, $\cdot OH$ and $HO_2\cdot$, are usually oxidizing agents. They are generally formed by X-ray, $\gamma$, or neutron irradiation. This is in contrast to $\alpha$ irradiation which favors the formation of molecular products which usually act as reducing agents (36). In plutonium nitrate solutions which were irradiated with X-rays, it was found (68), in fact, that plutonium was oxidized. This oxidation was attributed to $\cdot OH$ formed during X-ray irradiation.

Although both hydrogen peroxide and nitrous acid usually reduce plutonium, they can, under certain circumstances, oxidize it as well. Hydrogen peroxide, for example, can oxidize Pu(III) to Pu(IV) or Pu(V) to Pu(VI) (30, 48). The mechanisms for these oxidations are not clear. Some work (58) indicates that the Pu(III) is oxidized by nitric acid after the hydrogen peroxide has been destroyed catalytically by plutonium. In other experiments containing trace amounts of Pu(IV) (21), the oxidation by hydrogen peroxide of Pu(IV) to Pu(VI), or possibly Pu(V), appeared to be catalyzed by Fe(III).

Nitrous acid, acting as an oxidizing agent, can oxidize Pu(III) to Pu(IV). In nitric acid solutions this oxidation apparently involves NO and $NO_2$ as well as $HNO_2$ (22).

Thus under some conditions, radiolysis products may oxidize plutonium while under other conditions they may reduce it. This obviously complicates the understanding and interpretation of the reactions involved.

As part of a thorough investigation of the chemical behavior of Pu(V) in weak nitric acid solutions, Gel'man and Zaitseva systematically considered all possible reactions involving the radiolysis products of water with Pu(V) (31). Using standard oxidation potentials of the radiolysis products of water and the following potentials for Pu(V)

$$\begin{aligned} PuO_2^+ &\rightarrow PuO_2^{2+} + e & E^\circ &= 0.92\text{ v} \\ PuO_2^+ + 4H^+ + e &\rightarrow Pu^{4+} + H_2O & E^\circ &= 0.93\text{ v} \end{aligned} \qquad \text{(Eq 12)}$$

reactions were written for the oxidation or reduction of Pu(V). The accompanying changes in free-energy values were calculated. Although a decrease in free energy is not the only prerequisite for postulating whether a particular reaction will take place, it served as a guide in selecting possible reactions. This, along with other information, was then used by the authors to explain the behavior of Pu(V) under varying conditions. As an example, they used the information to calculate the amount of Pu(V) reduced if only two of the radiolysis products of water, $\cdot H$ and $H_2O_2$, were involved in the reduction. This calculated amount was then compared with the experimental results. The calculated amount of reduction was 2.8%. This was somewhat lower than the average experimental result (3.9%). The difference between the two results is probably related to the fact that not all possible reduction reactions were considered. Moreover, no consideration was given to the presence of nitrate ion in the solution and reducing agents formed from it.

From this discussion of reactions involving the radiolysis products of nitric acid and plutonium, it is apparent that a complicated system exists. An understanding of reactions in this system requires both a knowledge of the radiolytic behavior of nitrate as well as a knowledge of the chemistry of plutonium.

### 2. *Reactions Involving Disproportionation of Plutonium*

Plutonium(IV) and plutonium(V) undergo disproportionation (self-oxidation and reduction) in aqueous solutions. The tendency for disproportionation is greater for plutonium than for any of the other actinide elements of lower atomic number.

For disproportionation to occur, an element must have at least three oxidation states stable in an aqueous medium; plutonium has four. A concomitant requirement is that these ions must be able to coexist in solution. Coexistence is governed by the oxidation potentials of the ions. An approximate guide is that if the potentials of two oxidation–reduction couples do not differ by more than about 0.1 v, neither will completely oxidize the other, but an equilibrium will be established (85). Data given in Table IV indicate that the oxidation potentials involving plutonium(III), -(IV), -(V), and -(VI) in nitric acid do not differ by more than 0.1 v. Hence, it is possible for all of these oxidation states to exist simultaneously in solution.

The rates of the disproportionation reactions of plutonium are important in plutonium chemistry since they determine the rate of approach to equilibrium among the various oxidation states. Furthermore, these rates are involved in reactions of plutonium with oxidizing and reducing agents other than plutonium.

The disproportionation of Pu(IV) and Pu(V) has been investigated in hydrochloric (20, 23, 77) and perchloric acids (23, 71, 73). The only reported investigation of the disproportionation of these two ions in nitric acid specifically is that of Artyukhin, Medvedouskii, and Gel'man (8). The disproportionation of Pu(V) in nitric acid is mentioned, although not investigated, by Gel'man and Zaitseva (30, 31).

#### a. Disproportionation of Pu(IV)

Experimental work on the disproportionation of Pu(IV) in nitric acid was conducted in solutions $2 \times 10^{-3}$ to $7 \times 10^{-3}$ *M* in plutonium, as Pu(IV), and 0.1, 0.2, 0.3, and 0.4 *M* in nitric acid (7). The temperature was 25°. The concentration of plutonium in each of the various oxidation states was determined spectrophotometrically at periodic intervals. The disproportionation of Pu(IV) proceeded rapidly, reaching equilibrium within 15–20 hr at all of the nitric acid concentrations investigated. The rate and the extent of the disproportionation increased as the nitric acid concentration decreased. In the higher nitric acid concentrations (0.4 and 0.3 *M*), the net disproportionation of Pu(IV) could be represented by

$$3\mathrm{Pu(IV)} \rightleftharpoons 2\mathrm{Pu(III)} + \mathrm{Pu(VI)} \qquad \text{(Eq 13)}$$

In the lower nitric acid concentrations (0.2 and 0.1 *M*), this equation was not directly applicable, however, since Pu(V) is found in the solutions. The appearance of Pu(V) can be explained if Eq 13, which represents a net disproportionation reaction, occurs through the following mechanism.

$$\mathrm{Pu(IV)} + \mathrm{Pu(IV)} \overset{k_1}{\rightleftharpoons} \mathrm{Pu(III)} + \mathrm{Pu(V)}\ \text{(slow)} \qquad \text{(Eq 14)}$$

$$\mathrm{Pu(V)} + \mathrm{Pu(IV)} \overset{k_2}{\rightleftharpoons} \mathrm{Pu(VI)} + \mathrm{Pu(III)}\ \text{(fast)} \qquad \text{(Eq 15)}$$

At lower acidities Pu(V) becomes increasingly stable and can exist in solutions for measurable periods of time (47). In nitric acid, for example, Pu(V) is most stable in the pH range of 3.5 to 4.5 (31).

The rate-determining step in the disproportionation of Pu(IV) is the reaction in Eq 14. It is slower than the reaction in Eq 15 because it requires the formation of plutonium–oxygen bonds; Eq 15 requires only the transfer of electrons and no chemical bonds need to be formed or broken. This difference between the two reactions is apparent when they are rewritten using accepted formulas for hydrolyzed plutonium ions.

$$\mathrm{Pu^{4+}} + \mathrm{Pu^{4+}} \rightleftharpoons \mathrm{Pu^{3+}} + \mathrm{PuO_2^{+}}\ \text{(slow)}$$

$$\mathrm{Pu^{4+}} + \mathrm{PuO_2^{+}} \rightleftharpoons \mathrm{PuO_2^{2+}} + \mathrm{Pu^{3+}}\ \text{(fast)}$$

The reaction in Eq 15 is rapid and reversible and is found in practically all investigations involving the aqueous chemistry of plutonium. The equilibrium between all four oxidation states of plutonium which it represents is maintained at all times (73). The rate constant, $k_2$, for this reaction in nitric acid is not known.

The rate constant, $k_1$, for the slow, rate-determining step in the disproportionation of Pu(IV) is given in Table V for various nitric acid concentrations. From these data it is apparent that as the nitric acid concentration decreases from 0.4 to 0.1 *M*, the rate of the disproportionation increases by nearly 100-fold.

TABLE V

RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR THE DISPROPORTIONATION OF Pu(IV) IN $HNO_3$[a]

| $HNO_3$ concn, *M* | Pu concn, *M* × $10^3$ | $k_1$, l. mole$^{-1}$ hr$^{-1}$ | *K* |
|---|---|---|---|
| 0.4 | 7.7 | 1.1 | 0.0045 |
| 0.3 | 7.6 | 3.7 | 0.049 |
| 0.2 | 2.0 | 14 | 0.41 |
| 0.1 | 2.2 | 92 | 7.8 |

[a] Adapted from Artyukhin, Medvedouskii, and Gel'man (8).

The equilibrium constant for the net disproportionation reaction in Eq 13 is

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

Values for *K* are shown in Table V. These values, together with the rate constants, if extrapolated to higher acid concentrations, indicate that disproportionation of Pu(IV) in strong nitric acid solutions is negligible.

The equilibrium constants, if uncorrected for nitrate complex formation, are inversely proportional to the 5.3 power of the hydrogen ion concentration. Corrected for nitrate complex formation, the proportionality is reduced to a power of 4. Using the accepted formulas of plutonium ions in aqueous solution, Eq 13 can be rewritten to show the stoichiometry of the disproportionation of Pu(IV).

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

The equilibrium constant for this reaction is given by

$$K' = \frac{[\mathrm{Pu^{3+}}]^2[\mathrm{PuO_2^{2+}}][\mathrm{H^+}]^4}{[\mathrm{Pu^{4+}}]^3} = K[\mathrm{H^+}]^4$$

Values of $K'$ were calculated using data of Artyukhin, Medvedouskii, and Gel'man (8). These values, along with comparable data from perchloric and hydrochloric acids, are given in Table VI.

In nitric acid, the $K'$ values are not constant over the fourfold change in acid concentration. However, the *K* values were not corrected for any effects caused by hydrolysis of Pu(IV) or by oxidation or reduction reactions resulting from $\alpha$ radiolysis of the solutions. In perchloric and hydrochloric acid solutions, constant values of $K'$ were obtained only if corrections for these effects were applied (71, 77).

From a comparison of the equilibrium constants at 0.2 *M* acid, it appears that the tendency for disproportionation increases in the order $HNO_3 < HCl < HClO_4$. The stability of Pu(IV) complexes formed with the anions of these acids decreases in the same order. The association constant for the reaction $\mathrm{Pu^{4+}} + \mathrm{X^-} \rightleftharpoons \mathrm{PuX^{3+}}$, when $X^-$ is $NO_3^-$, varies from 2.9 (40) to 4.7 (91), depending on solution composition. The constant has a value of 2.1 when $X^-$ is $Cl^-$ (72), whereas $ClO_4^-$ does not form a complex at all with $Pu^{4+}$.

The rate of disproportionation of Pu(IV) decreases with an increase in the nitric acid concentration (see Table V). Similar behavior is found in perchloric and hydrochloric acids, and in both of these acids there is an inverse relationship between the rate of disproportionation and the third power of the hydrogen ion concentration (71, 77). Calculations, using rate constant data

Table VI

Equilibrium Constants for the Disproportionation of Pu(IV) in Various Acid Solutions

$$3\text{Pu(IV)} \rightleftharpoons 2\text{Pu(III)} + \text{Pu(VI)}$$

| Acid | $HClO_4$[a] | | HCl[b] | | $HNO_3$[c] | |
|---|---|---|---|---|---|---|
| concn, *M* | *K* | *K'*[d] | *K* | *K'*[e] | *K* | *K'*[f] |
| 0.5 | 0.11 | $8.4 \times 10^{-3}$ | 0.024 | $1.8 \times 10^{-3}$ | | |
| 0.4 | | | | | 0.0045 | $0.12 \times 10^{-3}$ |
| 0.3 | | | | | 0.049 | $0.39 \times 10^{-3}$ |
| 0.2 | 4.07 | $11.0 \times 10^{-3}$ | 0.77 | $1.9 \times 10^{-3}$ | 0.41 | $0.65 \times 10^{-3}$ |
| 0.1 | | | | | 7.8 | $0.78 \times 10^{-3}$ |

[a] Rabideau (71). [b] Rabideau and Cowan (77). [c] Calculated from data in Artyukhin, Medvedouskii, and Gel'man (8). [d] Corrected for radiolysis and hydrolysis. [e] Corrected for hydrolysis. [f] Uncorrected for radiolysis and hydrolysis.

from Artyukhin, Medvedouskii, and Gel'man (8), show this same inverse third-power relationship for the disproportionation of Pu(IV) in nitric acid. The rate constants in all three acids are given in Table VII. The values of the rates of disproportionation of Pu(IV) are similar in nitric and perchloric acids but are about five times faster in hydrochloric acid. No explanation has been given for this difference between acids.

Table VII

Disproportionation Rate Constants

$$\text{Pu(IV)} + \text{Pu(IV)} \overset{k_1}{\rightleftharpoons} \text{Pu(III)} + \text{Pu(V)}$$

| Acid | $HNO_3$[a] | | $HClO_4$[b] | | HCl[c] | |
|---|---|---|---|---|---|---|
| concn, *M* | $k_1$[d] | $k_1[H^+]^3$ | $k_1$[d] | $k_1[H^+]^3$ | $k_1$[d] | $k_1[H^+]^3$ |
| 0.5 | | | 0.88 | 0.11 | 4.79 | 0.60 |
| 0.4 | 1.1 | 0.07 | | | | |
| 0.3 | 3.7 | 0.10 | | | | |
| 0.2 | 14 | 0.11 | 14.2 | 0.12 | 71 | 0.56 |
| 0.1 | 92 | 0.09 | | | | |

[a] $k_1$ values from Artyukhin, Medvedouskii, and Gel'man (8); $k_1[H^+]^3$ values calculated. [b] Rabideau (71). [c] Rabideau and Cowan (77). [d] l. mole$^{-1}$ hr$^{-1}$.

Based on the above discussions it seems reasonable to assume that the disproportionation of Pu(IV) in nitric acid takes place by the same mechanism as its disproportionation in perchloric and hydrochloric acids.

### b. Disproportionation of Pu(V)

Experimental investigations of the disproportionation of Pu(V) in nitric acid were conducted in solutions of Pu(V) 0.1, 0.2, and 0.3 *M* in nitric acid (8). These solutions were prepared by reducing Pu(VI) with hydrogen peroxide at a pH of 3 to 4, then acidifying the reduced solution to the desired acid concentration. Sodium hydroxide was used to adjust the pH of the solutions prior to reduction so that the final solutions contained sodium nitrate. The total plutonium concentration in the solutions was not stated, but it is probably between $10^{-3}$ and $10^{-2}$ *M*.

At time intervals varying from 0 to 80 hr, the concentration of plutonium in the various oxidation states at each of the acidities was determined spectrophotometrically to establish their relative concentration. The disproportionation of Pu(V) reached an equilibrium within 30 hr at each of the $HNO_3$ concentrations investigated. The rate of disproportionation increased with increasing hydrogen ion concentration. This is the reverse of the situation that exists in the disproportionation of Pu(IV).

The disproportionation of Pu(V) differs from that of Pu(IV) in another way, also. Once the disproportionation of Pu(IV) begins, it proceeds at a constant rate until equilibrium is reached. The rate of disproportionation of Pu(V), on the other hand, is at first slow. But it soon accelerates in an autocatalytic manner before decreasing and becoming stationary. A plot of the rate of disproportionation of Pu(V) *vs.* time is shown in Figure 1.

A mechanism for Pu(V) disproportionation must account for the observed change in rate during the disproportionation process. A mechanism suggested by Artyukhin, Medvedouskii, and Gel'man (8) does this in the following manner. At the start, when only Pu(V) is present, the only possible reaction is

$$\text{Pu(V)} + \text{Pu(V)} \overset{k_3}{\rightleftharpoons} \text{Pu(IV)} + \text{Pu(VI)} \qquad \text{(Eq 16)}$$

The Pu(IV) in turn reacts readily with Pu(V) according to Eq 15.

$$\text{Pu(IV)} + \text{Pu(V)} \rightleftharpoons \text{Pu(III)} + \text{Pu(VI)}$$

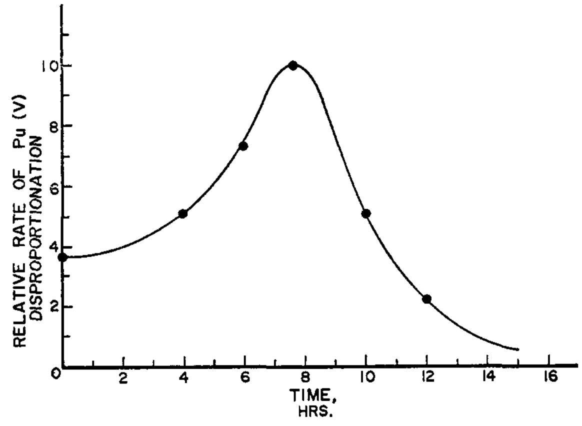

Figure 1. Relation between rate of disproportionation of Pu(V) and the time of reaction (0.2 *M* in $HNO_3$ and 0.2 *M* in $NaNO_3$): adapted from Artyukhin, Medvedouskii, and Gel'man (8).

As Pu(III) accumulates, the following reaction begins to predominate.

$$\mathrm{Pu(III)} + \mathrm{Pu(V)} \overset{k_4}{\rightleftarrows} 2\mathrm{Pu(IV)} \qquad \text{(Eq 17)}$$

It is this last reaction which results in the autocatalytic acceleration of the process.

The rate constants for the reactions in Eq 16 and 17 are given in Table VIII. The rate constant for the reaction in Eq 15 is not available in nitric acid, but it has a very large value in $HClO_4$ (78), and so presumably would be very large, compared to $k_3$ and $k_4$, in nitric acid.

TABLE VIII
RATE CONSTANTS FOR THE DISPROPORTIONATION OF Pu(V) IN NITRIC ACID SOLUTIONS[a]

| $HNO_3$ concn,[b] $M$ | Rate, l. mole$^{-1}$ hr$^{-1}$ $k_3$ | $k_4$ |
|---|---|---|
| 0.3 | 3.4 | 108 |
| 0.2 | 1.8 | 53 |
| 0.1 | 0.73 | 27.5 |

[a] Adapted from Artyukhin, Medvedouskii, and Gel'man (8).
[b] These solutions are also approximately 0.2 $N$ in $NaNO_3$.

Because of the low rate constant for the reaction in Eq 16, the initial disproportionation of Pu(V) is slow. As Pu(III) accumulates (*via* the reaction in Eq 15), the reaction in Eq 17 begins to predominate and the rate of Pu(V) disproportionation increases until the product [Pu(V)][Pu(III)] reaches a maximum. Subsequently, as the concentrations of Pu(V) and Pu(III) decrease, the rate of disproportionation falls to a steady state.

The disproportionation of Pu(V) in both hydrochloric and perchloric acids follows essentially the same mechanism outlined above for nitric acid. In the investigations of disproportionation in these acids, however, the conditions were such that autocatalysis was minimized. Connick, studying the disproportionation in hydrochloric acid, realized the possibility of autocatalysis; the rate data indicated $k_4$ was at least 35 times greater than $k_3$ in 0.5 $M$ HCl at room temperature (20). Absolute proof of autocatalysis could not be obtained, however, since the initial solutions contained significant quantities of both Pu(III) and Pu(VI). Rabideau, investigating the disproportionation of Pu(V) in perchloric acid, was concerned primarily with determining the rate of the reaction in Eq 16 (73). Starting solutions containing only Pu(V) were prepared, and rates were measured during a period when Eq 16 was apparently the only possible reaction.

The rate constant, $k_3$, in Eq 16 is directly proportional to the hydrogen ion concentration in the nitric acid solutions investigated (8). This is indicated by values of $k_3/[\mathrm{H}^+]$ in Table IX. Similar data are available for the reaction in perchloric acid (73). This suggests that the mechanism for the reaction in Eq 16 is the same as the mechanism postulated for the comparable reaction in perchloric acid (73), *viz.*

$$\mathrm{PuO_2}^+ + \mathrm{H}^+ \rightleftharpoons \mathrm{Pu(O)OH}^{2+}$$

$$\mathrm{PuO_2}^+ + \mathrm{Pu(O)OH}^{2+} \rightarrow \mathrm{PuO_2}^{2+} + \mathrm{Pu(O)OH}^+ \quad \text{(slow)}$$

$$\mathrm{Pu(O)OH}^+ \rightarrow \text{stable Pu(IV) species}$$

(The parentheses are placed around the oxygens to indicate a peroxide linkage is not intended.)

The rate constant, $k_4$, also appears to be directly proportional to the hydrogen ion concentration in nitric acid. This is indicated by the relatively constant values of $k_4/[\mathrm{H}^+]$ given in Table IX. Unfortunately, rate data in other acids are not available for calculating $k_4$.

TABLE IX
EFFECT OF ACIDITY ON RATE OF REACTION

$$\mathrm{Pu(V)} + \mathrm{Pu(V)} \overset{k_3}{\rightleftarrows} \mathrm{Pu(IV)} + \mathrm{Pu(VI)}$$

$$\mathrm{Pu(III)} + \mathrm{Pu(V)} \overset{k_4}{\rightleftarrows} 2\mathrm{Pu(IV)}$$

| $HNO_3$ concn,[a] $M$ | $k_3$[b,d] | $k_3/[\mathrm{H}^+]$[c] | $k_4$[b,d] | $k_4/[\mathrm{H}^+]$[c] |
|---|---|---|---|---|
| 0.3 | 3.4 | 11.3 | 108 | 360 |
| 0.2 | 1.8 | 9.0 | 53 | 265 |
| 0.1 | 0.73 | 7.3 | 27.5 | 275 |

[a] These solutions are also approximately 0.2 $M$ in $NaNO_3$. [b] Artyukhin, Medvedouskii, and Gel'man (8). [c] Calculated from data in Artyukhin, Medvedouskii, and Gel'man (8). [d] l. mole$^{-1}$ hr$^{-1}$.

A comparison of mechanisms shows the close relationship between the disproportionations of Pu(IV) and Pu(V). The initial reaction in the disproportionation of Pu(IV) is that of Eq 14.

$$\mathrm{Pu(IV)} + \mathrm{Pu(IV)} \rightleftharpoons \mathrm{Pu(III)} + \mathrm{Pu(V)} \quad \text{(slow)}$$

This is the reverse of the final reaction in the disproportionation of Pu(V) (Eq 17).

$$\mathrm{Pu(III)} + \mathrm{Pu(V)} \rightleftharpoons \mathrm{Pu(IV)} + \mathrm{Pu(IV)} \quad \text{(slow)}$$

Both disproportionation mechanisms include the reaction involving the attainment of equilibrium among all four oxidation states of plutonium as shown in Eq 15.

The disproportionation of Pu(V) is faster in nitric acid than is the disproportionation of Pu(IV). This is shown in Table X, which summarizes the rate constants for the slow reactions in each of the disproportionation mechanisms.

### 3. *Reactions Involving Common Oxidizing and Reducing Reagents*

The reactions of plutonium with common oxidation and reduction reagents were comprehensively reviewed by Connick (21) and subsequently summarized by Katz and Seaborg (48). In most cases, the investigations of the oxidation–reduction reactions were qualitative in

TABLE X
SUMMARY OF RATE CONSTANTS FOR DISPROPORTIONATION REACTIONS[a]

$$\mathrm{Pu(IV)}:\quad 2(\mathrm{IV}) \overset{k_1}{\rightleftarrows} (\mathrm{III}) + (\mathrm{V})$$

$$\mathrm{Pu(V)}:\quad 2(\mathrm{V}) \overset{k_3}{\rightleftarrows} (\mathrm{IV}) + (\mathrm{VI})$$

$$(\mathrm{III}) + (\mathrm{V}) \overset{k_4}{\rightleftarrows} 2(\mathrm{IV})$$

| $HNO_3$ concn, *M* | Rate, l. mole$^{-1}$ hr$^{-1}$ | | |
|---|---|---|---|
| | $k_1$ | $k_3$ | $k_4$ |
| 0.4 | 1.1 | | |
| 0.3 | 3.7 | 0.73 | 27.5 |
| 0.2 | 14 | 1.8 | 53 |
| 0.1 | 92 | 3.4 | 108 |

[a] Adapted from Artyukhin, Medvedouskii, and Gel'man (8).

nature, and true reaction rates were not determined. More recently the reaction of plutonium with several reagents has been investigated in greater detail. These include Ti(III) (75), V(III) (74), U(IV) (59, 80), and $O_2$ (60). Only the U(IV) (80) reaction was investigated in nitric acid, but, in general, it is expected that these reactions, as well as those summarized by Katz and Seaborg (48), would take place in nitric acid. They would be modified, however, by effects specific to nitric acid such as compatibility of the reagents with the acid and complex ion formation with nitrate.

### *4. Interrelationship of Oxidation and Reduction Reaction Mechanisms*

The oxidation and reduction of plutonium can involve two mechanisms as noted above: a direct reaction with an oxidizing or reducing agent other than plutonium and a disproportionation reaction in which plutonium acts as its own oxidizing or reducing agent. An oxidation or reduction of plutonium through more than one oxidation state can involve both of these mechanisms. In reductions of the type that occur with Pu(VI), for example, the reduction mechanism has been found to consist of two steps (20). The first step is a direct reduction of Pu(VI) to Pu(V). This is followed by a disproportionation of the Pu(V). The net result of these two reactions is reduction of the Pu(VI) to Pu(IV) and Pu(III).

The reduction of Pu(VI) to Pu(V) by a reducing agent is, in general, a faster reaction than the reduction of Pu(V) to Pu(IV) by a reducing agent (20). Furthermore, under some conditions, the reduction of Pu(V) by a reducing agent is slow compared to the disproportionation of Pu(V). Consequently, the reduction of Pu(V) can proceed through a disproportionation mechanism even though a reducing agent is present (20). This can be the case, for example, when hydrogen peroxide or nitrous acid acts as a reducing agent (20).

The oxidation of Pu(IV), just as the reduction of Pu(VI), may proceed through a combination of direct oxidation and disproportionation. No examples of this behavior have been definitely established in nitric acid, although it has been suggested that oxidation of Pu(IV) to Pu(VI) occurs *via* this mechanism (21).

In reactions involving both direct reduction and disproportionation, the rate of the reduction can be affected significantly by the plutonium concentration. In the case of the reduction of Pu(VI) to Pu(IV), this effects results because the disproportionation of Pu(V) is bimolecular with respect to plutonium. As the plutonium concentration gets smaller, the rate of the reduction of plutonium below Pu(V) decreases. A high plutonium concentration and a low concentration of reducing agent favor a disproportionation reaction mechanism for reduction. Conversely, a low plutonium concentration and a high concentration of reducing agent favor a direct reaction mechanism.

The possibility of direct energy transfer from an $\alpha$ particle to a plutonium ion with the resulting oxidation or reduction of the plutonium has been considered as an oxidation–reduction mechanism. It apparently has never been investigated specifically, however. In radiolysis studies reported in nitric acid (7, 68), plutonium concentrations have been kept low (approximately $10^{-3}$ *M*) to minimize any possibility of this direct reaction between $\alpha$ particles and the plutonium ions.

## B. INFLUENCE OF SOLUTION COMPOSITION PARAMETERS ON OXIDATION–REDUCTION REACTIONS OF PLUTONIUM IN NITRIC ACID SOLUTIONS

A number of factors can modify the rates and equilibrium of the fundamental oxidation and reduction reactions of plutonium in nitric acid solutions. These factors can be summarized as follows: (1) complex ion formation between plutonium and nitrate, (2) hydrolysis and polymerization of plutonium at low acidities, (3) presence of foreign cation or anions, (4) solution temperature, (5) plutonium concentration, and (6) initial concentration of the various plutonium ions. A number of variables relating to solution composition or treatment can influence the factors listed above. These solution variables, and their effects, are summarized in the following sections.

### *1. Nitrate Ion Concentration*

The rate of oxidation or reduction of plutonium is affected by the nitrate ion concentration. For example, it was found in one investigation that the rate of oxidation of Pu(IV) by radiolysis products decreases with an increase in the nitrate concentration (68). This decrease in rate at higher concentrations is attributed to the formation of Pu(IV) nitrate complexes which are more difficult to reduce than uncomplexed plutonium. In this investigation (68), the nitric acid concentration was constant at 0.3 $M$ and the added nitrate was varied from 0 to 1.76 $M$ using sodium nitrate. The plutonium concentration was $3 \times 10^{-4}$ $M$ and the plutonium was initially all in the "reduced form", *i.e.*, Pu(III) or Pu(IV). The solution was irradiated with an external X-ray source. With increasing nitrate ion concentration, the amount of plutonium oxidized decreased as a function of the absorbed energy.

In another investigation, the rate of reduction of Pu(VI) increased with an increase in the nitrate ion concentration (7). In this work, the initial nitric acid concentration was adjusted to give a solution with a pH of 3; nitrate was varied from 0.1 to 5 $M$ using sodium nitrate; plutonium concentration was $7 \times 10^{-3}$ $M$; and the only source of radiation was from the $\alpha$ particles of the contained plutonium. At all of the nitrate concentrations investigated, Pu(V) appeared almost immediately. After 15 to 25 days, Pu(IV) began to appear; the rate of appearance increased with an increase in the nitrate concentration. This increase can probably be attributed to the formation of stable Pu(IV) nitrate complexes at the higher nitrate ion concentrations, although a simple interpretation is complicated by the formation of polymeric Pu(IV) at the low acidity of the solutions.

Complex ion formation also hinders the oxidation of Pu(IV) by dichromate (21, 68). The oxidation is retarded more effectively by nitric acid than by a salt of equivalent nitrate ion concentration.

The thermal oxidation of plutonium in nitric acid is inhibited in solutions containing high concentrations of nitric acid or uranyl nitrate. This is indicated in Table XI. Again, the inhibiting effect is presumably due, at least in part, to Pu(IV)–nitrate complex formation (50). From the data in this table, it appears that there is little or no oxidation of Pu(IV) when relatively concentrated nitric acid–Pu(IV) solutions are heated.

TABLE XI
OXIDATION OF Pu(IV) TO Pu(VI).
EFFECT OF NITRATE CONCENTRATION[a] AT 80–95°

| $HNO_3$ concn, $M$ | $UO_2(NO_3)_2$ concn, $M$ | Time for 50% oxidn, min |
|---|---|---|
| 14 | | No oxidn detectable in 4.5 hr |
| 7.7 | | No oxidn detectable in 2.5 hr |
| 2 | | 230 |
| 2 | 1.26 | 275 |
| 0.5 | | *Ca.* 40 |
| 0.5 | 1.07 | 100 |

[a] Adapted from Connick (21).

### *2. Acid Concentration*

As with nitrate ion, the concentration of acid can affect the rate of oxidation and reduction of plutonium in nitrate solutions. This is indicated in an investigation in which Artyukhin, Medvedouskii, and Gel'man studied the rate of Pu(VI) reduction at several nitric acid concentrations (7). The nitrate concentration of the solutions was maintained relatively constant by adding sodium nitrate. Irradiation was from the $\alpha$ particles of the contained plutonium. The effect of the acidity on the distribution of the oxidation states is shown in Table XII for the lowest and highest acidities investigated.

At the very low acidities investigated in this study (pH 4.7 and 2), there was rapid initial reduction of Pu(VI) and a relatively large buildup of the Pu(V) concentration. As the acid concentration was increased from these low values, the initial rate of Pu(VI) reduction decreased and Pu(IV), as well as Pu(III), began to appear quite early. There was a corresponding decrease in the concentration of Pu(V). The authors attribute the reduction of Pu(VI) to a reaction in which hydrogen peroxide, generated by radiolysis, acts as a reducing agent. Hydrogen ion is a product of this reduction reaction involving the hydrogen peroxide. An increase in the acid concentration would therefore shift the equilibrium of this reduction reaction and decrease the amount of Pu(VI) reduced. No explanation is given for the decrease in the Pu(V) concentration with an increase in acid concentration, but it is almost certainly related to an increase in the rate of disproportionation of Pu(V) with an increase in acid concentration.

In a comparable investigation, the reduction of Pu(VI) by $\alpha$-particle irradiation was studied in solutions 0.0024 (pH 2.6), 0.3, 0.5, 1, 2, 3, 4, 6, and 8 $M$ in nitric acid (61). The solutions contained $1.85 \times 10^{-3}$ $M$

TABLE XII
REDUCTION OF PLUTONIUM. EFFECT OF ACID CONCENTRATION[a,b]

| Time exposed, days | Distribution of Pu oxidation states, $M \times 10^3$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | pH 4.7 | | | | 0.4 $N$[c] | | | |
| | (III) | (IV) | (V) | (VI) | (III) | (IV) | (V) | (VI) |
| 0 | 0 | 0 | 0 | 7.6 | 0 | 0 | 0 | 5.8 |
| 25 | 0 | 0 | 3.0 | 4.6 | 0 | 0.3 | 0 | 5.5 |
| 50 | 0 | 0.2 | 5.6 | 1.8 | 0.2 | 1.4 | 0.2 | 4.8 |
| 75 | 0 | 1.2 | 5.7 | 0.7 | 0.3 | 2.5 | 0.2 | 3.4 |
| 100 | 0 | 1.6 | 5.3 | 0.7 | 0.4 | 3.8 | 0.2 | 2.0 |

[a] Adapted from data by Artyukhin, Medvedouskii, and Gel'man (7). [b] Total irradiation energy from $\alpha$, $1.7 \times 10^{18}$ ev cm$^{-3}$ day$^{-1}$. Pu concn was $7 \times 10^{-3}$ $M$. Assuming all Pu is $^{239}$Pu, dosage is $10^{16}$ ev cm$^{-3}$ hr$^{-1}$ based on data by Pagés (64). [c] The total Pu concentration is not constant in these data. It was not in the original reference.

plutonium, present initially as Pu(VI). The contained plutonium was the only source of $\alpha$ particles. In the pH 2.6 solution, reduction of Pu(VI) began 3 days after sample preparation, forming Pu(V), but no Pu(IV). This agrees with previous results at this low acidity (7). In the 0.3–8 *M* acid solutions, there was no Pu(VI) reduction during the first 2 months, but in 10 month's time there was reduction in the 0.3, 0.5, and 1.0 *M* nitric acid solutions. In these solutions, the lower the acidity, the greater was the amount of Pu(VI) reduced. In the 0.3 *M* acid solution, 83% of the Pu(VI) was reduced to Pu(IV), while, in the 0.5 *M* solution, 61% was reduced; in the 1 *M* solution, 10% was reduced.

The effect of acid concentration on the oxidation of plutonium in nitric acid solutions has been investigated using radiation from an external X-ray source (68). There was less oxidation at a given radiation dose the higher the acidity of the solution. This agrees, at least qualitatively, with the work above (7) in which it was found that reduction of plutonium was favored by increased acidity.

In contrast to these results, no change in the relative concentration of the various oxidation states was found by Pagès (64) in plutonium nitrate solutions irradiated with $\gamma$ rays from an external $^{60}$Co source. The nitric acid concentration in this study varied from 0.5 to 1.5 *M* and the total plutonium from $3 \times 10^{-3}$ to $10^{-2}$ *M*. The solutions contained plutonium as Pu(VI) or mixtures of Pu(VI) and Pu(IV). The total dosage of radiation was higher than in comparable previous investigations (6, 64). More experimental work will be necessary to explain the difference between results obtained by different investigators under essentially comparable conditions.

The effect of acidity on the stability of Pu(V) in nitric acid has been studied by Gel'man and Zaitseva (31). Solutions were prepared to contain from 3.4 to 5 g of Pu(V)/l. in solutions whose initial pH values were 2, 3, 4, and 5. These solutions were analyzed at intervals over a period of 13 days to measure the conversion of the Pu(V) to other oxidation states. Solutions with an initial pH of 2 were characterized by a rapid lowering of the Pu(V) concentration. At a pH of 3, the decrease in the Pu(V) concentration was much less rapid. This same situation was true for solutions with initial pH values of 4 and 5. It was thus concluded that Pu(V) was most stable in solutions with an initial pH between 3.5 and 4.5. The decrease in the Pu(V) concentration at lower pH values was accompanied by the formation of relatively large amounts of Pu(VI) and Pu(IV), while, at the higher pH values, large amounts of Pu(IV) were formed but only negligible amounts of Pu(VI).

In another series of experiments by Gel'man and Zaitseva (31), the change, with time, in acid concentration of Pu(V) nitrate solutions was investigated. Solutions were prepared to contain from 4.5 to 5 g of Pu(V)/l. The initial pH values of the solutions were adjusted to 3, 4, and 5. In the solutions with initial pH values of 5 and 4, the pH decreased to approximately 3.5 within a period of 10 days. In the same period of time, the pH of the third solution increased from 3 to 3.5. These changes indicated reduction processes were predominate in solutions with pH >3.5 and oxidation processes predominate in solutions with pH <3. The authors concluded, on the basis of further work, that these oxidation and reduction reactions were caused by $\alpha$-radiolysis products of water and nitrate.

In a comparable investigation, the change in acid concentration was studied during the self-reduction of Pu(VI) by $\alpha$ radiation (61). The plutonium was initially present as Pu(VI) and, during the 37 days the reaction was followed, it was reduced only to Pu(V). The concentration of hydrogen ion increased during this reduction as shown in Table XIII, with the greatest increase occurring at the higher plutonium concentrations. The increase in hydrogen ion during the reduction of Pu(VI) was attributed (61) to two reactions. One involved the radiolysis of water

$$H_2O \xrightarrow{\alpha} H_2O^+ + e$$

$$H_2O^+ \rightarrow \cdot OH + H^+$$

and the other the ionization of hydrogen formed during the radiolysis.

TABLE XIII

SELF-REDUCTION OF Pu(VI). EFFECT ON ACIDITY[a]

| Initial Pu(VI) concn, $M \times 10^{-3}$ | Redn in Pu(VI) concn, %, in 37 days | pH of solution Initial | pH of solution After 37 days | Increase in $H^+$ concn, $M \times 10^3$ |
|---|---|---|---|---|
| 10 | 40 | 2.74 | 2.00 | 8.13 |
| 8 | 45 | 2.83 | 2.23 | 4.41 |
| 7 | 47.9 | 2.88 | 2.27 | 4.05 |
| 6 | 50 | 2.88 | 2.23 | 4.57 |
| 5 | 50 | 2.93 | 2.41 | 2.72 |
| 4 | 52.5 | 3.05 | 2.65 | 1.35 |
| 3 | 51.7 | 3.18 | 2.51 | 2.43 |
| 2 | 52.5 | 3.30 | 2.83 | 0.98 |
| 1 | 55 | 3.48 | 2.90 | 0.93 |

[a] Adapted from Nikol'skii, Pozharskaia, and Pozharskii (61).

The change in acid concentration during self-reduction of Pu(VI) by $\alpha$ radiation was followed in another investigation (16). This investigation differed from that of Nikol'skii, Pozharskaia, and Pozharskii (61) in that the total plutonium and acid concentrations were higher, and the plutonium was not all present initially as Pu(VI). Data on the experiments and the results are summarized in Table XIV.

In this work, the acidity decreased in the ratio of approximately 1 mole of hydrogen for every mole of Pu(VI) reduced. This decrease in acidity is in contrast

TABLE XIV

SELF-REDUCTION OF Pu(VI). EFFECT ON ACIDITY[a]

| Sample no. | Pu(VI) concn, % |  | $HNO_3$ concn, M |  | Decrease in $HNO_3$ concn, M |
|---|---|---|---|---|---|
|  | Initial | After 27 days | Initial | After 27 days |  |
| 1 | 53 | 2.3 | 2.05 | 1.75 | 0.30 |
| 2 | 52 | 2.6 | 2.07 | 1.82 | 0.25 |
| 3 | 46 | 2.5 | 3.06 | 2.88 | 0.18 |
| 4 | 45 | 2.2 | 3.19 | 2.98 | 0.21 |

[a] Adapted from Byrne, Delnay, Domning, Grill, and Miner (16). Total Pu concn., *ca.* 146 g/l.

to the increase in acidity observed by Nikol'skii, Pozharskaia, and Pozharskii (61). At present there is no explanation for the difference in the results obtained in the two investigations.

Nitric acid, as well as aluminum nitrate and sodium nitrate, inhibit the thermal oxidation of Pu(IV) nitrate solutions (24). Nitric acid was shown to be a more efficient inhibitor for the oxidation than either of the nitrate salts. The acid also has a greater inhibiting effect than the salts on the disproportionation of Pu(IV).

In solutions of low acidity, hydrolysis and polymerization of both Pu(VI) and Pu(IV) can occur, especially at elevated temperatures. The plutonium products of these reactions are resistant to oxidation or reduction. The acid concentration at which hydrolysis begins depends on a number of factors including the plutonium concentration, the presence or absence of complexing agents, and the temperature. The hydrolytic behavior of Pu(IV) in nitric acid has been reviewed (57).

### *3. Plutonium Concentration*

Both the total plutonium concentration and the relative concentration of its various oxidation states can affect the behavior of plutonium in nitric acid solutions. In all the work reported in which the effect of $\alpha$ self-radiation or radiation from external $\gamma$ or X-rays was investigated, the total concentration was kept low, as was indicated earlier. This was done to prevent possible direct transfer of energy from the $\alpha$ particles to the plutonium ions. It is unlikely, however, that there would be any such direct transfer of energy since the number of plutonium ions is quite small compared to the number of water molecules. Thus nearly all of the energy of the $\alpha$ particles would be consumed in ionizing, exciting, and dissociating the water molecules (21).

Disregarding, then, any direct reaction of $\alpha$ particles with plutonium, an increase in radiation accompanying an increase in the total plutonium concentration could increase, or perhaps even alter the radiolysis products of both water and nitrate. Any changes in these products would subsequently affect the behavior of plutonium. There has been no systematic investigation of the effect of increased plutonium concentration on radiolysis reactions in nitric acid solutions. There are references, however, to the gross behavior of plutonium nitrate solutions with plutonium concentrations varying from 44 to 570 g/l. (approximately 0.2 to 2.4 *M*) (16, 63). The composition of the gas evolved from some of these solutions was determined as was the rate of reduction of Pu(VI). In one study, a change in the acid concentration with elapsed time was also observed (16). There was no attempt in any of this work, however, to relate mechanisms to any of the reactions.

The initial concentration of the various oxidation states of plutonium also affects the oxidation and reduction reactions of plutonium in solution. In one investigation, plutonium nitrate solutions were irradiated with X-rays for given time intervals. The steady-state ratios of the oxidation states of plutonium varied and were dependent on the initial concentrations of Pu(V) and Pu(VI) (68). When the same type of experiment was conducted in perchloric acid, which eliminated any effect from nitrate radiolysis products, comparable steady-state ratios were obtained, even when part of the initial plutonium was in a reduced form (67).

In another investigation, nitrate solutions were prepared containing 5, 2.5, 1.25, and 0.6 g of plutonium/l., all in the pentavalent state (30). One series of the solutions was prepared at pH 4 and another at pH 5. The only irradiation was from the $\alpha$ activity of the contained plutonium. The solutions were analyzed over a period of 13 days to determine the concentration of the various oxidation states of plutonium. The Pu(V) concentration of each solution decreased with time, with the rate of decrease approximately proportional to the initial concentration of Pu(V). This would be expected from the disproportionation mechanism for Pu(V) discussed earlier (Eq 16, 15, and 17).

The initial concentration of Pu(IV) affects the rate at which it is oxidized to Pu(VI) in hot nitric acid solutions (24). Up to a point, if the concentration of Pu(IV) is increased, there is a corresponding increase in the rate of oxidation of Pu(IV), but, at high initial Pu(IV) concentrations, this rate decreases. This decrease is attributed to the effect of Pu(VI) on the disproportionation of Pu(IV).

### *4. Temperature*

An increase in temperature has the expected effect of increasing the rate of both oxidation and reduction reactions in plutonium nitrate solutions. The temperature coefficients of the rate of the plutonium disproportionation reactions have been determined in hydrochloric and perchloric acids (73, 77, 78), but not in nitric acid. However, there are some data showing the effect of temperature on the over-all rate of oxidation of Pu(IV) to Pu(VI) in nitric acid. These data are summarized in Table XV.

The rate constant for the oxidation of Pu(IV) to Pu(VI) in 1 *M* $HNO_3$ increased from 0.13 $l.^2$ $moles^{-2}$

TABLE XV

OXIDATION OF Pu(IV) TO Pu(VI). EFFECT OF TEMPERATURE

| $HNO_3$ concn, $M$ | Temp, °C | Initial Pu(IV) concn, $M \times 10^3$ | Time for 50% oxidn, min | Oxidn in 500 min, % | Ref |
|---|---|---|---|---|---|
| 0.2 | 75 | 1.05 | 16 | | 21 |
| 0.2 | *Ca.* 25 | 5.0 | $8 \times 10^4$ | | 21 |
| 1.7 | *Ca.* 110 | 1.03 | | 79 | 24 |
| 1.7 | 98 | 1.03 | | 63 | 24 |
| 1.7 | *Ca.* 25 | 4.13 | | 0 | 24 |

$min^{-1}$ at room temperature to $10^5$ $l.^2$ $moles^{-2}$ $min^{-1}$ at reflux temperature (*ca.* 100°) (24).

### 5. *Foreign Cations and Anions*

Foreign cations and anions can affect the oxidation and reduction of plutonium in nitrate solutions in a number of ways. If these foreign ions are oxidizing or reducing agents, and have the proper potentials in the given system, they can oxidize or reduce plutonium (see section III.A.3). If they are nitrate salts, the nitrate can complex Pu(IV) and alter its oxidation–reduction behavior (6, 24, 68). If they are ions such as $UO_2^{2+}$ which form nitrate complexes, they can alter the concentration of nitrate and again affect the oxidation–reduction behavior of Pu(IV) (24, 68). A detailed discussion of all of these possible reactions is beyond the scope of this review. Rather, the discussion will be limited to the two oxidation–reduction agents, hydrogen peroxide and nitrous acid, which are generated by radiolysis in plutonium nitrate solutions.

Nitrite will reduce the oxidized forms of plutonium. This reduction was studied in the early 1940's and is summarized by Connick (21). More recently, the use of sodium nitrite as a reducing agent for Pu(VI) has been investigated at Hanford (19). It was concluded that the reduction of Pu(VI) by nitrite is dependent on the nitrite concentration, temperature, acidity, ferric ion concentration, and time. Efficient reduction by nitrite is limited to solutions with a nitric acid concentration lower than 1.4 $M$ and a temperature above 50°. By proper control of conditions, it was possible to get at least 90% reduction of Pu(VI) to Pu(III). The total plutonium concentration in the solutions investigated was 0.01 $M$, and the most efficient concentrations of $NaNO_2$ and $HNO_3$ were 0.05 and 0.55 $M$, respectively.

The reaction of nitrite has also been investigated at the low concentrations produced by radiolysis (68). A solution containing plutonium in the oxidized form [Pu(VI) and Pu(V)] was exposed to X-ray irradiation. At intervals, the concentration of plutonium was determined in both the oxidized and the reduced [Pu(IV) and Pu(III)] forms. The nitrite concentration was determined at the same time. The total plutonium concentration was $3.4 \times 10^{-4}$ $M$.

Noticeable reduction of plutonium started only after the accumulation of a certain amount of nitrite (approximately $5 \times 10^{-4}$ $M$) and proceeded to a constant value which was determined by the nitrite concentration. The nitrite also reached a steady-state concentration which did not change during further irradiation.

A second experiment was conducted (68) in which nitrite was added prior to irradiation to give an amount slightly higher than the previously determined steady-state concentration. The plutonium was completely reduced soon after irradiation began, and, at the same time, the nitrite concentration diminished to the steady-state concentration.

Uranium was present, along with plutonium, in these last two nitrite experiments. This makes a quantitative interpretation of the data difficult since uranium can also react with nitrite. The authors indicate the role of nitrite in the plutonium reduction is unclear. They suggest it might retard plutonium oxidation normally expected in solutions exposed to X-ray irradiation, by acting as an acceptor for the $\cdot OH$ radical, which they feel is the oxidant for Pu(IV).

Nitrite can oxidize Pu(III). The kinetics and mechanism of this oxidation have been investigated using plutonium concentrations of $10^{-6}$ to $10^{-5}$ $M$ (27). The rate of oxidation is a function of the second power of the nitric acid concentration and the first power of the concentrations of hydrogen ion, nitrate ion, and nitrous acid. The oxidation of Pu(III) was autocatalytic in nitric acid if the concentration of nitrous acid was less than or equal to the concentration of plutonium. Mechanisms were suggested for the oxidation which involved $NO^+$ and $N_2O_4$ as the oxidizing agents.

Hydrogen peroxide can reduce plutonium; this is its primary effect in plutonium nitrate solutions. However, it can also oxidize plutonium. Thus, its behavior is complex and is dependent on conditions such as acidity and concentrations of catalytic impurities, plutonium, complexing agents such as nitrate, etc. As an example, in a nitrate solution at pH >4, a radiolysis product of water (which is assumed to be hydrogen peroxide) will reduce Pu(V), but at a pH <3 it will oxidize Pu(V) (30).

As discussed in section II of this review, hydrogen peroxide is formed in nitric acid solutions by the radiolysis of water. The rate of formation of hydrogen peroxide has apparently never been measured in plutonium nitrate solutions, although it has been measured in plutonium perchlorate solutions (76). There is no question of its presence, however.

Hydrogen peroxide has been investigated as a reducing agent for Pu(VI) in nitric acid solutions when added in quantities in excess of that produced by radiolysis (58). Specifically, its effect was examined as a function of the concentrations of nitric acid, plutonium, and iron. Results showed that pure solutions of Pu(VI) in nitric acid are rapidly reduced by hydrogen peroxide to Pu(IV), which is in turn reduced by peroxide to Pu(III). Reoxidation of Pu(III) to Pu(IV) occurs rapidly at high plutonium concentrations but slowly at low plutonium concentrations. This reoxidation of Pu(III) is believed to be effected by nitrate after the peroxide has been decomposed. Plutonium acts as a catalyst for the decomposition of the peroxide. Nitrate itself is thought to be inactive in oxidizing Pu(III), so probably intermediates such as NO or $NO_2$ are involved (21).

In this same investigation (58), it was found that the rate of reduction of Pu(VI) by peroxide increases with an increase in the plutonium concentration. Iron greatly reduces the rate of reduction and, in fact, can completely prevent reduction if present in concentrations greater than 1 g/l.

The amount of hydrogen peroxide present in excess of the amount required to reduce plutonium has little effect on the rate of the plutonium reduction. Likewise, the nitric acid concentration in the acid range studied (1.5 to 6 *M*) has only a minor effect on the rate of reduction with reduction being slightly more rapid in 3.5 *M* acid. Sunlight has no detectable effect on the reduction rate.

Plutonium can catalyze the decomposition of hydrogen peroxide, as noted earlier (21, 58). This catalytic effect has been investigated in some detail by Elson (28) using Pu(IV) alone as well as Pu(IV) in combination with metallic platinum and salts of Cu(II) and Fe(III). The results showed that Pt combined with Pu(IV) increases the rate of decomposition by about a factor of 2, with or without the presence of Fe(III) or Cu(II). The effect of adding Fe(III) and Cu(II), at 0.01 *M* each, to Pu(IV) was to lower the rate of decomposition as compared to lower concentrations of these two ions.

Data obtained when Pu(IV) and Pt were used as catalysts for the decomposition of hydrogen peroxide in nitric acid are summarized in Table XVI.

TABLE XVI
DECOMPOSITION OF $H_2O_2$.[a]
EFFECT OF Pu(IV) AND Pt ON RATE

| Temp, °C | Rate, $k \times 10^4$ sec$^{-1}$<br>Pt present[b] | Pt absent |
|---|---|---|
| −10.0 | 0.43 | |
| −9.1 | | 0.24 |
| −8.4 | 0.47 | |
| −8.1 | | 0.30 |
| −1.0 | | 0.88 |
| 9.1 | | 2.5 |
| 17.8 | | 4.1 |
| 18.3 | | 6.3 |
| 20.5 | | 18 |

[a] Adapted from Elson (28). Pu(IV), 1.25 *M*; $HNO_3$, 4.5 *M*; $H_2O_2$, 0.05–0.1 *M*. [b] 9 $cm^2$/10 ml of solution.

A mechanism suggested to explain the catalytic effect of Fe(III) and Cu(II) on the decomposition of hydrogen peroxide is based on an oxidation–reduction reaction involving hydrogen peroxide as both the oxidant and the reductant. This same mechanism is suggested to explain the catalytic behavior of Pu(IV) (28). Such a mechanism was shown to exist in the catalytic decomposition of hydrogen peroxide by Pu(IV) in hydrochloric, perchloric, and sulfuric acid media (11) and thus, may also function in nitric acid.

ACKNOWLEDGMENT.—The authors wish to thank their colleagues who read the manuscript and offered constructive criticisms and valuable suggestions. The review was prepared during the course of work under Contract AT(29-1)-1106 with the Atomic Energy Commission.

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