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***Nature of the Steady State of
Plutonium-238 in Dilute Nitric
and Hydrochloric Acids***

G. L. Silver

AEC Research and Development Report

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SUMMARY

The nature of the steady state of plutonium-238 in dilute nitric acid has been reexamined. The concentration of hexavalent plutonium at steady state is lower than previously reported, and depends upon the total plutonium concentration. The use of tristimulus colorimetry for studying plutonium solutions is discussed, and the preparation of solutions of pentavalent plutonium is described. The nature of the steady state of plutonium-238 in dilute hydrochloric acid is mentioned.

INTRODUCTION

In 1968, Silver and Buzzelli proposed that the autoreduction of hexavalent plutonium-238 in dilute nitric acid might proceed by an autocatalytic mechanism.¹ As an introduction to this study, they showed that the steady-state concentration of $^{238}\text{PuO}_2^{2+}$ in dilute nitric acid solutions of plutonium-238 was only a small fraction of the total plutonium present. The purpose of the present study was to examine in greater detail the nature of the steady state of plutonium-238 in dilute nitric acid in an attempt to obtain a better understanding of the nature of the valence state distribution of plutonium-238 species in this medium. As a supplement to this study, the valence state distribution of plutonium-238 in dilute hydrochloric acid was briefly examined.

EXPERIMENTAL

Spectrophotometric measurements were made with a Beckman DK-2A recording spectrophotometer using 1-cm cells. Spectra of plutonium solutions were analyzed by abbreviated complementary tristimulus colorimetry (CTC). The wavelengths 799 nm, 895 nm and 1012 nm were selected for monitoring. A ferrous chloride, ferric chloride buffer in hydrochloric acid was used as a potential standard for potential measurements. Since the hydrochloric acid concentration of the buffer was 1.5M, the potential of the buffer was taken as 700 mV.² Potential measurements were made with a Beckman pH meter using calomel and platinum electrodes. A hydrochloric acid solution of plutonium-238 was prepared by dissolving $^{238}\text{PuO}_2$ in 12M hydrochloric acid.

The plutonium used in these experiments consisted of a mixture of plutonium isotopes consisting largely (80%) of plutonium-238 with the balance (~20%) plutonium-239. A series of five solutions of $^{238}\text{Pu(IV)}$ containing 8.74 mg/ml total plutonium in various concentrations of nitric acid was prepared by dilution of a stock solution of $^{238}\text{Pu(IV)}$ which had been allowed to age in 0.5M nitric acid for one day. Five similar solutions of $^{238}\text{Pu(IV)}$ were prepared by dilution of a fresh solution of $^{238}\text{Pu(IV)}$ such that the total plutonium concentration was 2.92 mg/ml.

With the exception of Pu(V), reference solutions of the various plutonium species were prepared as described elsewhere.³ Solutions of pentavalent plutonium-238 were prepared by oxidizing small volumes of $^{238}\text{Pu(IV)}$ solutions to $^{238}\text{Pu(VI)}$ in 0.5-1M nitric acid with divalent silver oxide. The free acid was then neutralized with an excess of 1.5M pyridine-pyridinium nitrate buffer. When an excess of buffer had been added, a solution of 3% hydrogen peroxide was added dropwise with vigorous swirling until the orange color of PuO_2^{2+} was replaced by the pink color of PuO_2^+ . A few more drops of the peroxide were added, and the spectra of the pink solutions were obtained immediately. Such spectra did not reveal the absorbance of PuO_2^{2+} near 830 nm. This method of preparing solutions of PuO_2^+ is easier than the methods described by Silver³ because it is not necessary to remove silver ions from the solutions of PuO_2^{2+} prior to the reduction step.

The abbreviated CTC approach has been used previously for plutonium-238 solutions.³ Prior studies of plutonium-238 utilized the wavelength 475 nm because of experimental limitations. The use of 475 nm

for studying plutonium solutions leaves much to be desired. The extinction coefficient of Pu(IV) at this wavelength is larger than the extinction coefficients of other ionic plutonium species at many other suitable wavelengths, and this limits the useful range of plutonium concentrations which may be studied spectrophotometrically at this wavelength by the CTC approach. The absorbance peak at 475 nm is narrow, and the extinction coefficient of Pu(IV) is sensitive to nitric acid concentrations, so that at this wavelength the Beer-Lambert law is followed only approximately.⁴ Plutonium(IV) polymer also absorbs appreciably near 475 nm, so that even a small amount of the polymer in plutonium solutions may influence the absorption of light at 475 nm appreciably. For these reasons 799 nm, 895 nm and 1012 nm were selected for monitoring. Each of the selected wavelengths corresponds to the top of a broad absorption maximum for Pu(III), while 799 nm also corresponds to the top of an absorption maximum for Pu(IV). Doubtless other wavelengths could also be used.

One of the difficulties attending the use of the abbreviated CTC approach is the preparation of reliable standards.⁵ Since it was anticipated that only small amounts of Pu(VI) would be encountered in plutonium-238 solutions at steady state, a calibration curve of the Pu(VI) absorption maximum near 830 nm was prepared. This calibration curve is shown in Figure 1, and may be compared to a

FIGURE 1 - Absorbance as a function of concentration for PuO_2^{2+} near 830 nm.

similar calibration curve elsewhere.⁵ Concentrations of PuO_2^{2+} in experimental solutions were ascertained by the absorbance of PuO_2^{2+} near 830 nm using the calibration curve shown in Figure 1. This method of determining PuO_2^{2+} concentrations should be more accurate than application of CTC either directly or by difference. The determination of low concentrations of PuO_2^{2+} by CTC has been criticized by Silver.³

In solutions of plutonium consisting mainly of Pu(III) and Pu(IV) such that Pu(VI) makes an insignificant contribution to the absorption spectrum, the CTC approach degenerates to the analysis of the proportion of two variables whose sum is constant. It then becomes unnecessary to obtain accurate C° values for Pu(III) and Pu(IV), although it is necessary to obtain accurate complementary color points for these species. In this study, the color fractions of Pu(III) and Pu(IV) ($q_{(III)}$ and $q_{(IV)}$ respectively) were determined graphically. The failure of solution complementary color points to adhere to a line defined by the complementary color points of pure Pu(III) and Pu(IV) can be used as an indication of nonadherence to the Beer-Lambert law, or accidental error in obtaining or interpreting solution spectra. Evidence of gross nonadherence was not observed in this study.

In plutonium solutions containing only Pu(III) and Pu(IV), the concentration of each species is related to the total plutonium concentration via Equation 1:

$$Jq_{(III)} C_{(III)}^\circ + Jq_{(IV)} C_{(IV)}^\circ = C_T \quad (1)$$

where C_T represents the total plutonium concentration. Dividing this equation by the constant $C_{(III)}^\circ$ yields

$$Jq_{(III)} + Jq_{(IV)} [C_{(IV)}^\circ / C_{(III)}^\circ] = C_T / C_{(III)}^\circ \quad (2)$$

Thus, a plot of $Jq_{(III)}$ versus $Jq_{(IV)}$ should be a straight line of slope $[-C_{(IV)}^\circ / C_{(III)}^\circ]$ if adherence to the Beer-Lambert law is maintained. Such a plot obtained from solutions containing

8.74 mg/ml plutonium aged for 48 hr, 6 days and 2 weeks is shown in Figure 2.

FIGURE 2 - Plot of product of color fractions of Pu(III) and Pu(IV) and total absorbance for solutions containing 8.74 mg/ml of 80% plutonium-238.

The slope of the line is -1.32. Hence, the relative amounts of Pu(III) and Pu(IV) in plutonium-238 solutions which have reached steady state are $Jq_{(III)} / [Jq_{(III)} + Jq_{(IV)} (1.32)]$ and $Jq_{(IV)} (1.32) / [Jq_{(III)} + Jq_{(IV)} (1.32)]$. Although it is unnecessary by this approach to find accurate C^0 values for Pu(III) or Pu(IV), we find that C^0 for Pu(III) is approximately 5 mg/ml ($J = \Sigma A$).⁶

RESULTS AND DISCUSSION

In Table 1 is presented the valence state distribution of plutonium solutions containing 8.74 mg/ml of 80% plutonium-238 in various concentrations of nitric acid after selected aging periods. Examination of this table shows that the steady-state concentration of Pu(III) decreases with increasing nitric acid concentration, and that the steady-state concentration of Pu(IV) increases with increasing nitric acid concentration. The steady-state concentration of Pu(IV) is very low, and decreases with increasing acid concentration. Qualitatively, these results are in agreement with the results reported by Silver and Buzzelli in their brief examination of the steady state of plutonium-238 in dilute nitric acid. Table 2

Table 1

DISTRIBUTION OF PLUTONIUM VALENCE STATES FOR SOLUTIONS OF 80% PLUTONIUM-238 AFTER (a) 48 HOURS, (b) 6 DAYS, (c) 14 DAYS AS A FUNCTION OF SOLUTION ACIDITY^a

Acidity (M)	% III			% IV			% VI		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
0.18	74	73	75	25	26	24	0.9	0.9	0.9
0.26	67	66	68	32	34	31	0.7	0.6	0.7
0.34	57	55	57	43	45	43	0.4	0.4	0.5
0.48	38	37	39	62	63	61	0.3	0.3	0.3
0.63	24	24	25	76	76	75	0.2	0.2	0.2

^a Plutonium concentration = 8.74 mg/ml.

Table 2

DISTRIBUTION OF PLUTONIUM VALENCE STATES FOR SOLUTIONS
OF 80% PLUTONIUM-238 AFTER (a) 24 HOURS, (b) 6 DAYS,
(c) 14 DAYS AS A FUNCTION OF SOLUTION ACIDITY^a

Acidity (M)	% III			% IV			% VI		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
0.19	75	74	74	23	24	24	1.8	1.8	1.7
0.26	61	64	66	37	35	33	1.7	1.4	1.3
0.34	50	52	51	49	47	48	1.4	1.1	1.0
0.49	33	34	33	66	65	66	1.1	1.1	1.0
0.71	20	20	20	79	79	79	1.6	1.2	1.3

^aPlutonium concentration = 2.92 mg/ml.

shows similar results for a solution containing 2.92 mg/ml of 80% plutonium-238. Table 2 is more easily compared to the results of Silver and Buzzelli since the solutions described in Table 2 and the solutions described by Silver and Buzzelli contain nearly identical plutonium concentrations. Comparison of Table 2 with the results of Silver and Buzzelli shows general agreement, with two exceptions.

1. Silver and Buzzelli reported that very dilute nitric acid solutions of plutonium-238 (0.32M and 0.18M) contained 4% and 6%, respectively, of hexavalent plutonium. This seems surely to be an error, the excessively large amounts of Pu(VI) probably being the result of intrinsic errors in the CTC approach for measuring small quantities of Pu(VI), as well as use of the wavelength 475 nm. In higher acid concentrations, agreement between Table 2 and the results in reference 1 is better.
2. Examination of the tables of valency distribution given by Silver and Buzzelli shows that, curiously, their solutions had not quite reached steady state after 24 hr. Examination of Table 2 shows that some of the solutions described in this table also had not reached steady state after 24 hr, but that they were much

closer to steady state after this period than were the solutions described in reference 1. The reason for this is not clear. Perhaps Silver and Buzzelli inadvertently oxidized some Pu(IV) to Pu(VI) by accidental denitration of the tetravalent plutonium nitrate crystals during the preparation of their stock solution. Such accidental denitration occurs easily, and the resulting Pu(VI) would prolong the period required for the solutions to reach steady state. Alternately, the period required to reach steady state for solutions containing 2.9 mg/ml of 80 at. % plutonium-238 may be so close to 24 hr that a difference of about 2 hr near the end of the 24-hr period (i.e., the time required to obtain all spectrophotometric measurements) affects the valence state distribution.

Of considerable interest in the study of the steady state of plutonium-238 in dilute nitric acid is the potential-acidity behavior of solutions at steady state. In Figure 3 is shown a predominance region diagram for plutonium on which have been plotted the experimental potentials of the solutions described in Tables 1 and 2. These potentials were measured two weeks after the solutions had been prepared. Figure 3 is more complete than the similar diagram presented by

FIGURE 3 - Predominance region diagram for plutonium in dilute nitric acid.*

Silver and Buzzelli since it contains experimental potentials of two series of solutions of differing plutonium concentrations. Within experimental error, the points for each series of solutions plotted in Figure 3 form straight lines. These lines are parallel, with a slope of 0.10 and a separation of about 5 mV. Figure 3 indicates that the solutions of lower plutonium concentration have higher absolute potentials. This potential difference is also indicated by examination of Tables 1 and 2 where, for a given acidity, the ratio Pu(IV)/Pu(III) is slightly greater in solutions of lower plutonium concentration. This shift toward more positive potentials with a decrease in plutonium concentration is also reflected in a higher relative amount of PuO_2^{2+} , the highest common oxidation state of plutonium in acid solution, in

*See reference 7.

solutions of lower plutonium concentration.

It is of interest to speculate on the possible causes of the observed potential-acidity behavior of dilute solutions of plutonium-238. In this regard, the data of Silver and Buzzelli are helpful. They found, for solutions which evidently had not reached steady state, that a plot of potential versus $\log(\text{H}^+)$ was linear below $\log(\text{H}^+) = -0.4$. Examination of the diagram in reference 1 shows that the deviation from linearity of the data between $\log(\text{H}^+) = -0.4$ and $\log(\text{H}^+) = -0.3$ is very small, so that their data are essentially linear below $\log(\text{H}^+) = -0.3$. Above $\log(\text{H}^+) = -0.3$, however, their data show definite curvature. Examination of Figure 3 shows that the potential-acidity behavior for plutonium-238 solutions aged for two weeks is linear at least as high as $\log(\text{H}^+) = -0.2$. Silver and Buzzelli determined that the slope of the line determined by their potential-acidity data was 0.13. Since the predicted slope of a plot of potential versus $\log(\text{H}^+)$ should be about 0.12 if reaction 3

were potential-controlling, they speculated that the alpha radiations of plutonium-238 reduced nitrate ions to nitrous acid with the result that a nitric acid-nitrous acid buffer resulted which became potential-controlling. In their view, the behavior of the Pu(III)/Pu(IV) ratio could be explained in terms of the potential-acidity behavior of this buffer system. This point of view is generally compatible with the work of Miner et al.,⁹ who have shown that nitrous acid is an initial product of the alpha radiolysis of nitric acid. Interestingly, these workers have also shown that the presence of hydrogen peroxide in solutions containing nitrite need not be considered. For the solutions under consideration here, this apparently eliminates peroxide as a participant in a potential-controlling redox system.

While the absolute values of the potentials recorded by Silver and Buzzelli and those in Figure 3 are similar, their behavior with changes in acidity is

different. As mentioned above, it is not surprising that the potential-acidity behavior of plutonium nitrate solutions might correspond to the nitric acid-nitrous acid buffer system soon after the solutions were prepared. Experimental potentials plotted in Figure 3, however, were taken from solutions which had aged for 2 weeks. During this period, the accumulated nitrous acid may undergo alpha radiolysis or disproportionation. Either reaction should result in the introduction of nitric oxide into the solutions. Shaking the aged solutions immediately prior to the potential measurements caused effervescence. Presumably this effect was due to nitric oxide gas since the concentration of hydrogen peroxide, a precursor of oxygen gas, should have been very small.⁸ The presence of significant quantities of nitric oxide suggests two other reactions which might become potential-controlling in aged solutions of plutonium-238:

Whether or not Reaction 4 becomes potential-controlling is difficult to ascertain, since the concentration of nitrous acid was not determined and was probably not constant. The anticipated variation of the nitrous acid concentration as the nitric acid concentration changes,⁹ however, makes it unlikely that the potential-pH behavior of this system in plutonium nitrate solutions would be linear. Since the relation of potential with $\log(\text{H}^+)$ is linear, Reaction 4 may perhaps be eliminated on this basis. For Reaction 5:

$$E = 0.95 + (0.06/3)[\log(\text{NO}_3^-)(\text{H}^+)^4] - (0.06/3)[\log(\text{NO})] \quad (6)$$

In aged solutions, the last term in Equation 5 should be nearly constant, and since, in the solutions under consideration here, the nitrate ion concentration is approximately equal to the hydrogen ion concentration, the potential-acidity behavior for the nitrate-nitric oxide system will be in the form of Equation 7:

$$E = 0.95 - N + 0.10[\log(\text{H}^+)] \quad (7)$$

where "N" represents a constant term due to the presence of nitric oxide. Thus, for this buffer system, a plot of potential versus $\log(\text{H}^+)$ should be a straight line with a slope of 0.10, a value in agreement with the experimentally observed slope of 0.10. That nitric oxide and aqueous nitric acid can exist in a kinetically reversible equilibrium has been established.⁹

Similar lines of thought may be used to propose an explanation for the small but perceptible decrease in solution potential with increasing plutonium concentration. The higher the concentration of plutonium, the higher the level of internal radiation in the nitric acid solutions of plutonium nitrate. An increased level of radiation will correspond to an increased rate of radiolytic decomposition of nitrate ions and nitrous acid. This will result in a higher steady-state concentration of oxides of nitrogen, particularly nitric oxide, increasing the absolute value of "N" in Equation 7, and thus decreasing the absolute value of the solution potentials.

If the ratio Pu(III)/Pu(IV) responds to the potential-acidity behavior of a nitrogen redox system as postulated above, how can the relative abundance of hexavalent plutonium in the plutonium-238 solutions be explained? In solutions of plutonium at steady state, an equilibrium approximated by Equation 8 is established:

Taking the constant for this reaction¹⁰ as 1×10^{-4} in 0.34M nitric acid, and using concentrations of Pu(III) and Pu(IV) derived from Tables 1 and 2, the calculated relative steady-state concentration of Pu(VI) in a solution containing 8.74 mg/ml of plutonium is 0.5%, and in a solution containing 2.92 mg/ml of plutonium it is 1%. These values are in fair agreement with the observed values of hexavalent plutonium shown in Tables 1 and 2.

In Figure 4 is plotted the logarithm of the ratio Pu(IV)/Pu(III) for the two series of plutonium solutions. A smooth curve may be passed through the points for the solutions containing 8.74 mg/ml as shown in the diagram. An arbitrary dashed line of slope 2.00 has also been

FIGURE 4 - Plot of the logarithm of the Pu(IV)/Pu(III) ratio as a function of the logarithm of acidity at two different plutonium concentrations.

passed through the points to show that they lie very close to such a line as might be expected from the potential-acidity relationship of the solutions. The equation of the arbitrary dashed line is $\log[\text{Pu(IV)}/\text{Pu(III)}] = \log [8(\text{H}^+)^2]$. Hence, to a first approximation, the ratio $[\text{Pu(IV)}]/[\text{Pu(III)}]$ at steady state varies as the square of the nitric acid concentration.

PLUTONIUM-238 IN HYDROCHLORIC ACID

Dilute solutions of plutonium-238 in hydrochloric acid were prepared as described earlier. The solutions were allowed to stand for 2 weeks before they were examined.

Potentials of two series of plutonium-238 solutions are shown graphically in

FIGURE 5 - Potentials of 80% plutonium-238 solutions in dilute hydrochloric acid as a function of the logarithm of the acidity at two different plutonium concentrations.

Figure 5, which is a predominance region diagram for dilute hydrochloric acid.¹¹ Also sketched in the diagram is the Pu(III)/Pu(IV) potential boundary in dilute hydrochloric acid (dashed line).¹⁰ Examination of this diagram indicates that the potentials of dilute solutions of plutonium-238 in 1.2-1.8M hydrochloric acid are stabilized near the chlorine gas-chloride ion buffer region. As the acid concentration decreases below $\sim 1\text{M}$, there is a precipitous decrease in the solution potential. This precipitous drop in potential does not correspond to the Nernstian behavior of any easily apparent redox couple. The potential difference between 1.5M and 0.2M hydrochloric acid containing 0.01-0.02M plutonium-238 is approximately 850 mV. The relative concentrations of Pu^{4+} and Pu^{3+} in the solutions of plutonium-238 were approximately equal in 0.8M HCl; in solutions of

acidity lower than 0.6M, only Pu^{3+} was observed. In solutions whose potential was near the Cl_2/Cl^- buffer region, only Pu^{4+} and PuO_2^{2+} were found. The acidity

of solutions containing 5.81 mg/ml plutonium decreased 10% during a 2-week period.

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APPENDIX

One reason why the nature of the steady state of plutonium-238 in dilute acids is of interest is because the potential differences in such solutions allow the preparation of radioactive batteries which require only a small quantity of radioisotope for their operation. Hence, anode and cathode compartments of a cell containing 0.2M and 2M hydrochloric acid, respectively, and containing a few milligrams of dissolved plutonium-238 should be capable of developing a potential difference of several hundred millivolts. A few operational characteristics of a battery based upon nitric acid solutions of plutonium-238 have been evaluated.

Several solutions of plutonium-238 in nitric acid of various concentrations were prepared. Into one compartment of a wet cell was placed 100 ml of a 0.97M nitric acid solution containing plutonium-238 at a concentration of 2.4 mg/ml. Various other solutions of the same plutonium concentration but differing nitric acid concentrations were, in succession, placed in the other compartment of the wet cell. The two halves of the wet cell

were connected by means of two Leeds & Northrup salt bridges joined by a hollow glass tube filled with saturated potassium nitrate. A platinum foil electrode of 4 cm² total area was placed in each side of the wet cell. The voltages of the batteries so prepared were measured for each pair of plutonium solutions. Table A-1 presents the open circuit voltages of the battery, the voltages across a 10,000-ohm resistor, and the power developed for some typical plutonium-238 solutions of low acidity.

While the power developed by the nitric acid system is rather low, these data lead to interesting speculations. For example, Figure 5 shows that in hydrochloric acid solutions of plutonium-238 a maximum difference in potentials of 850 mV was observed. Table A-1 indicates that the voltage across a 10,000-ohm resistor for the nitric acid system was about half of the open circuit voltage. If this were also true of a hydrochloric acid wet cell, about 400 mV might be realizable. This corresponds to a power of 16 μ W. Now, it should be possible to use

Table A-1

SOME CHARACTERISTICS OF A PLUTONIUM-238/NITRIC ACID WET CELL

Solution Acidity (M)	Open Circuit Voltage (mV)	Voltage Across 10 ⁴ -Ohm Resistor (mV)	Power Generated (μ W)
0.13	72	34	0.116
0.19	65	28	0.078
0.23	54	25	0.063
0.45	35	16	0.026
0.52	23	11	0.012

small volumes (~2 ml) of solutions such that the total plutonium-238 requirement does not exceed 8 mg. This would correspond to an electrical conversion factor of ~2 mW per gram of isotope, which is greater than the thermal conversion factor of about 0.5 mW per gram of isotope in some presently employed radioisotope batteries. Moreover, many of the thermal conversion batteries presently employed do not contain energy storage devices (i.e., the heat is not stored for future use). In a chemical

system which is completely contained, it might be possible to store the radiation-generated redox agents (e.g., chlorine gas) in or above the electrolyte when the battery was not in use for utilization at a later time, thus using the energy of radioactive decay still more efficiently. Other cell designs (such as liquid junction cells) might also improve the efficiency, as might other factors such as electrodes of larger surface area.