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The Chemistry of Americium. IV. The Stability of Am(V) and Am(VI) in Nitric Acid Solutions and in the Solutions Containing Ozone Gas, Fluoride, or Phosphate Ions

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The coprecipitation technique with $BiPO_4$ and ThF_4 was applied to studying the stability of Am(V) and Am(VI) at concentrations lower than 10^{-6} M. It was found that ^{241}Am(V) and ^{241}Am(VI) were rapidly reduced to ^{241}Am(III) in nitric acid solutions at low acidities and at high temperatures, but the reduction was effectively inhibited by the presence of ozone gas or fluoride ions. On the other hand, ^{243}Am(V) and ^{243}Am(VI) were found to be rather stable in nitric acid solutions, while they were readily reduced to ^{243}Am(III) in phosphate solutions in the same manner as ^{241}Am(V) and ^{241}Am(VI).

Most investigations on the chemical properties of Am(V) and Am(VI) have been carried out by the use of an α-emitter $^{241}\mathrm{Am}(t_{1/2}=433\ \mathrm{y})$; its α-decay leads to the radiolytic reduction of Am(V) and Am(VI). In an Am(V) solution, Am(III) is observed as a product. Here the variation of Am(III) and Am(V) concentrations with time is expressed by an empirical equation:

$$-\frac{\mathrm{d[Am(V)]}}{\mathrm{d}t} = \frac{\mathrm{d[Am(III)]}}{\mathrm{d}t} = k_1[\mathrm{Am}]_\mathrm{T}, \qquad (1)$$

where k_1 is an apparent rate constant and $[\mathrm{Am}]_\mathrm{T}$ means the total americium concentration.

In an Am(VI) solution, Am(V) and Am(III) are observed as products. The decrease in the Am(VI) concentration with time can be expressed by an empirical equation:

$$-\frac{\mathrm{d[Am(VI)]}}{\mathrm{d}t} = k_2[\mathrm{Am}]_\mathrm{T}, \qquad (2)$$

where k_2 is an apparent rate constant. If no reactions other than the radiolytic reduction proceed, the growth of Am(V) can be expressed by an equation:

$$\frac{\mathrm{d[Am(V)]}}{\mathrm{d}t} = (k_2-k_1)[\mathrm{Am}]_\mathrm{T}. \qquad (3)$$

Values for k_1 and k_2 have been estimated to be 0.01 and 0.03 h^{-1}, respectively, in dilute acid solutions.[1,2]

When the long-lived isotope $^{243}\mathrm{Am}(t_{1/2}=7400\ \mathrm{y})$ is used, the radiolytic reduction is not so remarkable as that in ^{241}Am solutions.[3] On the other hand, ^{241}Am(V) and ^{243}Am(V) disproportionate to Am(VI) and Am(III) in moderately concentrated acids. The rate of disproportionation of ^{241}Am(V) in various media is expressed by the following equation,[4,5] but the rate law is rather complicated when ^{243}Am(V) is used:[3]

$$-\frac{\mathrm{d[Am(V)]}}{\mathrm{d}t} = k_3[\mathrm{Am(V)}]^2[\mathrm{H}^+]^4, \qquad (4)$$

where k_3 is an apparent rate constant.

This result has been obtained by the application of spectrophotometry to the ^{241}Am and ^{243}Am solutions at concentrations of 10^{-3} M or above. The ^{241}Am and ^{243}Am solutions diluted to about 10^{-7} M and 10^{-6} M, respectively, can be studied by radiometry. In dilute solutions, Am(V) may be free from any disproportionation, while the radiolytic reduction of ^{241}Am(V) and ^{241}Am(VI) may proceed, as suggested by Eqs. 1—4. Furthermore, Am(V) and Am(VI) may be reduced by small amounts of impurities.

The information concerning the instability of Am(V) and Am(VI) at low concentrations is rather poor. Only a little information was obtained by previous works[6,7] in which the instability of Am(V) in several media was studied by means of solvent extraction with 2-thenoyltrifluoroacetone and of column chromatography using bis(2-ethylhexyl) hydrogenphosphate (HDEHP) as an extractant, where the rapid reduction of ^{241}Am(VI) by HDEHP was observed.

When the solutions of Am(V) and Am(VI) were submitted to the coprecipitation method with some fluorides and phosphates at 0—5 °C, no change of oxidation states of americium was observed.[8,9] However, this finding can not always promise the high stability of Am(V) and Am(VI) in fluoride and phosphate solutions at room temperature or above.

In this work, the instability of Am(V) and Am(VI) in nitric acid solutions and in solutions containing ozone gas, fluoride, or phosphate ions was investigated. The change of oxidation state of americium with time was traced by means of the coprecipitation method with bismuth(III) phosphate and thorium(IV) fluoride.

Experimental

Reagents. Nitric acid solutions of ^{241}Am(III) and ^{243}Am(III) were prepared by the manners described before,[6,7] and the concentrations of ^{241}Am and ^{243}Am were determined by α-spectrometry using an Si detector connected to a multichannel pulse-height analyzer. Bismuth(V) sodium oxide was added in quantities of 10 mg/ml to a 0.1 M HNO_3 solution of Am(III), and the mixture was mechanically stirred for 50 min at room temperature and for additional 10 min at 0 °C. An Am(VI) solution was obtained by filtration of the mixture with a glass fibre filter-paper, Whatman GF/A.[10]

An Am(V) solution was prepared at 0 °C by passing the Am(VI) solution through a column of Celite 545 containing HDEHP as an extractant.[7] The solutions of nitric acid and ammonium fluoride or sodium dihydrogenphosphate were added to the Am(V) and Am(VI) solutions, making concentrations up to about 10^{-7} M and 10^{-6} M with respect to ^{241}Am and ^{243}Am, respectively.

Bismuth(V) sodium oxide, min 80 wt %, was used as an oxidant. For the coprecipitation test, bismuth(III) and thorium(IV) nitrates, sodium dihydrogenphosphate, and ammonium fluoride were used. These and other chemicals were of G.R. grade. Ozone gas, which was bubbled through the required solutions in order to eliminate as many reducing materials as possible, was supplied by an ozone generator.

Procedure. The Am(V) and Am(VI) solutions were stocked in a thermostat at a temperature kept constant with an accuracy of ±0.5 °C. Appropriate aliquots of the stock solutions were submitted to the coprecipitation test which was carried out under such conditions that Am(III) was quantitatively carried down, while most of Am(V) and Am(VI) remained in the solution.

Bismuth(III) phosphate and thorium(IV) fluoride were precipitated at 0 °C from the americium solution containing bismuth(III) and thorium(IV) ions, respectively, by the addition of excess precipitants under the following conditions:

Precipitate	$BiPO_4$	ThF_4
Volume	5 ml	3 ml
Acidity	0.5 M	0.1 M
Amounts of metal ion	Bi^{3+} 10 mg	Th^{4+} 1 mg
Time of mixing	7 min	10 min

The mixture was either filtered by glass fibre filter-paper or centrifuged at 6000 rpm for 5 min. The fraction of americium carried, Y, was determined by measuring the γ-activity in the mixture and the filtrate (or the supernatant). The γ-ray assay was performed by the use of a flat-type NaI(Tl) scintillation probe connected to a scaler or by the use of a Ge(Li) detector connected to a multi-channel pulse-height analyzer.

Results and Discussion

Stability of Am(V) and Am(VI) in HNO_3 Solutions. The $BiPO_4$ coprecipitation test was carried out on the nitric acid solutions of ^{241}Am(V) and ^{241}Am(VI) at proper time intervals. The results on the 0.5 M HNO_3 solutions at 0—40 °C and on the (0.125—2 M) HNO_3 solutions at 30 °C are shown in Figs. 1 and 2, respectively. The measured value for Y increased with time of storage, especially at high temperatures and at low acidities. Dependence of the increase in Y on acidity was found only for the Am(VI) solutions at temperatures higher than 20 °C.

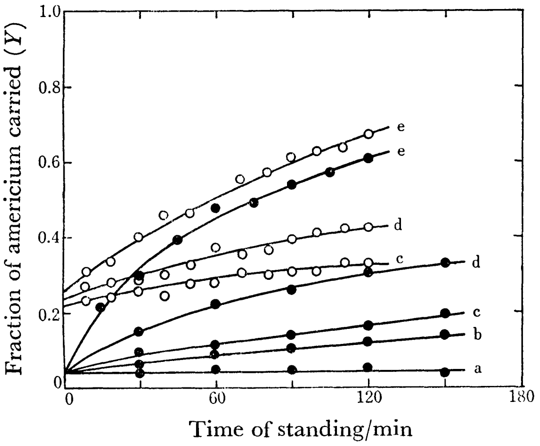

Fig. 1. The result of the $BiPO_4$ coprecipitation test carried out on the 0.5 M HNO_3 solutions of ^{241}Am(V) (○) and ^{241}Am(VI) (●) at 0 °C(a), 10 °C(b), 20 °C(c), 30 °C(d), and 40 °C(e).

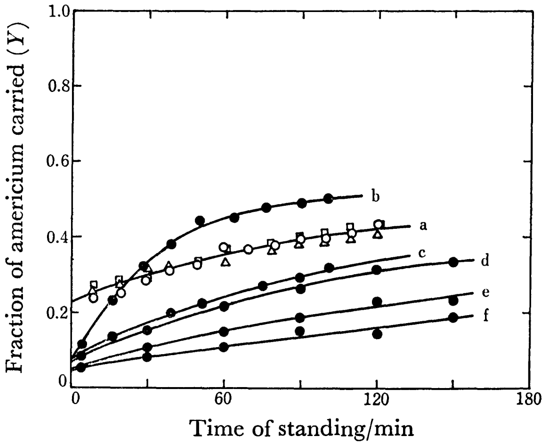

Fig. 2. The result of the $BiPO_4$ coprecipitation test carried out on the ^{241}Am(V) and ^{241}Am(VI) solutions at 30 °C.
a): ^{241}Am(V) solutions at the acidity of 0.125 M(○), 0.25 M(△), and 0.5 M(□). ●: ^{241}Am(VI) solutions at the acidity of 0.125 M(b), 0.25 M(c), 0.5 M(d), 1.0 M(e), and 2.0 M(f).

The increase in Y may be caused by the reduction of Am(V) and Am(VI) to Am(III) in the stock solutions, because Am(III) is more effectively carried by $BiPO_4$ than the others. When the mole fraction of each oxidation state of americium in the stock solution is expressed as f_X(X=III, V, and VI), Y may be given by the equation:[8]

$$Y = f_{III}Y_{III} + f_V Y_V + f_{VI} Y_{VI}, \tag{5}$$

where Y_X(X=III, V, and VI) means the fraction of Am(X) carried, which can be determined by the coprecipitation test on the corresponding single-component solution. The values for Y_X were determined as follows; $Y_{III}=0.99\pm0.01$, $Y_V=0.25\pm0.03$, and $Y_{VI}=0.05\pm0.02$ by the $BiPO_4$ coprecipitation test, and $Y_{III}=0.99\pm0.01$, $Y_V=0.12\pm0.02$, and $Y_{VI}=0.30\pm0.02$ by the ThF_4 coprecipitation test.

If the radiolytic reduction proceeds predominantly in the stock solutions of ^{241}Am, Eq. 5 can be expressed by the following equations, using the solutions of Eqs. 1—3: for the case of ^{241}Am(V) solutions,

$$Y = Y_V + (Y_{III} - Y_V)k_1 t \tag{6}$$

and for the case of ^{241}Am(VI) solutions,

$$Y = Y_{VI} + \{(Y_{III} - Y_{VI})k_1 + (Y_V - Y_{VI})k_2\}t. \tag{7}$$

Unfortunately, the linear relations expected by Eqs. 6 and 7 were valid only for the results on the stock solutions of high acidities and at low temperatures, as are shown in Figs. 1 and 2. It is clear that some reactions other than the radiolytic reduction also proceeded, especially at low acidities and at high temperatures. These reactions are assumed to be first-order reactions such as Am(VI)→Am(V) and Am(V)→Am(III), while the radiolytic reduction of Am(V) and Am(VI) are zero-order reactions with respect to Am(V) and Am(VI).

In contrast to Eqs. 1—3, the rate law for the above-mentioned reactions can be expressed as follows: in the case of ^{241}Am(V) solutions,

$$-\frac{\mathrm{d}[\mathrm{Am(V)}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Am(III)}]}{\mathrm{d}t} = k_1'[\mathrm{Am(V)}] \qquad (8)$$

and in the case of ^{241}Am(VI) solutions,

$$-\frac{\mathrm{d}[\mathrm{Am(VI)}]}{\mathrm{d}t} = k_2'[\mathrm{Am(VI)}], \qquad (9)$$

and $$\frac{\mathrm{d}[\mathrm{Am(V)}]}{\mathrm{d}t} = k_2'[\mathrm{Am(VI)}] - k_1'[\mathrm{Am(V)}], \qquad (10)$$

where k_1' and k_2' are apparent rate constants.

If first-order reactions proceed predominantly in the stock solutions, Eq. 5 can be written as follows, using the solutions of Eqs. 8—10:
for the case of ^{241}Am(V) solutions,

$$Y_{\mathrm{III}} - Y = (Y_{\mathrm{III}} - Y_{\mathrm{V}}) \exp(-k_1't), \qquad (11)$$

and for the case of ^{241}Am(VI) solutions,

$$Y_{\mathrm{III}} - Y = \frac{(Y_{\mathrm{III}} - Y_{\mathrm{V}})k_2'}{k_2' - k_1'} \exp(-k_1't) + \left\{(Y_{\mathrm{III}} - Y_{\mathrm{VI}}) + \frac{(Y_{\mathrm{III}} - Y_{\mathrm{V}})k_2'}{k_1' - k_2'}\right\} \exp(-k_2't). \qquad (12)$$

As Y_{III} is nearly equal to unity, Figs. 3 and 4 illustrate the plot of $\log(1-Y)$ *vs.* t, using the data shown in Figs. 1 and 2. The relationship expected by Eqs. 11 and 12 was confirmed for the stock solutions of low acidities and at high temperatures. Thus, it is reasonable to assume that the radiolytic reduction and first-order reactions compete in the dilute ^{241}Am solutions.

The values for k_1' and k_2' were estimated by means of curve-fitting techniques; the results are shown in Table 1. The values for k_1' and k_2' fluctuated, undoubtedly depending upon whether a nitric acid solution had been used to prepare the stock solutions just after or a little after the dilution of concd nitric acid. Therefore, a certain material which induced first-order reaction had been probably introduced into the stock solutions from the nitric acid.

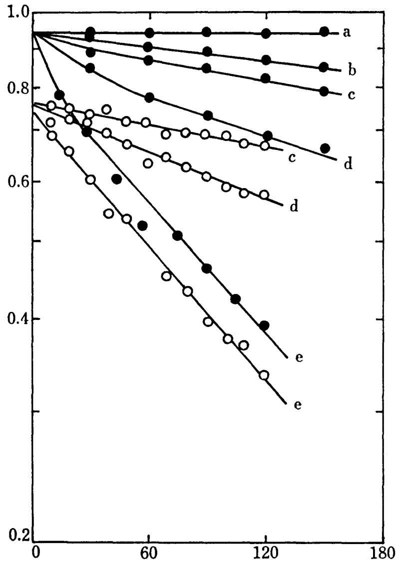

Fig. 3. The plot of $\log(1-Y)$ *vs.* t for the 0.5 M HNO_3 solutions of ^{241}Am(V)(○) and ^{241}Am(VI)(●) at 0 °C(a), 10 °C(b), 20 °C(c), 30 °C(d), and 40 °C(e).

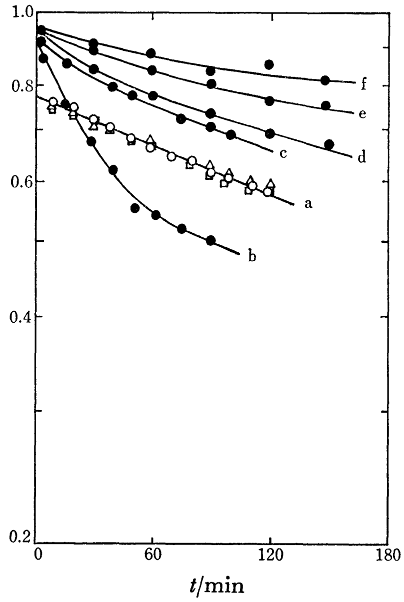

Fig. 4. The plot of $\log(1-Y)$ *vs.* t for the ^{241}Am(V) and ^{241}Am(VI) solutions at 30 °C. a): ^{241}Am(V) solutions at the acidity of 0.125 M(○), 0.25 M(△), and 0.5 M(□). ●: ^{241}Am(VI) solutions at the acidity of 0.125 M(b), 0.25 M(c), 0.5 M(d), 1.0 M(e), and 2.0 M(f).

TABLE 1. APPARENT RATE CONSTANTS FOR THE REDUCTION OF ^{241}Am(V) AND ^{241}Am(VI) IN HNO_3 SOLUTIONS

$[HNO_3]$ / M	Temperature / °C	Apparent rate constant/h^{-1}		
		k_1'[a)]	k_1'[b)]	k_2'[b)]
0.125	30	0.14±0.01	0.14±0.02	2.37±0.11
0.25	30	0.12±0.01	0.14±0.02	2.07±0.23
0.5	30	0.13±0.01	0.09±0.02	0.69±0.23
0.5	20	0.06±0.01	—	—
0.5	40	0.40±0.01	0.30±0.05	2.00±0.34

a) Result for Am(V) solutions. b) Result for Am(VI) solutions.

When the 0.05 M HNO_3 solutions of ^{243}Am(V) and ^{243}Am(VI) were investigated, no change in Y with time was observed even on the stock solutions at 30 °C. This finding may be explained only by the serious difference in emission rate of α-particles between ^{241}Am and ^{243}Am. Thus, first-order reactions are considered to be the radiation-induced reactions which may be caused by a product resulting from the interaction between the radiolysis product and the material introduced from the nitric acid.

This assumption was supported by a finding for the ^{241}Am(V) and ^{241}Am(VI) solutions containing ozone gas; that is, Y was constant for the time of storage during which the stimulative smell of ozone gas was still hanging about the vessel of the stock solutions. It can be said that ozone gas effectively eliminates any reducible materials in the same way as chlorine gas does.[4)]

Stability of Am(V) and Am(VI) in HNO_3-NH_4F Solutions. The coprecipitation test with ThF_4 was carried out on the 0.05 M HNO_3 solutions of ^{241}Am(V) and ^{241}Am(VI) containing the fluoride at 30 °C, and the result is shown in Fig. 5. The Y for the stock solutions

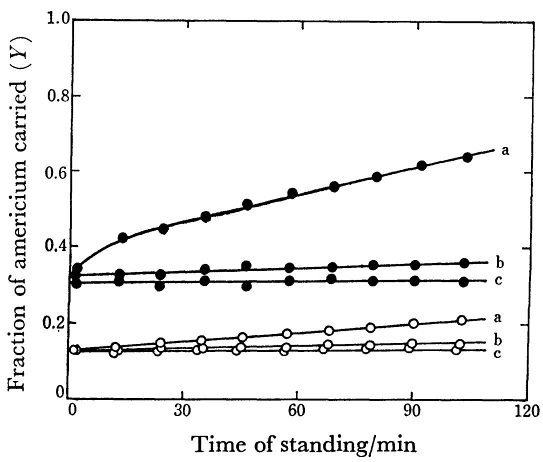

Fig. 5. The result of the ThF_4 coprecipitation test carried out on the 0.05 M HNO_3 solutions of ^{241}Am(V) (○) and ^{241}Am(VI) (●) at 30 °C. [NH_4F]: a) 0 M, b) 0.05 M, and c) 0.5 M.

containing the fluoride increased more slowly than for the case free from fluoride, and no change in Y was observed for the 0.5 M NH_4F solutions. The stock solutions of acidity higher than 0.05 M called for rather high concentrations of the fluoride in order to minimize the variation in Y.

This finding can be explained by the suggestion that ^{241}Am(V) and ^{241}Am(VI) become free from all reduction reactions if they form fluoro complexes, as in the cases of the acetate[7] and the chloride solutions[11] of ^{241}Am(V). The excellent stability of ^{243}Am(V) and ^{243}Am(VI) in the ozonized fluoride solutions was also confirmed as expected.

Stability of Am(V) and Am(VI) in HNO_3–NaH_2PO_4 Ozonized Solutions. The coprecipitation test with $BiPO_4$ was carried out on the 0.05 M HNO_3–(0—2 M) NaH_2PO_4 and the (0.025—0.2 M) HNO_3–0.5 M NaH_2PO_4 solutions of ^{241}Am(V) and ^{241}Am(VI) at 30 °C. The Y for these ozonized solutions increased rapidly with time of storage, especially at low acidities and at high phosphate concentrations. Figures 6 and 7 illustrate the plot of $\log(1-Y)$ *vs.* t; a good linearity was obtained in most cases.

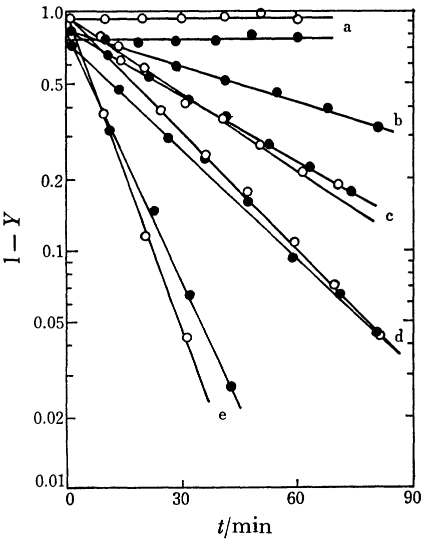

Fig. 6. The plot of $\log(1-Y)$ *vs.* t for the 0.05 M HNO_3 solutions of ^{241}Am(V) (○) and ^{241}Am(VI) (●) at 30 °C. [NaH_2PO_4]: a) 0 M, b) 0.1 M, c) 0.5 M, d) 1.0 M, and e) 2.0 M.

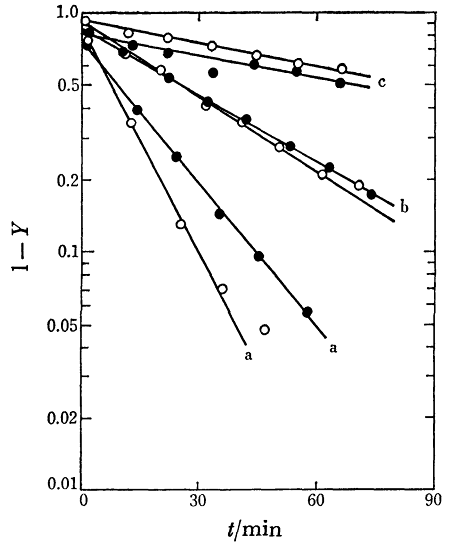

Fig. 7. The plot of $\log(1-Y)$ *vs.* t for the 0.5 M NaH_2PO_4 solutions of ^{241}Am(V) (○) and ^{241}Am(VI) (●) at 30 °C. [HNO_3]: a) 0.025 M, b) 0.05 M, and c) 0.2 M.

The same result was obtained both for the 0.05 M HNO_3–0.5 M NaH_2PO_4 solutions of ^{241}Am(V) and ^{241}Am(VI) at 0—40 °C and for the (0.05—0.5 M) HNO_3–1 M NaH_2PO_4 solutions of ^{243}Am(V) and ^{243}Am(VI) at 30 °C. Evidently, the variation in Y with time for the ozonized phosphate solutions of ^{241}Am(VI) and ^{243}Am(VI) can be explained neither by Eq. 7 nor by Eq. 12.

It is known that Am(VI) at such high concentrations as 2×10^{-3} M (^{243}Am 85% and ^{241}Am 15%) is reduced to Am(III) in phosphoric acid.[12] Then, it may be assumed that Am(V) and Am(VI) at low concentrations are also reduced to Am(III) in the ozonized phosphate solutions, and that the reduction rates are given by the following equations:

$$-\frac{d[\mathrm{Am(V)}]}{dt} = \frac{d[\mathrm{Am(III)}]}{dt} = k_1''[\mathrm{Am(V)}], \qquad (13)$$

and

$$-\frac{d[\mathrm{Am(VI)}]}{dt} = \frac{d[\mathrm{Am(III)}]}{dt} = k_2''[\mathrm{Am(VI)}], \qquad (14)$$

where k_1'' and k_2'' are apparent rate constants. If the change of oxidation states of americium in the ozonized phosphate solutions is predominantly caused by these reactions, Y can be expressed as follows, using the solutions of Eqs. 13 and 14:

for the case of Am(V) solutions,

$$Y_{\mathrm{III}} - Y = \exp(-k_1''t) \qquad (15)$$

and for the case of Am(VI) solutions,

$$Y_{\mathrm{III}} - Y = \exp(-k_2''t). \qquad (16)$$

As Y_{III} is nearly equal to unity, Eqs. 15 and 16 can explain the linearity obtained by the plot $\log(1-Y)$ *vs.* t, as are shown in Figs. 6 and 7. Therefore, it seems to be reasonable to assume that Am(V) and Am(VI) are reduced to Am(III) in the ozonized phosphate solutions.

Table 2. Apparent rate constants for the reduction of Am(V) and Am(VI) in HNO_3-NaH_2PO_4 ozonized solutions

$[HNO_3]$ / M	$[NaH_2PO_4]$ / M	Temperature / °C	Apparent rate constant/h^{-1}	
			k_1''[a)]	k_2''[a)]
0.05	0	30	-0.02 ± 0.03	-0.05 ± 0.02
0.05	0.1	30	—	0.67 ± 0.01
0.05	0.5	30	1.44 ± 0.04	1.28 ± 0.02
0.05	1.0	30	2.32 ± 0.05	2.13 ± 0.04
0.05	2.0	30	6.10 ± 0.04	4.78 ± 0.04
0.05	0.5	0	-0.06 ± 0.03	0.00 ± 0.02
0.05	0.5	15	0.14 ± 0.03	0.12 ± 0.02
0.05	0.5	40	7.63 ± 0.06	6.08 ± 0.06
0.025	0.5	30	4.23 ± 0.04	2.71 ± 0.02
0.1	0.5	30	0.65 ± 0.04	0.55 ± 0.04
0.2	0.5	30	0.40 ± 0.03	0.30 ± 0.05
0.05	0	30	0.02 ± 0.01[b)]	0.02 ± 0.02[b)]
0.05	0.1	30	1.00 ± 0.02[b)]	1.39 ± 0.02[b)]
0.05	1.0	30	10.5 ± 0.1[b)]	8.98 ± 0.02[b)]
0.5	1.0	30	2.89 ± 0.02[b)]	5.80 ± 0.03[b)]

a) Result for ^{241}Am solutions except as otherwise noted.
b) Result for ^{243}Am solutions.

Values for k_1'' and k_2'' were obtained from the slope of the straight lines. They were found to be rather large for the stock solutions of low acidities, at high phosphate concentrations, and at high temperatures, as are summarized in Table 2. The reduction of $^{243}Am(V)$ and $^{243}Am(VI)$ preceeded more rapidly than that of $^{241}Am(V)$ and $^{241}Am(VI)$ because the ^{243}Am concentration was about ten times higher than the ^{241}Am concentration.

The available information concerning the behavior of americium in phosphoric acid[12)] and the phosphato-complex formation of neptunium and plutonium[13,14)] suggests that Am(V) and Am(VI) may form the phosphato complexes such as $AmO_2H_2PO_4$ and $AmO_2H_2PO_4^+$, respectively, in the phosphate solutions examined. Therefore, the rapid reduction of Am(V) and Am(VI) might result from the intramolecular electron transfer in phosphato complexes.

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