Hydrolysis Reactions of Am(III) and Pu(VI) Ions in Near-Neutral Solutions

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Hydrolysis reactions of Am(III) and Pu(VI) ions in CO_2-free solutions of 0.1 M $NaClO_4$ were studied by means of solubility experiments using the oxide or hydroxide of ^{241}Am and ^{238}Pu. The pH of solutions was varied from 3 to 13.5. All experiments were carried out under an argon atmosphere. The speciation of dissolved species was determined as far as possible by spectrophotometry. Various ultrafiltration membranes were applied to examine the proper phase separation. Stability constants of all possible hydrolysis products are presented and compared with literature data.

Hydrolysis reactions are common to all actinide ions in near-neutral solutions, and take place either in parallel with or predominantly over other complexation reactions. In connection with the migration studies of actinide ions in natural waters, attention recently has been focused on hydrolysis reactions of actinides since these reactions are important in determining the solubility of the actinide hydroxide or oxide. Although numerous studies have been made (1-4) to determine stability constants of various hydrolysis products, much of the necessary data are still lacking. The acquisition of these data and further improvement or verification of the existing data is desirable.

In a series of investigations to assess geochemical parameters of various complexation reactions, the present paper concentrates on hydrolysis reactions of the Am^{3+} and PuO_2^{2+} ions in the pH range from 3 to 13.5. For the Am^{3+} ion, a number of papers (5-10) report the formation constant of the monohydroxide species $Am(OH)^{2+}$. While the present experiment was in progress, Rai et al. (5) presented the data for various hydrolysis products. In contrast to the Am^{3+} ion, much more data are available for the hydrolysis reactions of the PuO_2^{2+} ions including its polymerization reactions (11-19). The present study therefore complements and verifies the hitherto existing data for hydrolysis reactions of the two actinide ions.

Experimental

The present experiment comprises solubility measurements as a function of the pH (3 ~ 13.5). In order to obviate the dissolution of CO_2 from air, especially in solutions with pH > 7, all experiments were carried out under an argon atmosphere. For the same reason, only CO_2-free chemicals, e.g., NaOH and $NaClO_4$, were used and handled in an inert gas (argon) box. Sodium hydroxide from Baker Co. was heated in an inert gas oven for several hours at 150°C and the $NaClO_4$ solution was prepared by mixing NaOH and $HClO_4$ solutions in the inert gas box. The doubly distilled water was pretreated by deaerating with argon and stored in the inert gas box prior to preparation of desired experimental solutions.

Am(III) Hydrolysis.

For studying hydrolysis reactions of the Am^{3+} ion, two solid compounds of ^{241}Am, namely AmO_2 and $Am(OH)_3 \cdot nH_2O$, were used. The AmO_2 was treated in a thermogravimetric oven at 1,000°C for one hour under oxygen gas to ensure formation of the dioxide. The $Am(OH)_3 \cdot nH_2O$ was prepared by dissolving AmO_2 in 0.1 M $HClO_4$ and precipitating the hydroxide through addition of a slightly over stoichiometric amount of concentrated NH_4OH. The precipitate was filtered, washed with doubly distilled water until the wash solution reached a pH of 7, and dried in the inert atmosphere box to eliminate surface moisture. Experimental solutions of different pH containing 0.1 M $NaClO_4$ were prepared by addition of 0.1 M $HClO_4$ or 0.1 M NaOH. To each 25 mL of solution in a glass vial, about 3 mg AmO_2 or about 6 mg of $Am(OH)_3 \cdot nH_2O$ (15 mg AmO_2 to solutions of pH < 4) was introduced and all solutions were stored under argon gas.

In a separate experiment, the hydroxide precipitate of americium was produced directly in each experimental solution: 10 mL solution of 0.1 M $HClO_4$ containing 1.3×10^{-3} M americium was mixed with 10 mL of 0.1 M $NaClO_4$ and made alkaline to produce the hydroxide precipitate by adjusting the pH with addition of NaOH. Solutions thus prepared were left under argon gas to attain the solubility equilibrium.

Pu(VI) Hydrolysis.

For easy radiometric measurement, ^{238}Pu was chosen for this experiment. The PuO_2 was dissolved in boiling 1 M $HClO_4$ (8.6×10^{-3} M plutonium). The dissolved plutonium ion appeared to be hexavalent as verified by spectrophotometric analysis. One milliliter of this solution was diluted to 40 mL with 0.075 M $NaClO_4$ and the pH adjusted by addition of dilute NaOH or $HClO_4$. The PuO_2^{2+} ion originally introduced is immediately precipitated by increasing the pH of the solution. The solutions were stored under argon gas for several days before beginning solubility measurements.

<u>Sampling and Measurements</u>. The determination of dissolved actinide concentration was started a week after the preparation of solutions and continued periodically for several months until the solubility equilibrium in each solution was attained.   Some solutions, in which the solubilities of americium or plutonium were relatively high, were spectrophotometrically analyzed to ascertain the chemical state of dissolved species. For each sample, 0.2 to 1.0 mL of solution was filtered with a Millex-22 syringe filter (0.22 µm pore size) and the actinide concentration determined in a liquid scintillation counter. After filtration with a Millex-22, randomly chosen sample solutions were further filtered with various ultrafilters of different pore sizes in order to determine if different types of filtration would affect the measured concentration.   The chemical stability of dissolved species was examined with respect to sorption on surfaces of experimental vials and of filters. The experiment was performed as follows: the solution filtered by a Millex-22 was put into a polyethylene vial, stored one day, filtered with a new filter of the same pore size and put into another polyethylene vial. This procedure was repeated twice with two new polyethylene vials and the activities of filtrates were compared. The ultrafiltration was carried out by centrifugation with an appropriate filter holder. The results show that the dissolved species in solution after filtration with Millex-22 (0.22 µm) do not sorb on surfaces of experimental materials and that the actinide concentration is not appreciably changed with decreasing pore size of ultrafilters. The pore size of a filter is estimated from its given Dalton number on the basis of a hardsphere model used in the previous work (<u>20</u>).
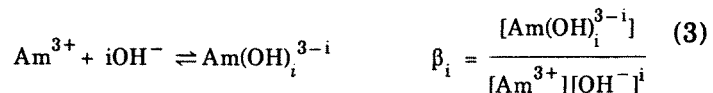
Results and Discussion

<u>Solubility of Americium Hydroxide</u>. Solutions containing greater than 10^{-6} M americium were examined by spectrophotometry to verify whether or not polymers were present.   The molar extinction coefficient measured for the 503 nm absorption band was found to remain constant at $\varepsilon = 390 \pm 5$ for all investigated solutions at pH = 3 ~ 6. Spectra recorded up to 850 nm in this pH range show the typical absorption bands of the Am^{3+} ion, which are similar to those observed in a dilute $HClO_4$ solution, without broadening or displacement. The concentration of americium ions in equilibrium solutions, [Am]s, is, therefore, considered a composite of only monomer species:

$$[Am]s = [Am^{3+}] + [Am(OH)^{2+}] + - - - + [Am(OH)_i^{3-i}] \qquad (1)$$

Since experiments are carried out at a constant ionic strength (I) and equilibrium concentrations of americium in solutions are found to be less than $10^{-4.8}$ M, all calculations are made on the

concentration basis. Equation 1 can be transformed into a function of the free proton or hydroxide ion concentration which contains the solubility product Ksp and formation constant β_i:

$$Am(OH)_3 \rightleftharpoons Am^{3+} + 3\,OH^- \qquad\qquad K_{sp} = [Am^{3+}][OH^-]^3 \quad (2)$$

$$Am^{3+} + iOH^- \rightleftharpoons Am(OH)_i^{3-i} \qquad \beta_i = \frac{[Am(OH)_i^{3-i}]}{[Am^{3+}][OH^-]^i} \quad (3)$$

and hence gives

$$[Am]_s = \frac{K_{sp}}{[OH^-]^3} \sum_{i=0} \beta_i[OH^-]^i \qquad\qquad (4)$$

The free hydroxide concentration is calculated from the pH measurement at the equilibrium state of each solution, using the ion product of water $Kw = 10^{-13.78}$ at $I = 0.1$ (1).

Calculation of the constants Ksp and β_i, using Equation 4, is made with the help of a least square fitting of the well known Simplex algorithm. As is apparent from the experimental points plotted as a function of the OH⁻ concentration, shown in Figure 1 (curve a), the i value does not exceed 3. The hydrolyzed species of americium therefore consist of $Am(OH)^{2+}$, $Am(OH)_2^+$ and $Am(OH)_3^0$. Calculated Ksp and β_i values are given in Table I, together with the literature data which are converted by the relation:

$$\beta_i = \frac{\beta_i^*}{Kw^i} \qquad\qquad (5)$$

where β_i^* is the constant for the reaction: $Am^{3+} + iH_2O \rightleftharpoons Am(OH)_i^{3-i} + iH^+$. For the conversion, Kw is taken from the literature (1) acording to the ionic strength used by each author. The values of Ksp and β_i reported for this work were calculated from an average of two experimental runs (the second run is not given). Estimated values for Ksp and β_i reported in the literature (2) are not included in this table. Only experimental values (6-10) are given. Except the work of Rai et al. (5), four other authors report β_1 values, one β_2 and none β_3. The solubility product of $Am(OH)_3$ by Rai et al. appears somewhat higher than ours, by 4 logarithmic units. Given the difficulties involved in the experiment, the discrepancy observed in the results from the two laboratories is not surprising. There is no doubt, however, that a better agreement is desirable. As described above, the present experiment was conducted using two different methods, either starting with a solid americium hydroxide present in solution or
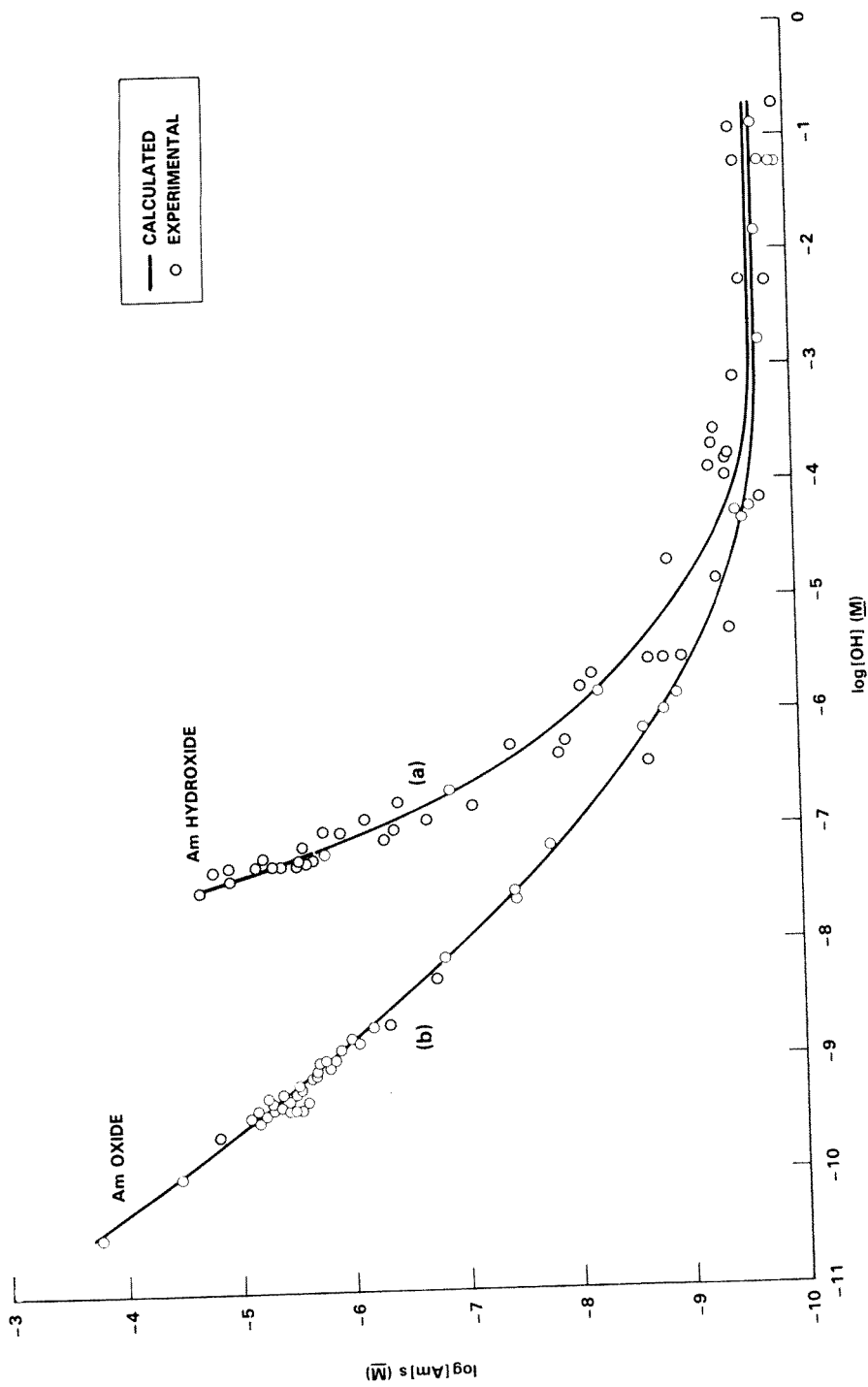
Figure 1. Solubilities of AmO_2 and $Am(OH)_3 \cdot nH_2O$ as a Function of the Equilibrium OH^- Concentration. The Solid Lines represent Calculations by Equations 4 and 12.

Table I. The Stability Constants and Solubility Products
of Am(III) Hydroxides (cf. Equations 2 and 3)[a]

log Ksp	log β_1	log β_2	log β_3	Medium	Reference
-27.16 ± 0.47 (-28.56)[c]	7.44 ± 0.83 (8.03)	13.92 ± 0.63 (14.93)	18.47 ± 0.52 (19.70)	0.1 M NaClO$_4$	This work
-24.34 (-24.62)	≥5.96 (≥5.96)	10.94 (10.94)	≥14.53 (≥14.53)	0.003 M CaCl$_2$	5
–	10.7 (10.9)	20.9[b] (21.2)	–	0.005 M NH$_4$ClO$_4$	6
–	11.3 (11.5)	–	–	0.001 M KCl	7
–	6.77 (7.90)	–	–	1 M NaClO$_4$	8
–	7.86 (8.47)	–	–	0.1 M NaClO$_4$	9
–	–	12.8 (14.6)	–	0.2 M NaClO$_4$	11

[a]The literature values are converted with the Kw values from Reference (1).
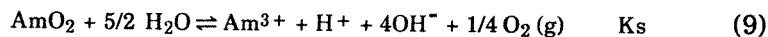[b]Estimated value.
[c]The values in parentheses are thermodynamic data calculated by the method and
input constants given in Reference (1).

producing a precipitate directly in each experimental solution. Both processes result in the same solubilities over a wide range of pH. Therefore, the present experiment involves reversible as well as reproducible reactions. Should polymers be produced in these solutions, the experiment in which the precipitation is made directly in solution by introducing an excess amount of the americium ion would result in higher solubility due to polymer formation than the experiment that is started with the solid americium hydroxide in solution. Once polymers are formed, they are not expected to depolymerize easily in near neutral solutions.

Spectrophotometric experiments, however, do not provide straightforward evidence for the existence of small amounts of americium hydroxypolymers. In order to compare the literature data with one another and with our data, they are transformed to thermodynamic data at I = 0 according to Baes and Mesmer (1), using the salt effect constants assessed by them. These data are given in parentheses in Table I. The first hydrolysis constants given in the literature differ from one another considerably. For lanthanide ions, log β_1 values are reported from 3.7 to 6.3 (1), which are distinctly lower than that of americium shown in Table I.

It has been suggested that the lattice parameter or ionic radii may be correlated with the hydrolysis constants of lanthanides and solubility products of Ln(OH)$_3$ (1). Whether such a correlation can be extended to trivalent actinides is not certain because supporting evidence is lacking. The similarity of Am^{3+} to Nd^{3+} assumed for hydrolysis behavior (5) still requires experimental foundation. The β_1 values known hitherto for americium (5-9) by no means corroborate this assumption. The β_1 value from this work is found to be close to the values from Desire et al. (9) and Nair et al.(8). Only two β_2 values are given in the literature, (5)(11) except for the estimated one (6). Our results are in fair agreement with the value of Bidoglio (10). The β_3 value of Rai et al. is given as a lower limit, so that the real value may be higher. In this respect our β_3 value seems to be in the correct direction. The log β_2 and log β_3 values for lanthanide ions are about 12 and 17 (1), respectively, which are somewhat lower than our values for the americium ion. In the present experiment there is no indication of formation of anionic hydrolysis products, not even the Am(OH)$_4^-$ species, although an analogous product is considered to form with lanthanides (1).

Solubility of Americium Oxide. The dissolution process of AmO$_2$ under normal or anoxic conditions in near neutral to alkaline solution includes the reduction of Am^{4+} to Am^{3+}, which turns the solution phase gradually into an oxidizing medium as AmO$_2$ dissolves. For this reason, the solubility of AmO$_2$ with respect to pH differs distinctively from that of Am(OH)$_3$ at pH < 9. The primary dissolution process may be expressed as follows:

$$AmO_2 + 2H_2O \rightleftharpoons Am^{4+} + 4OH^- \qquad\qquad K_1 \qquad (6)$$

$$Am^{4+} + e^- \rightleftharpoons Am^{3+} \qquad\qquad K_2 \qquad (7)$$

$$1/2\ H_2O \rightleftharpoons H^+ + e^- + 1/4\ O_2(g) \qquad\qquad K_3 \qquad (8)$$

$$AmO_2 + 5/2\ H_2O \rightleftharpoons Am^{3+} + H^+ + 4OH^- + 1/4\ O_2(g) \qquad Ks \qquad (9)$$

and the dissolution constant Ks is given by

$$Ks = K_1 K_2 K_3 = [Am^{3+}][OH^-]^3\ Kw[O_2(g)]^{0.25} \qquad (10)$$

The total concentration of trivalent americium species produced in the dissolution process is equivalent to $[O_2(g)]^{0.25}$. If all of these species are assumed to remain in solution, the following relation can be postulated:

$$[Am]_s{}^x = [O_2(g)]^{0.25} \qquad (11)$$

where $[Am]_s{}^x$ is the total concentration of americium in solution dissolved from AmO_2. In solution, all dissolved species are considered to be the same as those given by Equation 1, so that the solubility function of AmO_2 can be expressed on the basis of Equations 1, 3, 10, and 11 such that:

$$[Am]_s{}^x = \frac{Ks}{Kw[Am]_s[OH^-]^3} \sum_{i=0} \beta_i[OH^-]^i \qquad (12)$$

The method used for solution of Equation 12 for Ks and β_i values was similar to that used for Equation 4.

As mentioned above, because of the dissolution of AmO_2, the redox potential of an equilibrium solution is changed as a function of pH as well as $[Am]_s{}^x$. A combination of Equations 8 and 11 leads to the relationship:

$$pe + pH = 20.78 + log[Am]_s{}^x \qquad (13)$$

where 20.78 is calculated from the free energy of formation for a half mole water $[1/2\ \Delta G_f{}^\circ\ (H_2O) = 56.69$ kcal/mole and the redox potential, $Eh(mV) = 59.2\ pe]$. In the present experiment $pe + pH$ is constant only at the region where the $[Am]_s{}^x$ remains unchanged with pH (>9) and hence $pe + pH = 11.08$. This value increases gradually with increasing $[Am]_s{}^x$ and consequently the solution becomes more oxidizing with decreasing pH. Therefore, the dissolution of AmO_2 differs from that of $Am(OH)_3$ as observed in Figure 1 (curve b).

The situation may be comparable to deep groundwater, which is also an anoxic system. The change of pe + pH in the present experiment is shown in Figure 2.

The hydrolysis constants of the Am^{3+} ion from the AmO_2 solubility experiment are only in fair agreement with those from the $Am(OH)_3$ experiment. They are determined to be $\log \beta_1 = 8.82$, $\log \beta_2 = 14.68$, and $\log \beta_3 = 19.00$, which are slightly higher than the values given in Table I with the difference in order: $\Delta\beta_1 > \Delta\beta_2 > \Delta\beta_3$. To a certain extent, but not satisfactorily, these results justify the postulation of Equation 11. The reason for these results is not yet fully understood.

Solubility of PuO_2^{2+} Hydroxide. Solubilities of plutonium in equilibrium solutions are given in Figure 3 as a function of the pH. Dissolved hydrolysis products of the PuO_2^{2+} ion are examined up to the limit of spectrophotometric sensitivity, namely $[PuO_2^{2+}] > 10^{-5}$ M, to characterize their species. A few samples at pH = 5.5 to 6.5 show the concentration of dissolved plutonium to be high enough to be analyzed by spectrophotometry. A typical analytical result is shown in Figure 4. After the filtration with a Satorius 14529 membrane, the solution having $10^{-4.2}$ M plutonium at pH $\simeq 5.8$ manifests no typical features of the PuO_2^{2+} ion spectrum in the UV and NIR region. When the solution is brought to pH $\simeq 1$ by addition of a few drops of 1 M $HClO_4$, the peak at 830 nm appears after 25 minutes, growing slowly, and after 24 hours turns into a spectrum that can be ascribed to the PuO_2^{2+} ion. Upon acidification with HNO_3, the same result is obtained after 2 days. The observation at pH ~6 differs completely from studies reported in the literature (14)(18) which show the distinctive spectra of Pu(VI) solutions at the same pH. Their plutonium concentrations are $10^{-3.6}$ M (14) and $10^{-2.8}$ M (18), which are higher than can be maintained in the solution at pH ~6. The concentration we observed for this condition is about $10^{-4.2}$ M and does not change during several weeks of dissolution. At pH >6, the concentration of plutonium in solution decreases rapidly and at pH >9 reaches $[Pu]_s = 10^{-7.5}$ M. Spectra presented in the literature (14)(18) at pH = 6.5 to 11.0 cannot be reproduced in these experiments. The present experiment demonstrates that the solution at pH ~6 contains polymers, possibly devoid of the free PuO_2^{2+} ion which can be produced only by acidification. If the acidified solution is again made alkaline to pH >9, the plutonium concentration decreases to $< 10^{-7.5}$ M.

This result supports the conclusion that in the reasonably short time of these experiments no oxidation states are involved other than the Pu(VI) species, and that the hydrolysis reaction of the PuO_2^{2+} ion includes polymerization. Since there is no straightforward method to specify each polymer species involved, the most plausible species known in the literature (1)(17)(19) are considered (i.e., x,y = 2,2 and 3,5 of $M_x(OH)_y$).
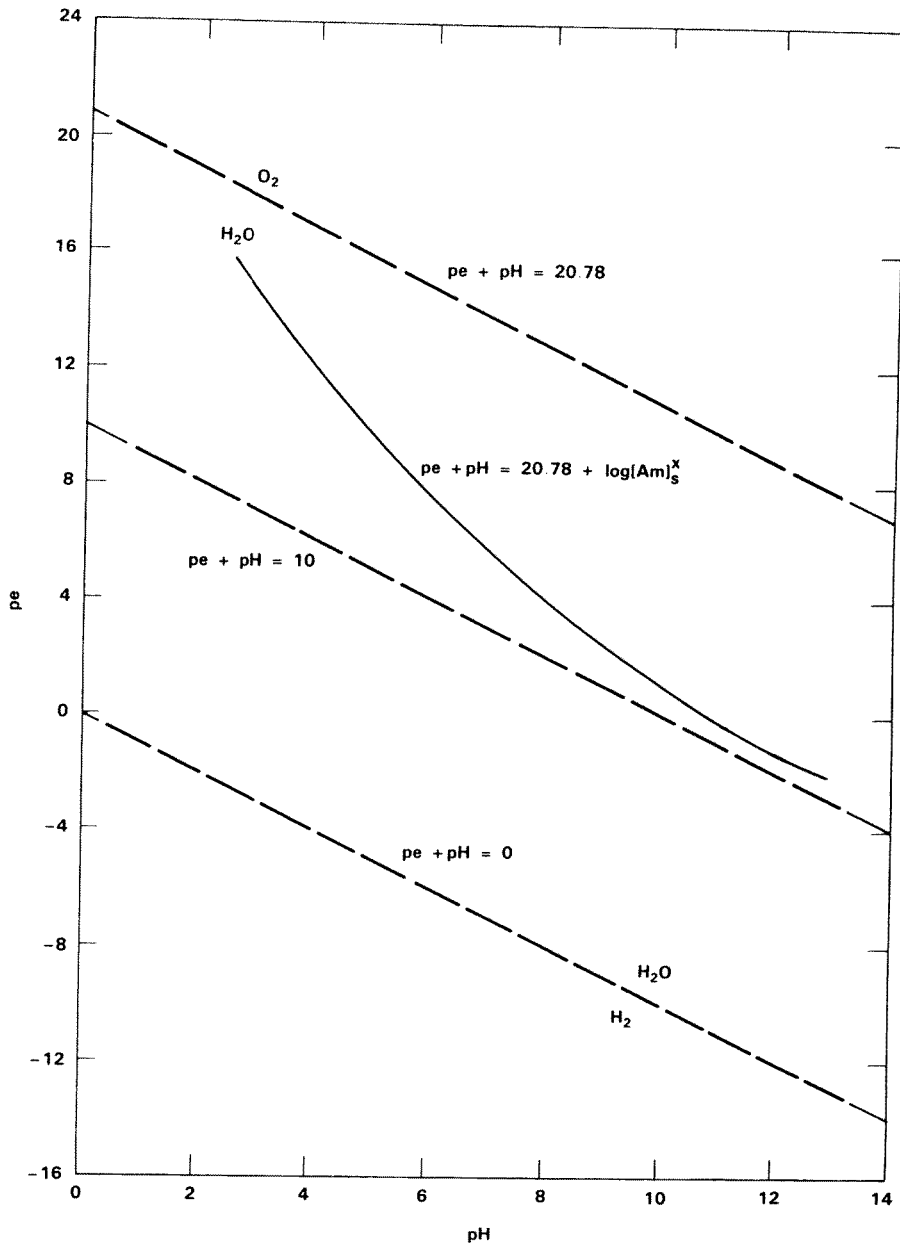
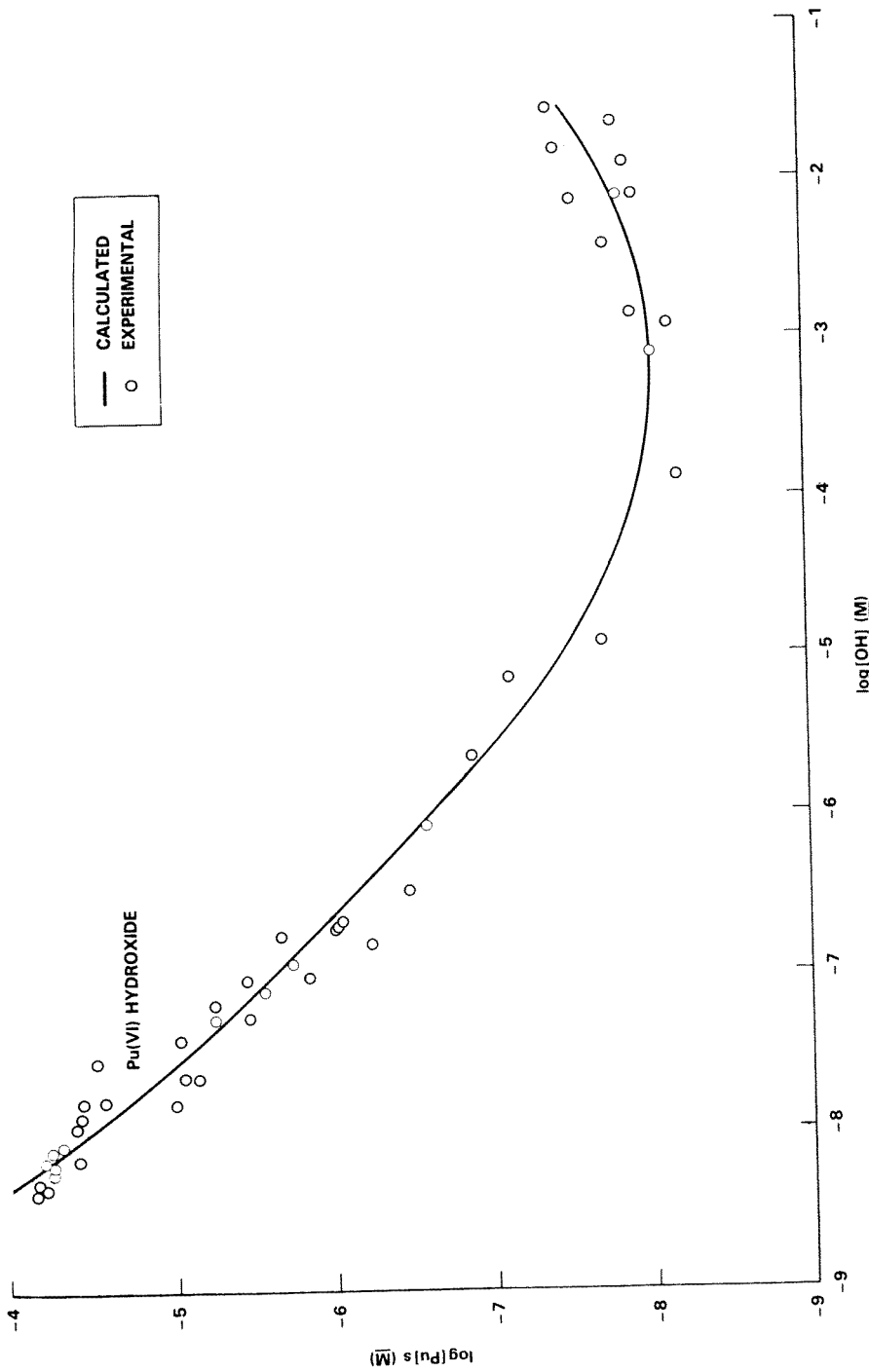Figure 2. The Change of pe + pH in Dissolution Equilibria of AmO_2 (see Equation 13).

Figure 3. Solubilities of $PuO_2(OH)_2 \cdot nH_2O$ as a Function of the Equilibrium OH^- Concentration. The Solid Line Represents Calculation by Equation 15.
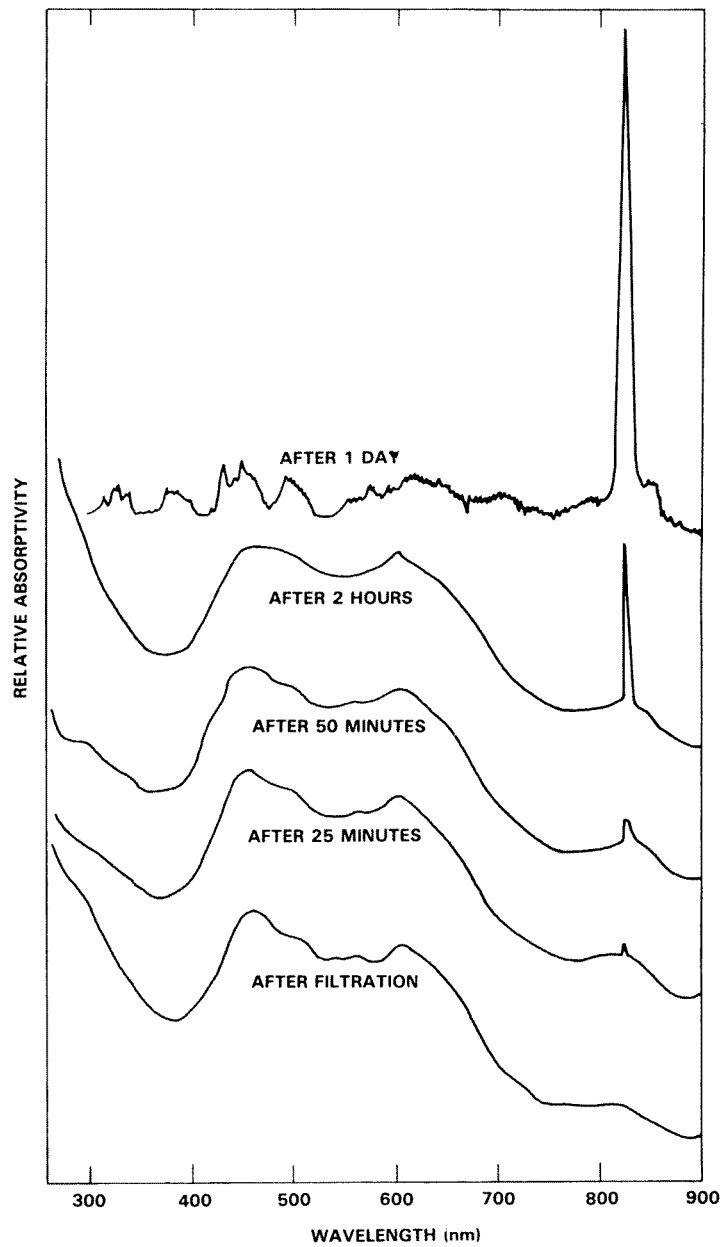
Figure 4. Absorption Spectra of the Pu(VI) Solution ([Pu]s = $10^{-4.2}$ M) Which Change Gradually After Acidification to pH = 1. The Initial Solution at pH = 5.8 is Filtered with a Satorious 14528 Filter (~0.6 nm pore size).

The dissolved Pu(VI) species are therefore considered to include the following hydrolysis products:

$$[Pu]s = [PuO_2^{2+}] + [PuO_2(OH)^+] + \text{- - -} + [PuO_2(OH)_i^{2-i}]$$
$$+ [(PuO_2)_2(OH)_2^{2+}] + [(PuO_2)_3(OH)_5^+] \quad (14)$$

which can be expressed by a general solubility function:

$$[Pu]s = \frac{Ksp}{[OH]^2} \sum_{i=0} \beta_i[OH]^i + \frac{Ksp^2}{[OH]^2} \beta_{2,2} + \frac{Ksp^3}{[OH]} \beta_{3,5} \quad (15)$$

Calculation of experimental constants in Equation 15 was performed by the same least square fitting computer program as used for the americium experiments. The stability constants of hydrolysis products thus determined for the PuO_2^{2+} ion are given in Table II together with the data from the literature. The solubility product from the present work is fortuitously in good agreement with the literature values (14)(18) although somewhat better with the data of Moskvin and Zaitseva (14) than that of Musante and Porthault (18). These data, including our value, can be considered only as tentative ones since the determination of the solubility product in the presence of polymers is not absolutely reliable. The stability constant of the first hydrolysis product is found to be closer to the values of Cassol et al. (17) and Kraus and Dam (12) than those of other authors (13-14)(18), whereas for the second and third hydrolysis products our values are lower than the literature data. The present experiment demonstrates the higher stability of the polymers in question as shown by their formation constants which appear to be larger than those from the literature (17)(19). Obviously, the formation of polymers is enhanced at the expense of monomer hydrolysis products. Due to the arbitrary choice of the polymer species for the calculation with Equation 15, it is not ventured to evaluate errors for the constants given in Table II. For the same reason, assessment of thermodynamic values is not attempted.

Speciation of Dissolved Species. Since there is no straightforward method to identify the dissolved species in solubility experiments, indirect approaches were applied in this experiment.

To verify whether or not colloid species were present in solution, phase separation was thoroughly examined with different ultrafilters. Tables III and IV show results from various ultrafiltrations for the Am(III) and Pu(VI) solutions, respectively. The solution at solubility equilibrium was first filtered with the Millex-22 (0.22 μ) filter and further passed through different ultrafilters of nearly the same pore size (~2 nm). Table III demonstrates that the americium concentration in filtrates

remains constant, although a small decrease of concentration is observed after filtration with Amicon CF 25 and Amicon YMT. This effect may be due to surface sorption. A similar experiment for the Pu(VI) solution with other ultrafilters of different pore sizes shown is presented in Table IV. The plutonium concentration was unchanged by filtration. From these filtration experiments it may be concluded that the dissolved species in filtrates are monomer and polymer hydrolysis products and do not include colloidal species.

The sorption of dissolved species onto the surface of experimental vials was also examined for Pu(VI) solutions. The results, shown in Table V for different pH values, indicate that after filtration with the Millex-22 filter $(0.22 \, \mu)$ the solutions remain stable, even if the solutions are transferred several times to new vessels.

The solutions from solubility experiments have shown a continuous decrease in pH with time due to radiolysis and/or hydrolysis. As shown in Figure 1, a large number of experimental points were obtained at the lower pH which were originally solutions of higher pH (up to 13.5). The same tendency was also observed in the Pu(VI) solutions (Figure 3). The solubility was changed as a result of this change in pH. When the americium solution was made alkaline to pH >9 by addition of NaOH, the solubility was decreased and it follows the curve shown in Figure 1. The reaction is therefore reversible with respect to pH. The results of this experiment imply that no colloid forms in these experimental solutions.

Direct speciation of dissolved americium and plutonium is possible only for solutions with appreciable concentration ($[Am(III)] \geq 10^{-6} \, M$ and $[Pu(VI)] \geq 10^{-5} \, M$) using a spectrophotometer with cumulative data recording ([21]). Typical spectra measured for the Am^{3+} ion at pH = 6.5 are shown in Figure 5 for 1, 5, 10, and 40 times cumulation at 503 nm. With this method it is shown that only trivalent americium ions are present in both equilibrium solutions from AmO_2 and $Am(OH)_3 \cdot nH_2O$ solids. For plutonium solutions, the spectrophotometric study indicates the presence of polymers as shown in Figure 4.

Calculated concentrations of possible hydrolysis species as a function of the equilibrium pH are given in Figures 6 and 7 for americium ions and plutonium ions, respectively. In the americium solution, the predominant species at pH <7 are the Am^{3+} and $Am(OH)^{2+}$ ions, whereas in the plutonium solution the PuO_2^{2+} ion is not the dominating species at near neutral media but polymers as postulated: $(PuO_2)_2(OH)_2^{2+}$ and $(PuO_2)_3(OH)_5^{+}$.

Table II. The Stability Constants and Solubility Products of Pu(VI) Hydroxides (cf. Equations 14 and 15) *

log Ksp	log β_1	log β_2	log β_3	log $\beta_{2,2}$	log $\beta_{2,3}$	log $\beta_{2,5}$	log $\beta_{3,5}$	log $\beta_{7,4}$	Medium	Reference
-23.00	8.26	14.91	16.90	21.98	-	-	56.28	-	0.1 M NaClO$_4$	This work
-	-	-	-	19.83	-	-	-	27.01	3 M NaClO$_4$	19
-24.05	9.93	16.31	20.27	-	30.74	-	-	-	0.1 M NaClO$_4$	18
-	7.80	-	-	19.01	-	-	46.64	-	1 M NaClO$_4$	17
-22.74	10.62	19.36	23.85	-	35.72	47.90	-	-	NH$_4$ClO$_4$	14
-	10.57	23.75	-	-	-	-	-	-	0.01 M NaNO$_3$	13
-	8.05	16.10	20.16	-	-	-	-	-	1 M NaClO$_4$	12

*The literature values are converted with the Kw values from Reference (7).

Table III. Comparison of Different Filtrations for the Determination of Solubilities of AmO$_2$: The Data are log [Am]$_s$ (M) Values

Sample number	pH	Filters used			
		Millex-22[a]	Amicon CF 25[b]	Amicon YMT	Satorius Sm 14549[d]
1	4.34	-4.68 ± 0.01[c]	-4.80 ± 0.02	-4.72 ± 0.01	-4.68 ± 0.01
2	5.33	-6.00 ± 0.01	-6.12 ± 0.02	-6.26 ± 0.02	-6.01 ± 0.01
3	7.97	-8.94 ± 0.05	-8.96 ± 0.13	-9.08 ± 0.08	-8.96 ± 0.10

[a] Average pore size 220 nm.
[b] Average pore size 1.9 nm.
[c] Average pore size 2.1 nm.
[d] Average pore size 1.8 nm.
Average from four experiments.

Table IV. Comparison of Different Filtrations for the Determination of
Solubilities of $PuO_2(OH)_2$: The Data are log [Pu]s (M) Values

Sample number	pH	Filters used				
		Millex-22[a]	Millipore CX-30[b]	Millipore CX-10[c]	Satorius SM 14539[d]	Satorius 14529[e]
1	4.12	-4.19 ± 0.03	-4.19 ± 0.03	-4.36 ± 0.03	-4.20 ± 0.01	-4.21 ± 0.01
2	6.72	-4.22 ± 0.02	–	-4.36 ± 0.03	-4.22 ± 0.03	–
3	9.36	-5.47 ± 0.05	–	-5.47 ± 0.05	–	–
4	9.97	-6.20 ± 0.01	–	-6.24 ± 0.02	–	–

[a] Average pore size: 220 nm.
[b] Average pore size: 2.1 nm.
[c] Average pore size: 1.4 nm.
[d] Average pore size: 1.2 nm.
[e] Average pore size: 0.6 nm.
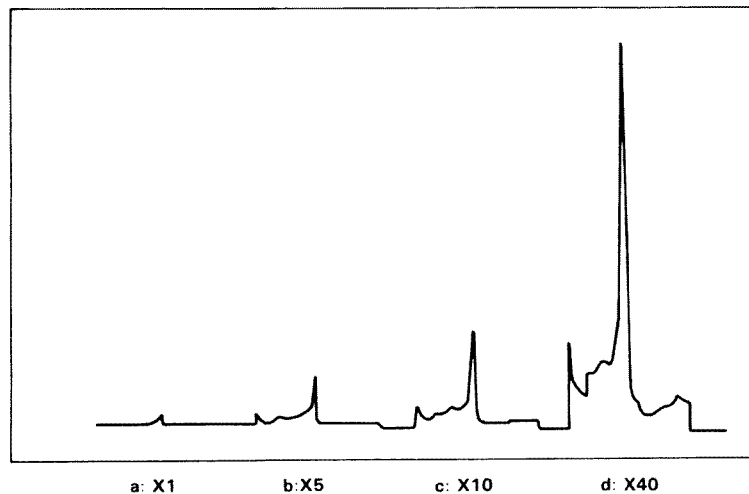
a: X1   b:X5   c: X10   d: X40

Figure 5.   Absorption Spectra of the Am(III) Solution ([Am]s = $10^{-5.5}$ M) in the Region of 503 nm Recorded by a Spectrum Accumulator. The Spectrum a: x1, b: x5, c: x10, and d: x40 Accumulations.

Table V. Sorption Test of the Dissolved PuO_2^{2+} Ion on the Surface of Different Experimental Vials: The Data are log [Pu]s (M) Values

Sample number	pH	Different vials			
		Polyethylene I*	Polyethylene II	Polyethylene III	Polyethylene IV
1	4.12	− 4.14 ± 0.03	− 4.13 ± 0.03	− 4.19 ± 0.03	− 4.18 ± 0.03
2	6.72	− 4.18 ± 0.02	− 4.18 ± 0.02	− 4.23 ± 0.02	− 4.20 ± 0.02
3	9.36	− 5.47 ± 0.05	− 5.48 ± 0.01	− 5.47 ± 0.01	− 5.46 ± 0.02
4	9.97	− 6.22 ± 0.01	− 6.28 ± 0.03	− 6.27 ± 0.03	− 6.19 ± 0.02

*After filtration at 0.22 μ.
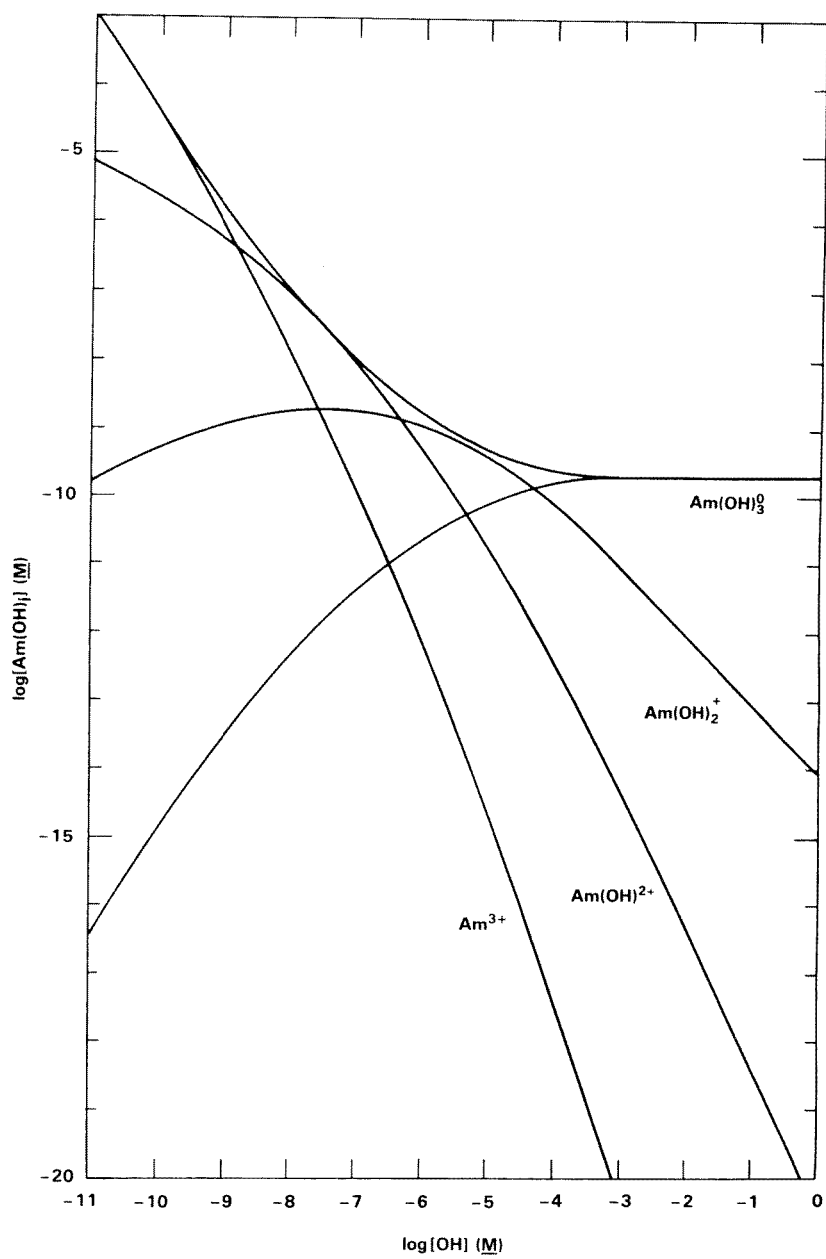
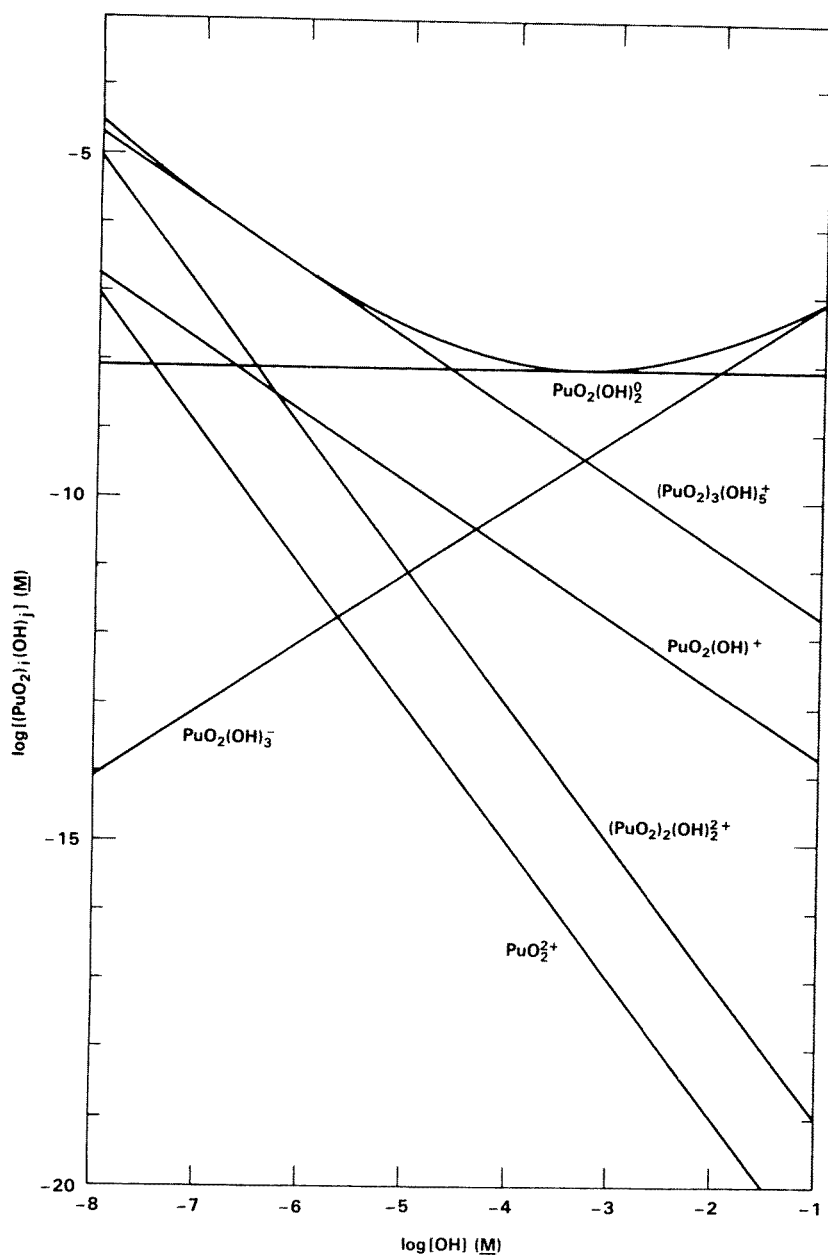Figure 6. Concentrations of Am(III) Hydrolysis Products as a Function of the OH⁻ Concentration in AmO₂ Dissolution.

Figure 7. Concentrations of Pu(VI) Hydrolysis Products as a Function of the OH⁻ Concentration.

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