

a pure solution of any one of them. Natural waters low in organics, however, may have Pu^{V} as the dominant species.

The pale colors of Ln^{3+} show some similarity between those with electron structures $[\text{Xe}]4f^n$ and those with $[\text{Xe}]4f^{14-n}$, but the explanation is beyond our scope. The $5f$ electrons in An^{3+} are more exposed, making their colors more intense and less patterned; moreover, some are of course less well known. See Table 3.4.

Table 3.4. The colors of Ln^{3+} and An^{3+} , necessarily omitting nuances

<i>n</i>	$4f^n$			$4f^{14-n}$	$5f^n$		$5f^{14-n}$
0	$_{57}\text{La}$	none	none	$_{71}\text{Lu}$	$_{89}\text{Ac}$	none	$_{103}\text{Lr}$
1	$_{58}\text{Ce}$	none	none	$_{70}\text{Yb}$	$_{90}\text{Th}$	dp blue	$_{102}\text{No}$
2	$_{59}\text{Pr}$	yl-grn	lt grn	$_{69}\text{Tm}$	$_{91}\text{Pa}$	dk blue	$_{101}\text{Md}$
3	$_{60}\text{Nd}$	violet	pink	$_{68}\text{Er}$	$_{92}\text{U}$	red-prp	$_{100}\text{Fm}$
4	$_{61}\text{Pm}$	pink	yl-pink	$_{67}\text{Ho}$	$_{93}\text{Np}$	purple	lt pink
5	$_{62}\text{Sm}$	dk yl	yellow	$_{66}\text{Dy}$	$_{94}\text{Pu}$	blue	green
6	$_{63}\text{Eu}$	lt pink	lt pink	$_{65}\text{Tb}$	$_{95}\text{Am}$	yl-pink	yl-grn
7	$_{64}\text{Gd}$	none	none	$_{64}\text{Gd}$	$_{96}\text{Cm}$	~ none	~ none

Abbreviations: dk, dark; dp, deep; grn, green; lt, light; prp, purple; yl, yellow; ~ none, pale yellow-green.

3.4 The Lanthanoids Ln(IV) and Actinoids An(IV)

The important ores pitchblende and/or uraninite are variously formulated as UO_2 or U_2O_5 up to the dark green oxide U_3O_8 , also more realistically in some cases as $\text{Ae}^{2+}_j\text{Rth}^{3+}_{2k}\text{Th}^{4+}_l\text{U}^{4+}_m\text{U}^{6+}_n\text{O}^{2-}_{j+3k+2l+2m+3n}$, $2m \geq n$, or $\text{Ae}^{2+}_j\text{Rth}^{3+}_{2k}\text{Th}^{4+}_l\text{U}^{5+}_{2m}\text{U}^{6+}_n\text{O}^{2-}_{j+3k+2l+5m+3n}$, $m \geq 2n$. The instability of aqueous UO_2^{+} (below) does not discredit any evidence for U_3O_8 as $\text{U}^{\text{V}}_2\text{U}^{\text{VI}}\text{O}_8$, but the ores may be mentioned here under both U^{IV} and U^{V} .

3.4.1 Reagents Derived from Hydrogen and Oxygen

Dihydrogen. Neptunium(> III) plus H_2 on Pt give Np^{III} , stable in H_2O .

Water. The most common thorium salt, $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and the chloride are soluble (forming $[\text{ThCl}_2(\text{H}_2\text{O})_n]^{2+}$). Anhydrous $\text{Th}(\text{SO}_4)_2$ is soluble in ice water, but it separates as a hydrate on heating. If the solution is allowed to stand without boiling, a series of hydrates will separate, their compositions depending on conditions. This behavior can separate Th^{IV} quantitatively at 0°C from the soluble Rth sulfates.

The ligancies of hydrated An^{4+} ions seem to vary from $[\text{Th}(\text{H}_2\text{O})_{11}]^{4+}$ down to $[\text{An}(\text{H}_2\text{O})_8]^{4+}$. Some only slightly soluble salts include $\text{ThOCO}_3 \cdot 8\text{H}_2\text{O}$, $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$, $\text{K}_2[\text{ThF}_6] \cdot 4\text{H}_2\text{O}$, $\text{K}_4[\text{Th}(\text{SO}_4)_4] \cdot \text{H}_2\text{O}$ and $\text{Th}[\text{Fe}(\text{CN})_6]$. The phosphates and iodates of M^{4+} are insoluble.

The ions Ce^{IV} (slowly but catalyzed by RuO_2 in 5-dM H_2SO_4 , or by MnO_2 or $\text{Co}_2\text{O}_3 \cdot \text{aq}$), Pr^{IV} , Nd^{IV} , Tb^{IV} and Dy^{IV} oxidize H_2O to O_2 , going to Ln^{III} . Water also reduces Am^{IV} , especially if warm and in high $c(\text{H}_3\text{O}^+)$, likewise Cm^{IV} in any case if not strongly complexed, giving An^{III} .

The $\text{An}(\text{H}_2\text{O})_n^{4+}$ ions hydrolyze in the order $\text{U}^{4+} > \text{Np}^{4+} < \text{Pu}^{4+}$ even at a pH as low as 0 for the smaller (higher- Z) ions, or more than 1 for U^{4+} . Aqueous Th^{4+} goes to $\text{Th}(\text{OH})_n^{(4-n)+}$ with $\text{Th} < 1 \text{ mM}$, otherwise to polymers. Below pH 6 these include $\text{Th}_4(\text{OH})_8^{8+}$, $\text{Th}_4(\text{OH})_{12}^{4+}$, $\text{Th}_6(\text{OH})_{14}^{10+}$ and $\text{Th}_6(\text{OH})_{15}^{9+}$, also perhaps $\text{U}_6(\text{OH})_{15}^{9+}$. The precipitation of hydroxides greatly complicates the study of the An^{IV} hydrolyses.

Natural waters may contain $\text{Th}(\text{OH})_4$, ThF_2^{2+} , $\text{Th}(\text{HPO}_4)_2$, $\text{Th}(\text{HPO}_4)_3^{2-}$ or $\text{Th}(\text{SO}_4)_2$, and some hot natural waters may contain, e.g., $[\text{Th}(\text{CO}_3)_5]^{6-}$.

Uranium tetrafluoride, UF_4 , can give hydrates such as $\text{UF}_4 \cdot \text{H}_2\text{O}$.

Water hydrolyzes U^{4+} only slightly in 1-M H_3O^+ and does not oxidize it. A pH not much over 3 forms $\text{U}(\text{OH})_3^+$ etc. Fairly acidic media let Pu^{IV} hydrolyze to colloidal polymers, irreversibly on aging.

Above pH 1, Pu^{4+} tends, retarded by UO_2^{2+} , to hydrolyze to a colloid. Above pH 4 it precipitates $\text{Pu}(\text{OH})_4$, becoming quite insoluble on aging.

Heat, $\text{Pu}(\text{SO}_4)_2$ and H_2O precipitate $\text{Pu}(\text{OH})_2(\text{SO}_4) \cdot 4\text{H}_2\text{O}$.

Without complexants, Am^{4+} and H_2O form Am^{III} and O_2 .

Oxonium. Thorium hydroxide, when freshly precipitated, is readily soluble in acids but after drying is more resistant. The oxide ThO_2 , e.g., from igniting $\text{Th}(\text{OH})_4$, dissolves only in HF/HNO_3 .

The salts $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$, ThF_4 and $\text{Th}_3(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ are insoluble even in high $c(\text{H}_3\text{O}^+)$. The uranium(IV) salts are similarly insoluble.

Little affected by the anions, H_3O^+ and $\text{Am}(\text{OH})_4$ react as Am^{4+} :



Chemiluminescence occurs on dissolving $\text{Li}_x\text{Cm}^{\text{IV}}\text{O}_y$ in H_3O^+ , with its reduction to Cm^{III} .

Hydroxide. Raising the pH on Ce^{4+} gives CeOH^{3+} , then polymers and yellow, gelatinous $\text{CeO}_2 \cdot \text{aq}$.

A preliminary separation of very dilute An^{IV} (from large amounts of less-acidic cations) may coprecipitate them as $\text{An}(\text{OH})_4 \cdot \text{aq}$, e.g., with $\text{ZrO}_2 \cdot \text{aq}$ by OH^- (after adding a little Zr^{IV} carrier if needed).

Aqueous Th^{IV} forms an insoluble, gelatinous, white $\text{Th}(\text{OH})_4 \cdot \text{aq}$ with OH^- at about pH 6 after, for example, ThOH^{3+} and especially $\text{Th}_6(\text{OH})_{15}^{9+}$. The precipitate is insoluble in excess but is not formed in the presence of chelators like tar-

trate (separation from yttrium). The basic salts $\text{Th}(\text{OH})_2\text{CrO}_4 \cdot \text{H}_2\text{O}$ and $\text{Th}(\text{OH})_2\text{SO}_4 \cdot \text{H}_2\text{O}$ are known. The oxalato complexes also give $\text{Th}(\text{OH})_4 \cdot \text{aq}$ with OH^- . Digesting $\text{Th}_3(\text{PO}_4)_4$ from ores (e.g., monazite) with OH^- (e.g., several h at 150°C) yields $\text{Th}(\text{OH})_4$, insoluble in HCl at pH 3–4 but $\text{Ln}(\text{OH})_3$ dissolve as Ln^{3+} .

Aqueous OH^- gives with U^{IV} a pale green precipitate, nearly insoluble in excess reagent but giving some $\text{U}(\text{OH})_5^-$ above pH 6, rapidly oxidized in air to a brown color. No precipitate is obtained with chelating organic hydroxy-acid anions or excess CO_3^{2-} . Likewise OH^- does not precipitate Pu^{IV} from carbonates below a pH of 11 or 12 without reduction to Pu^{III} , e.g., as $\text{Pu}_3(\text{OH})_3(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$.

Concentrated OH^- converts insoluble AnF_4 to acid-soluble $\text{An}(\text{OH})_4$.

The amorphous $\text{An}(\text{OH})_4 \cdot \text{aq}$ ($\text{AnO}_2 \cdot \text{aq}$) structures are poorly known.

Peroxide. Cerium(IV) is readily reduced to Ce^{III} by H_2O_2 in acid.

Especially on warming neutral or slightly acidified Th^{IV} , H_2O_2 precipitates a variable hydrated peroxide, used to confirm thorium, soluble in excess H_2SO_4 . One product is $\text{Th}_6(\text{O}_2)_{10}(\text{NO}_3)_4 \cdot 10\text{H}_2\text{O}$.

Carbonate and O_2^{2-} dissolve $\text{U}^{<\text{VI}}$ minerals as $\text{CO}_3^{2-}\text{-UO}_2^{2+}$ complexes.

Aqueous H_2O_2 in dilute H_3O^+ precipitates Np^{IV} or Pu^{IV} as $\text{MO}_4 \cdot \text{aq}$, apparently really $\text{M}^{\text{IV}}(\text{O}_2)_2 \cdot \text{aq}$, but also reduces Pu^{IV} to Pu^{3+} . A low $c(\text{H}_2\text{O}_2)$ forms $\text{Pu}_2(\mu\text{-O}_2)_2^{4+}$.

Alkaline peroxide and $\text{Np}^{<\text{VII}}$ or $\text{Pu}^{<\text{VII}}$ form Np^{VII} or Pu^{VII} ; see 3.6.1.

Solids are known containing $[\text{Pu}^{\text{IV}}_2(\text{CO}_3)_6(\mu\text{-O}_2)_2]^{8-}$, or what might be elaborated as $[\{\text{Pu}(\eta^2\text{-CO}_3)_3\}_2\{\mu\text{-}(1,2\text{-}\eta\text{:}1,2\text{-}\eta)\text{-O}_2\}_2]^{8-}$, with liganacy 10, i.e., having side-by-side O_2 bridges (in two Pu_2O_2 rhombi, bent at O-O).

Aqueous H_2O_2 easily reduces Bk^{IV} to Bk^{III} even in concentrated HNO_3 .

Di- and trioxigen. Air oxidizes Pa^{IV} rapidly to Pa^{V} . It also oxidizes U^{IV} or Np^{IV} , but not Pu^{IV} , slowly to UO_2^{2+} or NpO_2^{2+} , although all U^{IV} carbonate complexes go easily to U^{VI} in the air. In 2-M CO_3^{2-} at pH over 11.7, Np^{IV} becomes Np^{V} .

Hot air (or H_2O_2 , faster) helps isolate uranium from some ores, and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ exemplifies the many redox catalysts for it:



Adding NaOH up to pH 11 then recovers $\text{Na}_2\text{U}_2\text{O}_7$.

Aqueous U^{IV} , Np^{IV} or Pu^{IV} plus O_3 form MO_2^{2+} and even, with concentrated OH^- , Np^{VII} or Pu^{VII} (likewise Am^{VII}); see 3.6.1 trioxigen.

Ozone in 1-dM OH^- converts $\text{Am}(\text{OH})_4$ to soluble, yellow Am^{VI} .

3.4.2 Reagents Derived from the Other 2nd-Period Non-Metals, Boron through Fluorine

Carbon oxide species. Cerium(IV) and Na_2CO_3 can yield $\text{Na}_6[\text{Ce}(\eta^2\text{-CO}_3)_5] \cdot 12\text{H}_2\text{O}$ with the liganacy (c. n.) 10.

Thorium(IV) and CO_3^{2-} precipitate a basic carbonate, readily soluble in concentrated, difficultly in dilute, CO_3^{2-} . The complex is decomposed and precipitated by OH^- but not by NH_3 , F^- or PO_4^{3-} . Treating $\text{Th}(\text{OH})_4$ with CO_2 or “ $(\text{NH}_4)_2\text{CO}_3$ ” yields ThOCO_3 or $(\text{NH}_4)_2\text{Th}(\text{CO}_3)_3$ in turn.

Alkali carbonates or bicarbonates give pale-green $\text{U}(\text{OH})_4$ with U^{IV} . The precipitate is soluble in HCO_3^- or “ $(\text{NH}_4)_2\text{CO}_3$ ” and reprecipitated on boiling and destroying the excess reagent. Barium carbonate completely precipitates both Th^{IV} and U^{IV} even in the cold.

Solutions of U^{IV} in KHCO_3 or “ $(\text{NH}_4)_2\text{CO}_3$ ”, treated with $\text{C}_2\text{H}_4(\text{NH}_3^+)_2$, are found to precipitate $\text{C}_2\text{H}_4(\text{NH}_3)_2[\text{U}(\text{CO}_3)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$. We may also form the guanidinium salt $[\text{C}(\text{NH}_2)_3]_4[\text{U}(\text{CO}_3)_4]$. Better known are the pentacarbonato salts of Th and U: $\text{M}_6[\text{An}(\text{CO}_3)_5] \cdot \text{aq}$, where $\text{M}_6 = \text{Na}_6, \text{K}_6, \text{Ti}_6, [\text{C}(\text{NH}_2)_3]_6, [\text{Co}(\text{NH}_3)_6]_2$, etc. E.g., dissolving fresh $\text{U}(\text{OH})_4 \cdot \text{aq}$ in KHCO_3 yields $\text{K}_6[\text{U}(\text{CO}_3)_5] \cdot 6\text{H}_2\text{O}$. Or one may treat warm $\text{U}(\text{SO}_4)_2$ with $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ and cool to get the guanidinium salt. Complexes of Pu^{IV} and Am^{IV} also go up to $[\text{M}(\text{CO}_3)_5]^{6-}$. In $\text{M}_6[\text{An}(\text{CO}_3)_5] \cdot \text{aq}$ generally the carbonate is didentate. In natural waters the predominant Th species will often be $[\text{Th}(\text{CO}_3)_5]^{6-}$, but Pu^{IV} is more likely hydrolyzed to colloidal $\text{Pu}(\text{OH})_4$. (Uranium will be U^{VI} in those waters.) Whether the mixed $\text{An}(\text{OH})_n(\text{CO}_3)_2^{n-}$ complexes predominate is often unclear.

Even higher Pu^{IV} complexes can arise from dissolving the oxalate in Na, K or NH_4 carbonates, giving $\text{M}_1^{(2n-4)}\text{Pu}(\text{CO}_3)_n \cdot \text{aq}$ with $n = 4, 5, 6$ or 8 , although some of the carbonate may be uncomplexed in at least the 8-salt, and we therefore omit the brackets, $[\]$, that would indicate definite complexes. Aqueous $[\text{Pu}(\text{CO}_3)_5]^{6-}$ has 10-coordination. One finds various greenish, amorphous, water-soluble powders after treating the initial ethanol-produced oils with more ethanol or drying by heat.

More reactions than we can mention here give $\text{AnO}(\text{CO}_3) \cdot n\text{H}_2\text{O}$, $\text{Th}(\text{OH})_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$, $\text{An}(\text{CO}_3)_2 \cdot \text{aq}$, $\text{Na}[\text{Th}(\text{OH})(\eta^2\text{-CO}_3)_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$, $\text{Alk}_2[\text{Th}(\text{OH})_2(\eta^2\text{-CO}_3)_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$, $(\text{Na}, \text{NH}_4)_2[\text{U}(\text{H}-\eta^2\text{-CO}_3)_2\text{F}_4]$, $(\text{NH}_4)_2[\text{Th}(\eta^2\text{-CO}_3)_3] \cdot \text{H}_2\text{O}$, $\text{K}_3[\text{Th}(\text{OH})(\eta^2\text{-CO}_3)_3(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, $[\text{C}(\text{NH}_2)_3]_5[\text{Th}(\eta^2\text{-CO}_3)_3\text{F}_3]$, $(\text{Alk}, \text{NH}_4)_4[\text{An}(\eta^2\text{-CO}_3)_4] \cdot n\text{H}_2\text{O}$, $\text{Na}_5[\text{Th}(\text{OH})(\eta^2\text{-CO}_3)_4(\text{H}_2\text{O})] \cdot 8\text{H}_2\text{O}$, $(\text{Alk}, \text{Ti}, \text{NH}_4)_6[\text{An}(\eta^2\text{-CO}_3)_5] \cdot n\text{H}_2\text{O}$, $\text{Ac}_3[\text{Th}(\eta^2\text{-CO}_3)_5] \cdot 7\text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_6]_2[\text{An}(\eta^2\text{-CO}_3)_5] \cdot (4,5)\text{H}_2\text{O}$, and $(\text{Alk}, \text{NH}_4)_8[\text{Pu}(\eta^2\text{-CO}_3)_6] \cdot n\text{H}_2\text{O}$. Also, the mineral tuliokite is found to be $\text{Na}_6\text{Ba}[\text{Th}(\eta^2\text{-CO}_3)_6] \cdot 6\text{H}_2\text{O}$.

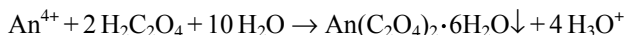
Cyanide species. We also find $[\text{An}(\text{NCS})_4(\text{H}_2\text{O})_4]$, $\text{Rb}[\text{Th}(\text{NCS})_5(\text{H}_2\text{O})_3]$, $\text{Na}_2[\text{Th}(\text{NCS})_5(\text{OH}) \cdot \text{aq}]$, $(\text{NH}_4)_3\text{Th}(\text{NCS})_7 \cdot 5\text{H}_2\text{O}$, $\text{M}_4[(\text{Th}, \text{U})(\text{NCS})_8] \cdot \text{aq}$ (cubic coordination! with $\text{M} = \text{Alk}$ or NH_4) and $(\text{Et}_4\text{N})_4(\text{U}, \text{Np})(\text{NCS})_8$.

Some “simple” organic species. Alcohols etc. dissolve $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$.

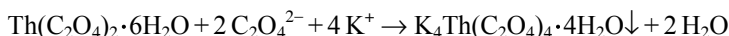
Boiled with CH_3CO_2^- , Th^{IV} precipitates a basic acetate, but other An^{IV} formates and acetates are too numerous even to summarize here.

Cerium(IV) is readily reduced to Ce^{III} by $\text{C}_2\text{O}_4^{2-}$.

Oxalic acid precipitates An^{IV} from an inorganic-acid solution as $An(C_2O_4)_2 \cdot 6H_2O$ (distinction from Al and Be but not the rare earths):



This is practically insoluble in an excess of the cold dilute reagent and only slightly soluble in dilute inorganic acids, but soluble in warm, concentrated HCl. For Th^{IV} at least, the oxalate is readily soluble in a mixture of acetate anion and acetic acid (distinction from the rare earths), also soluble in a hot concentrated oxalate solution, forming, e.g., $Th(C_2O_4)_4^{4-}$, reprecipitated by H_3O^+ . Igniting the oxalate gives the dioxide. Cooling the solution and adding ethanol produce a white salt, which breaks down somewhat in water:



Excess $C_2O_4^{2-}$ converts U^{IV} to $U(C_2O_4)_4^{4-}$ and to, for example, light-green $K_4U(C_2O_4)_4 \cdot 5H_2O$, precipitated by ethanol, alternatively to $K_2(Ca, Sr)U(C_2O_4)_4 \cdot 8H_2O$ or $Ba_2U(C_2O_4)_4 \cdot 9H_2O$. They all reduce Ag^+ .

At 98 °C, $H_2C_2O_4$ in 5-M HNO_3 or $NaNO_3$ reduces Pu^{IV} to Pu^{III} .

Cupferron, $C_6H_5N_2O_2^-$, is interesting in precipitating U^{IV} but not UO_2^{2+} . Therefore we can isolate uranium(VI) in a mixture by first precipitating Ti, Zr, V, Fe etc. with the $PhN_2O_2^-$, from H_2SO_4 solution. After that separation the UO_2^{2+} can be reduced to U^{IV} , precipitated with more cupferron, and thus separated also from Cr, Mn, Al, P and so on.

Reduced nitrogen. Thorium(IV) forms insoluble, gelatinous, white $Th(OH)_4$ with NH_3 . The precipitate is insoluble in excess of the reagent but is not formed in the presence of chelating organic hydroxy-acid anions (separation from yttrium).

The precipitation of $Zr(OH)_4 \cdot aq$ etc. by NH_3 (after adding small amounts of the carrier compound if needed) may be used for the preliminary separation of very small quantities of An species (from large amounts of the less-acidic cations) by coprecipitating them.

Ammonia gives with U^{IV} a pale green precipitate of $U(OH)_4$, insoluble in excess and rapidly oxidized in the air, changing to a brown color. No precipitate is obtained in the presence of, e.g., tartrate or excess CO_3^{2-} .

Ammonia and Bk^{IV} precipitate $Bk(OH)_4 \cdot aq$.

Aqueous Ce^{4+} oxidizes $N_2H_5^+$ to the radical ion $N_2H_4^{\bullet+}$, which reduces Fe^{3+} and Cu^{2+} for example.

Plutonium(> III) and $N_2H_5^+$ or NH_3OH^+ form Pu^{3+} , with conveniently gaseous byproducts. This allows separation from the unaffected UO_2^{2+} .

Thorium(4+) and HN_3 yield a strongly reducing amber complex. However, boiling N_3^- with Th^{IV} precipitates $Th(OH)_4$. The test is distinctive in the absence of unreduced Ce^{IV} and any other M^{IV} .

Oxidized nitrogen. Nitrous acid readily reduces Ce^{IV} to Ce^{3+} . It quickly oxidizes U^{IV} , however, to UO_2^{2+} , releasing NO.

Cerium(IV) in $(\text{NH}_4)_2[\text{Ce}(\eta^2\text{-NO}_3)_6]$ is a standard volumetric oxidant.

Nitric acid does not dissolve $\text{Ce}(\text{IO}_3)_4$, and dissolves ThO_2 poorly.

Uraninite, $\sim\text{UO}_{\geq 2}$, dissolves in HNO_3 and aqua regia slowly, and U^{4+} reacts with HNO_3 forming HNO_2 slowly, both resulting in UO_2^{2+} .

Solids, from dissolving hydroxides or carbonates in higher or lower $c(\text{HNO}_3)$, include $[\text{Th}(\eta^2\text{-NO}_3)_4(\text{H}_2\text{O})_4]$ and $[\text{Th}(\eta^2\text{-NO}_3)_6]^{2-}$ with liganacy (c.n.) 12 and $[\text{Th}(\eta^2\text{-NO}_3)_4(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ with liganacy 11 also in, e.g., $\text{AlkTh}(\text{NO}_3)_5 \cdot n\text{H}_2\text{O}$ and $(\text{Alk}, \text{Ti}, \text{NH}_4)_2[\text{An}(\text{NO}_3)_6]$. The following hexanitrate-complexes are derived from 8 to 14-M HNO_3 , with sulfamic acid added to prevent the oxidation of any uranium(IV) by any HNO_2 , i.e., $[(\text{Mg}, \mathbf{3d})(\text{H}_2\text{O})_6][\text{An}(\text{NO}_3)_6] \cdot 2\text{H}_2\text{O}$ plus $\text{K}_3\text{H}_3(\text{Th}, \text{U})(\text{NO}_3)_{10} \cdot n\text{H}_2\text{O}$ etc. Partial hydrolysis gives $[\{\text{Th}(\text{NO}_3)_3(\text{H}_2\text{O})_3\}_2(\mu\text{-OH})_2] \cdot 2\text{H}_2\text{O}$, liganacy 11.

Concentrated HNO_3 oxidizes $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ to UO_2^{2+} .

In 3-M HNO_3 Pu^{IV} is mainly $\text{Pu}(\text{NO}_3)_2^{2+}$; in $\text{HNO}_3 > 10\text{ M}$ it has $[\text{Pu}(\text{NO}_3)_6]^{2-}$, like Ce^{IV} , Th^{IV} etc., hence $(\text{Rb}, \text{Cs}, \text{NH}_4)_2[\text{Pu}(\text{NO}_3)_6] \cdot 2\text{H}_2\text{O}$, also, from 16-M HNO_3 , green $[\text{Pu}(\eta^2\text{-NO}_3)_4(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$, liganacy 11.

Warm 3-dM HNO_3 and Pu^{4+} form PuO_2^{2+} , apparently via the Pu^{4+} dismutation to PuO_2^{2+} and Pu^{3+} , which is then oxidized back to Pu^{4+} etc.

Hot HNO_3 with Np^{IV} gives HNO_2 and NpO_2^{2+} , which is stable in neutral solution but dismutates slowly at low pH.

Fluorine species. Adding F^- to Ce^{IV} precipitates $\text{CeF}_4 \cdot \text{H}_2\text{O}$. Concentrated NH_4F yields $(\text{NH}_4)_4[\text{CeF}_8]$, or $(\text{NH}_4)_6[\text{Ce}_2\text{F}_{14}] \cdot 2\text{H}_2\text{O}$ at lower $c(\text{NH}_4\text{F})$; this becomes $(\text{NH}_4)_2\text{CeF}_6$ and $(\text{NH}_4)_4[\text{CeF}_8]$ if dried.

Adding HF or F^- to dissolved Th^{IV} precipitates a bulky white ThF_4 , insoluble separately in excess fluoride or strong acid (separation from Be, Ti, Zr and Al), but fluoride helps HNO_3 dissolve ThO_2 , and a mixture containing 5-cM HF, 1-dM $\text{Al}(\text{NO}_3)_3$ (to buffer F^-) and 13-M HNO_3 can be used to dissolve ThO_2/UO_2 fuel, giving Th^{IV} , Pa^{V} and U^{VI} .

Uranium(IV) and HF or F^- precipitate green UF_4 , $\text{UF}_4 \cdot \text{H}_2\text{O}$ or UOF_2 . In air slowly, or 16-M HNO_3 vigorously, this all dissolves as UO_2^{2+} . The tetrafluoride dissolves little in dilute H_3O^+ ; hot OH^- forms black UO_2 .

Plutonium complexes such as PuF^{3+} and PuF_2^{2+} are quite stable, and other stabilities vary as $\text{Th}^{4+} < \text{U}^{4+} > \text{Np}^{4+} \geq \text{Pu}^{4+}$.

Concentrated alkali fluorides dissolve fresh $\text{Am}(\text{OH})_4 \cdot \text{aq}$ and CmF_4 as intensely colored An^{IV} complexes, and Am^{IV} in 13-M NH_4F or concentrated RbF precipitates $(\text{NH}_4)_4[\text{AmF}_8]$ or Rb_2AmF_6 , although $\text{Am}(\text{OH})_4$ dissolves in 13-M NH_4F at 25 °C only up to 2 cM. In solution, Am^{IV} persists generally only with strong complexers (see, e.g., phosphates just below and polytungstates in **3.4.4 Other reactions**). The fluoro-complexes do not dismutate even on heating to 90 °C. However, O_3 oxidizes them to Am^{VI} , and I^- reduces them to Am^{III} .

The fluoride CmF_4 in 15-M AlF_3 forms a Cm^{IV} complex. This is stable for 1 h at ambient T , but oxidizes H_2O . The An^{IV} ions form various further complexes, including $[\text{An}_6\text{F}_{31}]^{7-}$.

3.4.3 Reagents Derived from the 3rd-to-5th-Period Non-Metals, Silicon through Xenon

Phosphorus species. Phosphate precipitates Ce^{IV} as a phosphate. Adding phosphate or H_3PO_4 to Th^{IV} produces a gelatinous precipitate of $\text{Th}_3(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$, insoluble even in strong acids except hot, concentrated H_2SO_4 . Uranium(IV) or Pu^{IV} , and H_3PO_4 , precipitate $\text{An}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$. Also precipitable are $\text{Pu}_3(\text{PO}_4)_4 \cdot n\text{H}_2\text{O}$, $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot n\text{H}_2\text{O}$, $\text{Cu}^{\text{I}}\text{Th}_2(\text{PO}_4)_3$, $\text{Pb}_{1/2}\text{Th}_2(\text{PO}_4)_3$, $\text{An}[\text{P}_2\text{O}_7]$ such as $\text{Th}[\text{P}_2\text{O}_7]$ at pH 1, and $[\text{An}(\text{PO}_3)_4]_n$ (the metaphosphates). Ferroelectricity appears in $(\text{Na},\text{K})\text{Th}_2(\text{PO}_4)_3$.

The precipitation of BiPO_4 may be used for the preliminary concentration of small quantities of Np^{IV} , Pu^{IV} and Bk^{IV} by coprecipitation. Sulfuric acid keeps UO_2^{2+} complexed and dissolved. Zirconium phosphate can also carry Pu^{IV} etc. into its precipitate.

The many phosphate complexes of An^{IV} include, for example, $\text{An}(\text{H}_3\text{PO}_4)_x(\text{H}_2\text{PO}_4)_y(\text{HPO}_4)_z^{(y+2z-4)-}$, with high acidity naturally favoring high x , and high basicity high z . Concentrated H_3PO_4 stabilizes even Am^{IV} against the otherwise easy reduction to Am^{III} . Also, $[\text{P}_2\text{O}_7]^{4-}$ stabilizes Am^{IV} . Even Tb^{IV} is stabilized in $[\text{P}_3\text{O}_{10}]^{5-}$, but can then oxidize Ce^{3+} or Mn^{2+} in acid. Aqueous $[\text{P}_2\text{O}_7]^{4-}$ precipitates and separates Th^{IV} from all the Rth^{III} ions in approximately a 1.5-dM sulfate or 3-dM chloride solution. The insolubility of this $\text{Th}[\text{P}_2\text{O}_7]$ in dilute acid provides an excellent quantitative separation of Th^{IV} from cerium (reduced from Ce^{IV} to Ce^{III}) and determination of the thorium.

Reduced chalcogens. Sulfane, H_2S , reduces Ce^{IV} to Ce^{III} .

Sulfides in acid do not affect Th^{IV} or U^{IV} . Alkaline sulfides give $\text{Th}(\text{OH})_4$. “Ammonium sulfide” forms, with U^{IV} in neutral solution, a pale green, rapidly darkened precipitate.

Oxidized chalcogens. Boiling $\text{S}_2\text{O}_3^{2-}$ and Th^{IV} precipitates $\text{Th}(\text{OH})_4$ and sulfur (distinction from Ce).

Cerium(IV) is readily reduced to Ce^{III} by SO_2 .

Plutonium(> III) and SO_2 form Pu^{III} , stable to H_2O and O_2 . Sulfite solids include $\text{Th}(\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $(\text{Alk},\text{NH}_4)_2\text{Th}(\text{SO}_3)_3 \cdot n\text{H}_2\text{O}$, also $(\text{Na},\text{NH}_4)_4\text{Th}(\text{SO}_3)_4 \cdot n\text{H}_2\text{O}$, $\text{Na}_{2n}\text{U}(\text{SO}_3)_{n+2} \cdot \text{aq}$ and mixed complexes.

From $\text{Am}^{>\text{III}}$, SO_2 yields stable Am^{3+} , a weak reductant.

Mixing the appropriate ions can precipitate, say, $\text{An}(\text{SeO}_3)_2 \cdot \text{aq}$, $\text{Th}(\text{SeO}_4)_2 \cdot 9\text{H}_2\text{O}$, or $\text{An}(\text{TeO}_3)_2 \cdot \text{aq}$, likewise either $\text{ThO}(\text{TeO}_4) \cdot n\text{H}_2\text{O}$ or $\text{ThO}(\text{H}_4\text{TeO}_6) \cdot (n-2)\text{H}_2\text{O}$.

Fairly concentrated, hot H_2SO_4 dissolves CeO_2 somewhat slowly, then concentrating this with alkali sulfates gives, e.g., $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$.

Heating H_2SO_4 with aqueous Th^{IV} may precipitate a basic sulfate which will dissolve on cooling. Some simple sulfate hydrates, $\text{Th}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$, $n=8$ or 9 , also crystallize at ambient T .

With Th^{IV} a saturated solution of K_2SO_4 forms an insoluble double salt that is not affected by an excess of the reagent but is dissolved by hot water (separation from the yttroids). The corresponding sodium and ammonium double salts are soluble in water and in SO_4^{2-} (distinction from the ceroids), and $\text{Th}(\text{SO}_4)_2$, $\text{Th}(\text{SO}_4)_3^{2-}$ and $\text{Th}(\text{SO}_4)_4^{4-}$ are known. The 0.03 mM solubility of $^{7/2}\text{K}_2\text{SO}_4 \cdot \text{Th}(\text{SO}_4)_2$ in 3.5 dM K_2SO_4 separates it from the soluble Ln^{III} sulfates.

Thorium oxide, ThO_2 , is insoluble in acids except hot, concentrated H_2SO_4 . The thorium and other phosphates in monazite sand dissolve slowly in hot concentrated H_2SO_4 . (Cold H_2O then allows removing residues of silica, rutile, zircon, etc., and H_2S can eliminate certain metals.) Careful neutralization reprecipitates the phosphate.

Uranium dioxide is difficultly soluble in H_2SO_4 . In contrast to other U^{IV} salts, the sulfate, $\text{U}(\text{SO}_4)_2$, is fairly stable in air.

From Pu^{4+} and HSO_4^- arise PuSO_4^{2+} , $\text{Pu}(\text{SO}_4)_2 \cdot \text{aq}$ or $\text{K}_4\text{Pu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$.

Sulfuric acid dissolves $\text{Am}(\text{OH})_3$, very quickly forming the Am^{3+} and AmO_2^{2+} sulfato complexes; cf. **3.4.1 Oxonium**.

Insoluble AnF_4 become soluble sulfates on evaporation with H_2SO_4 .

Anomalous mixed crystals of Pu^{IV} coprecipitate with K_2SO_4 .

Sulfate ions complex An^{IV} firmly. Complexes include $\text{An}(\text{SO}_4)_n^{(2n-4)-}$, with the tetrasulfato dominating at $c(\text{SO}_4^{2-}) > 2 \text{ dM}$.

Solid phases are found to include $[(\text{Th}, \text{U}, \text{Pu})(\text{SO}_4)_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$, $\text{UOSO}_4 \cdot 2\text{H}_2\text{O}$ from a pH of about 7, $(\text{Alk}, \text{Ti}^{\text{I}}, \text{NH}_4)_2[\text{An}(\text{SO}_4)_3] \cdot n\text{H}_2\text{O}$, $(\text{Alk}, \text{NH}_4)_4[\text{An}(\text{SO}_4)_4] \cdot n\text{H}_2\text{O}$ (green for Pu^{IV}), the pentasulfato $(\text{Alk}, \text{NH}_4)_6[\text{An}(\text{SO}_4)_5] \cdot n\text{H}_2\text{O}$, the hexasulfato $(\text{NH}_4)_8[\text{An}(\text{SO}_4)_6] \cdot n\text{H}_2\text{O}$, plus $\text{Na}_6[\text{U}_2(\text{SO}_4)_7] \cdot 4\text{H}_2\text{O}$ and mixed complexes with $\text{C}_2\text{O}_4^{2-}$ for example.

Reduced halogens. Complexes of Ce^{IV} include $[\text{CeCl}_6]^{2-}$.

Anion-exchange resins retain AnCl_6^{2-} from 12-M HCl .

Thorium (mono)phosphates dissolve in HCl .

Uranium dioxide is difficultly soluble in HCl and HBr .

Adding CsCl in 6-M HCl to Pu^{IV} in 9-M HCl precipitates $\text{Cs}_2[\text{PuCl}_6]$, but Th^{IV} does not act similarly.

An interesting formula for a solid is $[\text{UBr}(\text{H}_2\text{O})_8]\text{Br}_3 \cdot \text{H}_2\text{O}$.

Cerium(IV) is readily reduced to Ce^{III} by HI .

From $\text{Am}(> \text{III}) \text{I}^-$ yields (chemically) stable Am^{3+} , a weak reductant.

Elemental and oxidized halogens. If ThO_2 is suspended in OH^- and the system saturated with Cl_2 , no dissolution occurs (distinction from many other oxides but

not cerium oxide). Chlorine, Np^{IV} and 1-M HCl at 75 °C form NpO_2^{2+} ; BrO_3^- or fuming HClO_4 does the same.

Concentrated HCl with Cl_2 and a 20 % excess of Cs^+ , saturated with HCl at –23 °C, dissolves $\text{Bk}(\text{OH})_4 \cdot \text{aq}$ giving a red solution and, promptly, an orange-red precipitate of Cs_2BkCl_6 .

Heating $\text{Am}(\text{OH})_3 \cdot \text{aq}$ and ClO^- in 2-dM OH^- , 90 °C, forms $\text{Am}(\text{OH})_4$.

Chlorate and H_2SO_4 dissolve U^{IV} ores as UO_2^{2+} sulfates.

Bromate, with $\text{An}^{<\text{VI}}$, gives UO_2^{2+} , NpO_2^{2+} , PuO_2^{2+} and AmO_2^{2+} .

The precipitation of $\text{Ce}(\text{IO}_3)_4$, with BrO_3^- as oxidant, may be used to separate small amounts of Bk^{IV} from other transplutonium elements by coprecipitation as $\text{Bk}(\text{IO}_3)_4$ in quite dilute HNO_3 . This can also coprecipitate Th, Group 4, Mn, Ag, Sn^{IV} , Pb and Bi, but not Group 1, Group 2, Rth^{III} , An^{III} , U, Cr, Mo, Fe, Co, Ni, Cu, Group 12, etc.

Iodate precipitates $\text{An}(\text{IO}_3)_4$, even from 6-M HNO_3 but not H_2SO_4 , thus separating them from other elements after reducing Ce^{IV} , perhaps by warming with H_2O_2 in acidic solution, to Ce^{III} .

Thorium perchlorate crystallizes as colorless $\text{Th}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$.

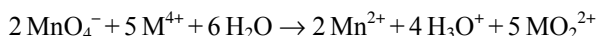
Periodate and Th^{IV} precipitate $\text{ThHIO}_6 \cdot 5\text{H}_2\text{O}$.

The $\text{Pu}^{<\text{VII}}$ ions plus $\text{H}_2\text{IO}_6^{3-}$ and OH^- form Pu^{VII} ; cf. **3.6.1 Peroxide**.

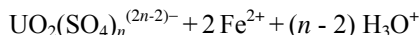
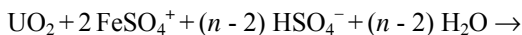
Xenon species. The $\text{Pu}^{<\text{VII}}$ ions react with XeO_3 and OH^- , or with XeO_6^{4-} , to form Pu^{VII} ; again cf. **3.6.1 Peroxide**.

3.4.4 Reagents Derived from the Metals Lithium through Uranium, plus Electrons and Photons

Oxidation. With $\text{An}^{<\text{VI}}$, the oxidants Ce^{4+} , MnO_4^- or Ag^{II} give UO_2^{2+} , NpO_2^{2+} , PuO_2^{2+} and AmO_2^{2+} , for example:



Leaching uranium from U^{IV} ores often best uses the concomitant, limited, Fe^{III} , with enough H_2SO_4 to prevent precipitation of phosphate, arsenate etc., and, say, ClO_3^- or MnO_2 to reoxidize the Fe^{II} , e.g.,:

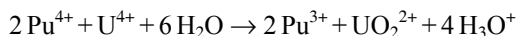


Aqueous $[\text{Fe}(\text{CN})_6]^{3-}$ reacts with U^{IV} to form $[\text{Fe}(\text{CN})_6]^{4-}$ and UO_2^{2+} ; these then give a red precipitate; see **3.6.4 Other reactions**, below.

Treating Np^{IV} with Fe^{III} yields Np^{V} and Fe^{2+} .

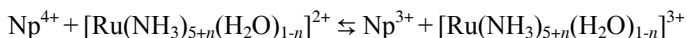
Uranium(IV) in acid precipitates metallic Ag, Au etc. from their solutions and goes to U^{VI} .

Reduction. Uranium(IV), e.g., from cathodic e^- , quickly reduces $\text{Pu}^{>\text{III}}$:

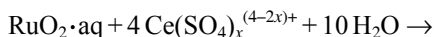


Iron(2+) in acid readily reduces Ce^{IV} or Pu^{IV} to M^{3+} , thus allowing a separation of Pu^{3+} , e.g., by solvent extraction, from unaffected UO_2^{2+} .

In nearly 1-M HCF_3SO_3 Ru^{II} reduces Np^{IV} in an equilibrium, $n \geq 0$:



Excess Ce^{IV} goes to Ce^{III} , oxidizing Ru^{IV} oxide in 5-dM H_2SO_4 completely to RuO_4 , accompanied by some Ru-catalyzed release of O_2 :



Neptunium(> III) plus Zn_{Hg} give Np^{3+} , stable in H_2O .

The very slow reduction of Ce^{IV} by Tl^+ is catalyzed by Ag^+ ; see **13.5.4 Oxidation**. Light (UV) also forms Ce^{III} and O_2 from Ce^{IV} and H_2O .

Other reactions. Traces of Np^{IV} , Pu^{III} and Pu^{IV} (and Ln^{III} and Th^{IV}) can be isolated by coprecipitation with LaF_3 , MnO_2 , $\text{Fe}(\text{OH})_3 \cdot \text{aq}$ or BiPO_4 .

Comparable to $\text{M}^{\text{I}}\text{Th}_2(\text{PO}_4)_3$ are $(\text{K}, \text{Rb})\text{Th}_2(\text{VO}_4)_3$.

Dichromate or basic CrO_4^{2-} precipitates Th^{IV} as $\text{Th}(\text{CrO}_4)_2 \cdot (3,1)\text{H}_2\text{O}$ or $\text{Th}(\text{OH})_2\text{CrO}_4 \cdot \text{H}_2\text{O}$ in turn. Here clarity with the name dichromate for both $\text{K}_2\text{Cr}_2\text{O}_7$ and a $\text{Th}(\text{CrO}_4)_2$ may require longer structural names such as μ -oxo-hexaoxodichromate(VI) and bis[tetraoxochromate(VI)].

A molybdate, Alk^+ and Th^{IV} yield $\text{Alk}_{2j}\text{Th}_k(\text{MoO}_4)_{j+2k}$, including a $\text{K}_8[\text{Th}(\eta^1\text{-MoO}_4)_4(\eta^2\text{-MoO}_4)_2]$ (ligancy 8), and a hydrated $\text{Th}(\text{MoO}_4)_2$.

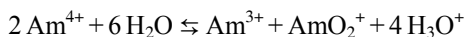
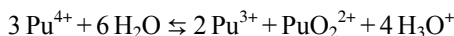
The An^{4+} ions do complex, often strongly and as either 1:1 or 1:2, $[\text{Nb}_6\text{O}_{19}]^{8-}$, $[\text{W}_{10}\text{O}_{36}]^{12-}$, $[\text{W}_{12}\text{O}_{42}]^{12-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, $[\text{P}_5\text{W}_{30}\text{O}_{110}]^{15-}$ (encapsulating An^{4+}), $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, $[(\text{B}^{\text{III}}, \text{Si}^{\text{IV}}, \text{P}^{\text{V}}, \text{As}^{\text{V}})\text{W}_{11}\text{O}_{39}]^{n-}$ etc.

Americium(IV) is stabilized against reduction (except by its own radiolysis) in, e.g., $\text{AmP}_2\text{W}_{17}\text{O}_{61}^{6-}$. Related Cm^{IV} complexes are chemiluminescent during the reduction to Cm^{III} by H_2O . Even Cf^{IV} may perhaps be stabilized by phosphotungstates.

Treated with $[\text{Fe}(\text{CN})_6]^{4-}$, Th^{IV} gives a white precipitate of $\text{Th}[\text{Fe}(\text{CN})_6]$, a very sensitive test, in neutral or slightly acidic solutions. Aqueous $[\text{Fe}(\text{CN})_6]^{4-}$ gives with U^{IV} a yellow-green precipitate, gradually being oxidized to red brown.

Uranium(IV) and $[\text{Fe}(\text{CN})_6]^{4-}$ form $\text{U}[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$; $[\text{Ru}(\text{CN})_6]^{4-}$ or $[\text{Os}(\text{CN})_6]^{4-}$ precipitate $\text{U}[\text{M}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$.

Low H_3O^+ favors dismutation for Pu^{4+} (catalyzed by UO_2^{2+} but stable in concentrated acid) or Am^{4+} :



but AmO_2^+ then also dismutates to Am^{3+} and AmO_2^{2+} .

The colors of Ln^{4+} are: Ce $4f^0$, yellow-orange; Pr $4f^1$ yellow; Nd $4f^2$, blue-violet; Tb $4f^7$, red-brown; and Dy $4f^8$, yellow-orange. The colors of An^{4+} are: Th $5f^0$, none; Pa $5f^1$, pale yellow; U $5f^2$, green; Np $5f^3$, yellow-green; Pu $5f^4$, tan; Am $5f^5$, orange; Cm $5f^6$, pale yellow; Bk $5f^7$, brown; Cf $5f^8$, green; neither Ln^{4+} nor An^{4+} can show the pattern of Table 3.4, because H_2O is pulled in, interacting too strongly with the f electrons.

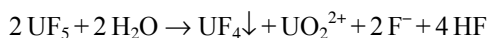
3.5 The Actinoids An(V)

3.5.1 Reagents Derived from Hydrogen and Oxygen

Water. The formulas for the simple An^V species, except Pa^V , in water are (linear) AnO_2^+ , where $\text{An} = \text{U}, \text{Np}, \text{Pu}$ or Am (unlike Nb or Ta). The apparent ionic charge of, e.g., PuO_2^+ felt by a ligated X^- is $\sim 2.2^+$.

Protactinium(V) is hydrolyzed, much more strongly than the higher- Z , *smaller*, An^V ions; it forms $\text{Pa}_2\text{O}_5 \cdot \text{aq}$ and colloids that are adsorbed on containers and interfere greatly with its study; it may be $\text{PaO}(\text{OH})^{2+}$, $\text{Pa}(\text{OH})_3^{2+}$ or $\text{PaO}(\text{OH})_2^+$, unlike the others (AnO_2^+) and with chemistry more like those of Nb^V and Ta^V than like those of other An^V .

Uranium pentafluoride reacts violently, giving UF_4 or UOF_2 :



Hydrolysis makes UO_2^+ , NpO_2^+ , PuO_2^+ and AmO_2^+ especially as $[\text{AnO}_2(\text{H}_2\text{O})_5]^+$ with linear AnO_2 from their AnX_5 . The AnO_2^+ ions (excluding Pa^V) do not readily hydrolyze further at a $\text{pH} < 7$ or 9 (higher than for the other oxidation states). Then we get AnO_2OH , $\text{AnO}_2(\text{OH})_2$ etc..

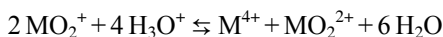
Some controversy may remain about Cf^V (\sim stable $5f^{7?}$) in OH^- .

Seawater is found now to contain Pu^V as $\sim 10^{-14}$ -M PuO_2^+ .

Oxonium. Uranium(V) dismutates rapidly but least at $\sim \text{pH } 3$:



High $c(\text{H}_3\text{O}^+)$ promote similar reactions of Np^V and Pu^V :



<http://www.springer.com/978-3-540-73961-6>

Inorganic Reactions in Water

Rich, R.

2007, XXII, 521 p. 17 illus., Hardcover

ISBN: 978-3-540-73961-6