DE LA RECHERCHE À L'INDUSTRIE

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Plutonium chemistry and other actinides in aqueous solutions

Part 2a

Homogeneous system

Ph. MOISY

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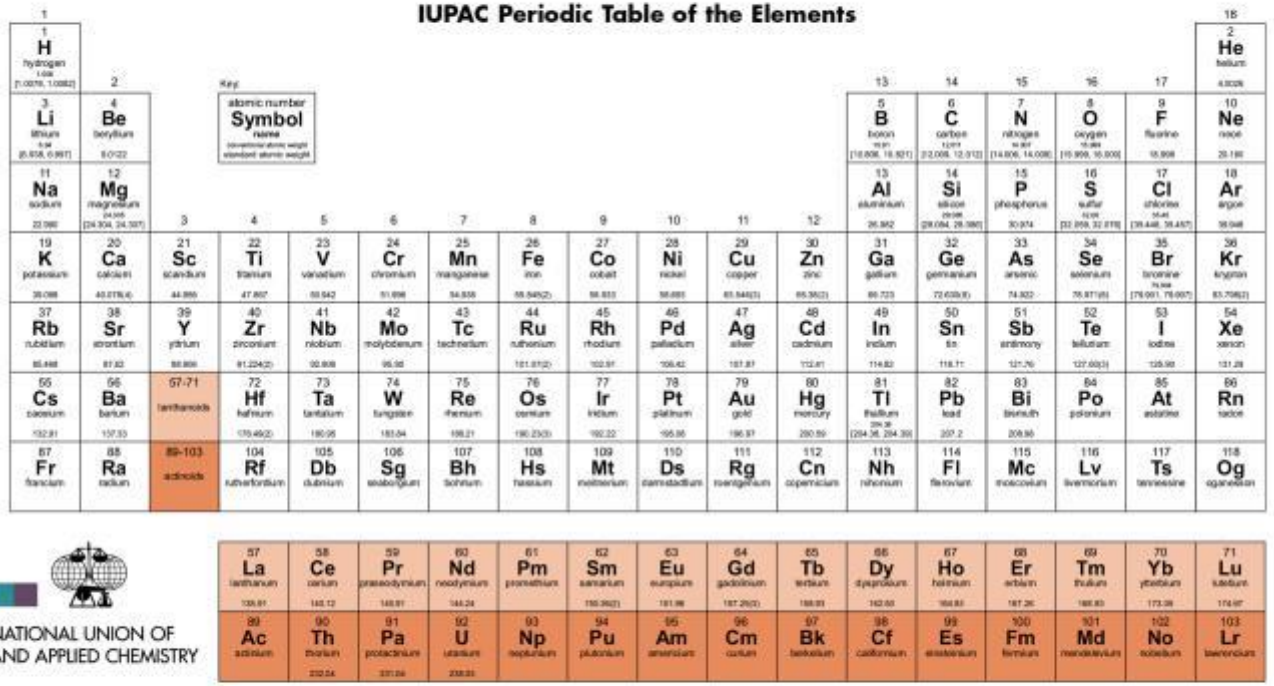
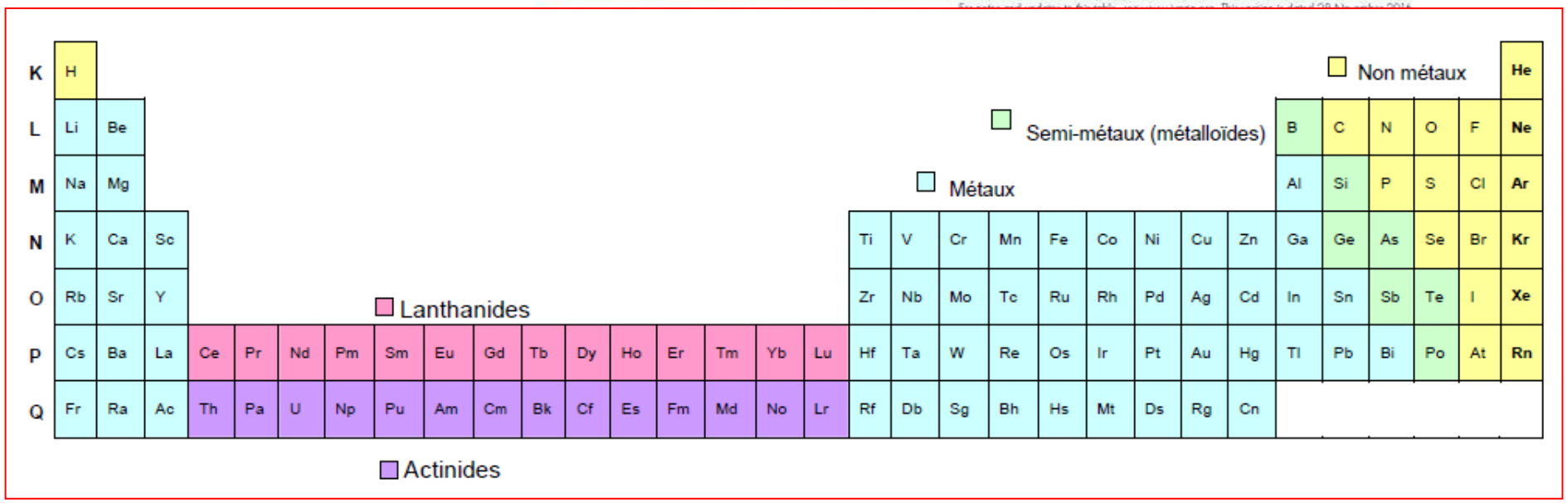
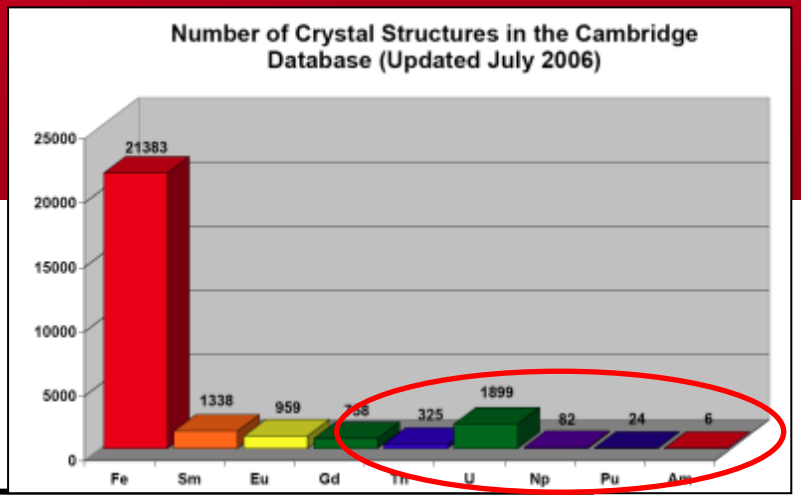
FROM RESEARCH TO INDUSTRY
cea den


IUPAC Periodic Table of the Elements
Key
atomic number
Symbol
name
INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY


K
L
M
N
O
P
Q
Non métaux
Semi-métaux (métalloïdes)
Métaux
Lanthanides
Actinides

Actinide family: 15 (14?) elements



From Actinium Ac (Z=89) to Lawrencium Lr (Z=103)

(Ac: $7s^2 6d^1$: 14 An?)

Element		Natural/Artificial	Knowledge
Thorium	Z= 90	Natural	Good
Uranium	Z= 92		
Neptunium	Z= 93		
Plutonium	Z= 94	Artificial	Good
Américium	Z= 95		
Curium	Z= 96		
Protactinium	Z= 91	Natural	Low
Berkelium	Z= 97		
↓		Artificial	Bad (very bad)
Lawrencium	Z= 103		
Einsteinium	Z= 99	**Last elements prepared in ponderable scale**	

Fermium (Z=100) ➔Lawrencium (Z=103) : Trace Chemistry

		Atom (g)	M^{2+} (g)	M^{3+} (aq)	M^{4+} (g)
	Actinium	$6d7s^2$	$7s$		
	Thorium	$6d^27s^2$	$5f6d$		
$6d^1$	Protactinium	$5f^26d7s^2$	$5f^26d$		$5f^1$
	Uranium	$5f^36d7s^2$	$5f^36d$	$5f^3$	$5f^2$
	Neptunium	$5f^46d7s^2$	$5f^5$	$5f^4$	$5f^3$
	Plutonium	$5f^67s^2$	$5f^6$	$5f^5$	$5f^4$
	Americium	$5f^77s^2$	$5f^7$	$5f^6$	$5f^5$
	Curium	$5f^76d7s^2$	$5f^8$	$5f^7$	$5f^6$
	Berkelium	$5f^97s^2$	$5f^9$	$5f^8$	$5f^7$
	Californium	$5f^{10}7s^2$	$5f^{10}$	$5f^9$	$5f^8$
	Einsteinium	$5f^{11}7s^2$	$5f^{11}$	$5f^{10}$	$5f^9$
	Fermium	$5f^{12}7s^2$	$5f^{12}$	$5f^{11}$	$5f^{10}$
	Mendelevium	$5f^{13}7s^2$	$5f^{13}$	$5f^{12}$	$5f^{11}$
	Nobelium	$5f^{14}7s^2$	$5f^{14}$	$5f^{13}$	$5f^{12}$
	Lawrencium	$5f^{14}6d7s^2$	$5f^{14}7s$	$5f^{14}$	$5f^{13}$

Actinide family: 15 (14?) elements

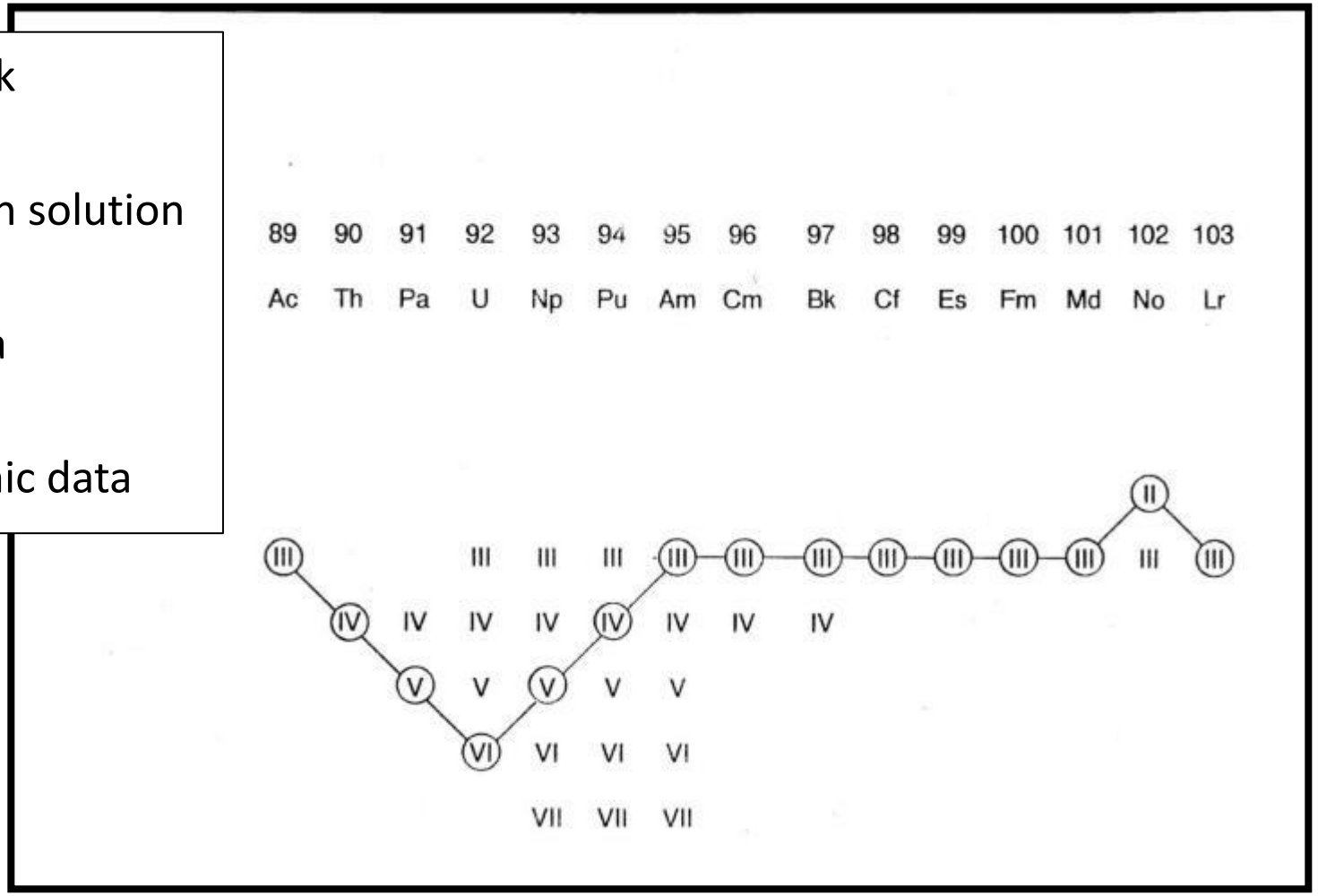
Oxidation State (Valency) of Actinide in Aqueous Solution

Outlook

1- Actinide ions in solution

2- Structural data

3- Thermodynamic data



Hydration sphere

Actinide ions in aqueous solution:

M(III) and M(IV):

$M(H_2O)_n^{3+}$ and $M(H_2O)_n^{4+}$ with *n = 8 or 9*

$Am(H_2O)_8^{3+}$, $Pu(H_2O)_8^{4+}$

M(V) and M(VI):

$MO_2(H_2O)_n^{+}$ and $MO_2(H_2O)_n^{2+}$ with M = U, Np, Pu and Am

$PuO_2^{2+}(H_20)_5$, $AmO_2^{2+}(H_20)_5$

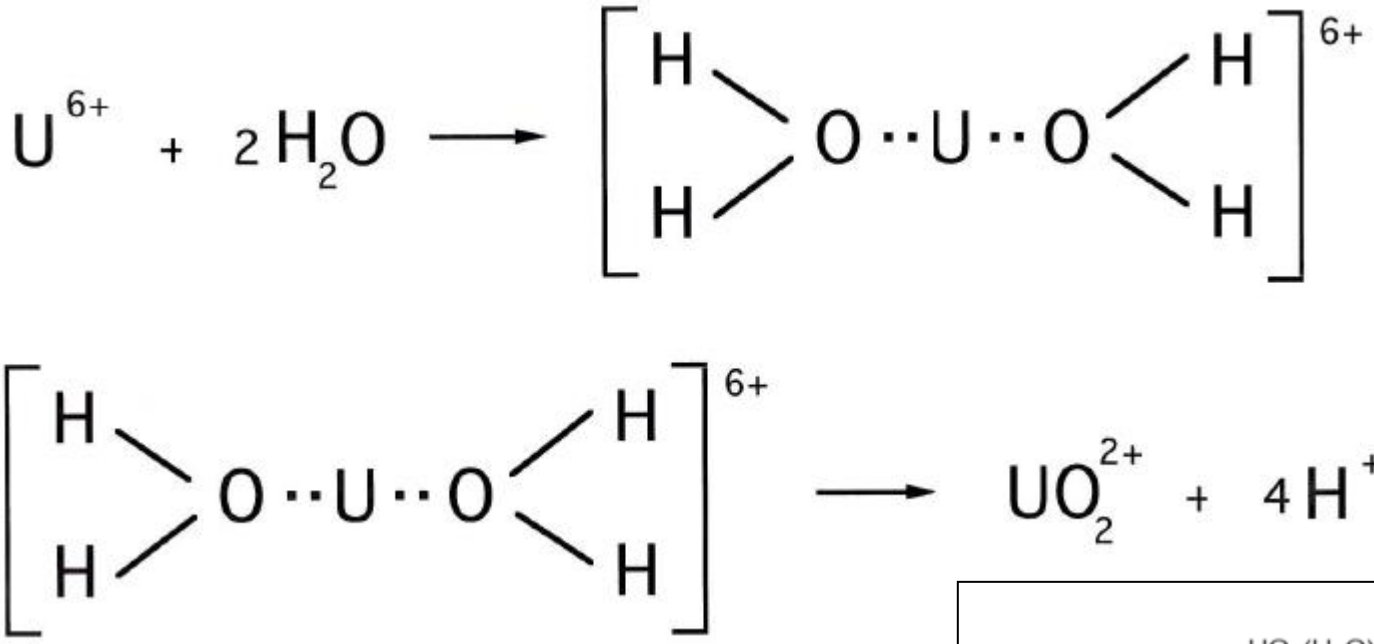
For Pa(V): $PaOOH(H_2O)_x^{2+}$

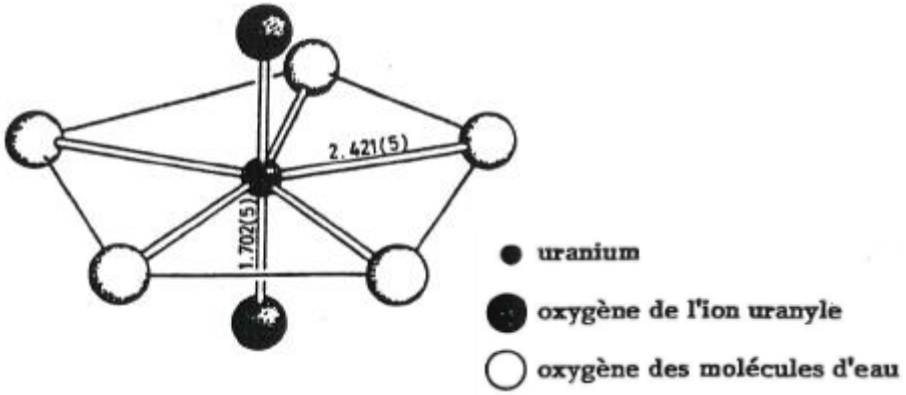
M(VII):

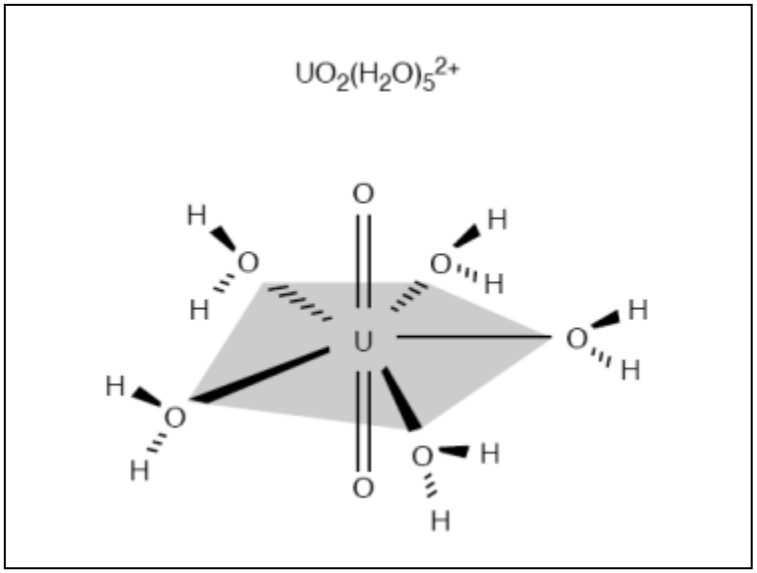
$NpO_3(H_2O)_y^{+}$ (in acid media), Pu(VII) and Am(VII) are unstable

$MO_4(OH)_2(H_2O)_z^{3-}$ with M = Np, Pu and Am (in basic media)

Special case for Oxidation State +6 and +5

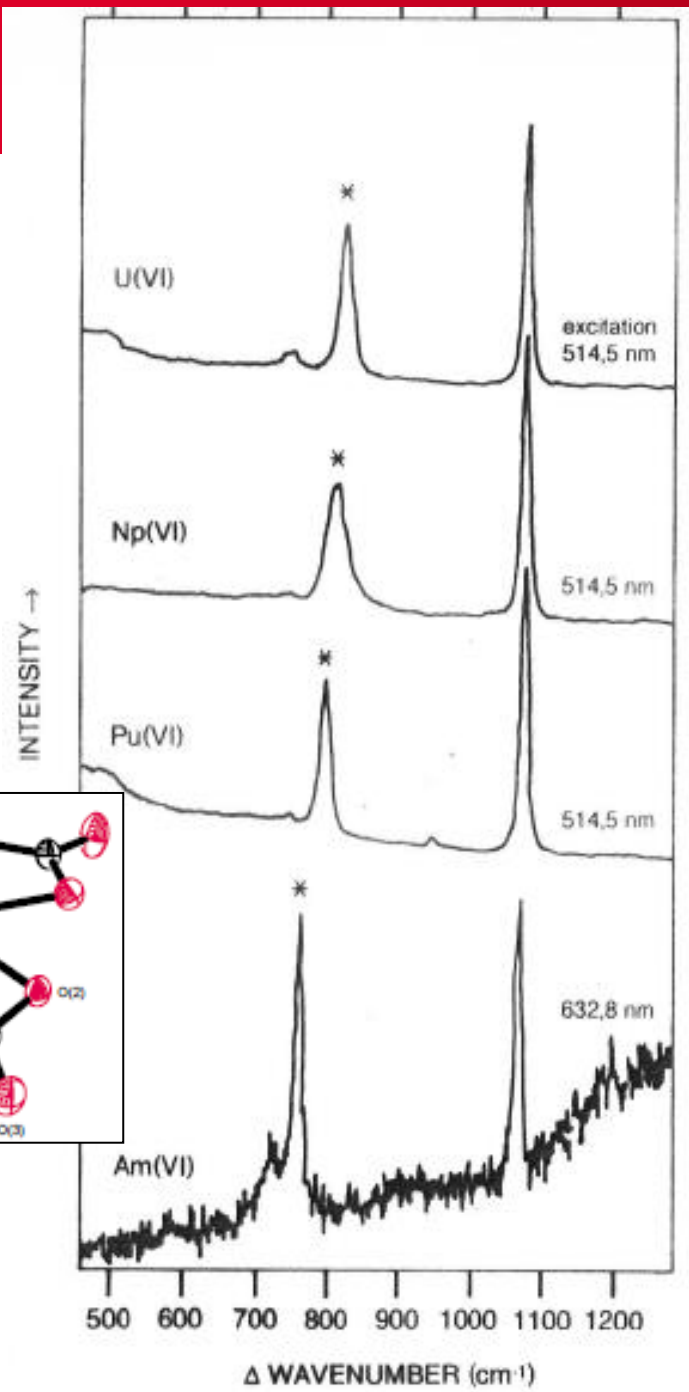


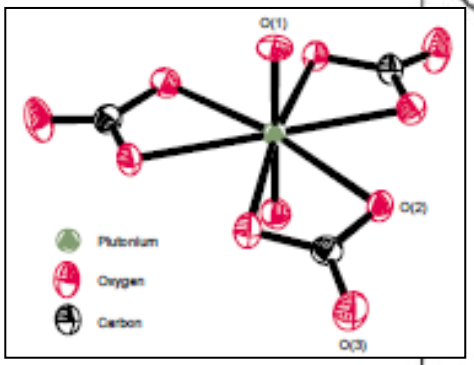




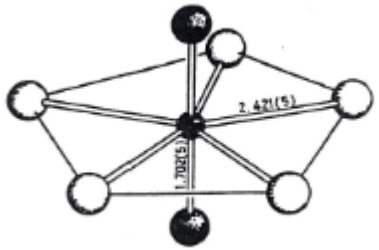
Structural Data: Actinyl (Oxidation state +V and +VI)

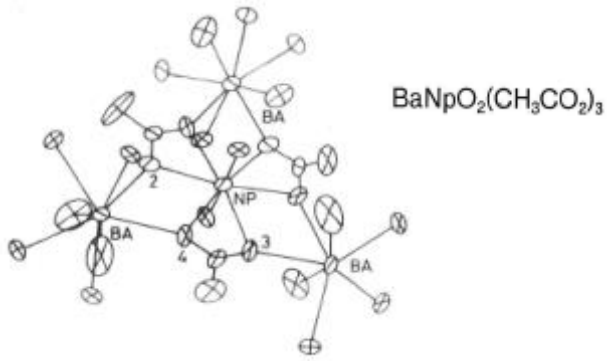
M(VI) in carbonate media (2 M) by Raman spectrocopy

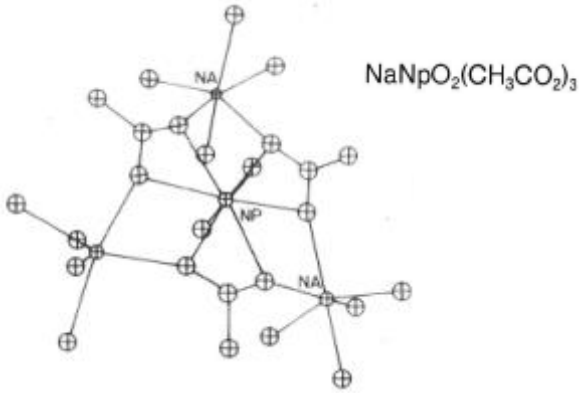




U(VI)-aquo by cristallography

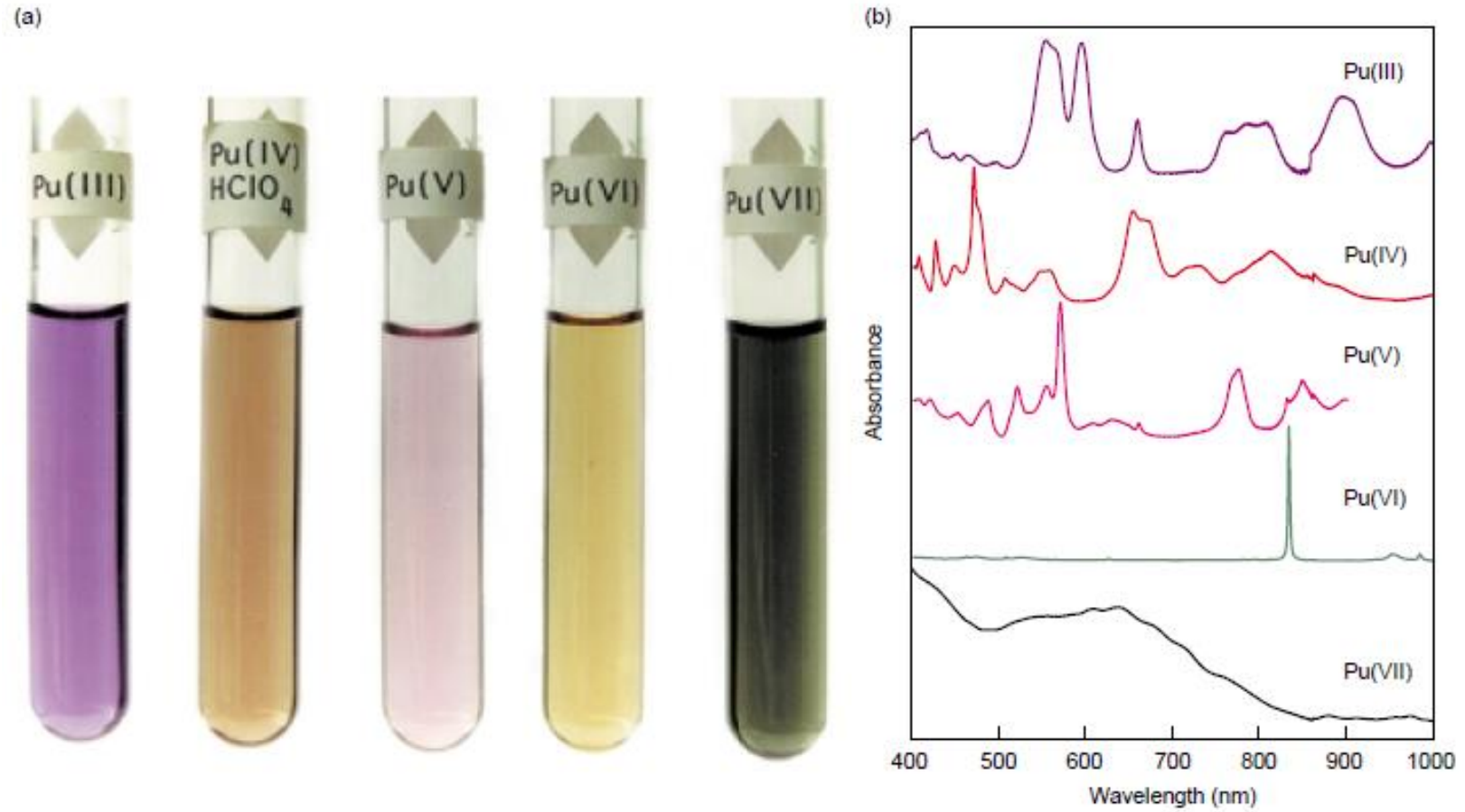






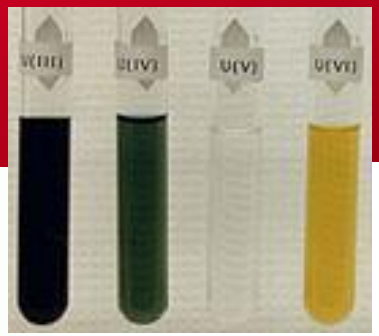
Np(V) and Np(VI) – acetate by cristallography

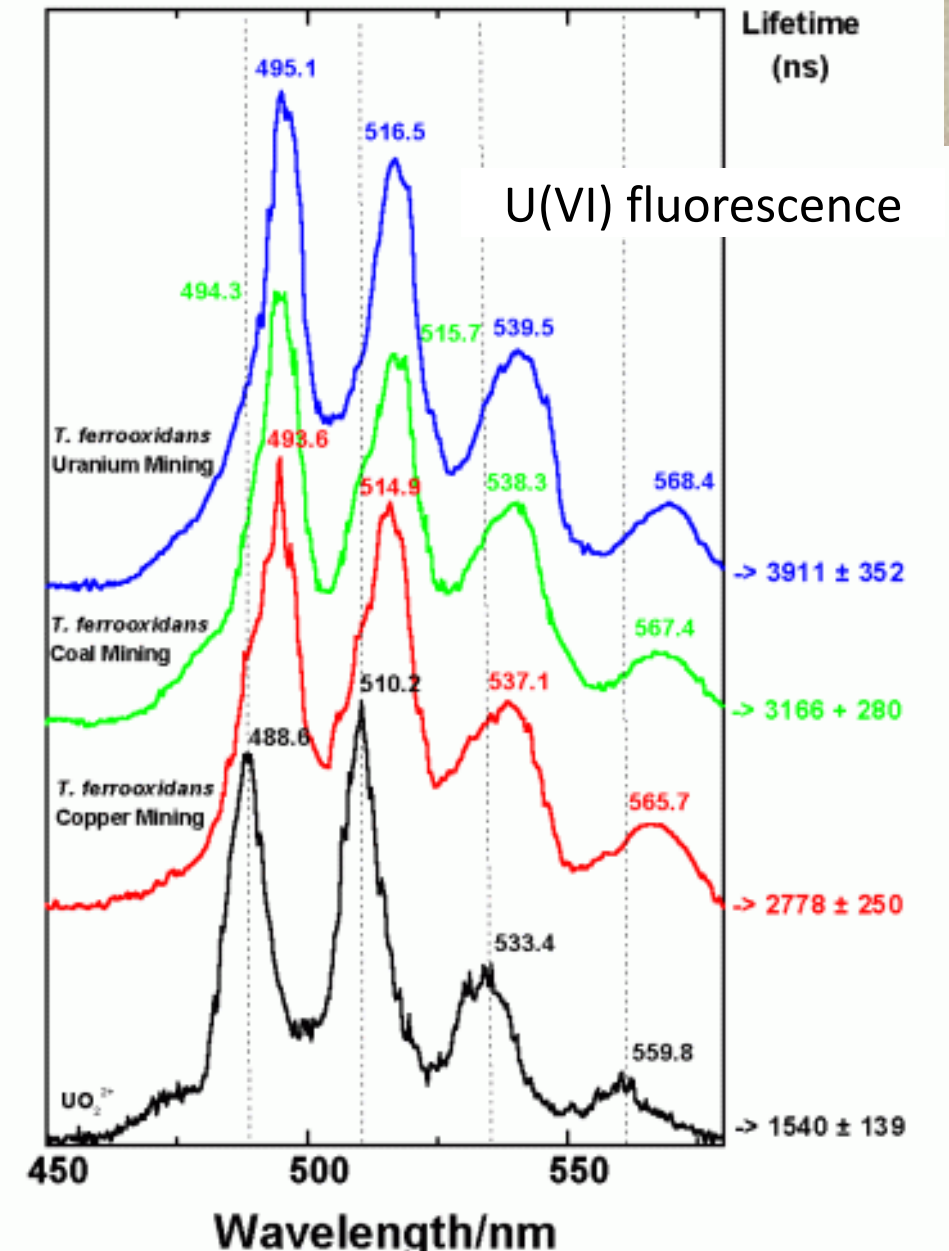
Plutonium



(a) Each of the plutonium oxidation states has a characteristic color in solution. The colors are specific and depend on the type and number of ligands. The photograph shows the aquo ions in 1 M perchlorate ($HClO_4$) solution. (Pu(V) is in $NaClO_4$ at pH = 7, Pu(VII) is in 2.5 M NaOH.) (b) The electronic absorption spectra of the plutonium aquo ions are compared here. (The relative absorbance values are not to scale.) The solution conditions are the same as in (a). Pu(VII) is a relatively rare oxidation state, but it can be formed under alkaline solution conditions. Each oxidation state can be identified by its characteristic absorption fingerprint.

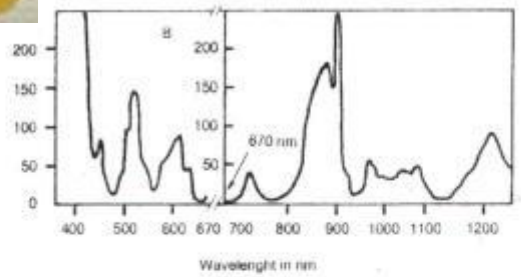
Uranium



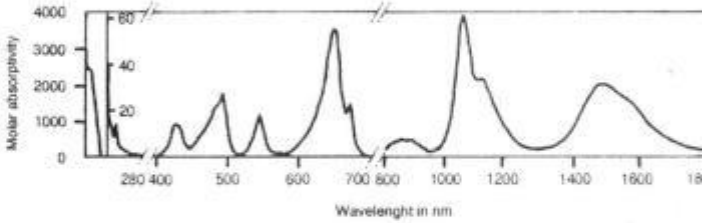


U(VI) fluorescence

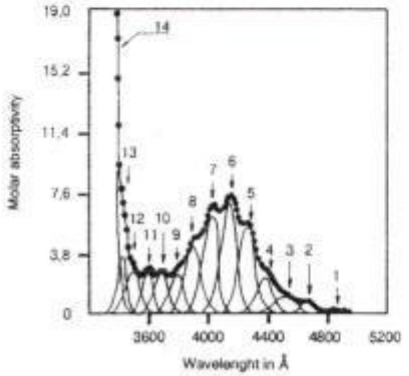
1 U(III) /M $HClO_4$



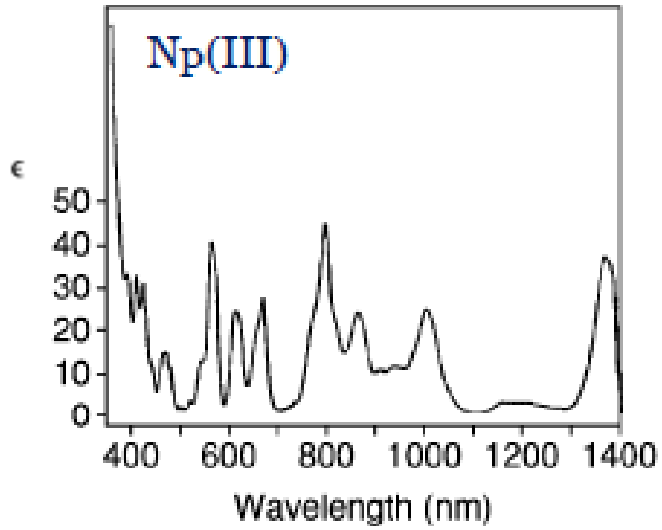
2 U(IV) /M $HClO_4$

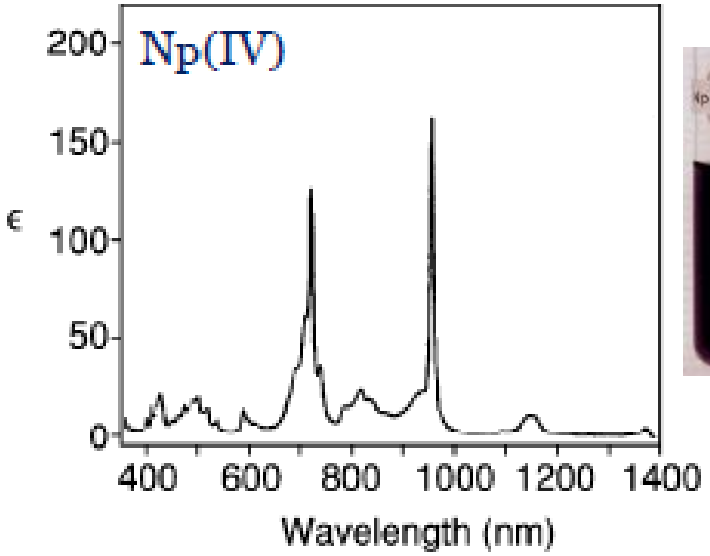


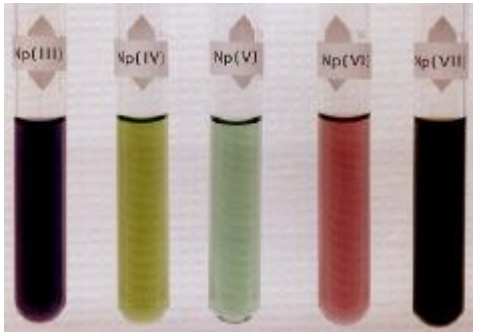
3 U(VI) 0,014M $HClO_4$ (μ = 3,0) Θ = 25°C

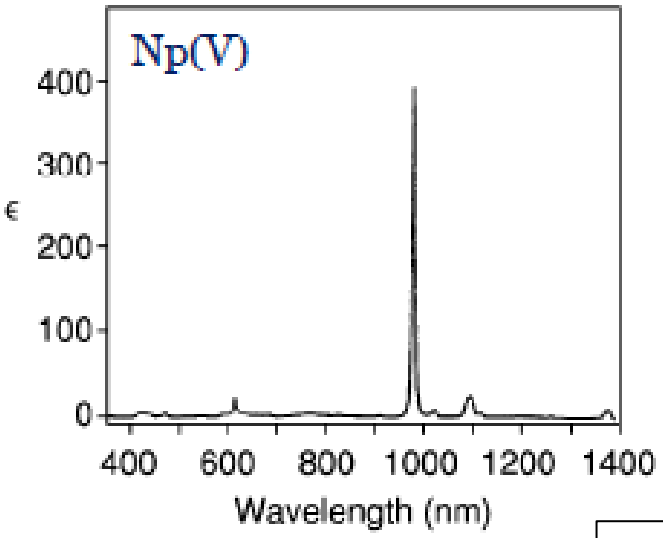


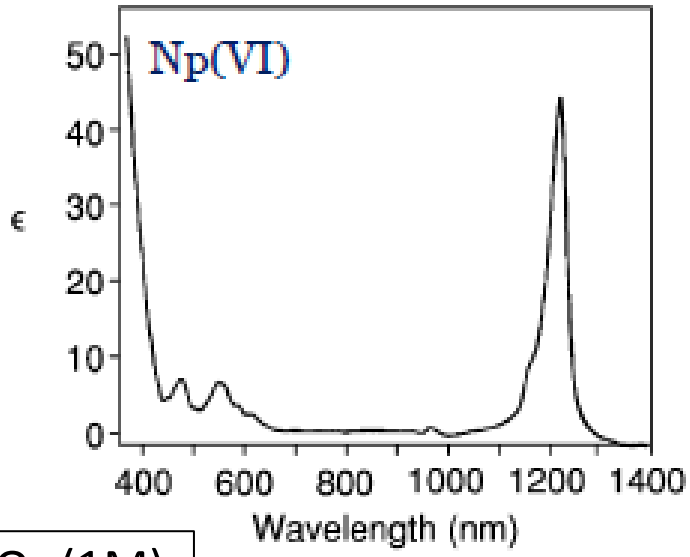
Neptunium

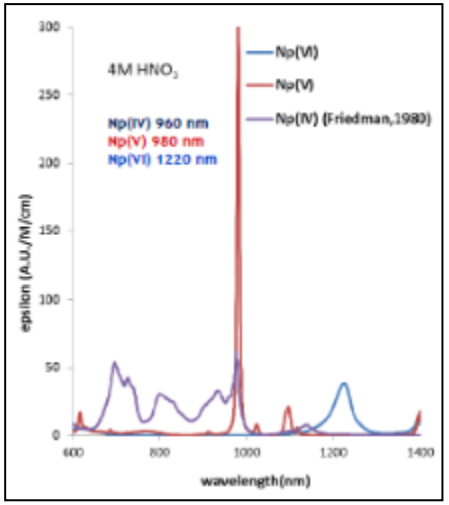






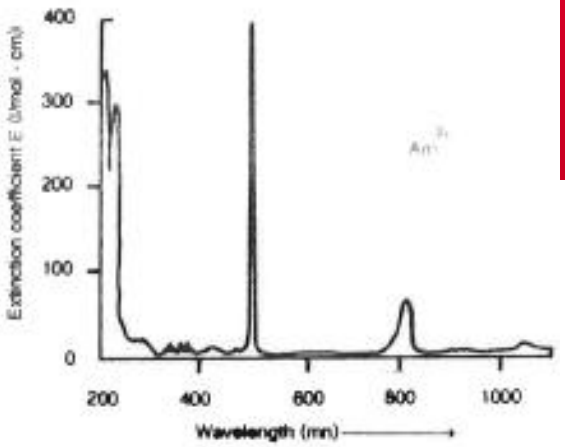


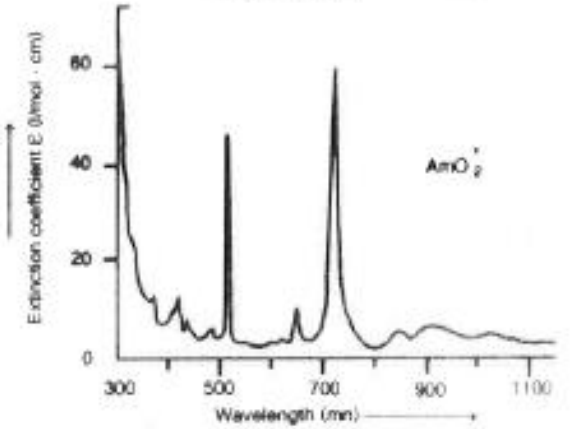


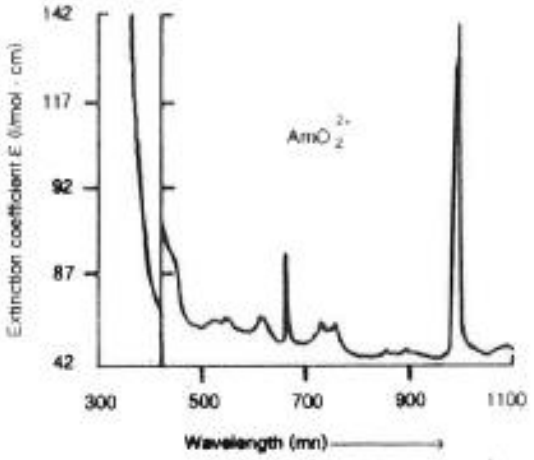


$HClO_4$ (1M)

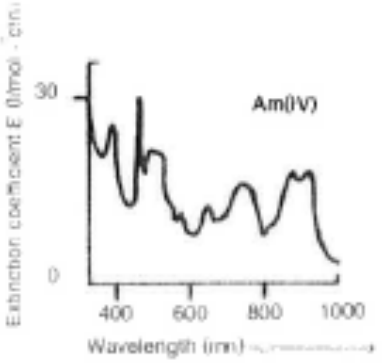
Americium and Curium



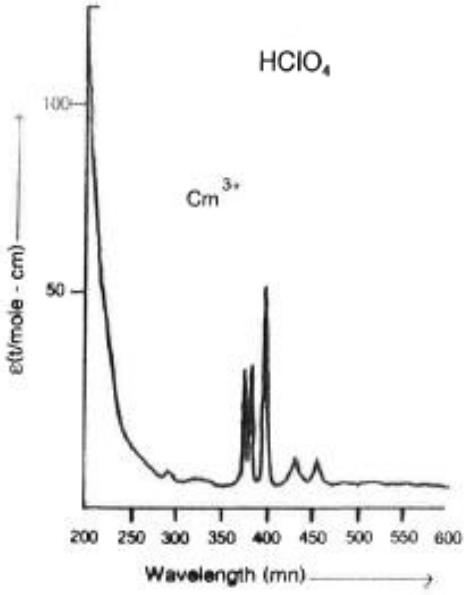




MILIEU = $HClO_4$ = 1M

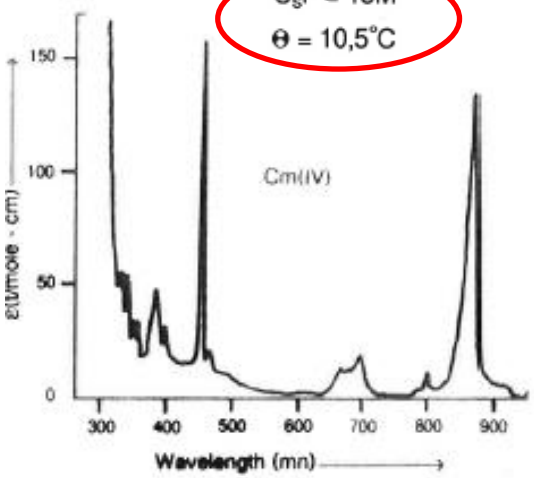


MILIEU = NH_4F = 13M



C_sF = 15M

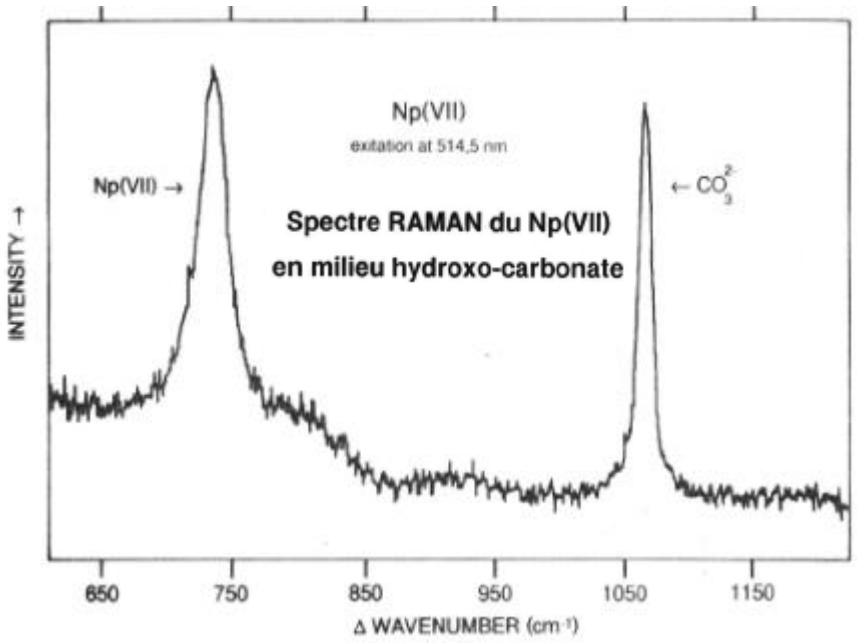
Θ = 10,5°C

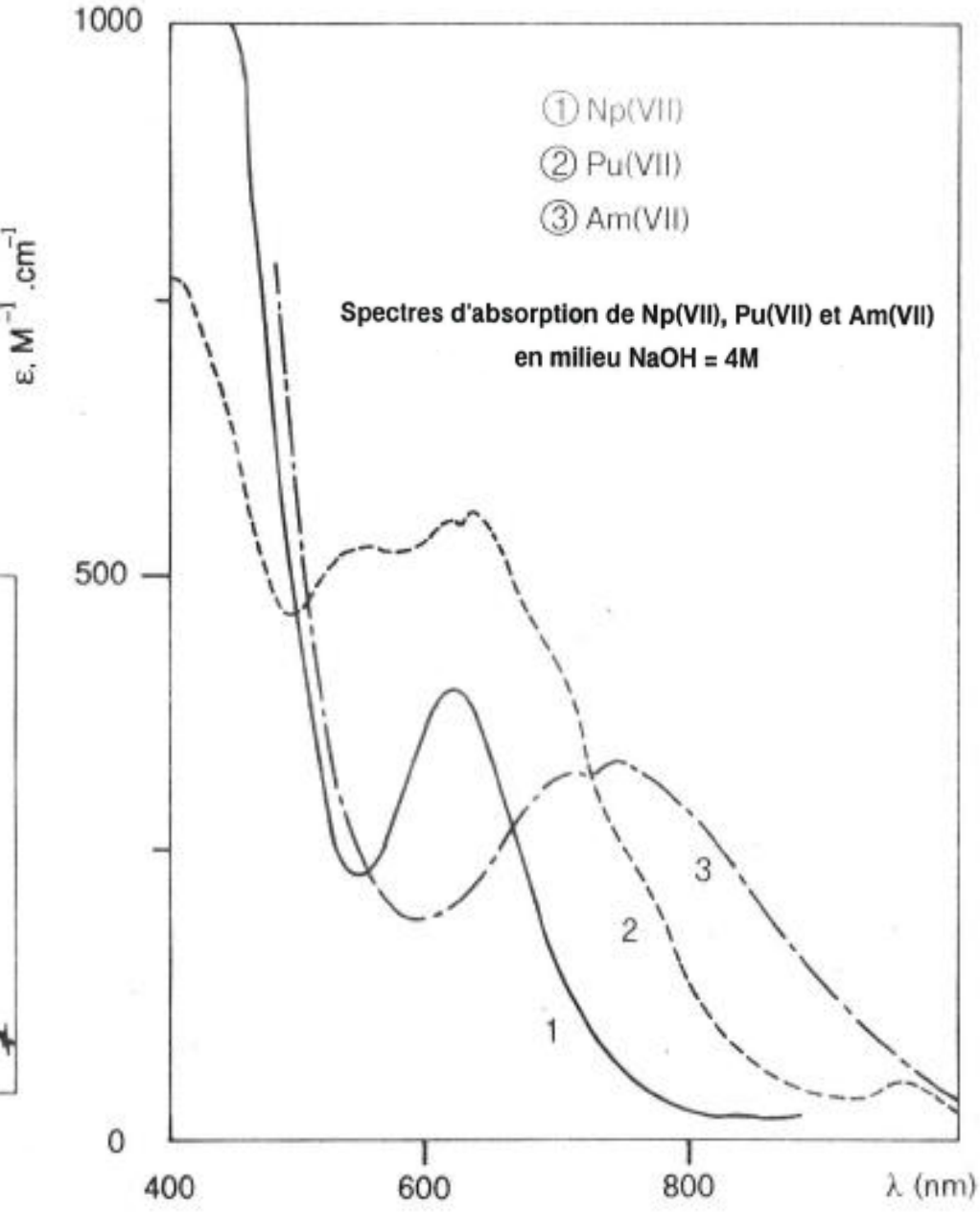


The case of An(VII)

Acidic media: $MO_3(H_2O)_x^+$ (only Np)

Basic media : MO_4^- (Np, Pu and Am)





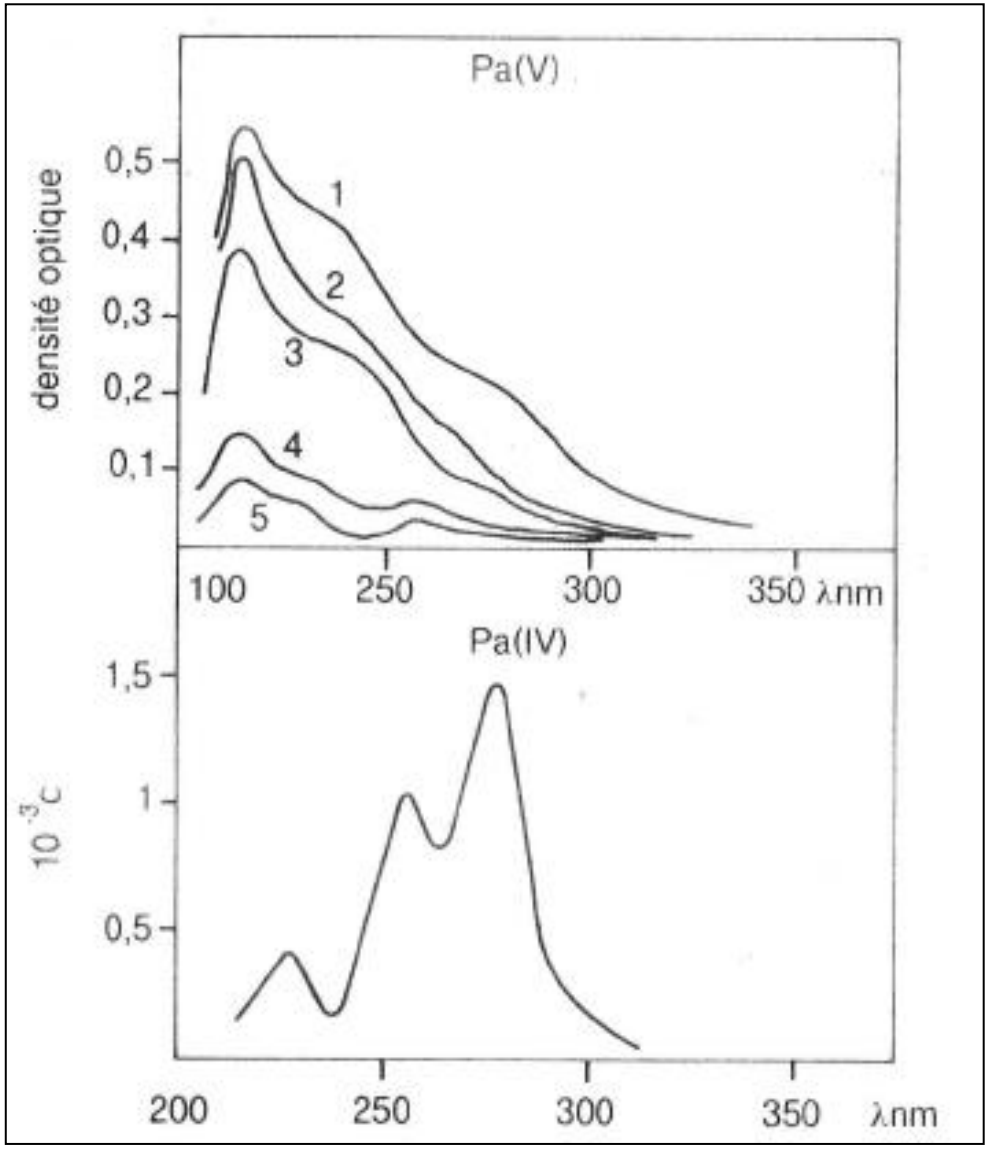
Protactinium: an irregularity in the Mendeleev Table

Pa(V) = PaO^{3+} $(PaO(OH)_x(H_2O)_y^{3-x})$
PaF_z^{5-z} (z = 6 and 7)

Polymerisation of Pa(V) (colloïdal form)

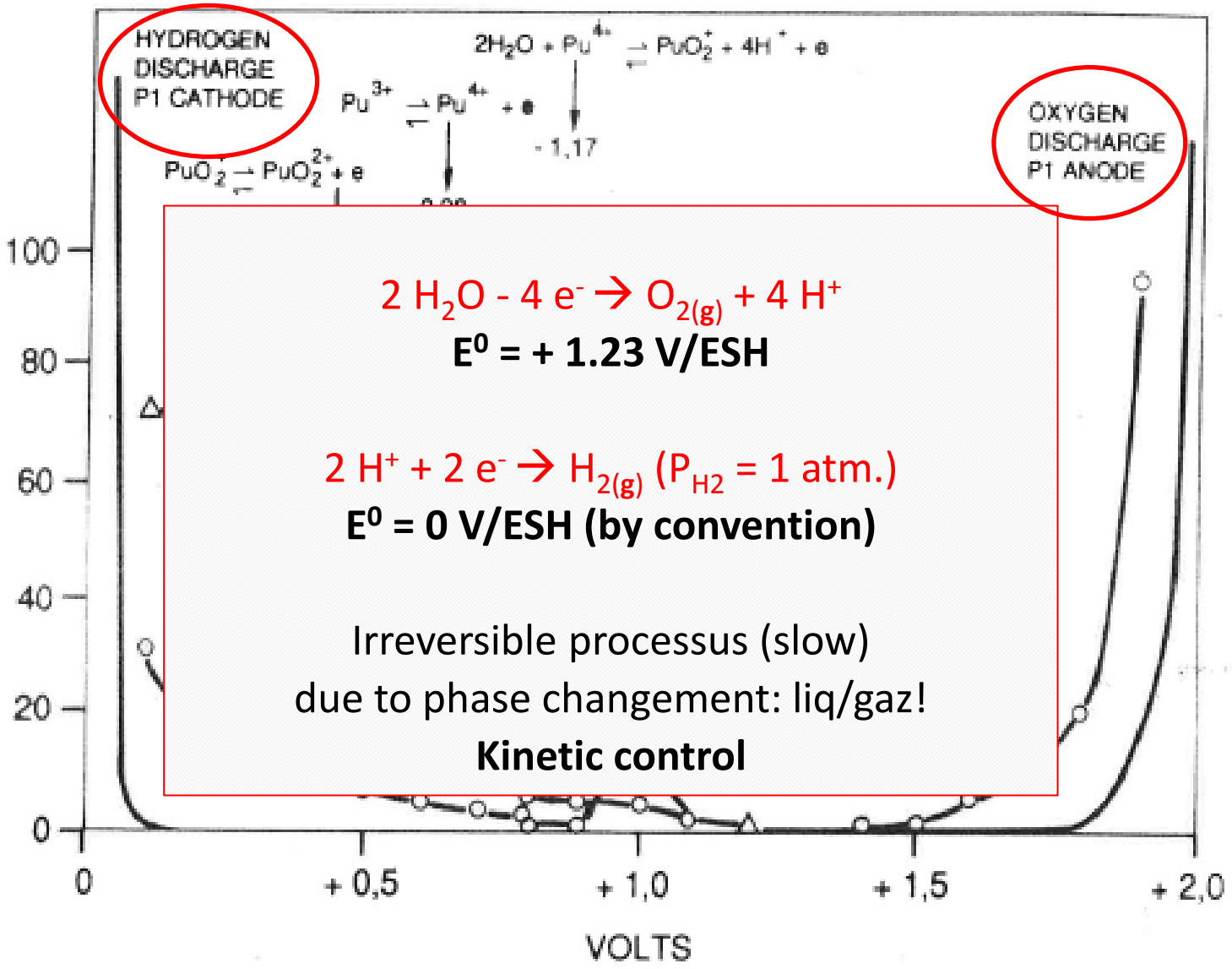
Adsorption (glass wall, …)
Chemical analog: Ta(V) and Nb(V)

Pa(IV) = ?



Spectres d'absorption de Pa(V) et Pa(IV) en milieux perchlorique.
Pa(V). Solutions fraichement préparées par dilution d'une solution-stock de protactinium dans $HClO_4$ 11,5M.
C_{Po} ~ 10^{-2}M - spectres : 1. $HClO_4$ 11,5M ; 2. $HClO_4$ 3M ;
3. μ = 3 $[H^+]$ = 0,95M ; 4. μ = 3, $[H^+]$ = 0,14M ; 5, μ = 3, $[H^+]$ = 10^{-2}M
Pa(IV) - $HClO_4$ 1,5M. Solutions préparées par dissolution de $PaCl_4$

Kinetic control of water electroactivity



$2\ H_2O - 4\ e^- \rightarrow O_{2(g)} + 4\ H^+$

E^0 = + 1.23 V/ESH

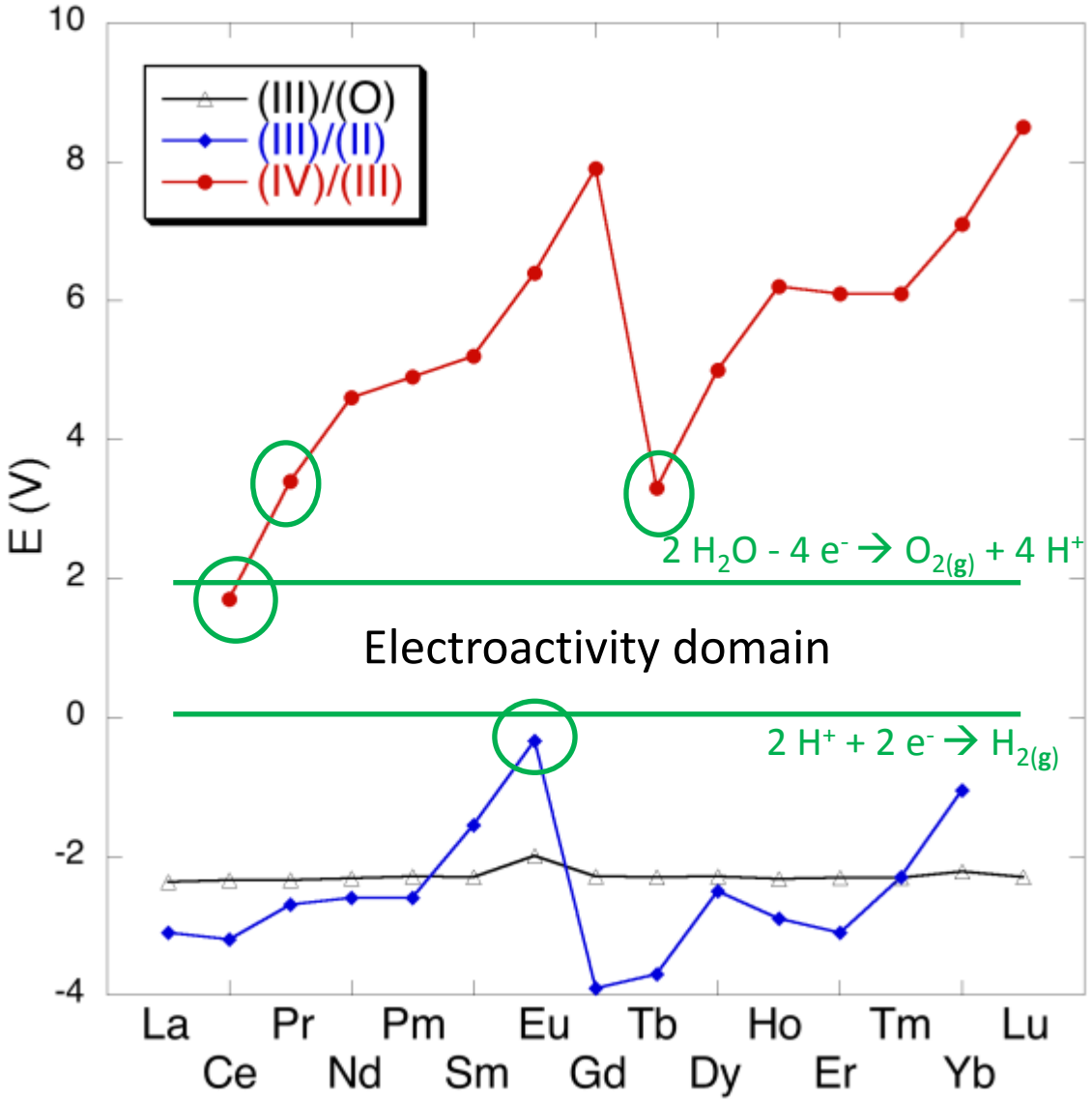
$2\ H^+ + 2\ e^- \rightarrow H_{2(g)}$ (P_{H2} = 1 atm.)

E^0 = 0 V/ESH (by convention)

Irreversible processus (slow)
due to phase changement: liq/gaz!

Kinetic control

Stability of Lanthanide in aqueous solution

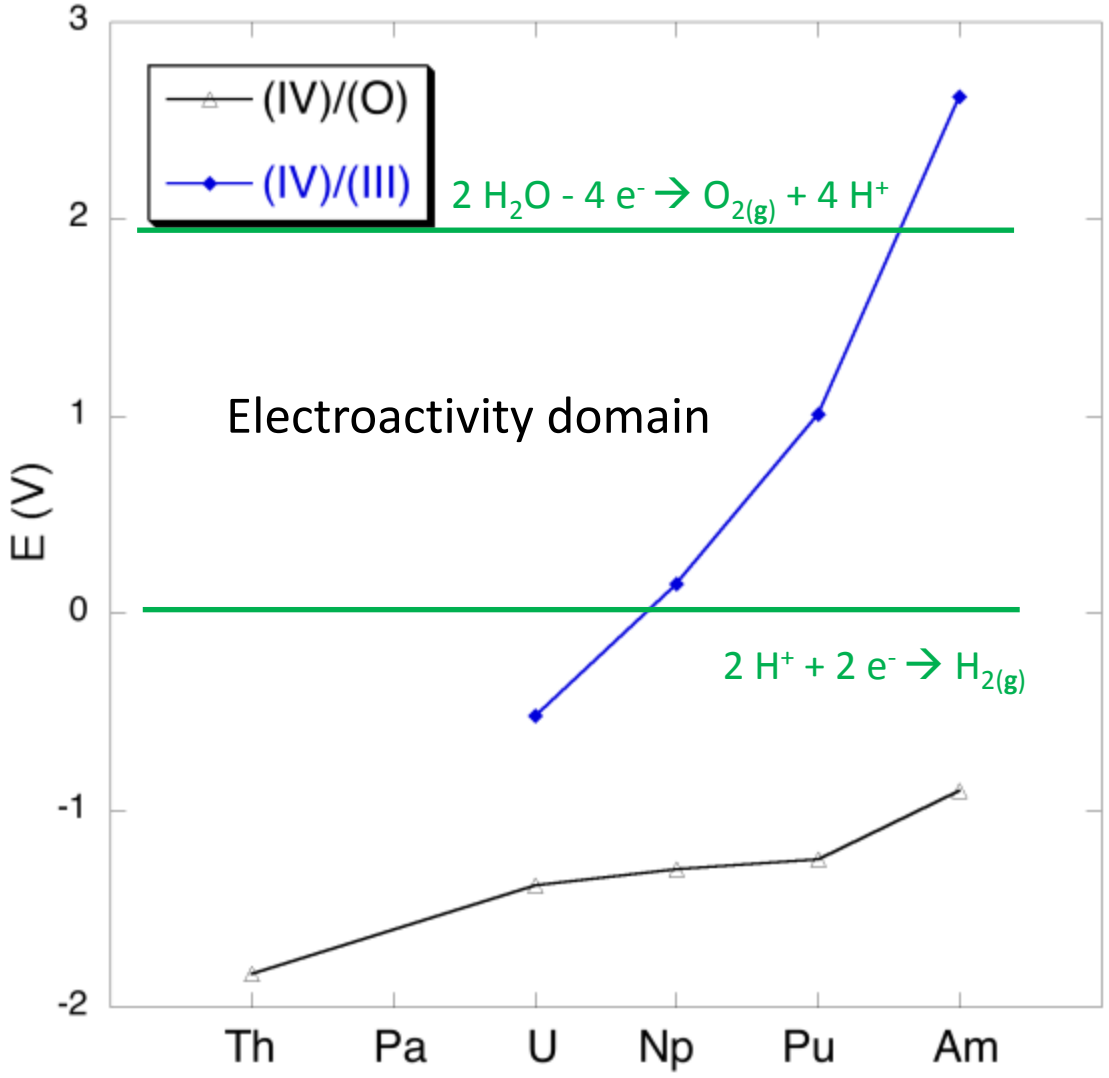


Stability of Ce(IV) and « Metastability » of Pr(IV), Tb(IV) and Eu(II)

Oxidation of Ln(0)
Reduction of Ln(IV)
Stability of Ln(III) only!

$Ln(0) + 3\ H^+ \rightarrow Ln_{aq}^{3+} + 3/2\ H_{2(g)}$

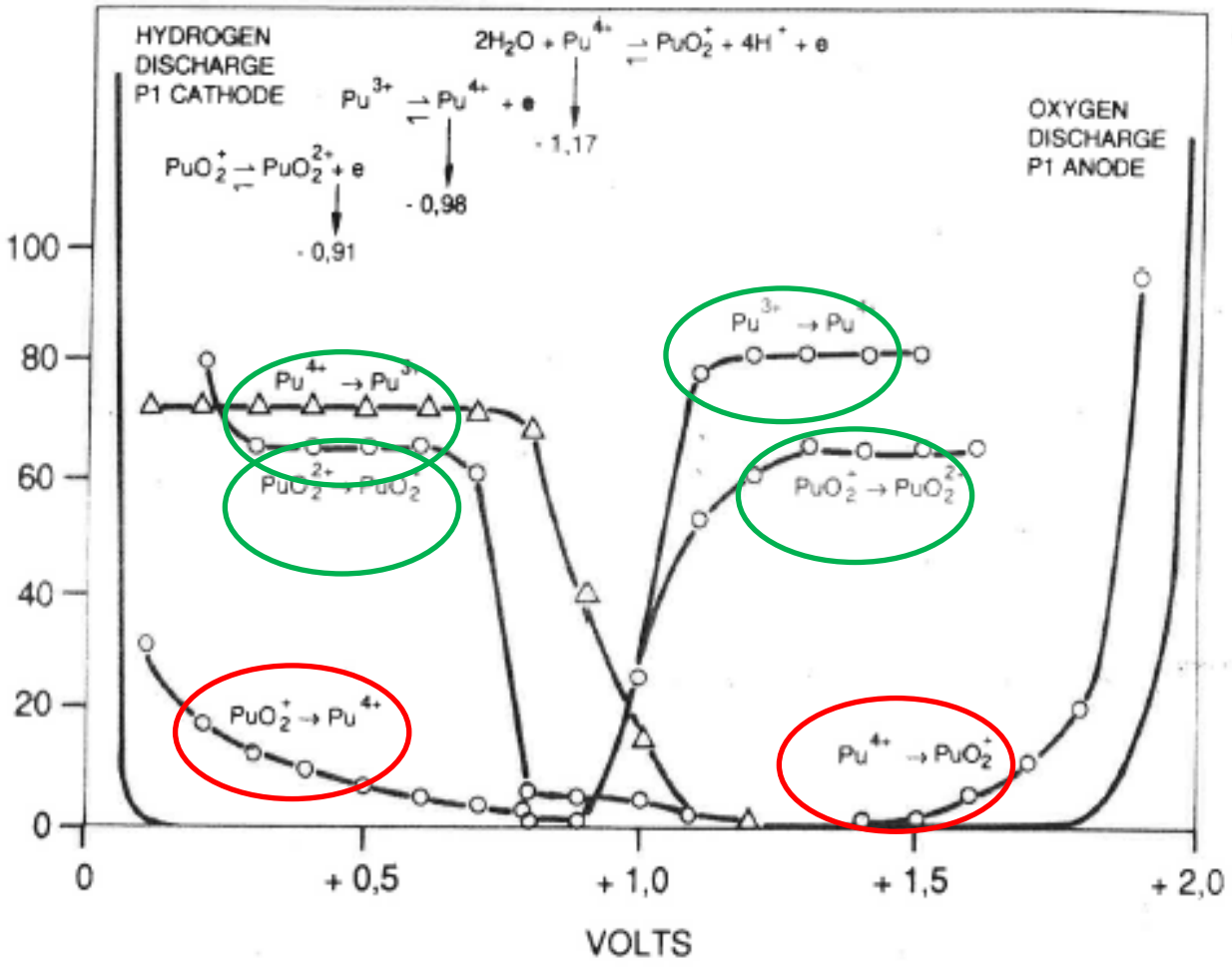
Stability of Actinide in aqueous solution



Oxidation of An(0)
Oxidation of U(III)
Reduction of Am(IV)
Stability of An: +III, +IV etc…

$Pu(\alpha) + 3\ H^+ \rightarrow Pu_{aq}^{3+} + 3/2\ H_{2(g)}$

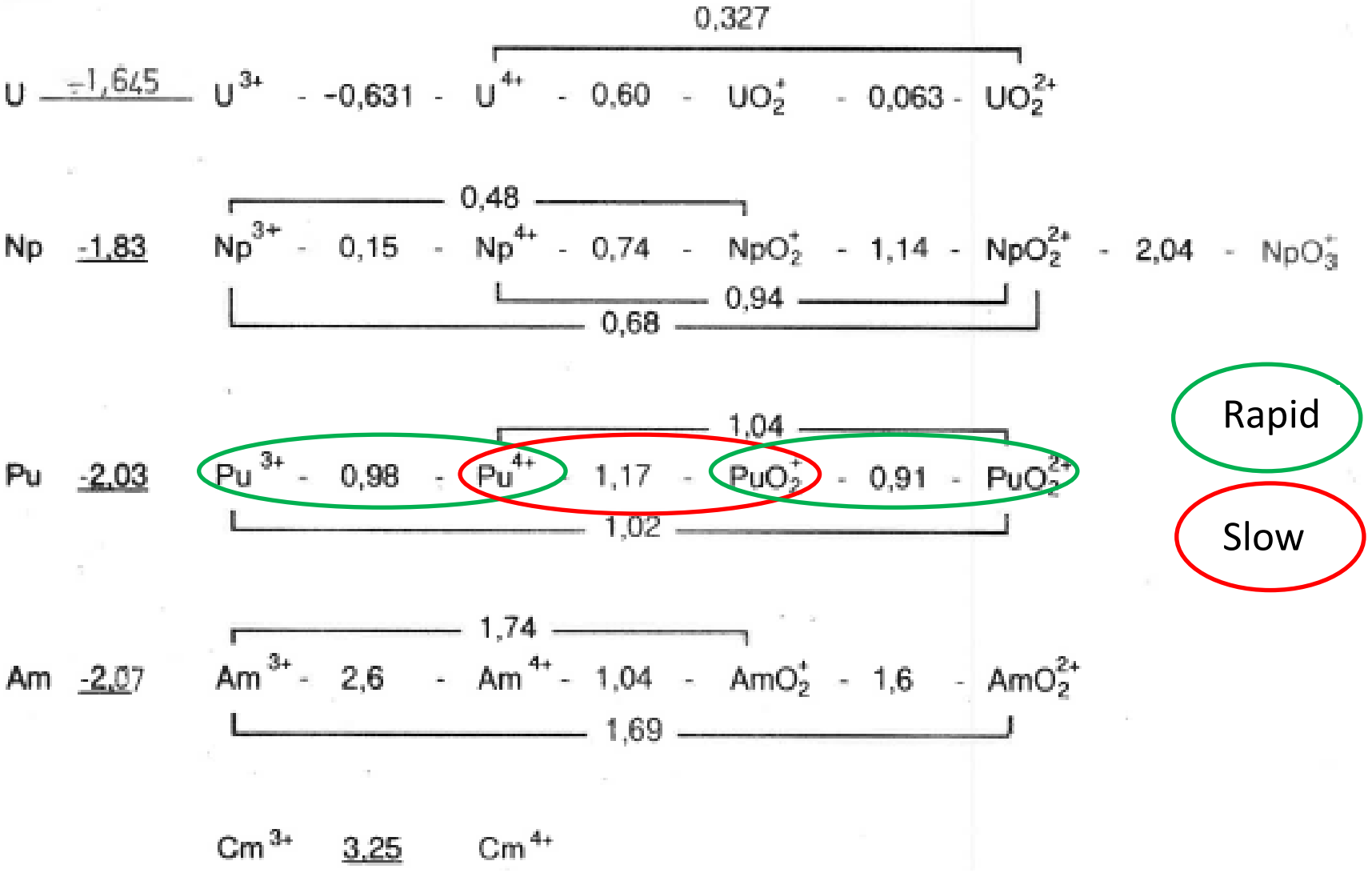
Redox behavior of An: Thermodynamic or Kinetic control



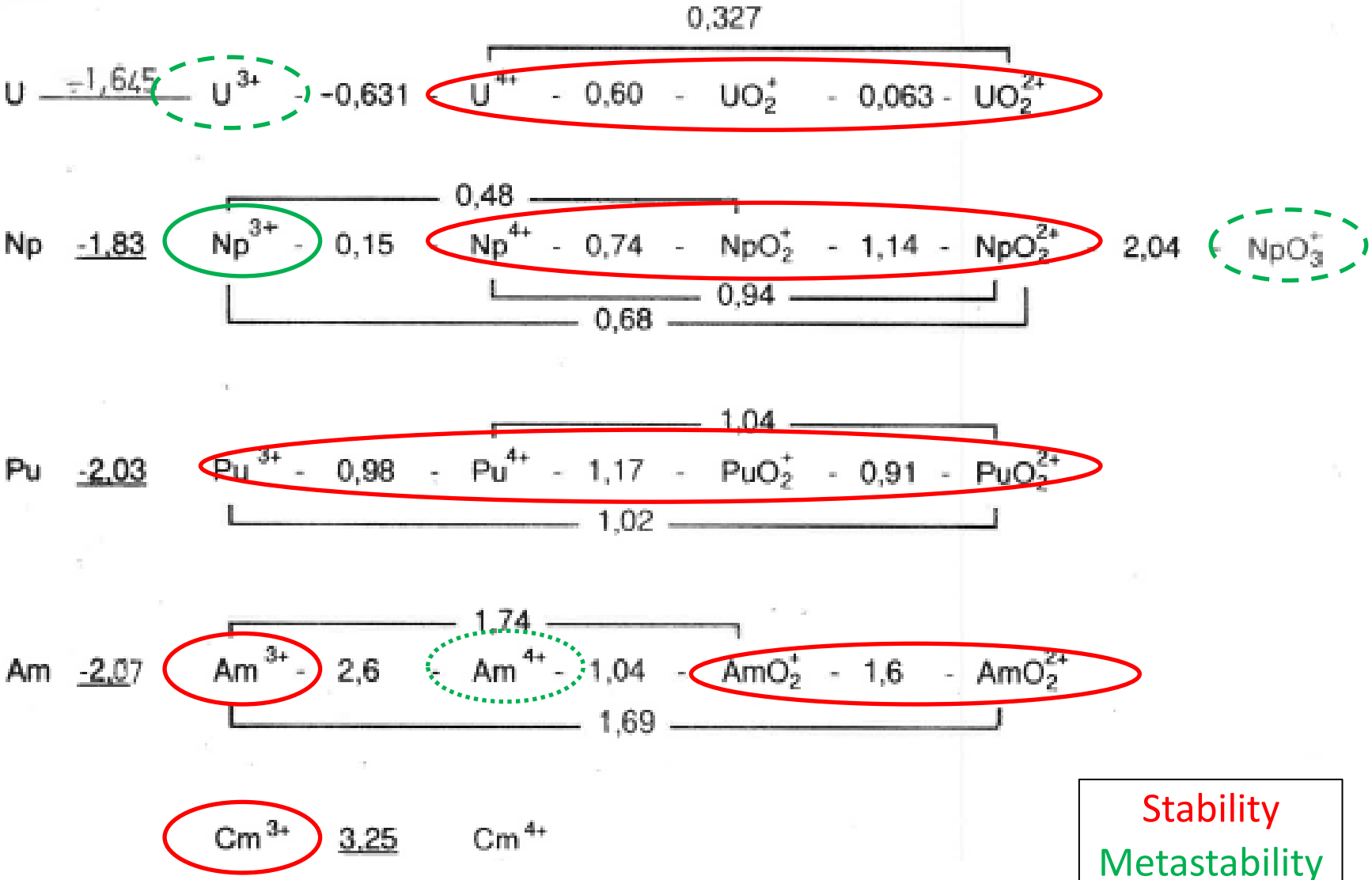
Only one charge transfert:
An^{n+} / $An^{(n+1)+}$ and
AnO_2^{n+} / $AnO_2^{(n+1)+}$
Reversible process (rapid):
Thermodynamic control

Chemical reaction coupled with charge transfert:
An^{4+} / AnO_2^{+}
Irreversible process (slow):
Kinetic control

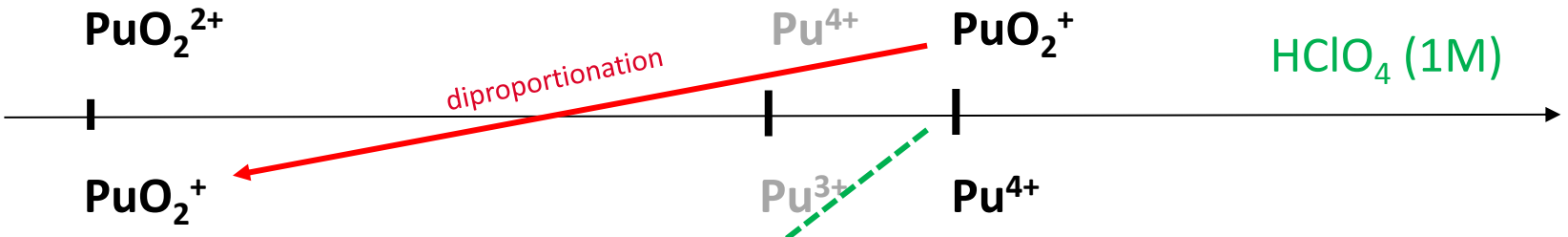
Latimer diagram for Actinide (aqueous solution, $HClO_4$ (1M), V/ESH)



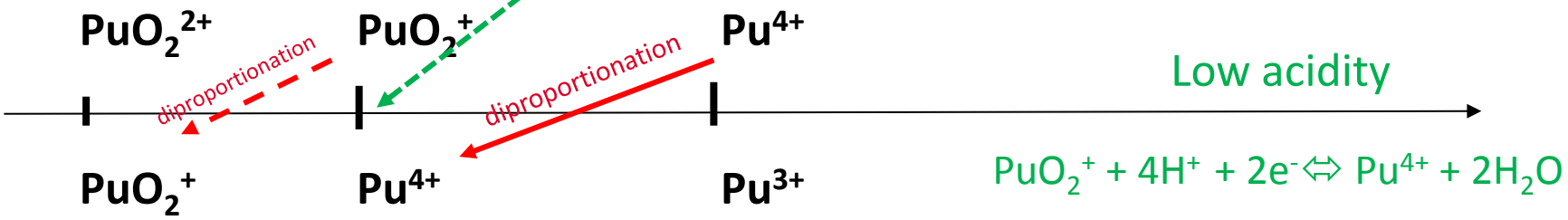
Stability (metastability) in acidic media ($HClO_4$ 1M)



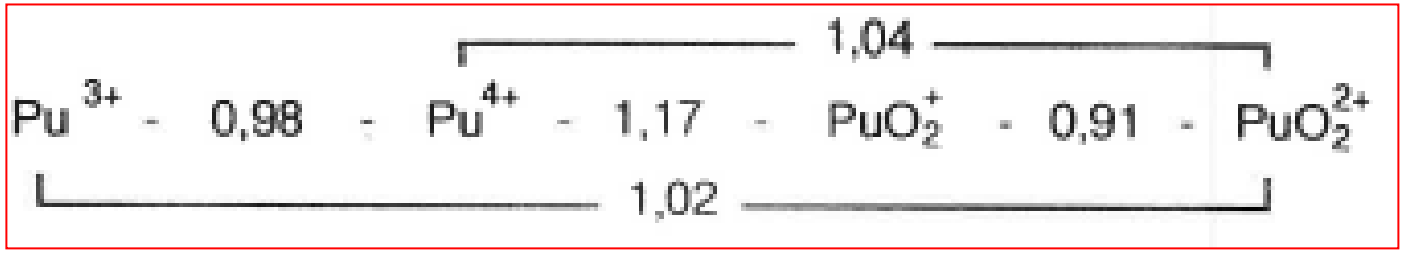
Disproportionation of Pu(IV) and Pu(V)



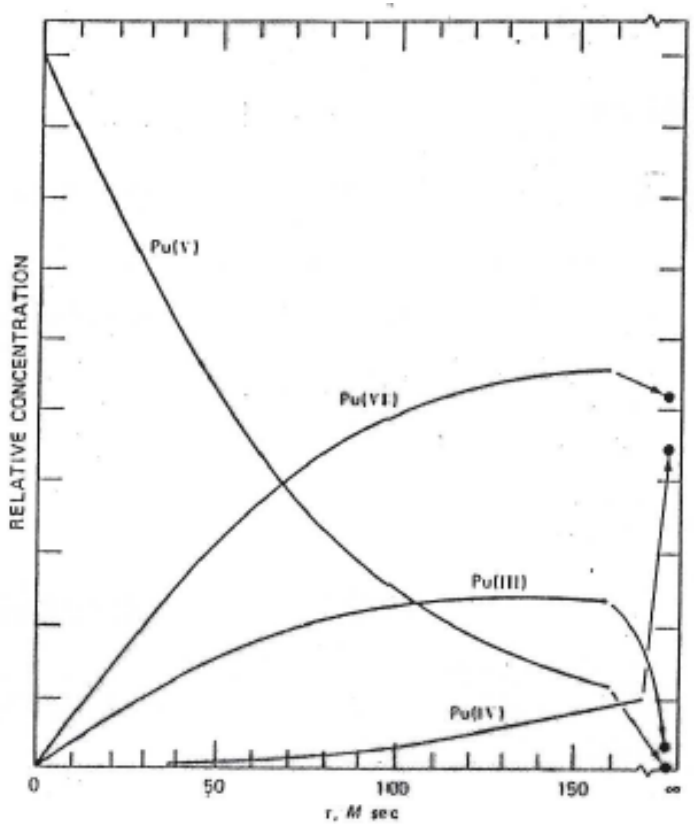
$$2PuO_2^{+} + 4H^{+} \Leftrightarrow Pu^{4+} + PuO_2^{2+} + 2H_2O$$



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



Disproportionation of Pu(V) (and redox reaction)



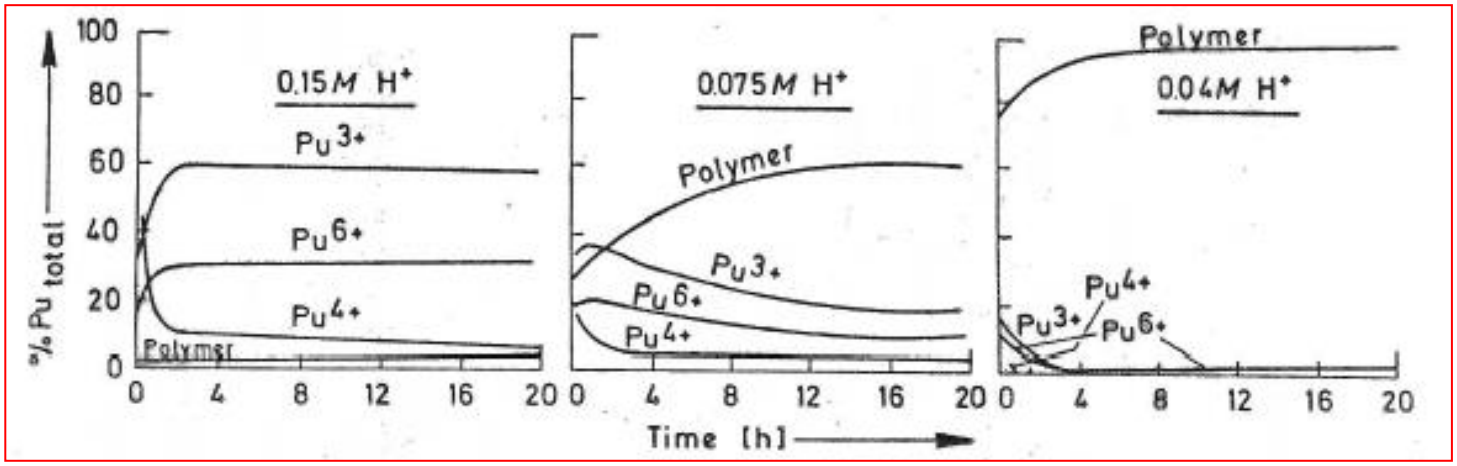
$$2PuO_2^+ + 4H^+ \Leftrightarrow Pu^{4+} + PuO_2^{2+} + 2H_2O \quad \text{slow}$$

$$PuO_2^+ + Pu^{4+} \Leftrightarrow PuO_2^{2+} + Pu^{3+} \quad \text{rapid}$$

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

Disproportionation of Pu(V) in $HClO_4$ (1M)

Disproportionation of Pu(IV) (and hydrolysis)



$$2Pu^{4+} + 2H_2O \Leftrightarrow Pu^{3+} + PuO_2^{+} + 4H^{+} \quad \text{slow}$$

$$Pu^{4+} + PuO_2^{+} \Leftrightarrow Pu^{3+} + PuO_2^{2+} \quad \text{rapid}$$

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

Kinetic law:

$$-d[Pu(IV)]/dt = [Pu^{4+}]^2 (k_1[H^+]^{-3} + k_1'[H^+]^{-4}) - [Pu^{3+}][PuO_2^+](k_2[H^+] + k_2')$$

$$Pu^{4+} + H_2O \rightleftharpoons PuOH^{3+} + H^+$$

$$Pu^{4+} + 2H_2O \rightleftharpoons Pu(OH)_2^{2+} + 2H^+$$

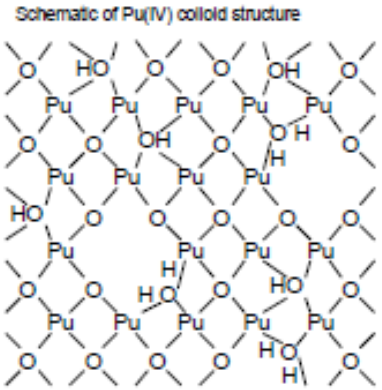
$$PuOH^{3+} + Pu(OH)_2^{2+} \longrightarrow Pu^{3+} + PuO_2H^{2+} + H_2O$$

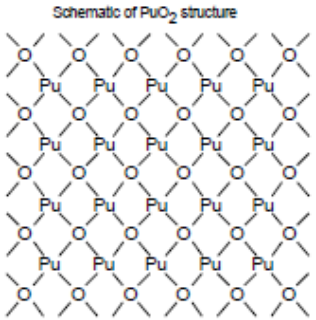
$$2Pu(OH)_2^{2+} \longrightarrow Pu^{3+} + PuO_2^{+} + 2H_2O$$

$$PuO_2H^{2+} \rightleftharpoons PuO_2^{+} + H^+$$

Chemical Behavior of Actinide in aqueous solution: outlook

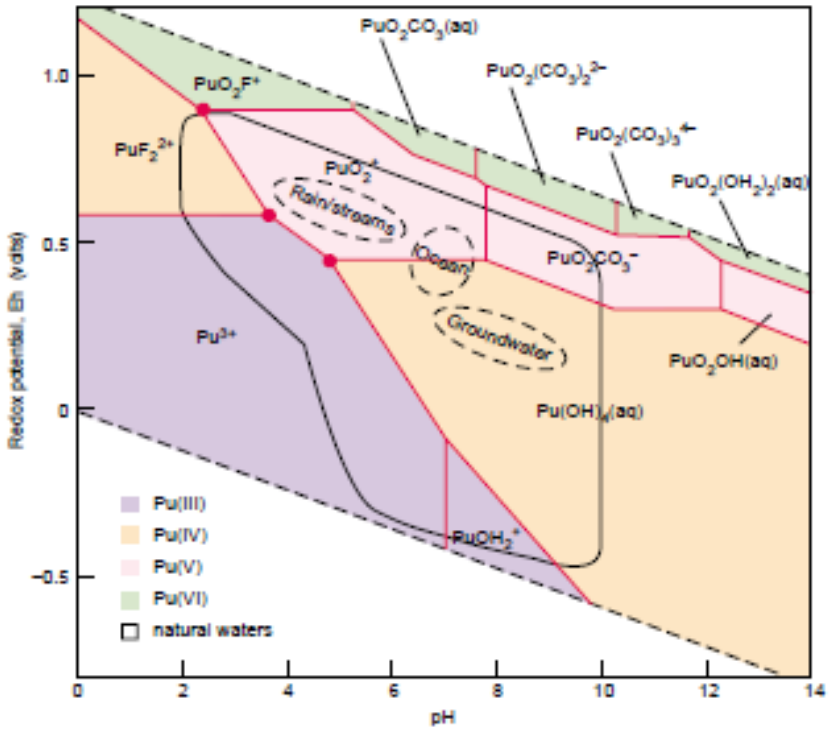
1- Hydrolysis





2- Complexation

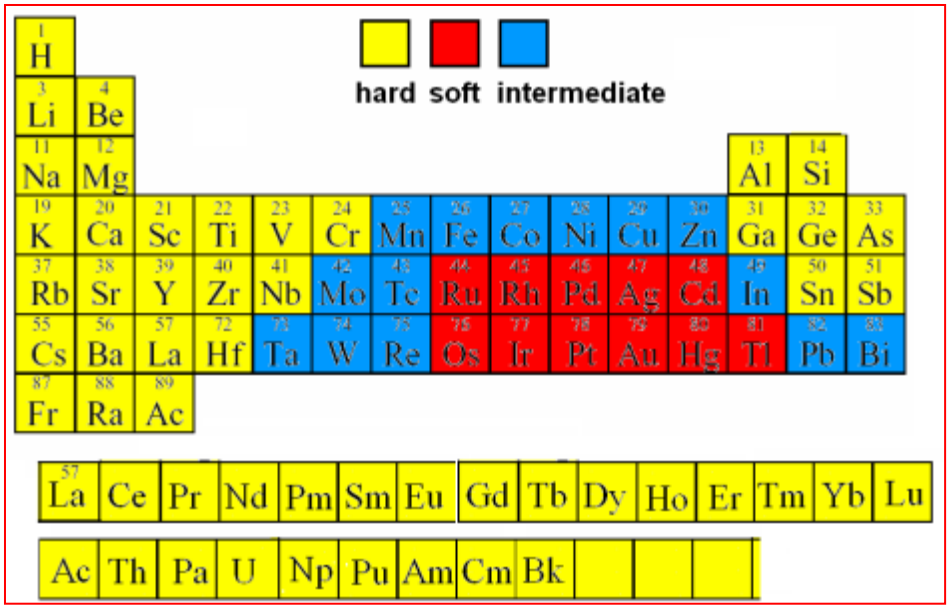
3- Pourbaix diagram



Chemical Behavior of Actinide in aqueous solution: basic knowledge

1- Actinide ions are hard acid cations (Pearson (1963) Hard and Soft Acids and Bases (HSAB)

For some metal ions, their chemistry is dominated by size and charge, while for others it is dominated by their Electronegativity

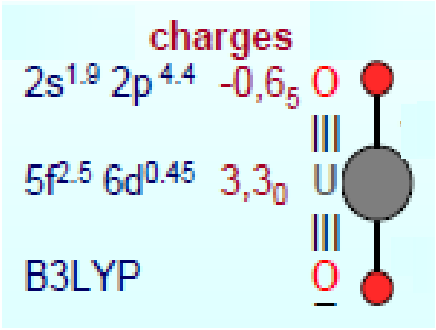


2- Electrostatic interaction (ionic potential z/r)

3- For Actinyl, z are the effective charge:

Oxidation state : $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$

Effective charge : +4 +3.3 +3 +2.3



Hydrolysis

Hydrolysis = special case of complexation (in water solvent)
Ligand = OH^- « hydroxyl anion »

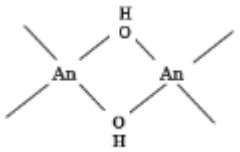
When pH increase: structure aquo ions is modified
One H^+ are expelled from inner water sphere to unbound water (into the bulk)

$$M(H_2O)_n^{Z+} + H_2O \Leftrightarrow MOH(H_2O)_{n-1}^{(z-1)+} + H_3O^+$$

$$M^{z+} + H_2O \Leftrightarrow MOH^{(z-1)+} + H^+$$

As hydroxyl anion is a bridger ligand, Hydrolysis produced hydroxopolynuclear compounds (and sometime polymer):

$$xM^{z+} + yH_2O \Leftrightarrow M_xOH_y^{(xz-y)+} + yH^+$$



Hydrolysis of Pu(IV)

Technical difficulties: 1) disproportionation

2) occurence of polymers

3) slow kinetics

	$\log K_{xy}$
$Pu^{4+} + H_2O \Leftrightarrow PuOH^{3+} + H^+$	-0,5
$Pu^{4+} + 2H_2O \Leftrightarrow Pu(OH)_2^{2+} + 2H^+$	-2,3
$Pu^{4+} + 3H_2O \Leftrightarrow Pu(OH)_3^{+} + 3H^+$	-5,3
$Pu^{4+} + 4H_2O \Leftrightarrow Pu(OH)_4 + 4H^+$	-9,5

For largest $[Pu^{4+}]$ concentrations: polymer with molecular mass 10^3 to 10^{10} g

$Pu(OH)_4$ green ; $[Pu^{4+}]\,[OH^-]^4$ = solubility product 10^{-55} !!

$Pu(OH)_4$ soluble if freshly prepared but insoluble if aged ($PuO_2 - nH_2O$)

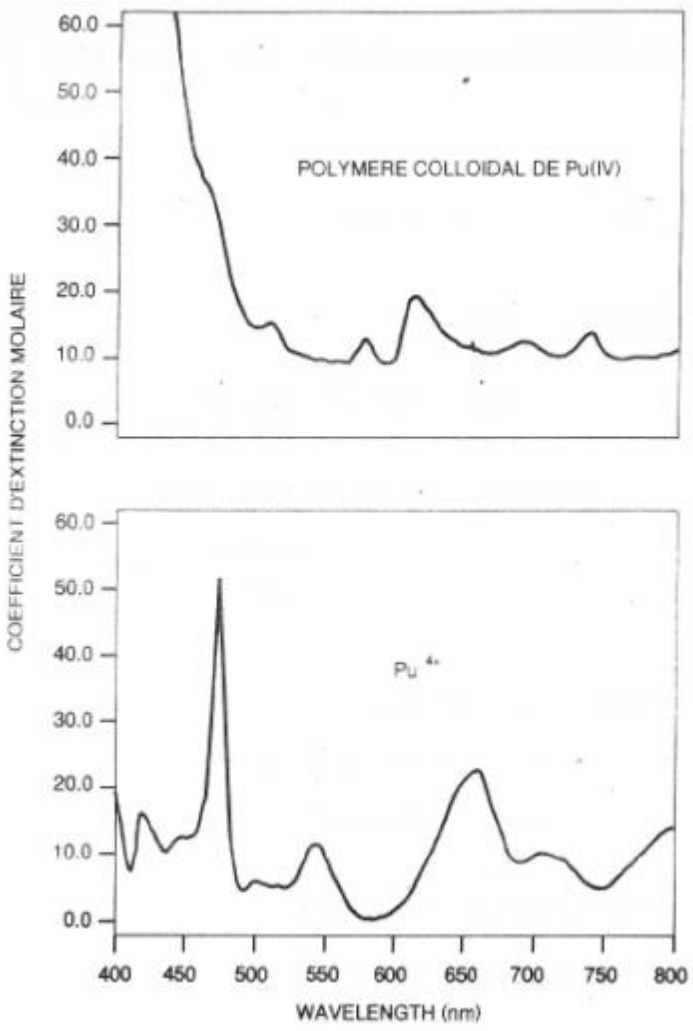
Pu(IV) polymeric form

-Low acidity (less than 0.5M, without complexing anions)

-Quick formation (dilution of an acidic Pu(IV) solution with water will frequently cause polymerisation in localized areas of low acidity, even when the final acidity of the solution is too high for polymerisation occur)

-Irreversibility (hight stability, no precipitation, ….)

-No reactivity (very slow with strong complexant anion such as F^-, or oxydo-reduction)



Hydrolysis of Pu(IV)

Ion (0.01 M)	Hydrolysis (10%) at pH
PuO_2^+	9
Pu^{3+}	7
PuO_2^{2+}	4
Pu^{4+}	0.5

For the same actinide, the hydrolysis increase with:

$$\mathbf{M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}}$$

no steric constraint with OH^- (the same size as H_2O) !

Complexation

Solution chemistry: Ionic potential (z/r), Acido-Basicity of Ligand (pKa) and Cation (hydrolysis), stoechiometry, speciation, activity coefficient, …

Coordination chemistry: inner-sphere or outer-sphere, atom donnor, coordination number, steric constraints, polyhedre, ….

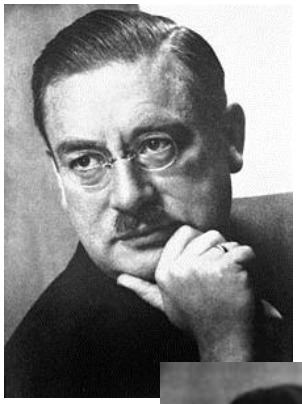
Redox chemistry (ligand and cation): Nernst law, intra-molecular, temperature effect, …

Electrolyte theory

Electrolyte theory provides a useful theory for thermodynamic application

Debye – Huckel models (and also more complicated model as Pitzer theory and others…)

$$I = \frac{1}{2}\sum_i m_i z_i^2$$



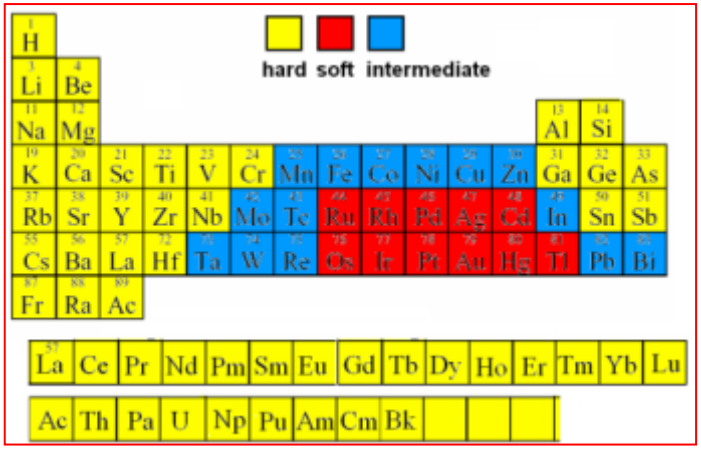
Debye-Hückel equation	$\log\gamma_i = -Az_i^2\sqrt{I}$
Extended Debye-Hückel equation	$\log\gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}}$
Davies equation	$\log\gamma_i = -Az_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right)$
Specific Ion Interaction Theory (SIT)	$\log\gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}} + \sum_k \varepsilon_{(i,k,I)} m_i$

A: Debye_Hückel slope. **B**: Debye_Hückel parameter; $\mathbf{a_i}$: effective distance
$\mathbf{z_i}$: ionic charge; **I**: ionic strength; $\mathbf{m_i}$: molality;
$\mathbf{e_{(i,k,I)}}$: interaction coefficients between ions i and k at a the ionic strength I.

Hard and Soft donnor

-Hard acids interact with Hard bases through ionic bonding

- Soft acids and bases interactions favour covalent bonding



List of Some Hard and Soft Acids and Bases

A. Acids

i. Hard.	+1 ions	H, Li to Cs
	+2 ions	Mg to Ba, Fe, Co, Mn
	+3 ions	Fe, Cr, Ga, In, Sc, Y, Ln, An
	+4 ions	Ti, Zr, Hf, Ln, An
	-yl ions	VO^{2+}, MoO_3, AnO_2, $Mn(VII)O_4^{1-}$
ii. Borderline.	+2 ions	Fe, Co, Ni, Cu, Zn, Sn, Pb
	+3 ions	Sb, Bi, Rh, Ir, Ru, Os
iii. Soft.	Neutral	BH_3
	+1 ions	Cu, Ag, Au, Hg, CH_3Hg,
	+2 ions	Cd, Hg, Pd, Pt

B. Bases

i. Hard.	Neutral	H_2O, ROH, NH_3, RNH_2, N_2H_4, R_2O, R_3PO, $(RO)_3PO$
	-1 ions	OH, RO, RCO_2, NO_3, ClO_4, F, Cl
	-2 ions	O, $R(CO_2)_2$, CO_3, SO_4
	-3 ions	PO_4
ii. Borderline.	Neutral	$C_6H_5NH_2$, C_5H_5N
	-1 ions	N_3, NO_2, Br
	-2 ions	SO_3
iii. Soft.	Neutral	C_2H_4, C_6H_6, CO, R_3P, $(RO)_3P$, R_3As, R_2S
	-1 ions	H, CN, SCN, RS, I
	-2 ions	S_2O_3

Water Radiolysis product: H_2O_2

Chemical properties in aqueous media:

- **Acido-basic**

  $H_2O_2 \Leftrightarrow HO_2^- + H^+$ $\quad pK_1 = 11,6$

  $HO_2^- \Leftrightarrow O_2^{2-} + H^+$ $\quad pK_2$ very high

- **Coordination**

  $M^{n+} + m\ H_2O_2 \Leftrightarrow M(O_2)_m^{(n-2m)+} + 2mH^+$

  Bidentate, « bridger », no steric constraint

- **Redox**

  $H_2O_2 + 2\ H^+ + 2\ e \Leftrightarrow 2H_2O$ $\quad E^0 = 1.77$ V/ENH

  $H_2O_2 - 2\ e \Leftrightarrow O_2 + 2H^+$ $\quad E^0 = 0.68$ V/ENH

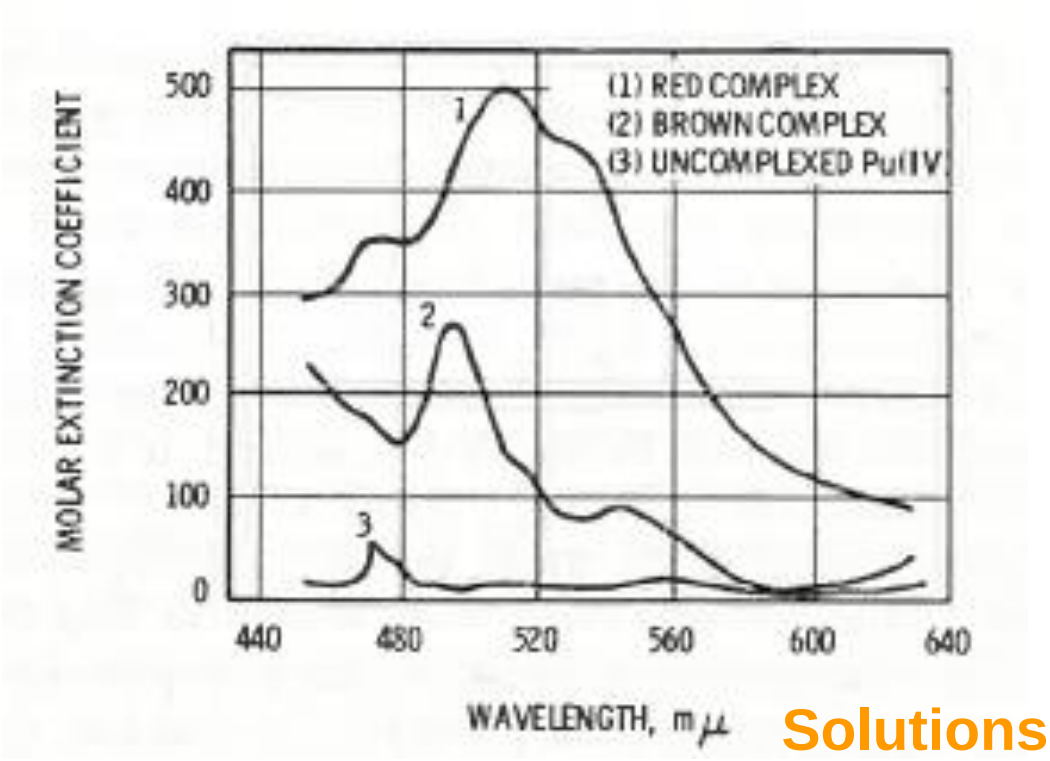
The case of $Pu - H_2O_2$ (1)

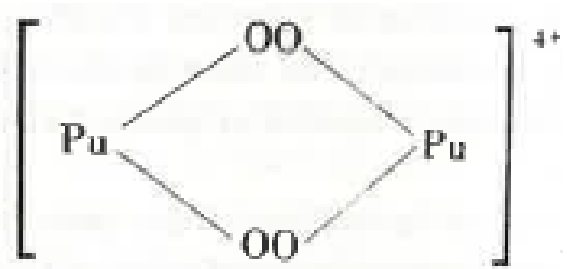
$2\ Pu^{4+} + H_2O_2 + H_2O \Leftrightarrow (Pu)_2(O_2)(OH)^{5+} + 3H^+$ $K_1 = 8{,}8 \times 10^6$ mol/L

brun (complex 2:1)

$2\ Pu^{4+} + 2H_2O_2 \Leftrightarrow (Pu(O_2))_2^{4+} + 4H^+$ $K_2 = 6{,}3 \times 10^8$ mol/L

rouge (complex 2:2 (1:1))





Solutions Pu^{4+} (HCl 0.5 M) + H_2O_2

The case of Pu – H_2O_2 (2)

$Pu^{4+} + 2\ H_2O_2 + H_2O \Leftrightarrow \mathbf{Pu(O_2)_2} + 4H^+$

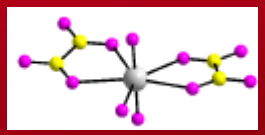
unsoluble complex 1:2

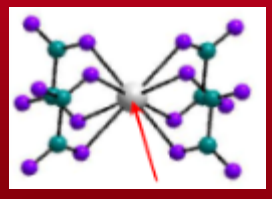
But Pu(IV) reduction to Pu(III) at low acidity (0.5 M) produce $(Pu^{IV}Pu^{III})(O_2)_{7/2}$

Calcination of this complex can be used to prepare PuO_2, but it is difficult to control the redox chemistry of Pu !

Reduction of Pu(VI) to Pu(IV) with H_2O_2, but U(VI) can be complexed to form an unsoluble compounds: $UO_2(O_2)$ (industrial application in front-end cycle)

The case of An(III and IV) with $C_2O_4^{2-}$: speciation





- Acido-basicity $H_2C_2O_4 \Leftrightarrow H^+ + HC_2O_4^-$ $pK_{a1} = 1.2$

$HC_2O_4^- \Leftrightarrow H^+ + C_2O_4^{2-}$ $pK_{a2} = 4.2$

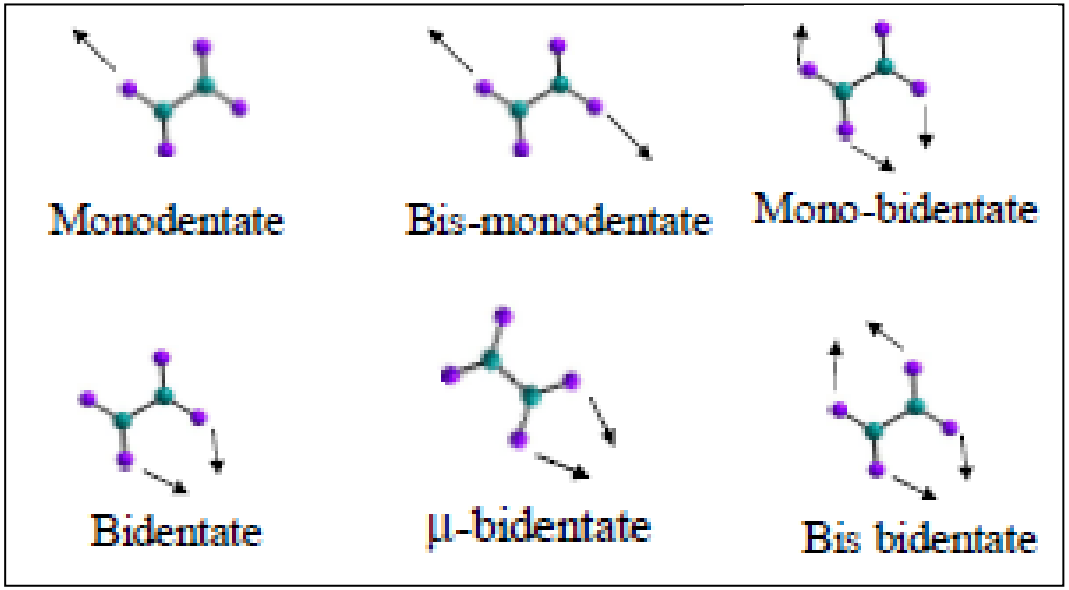
- No redox reaction (in normal pressure and temperature conditions)

-Bidendate, bridger, steric constraint:

Stoechiometry:

1:1 to 1:5 for An(III and IV)

1:1 to 1:3 for An(V and VI)

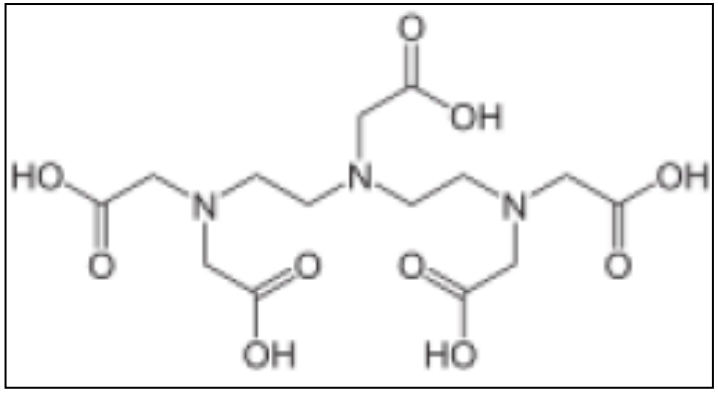


Unsoluble compounds for neutral species: $M_2(C_2O_4)_3.10H_2O$, $M(C_2O_4)_2.6H_2O$, $MO_2(C_2O_4).xH_2O$, …

Thermal treatment: oxide/dioxide (ThO_2, U_3O_8, NpO_2, PuO_2, AmO_2, CmO_2, …)

Polyaminocarboxylate complex of An(III and IV)

DTPA (Diethylene triamine pentaacetic acid, H_5Y) is perhaps the most effective for Pu excretion as anionic Pu(IV) chelate complexes (stoechiometry 1:1).



CN = 8, but steric constraint

Redox behavior (slow reductant at ambiant temperature

- 5 carboxylate functions and 3 nitrogen (CN = 8)
- Reduction of Pu(VI) to Pu(IV)

$$M^{n+} + H_5Y \Leftrightarrow MY^{(n-5)} + 5H^+$$

$Pu(IV)Y^-$ → log K = + 33

$An(III)Y^{2-}$ → log K = + 22 to + 23

DTPA is a medicine for the treatment of contaminated with Pu workers

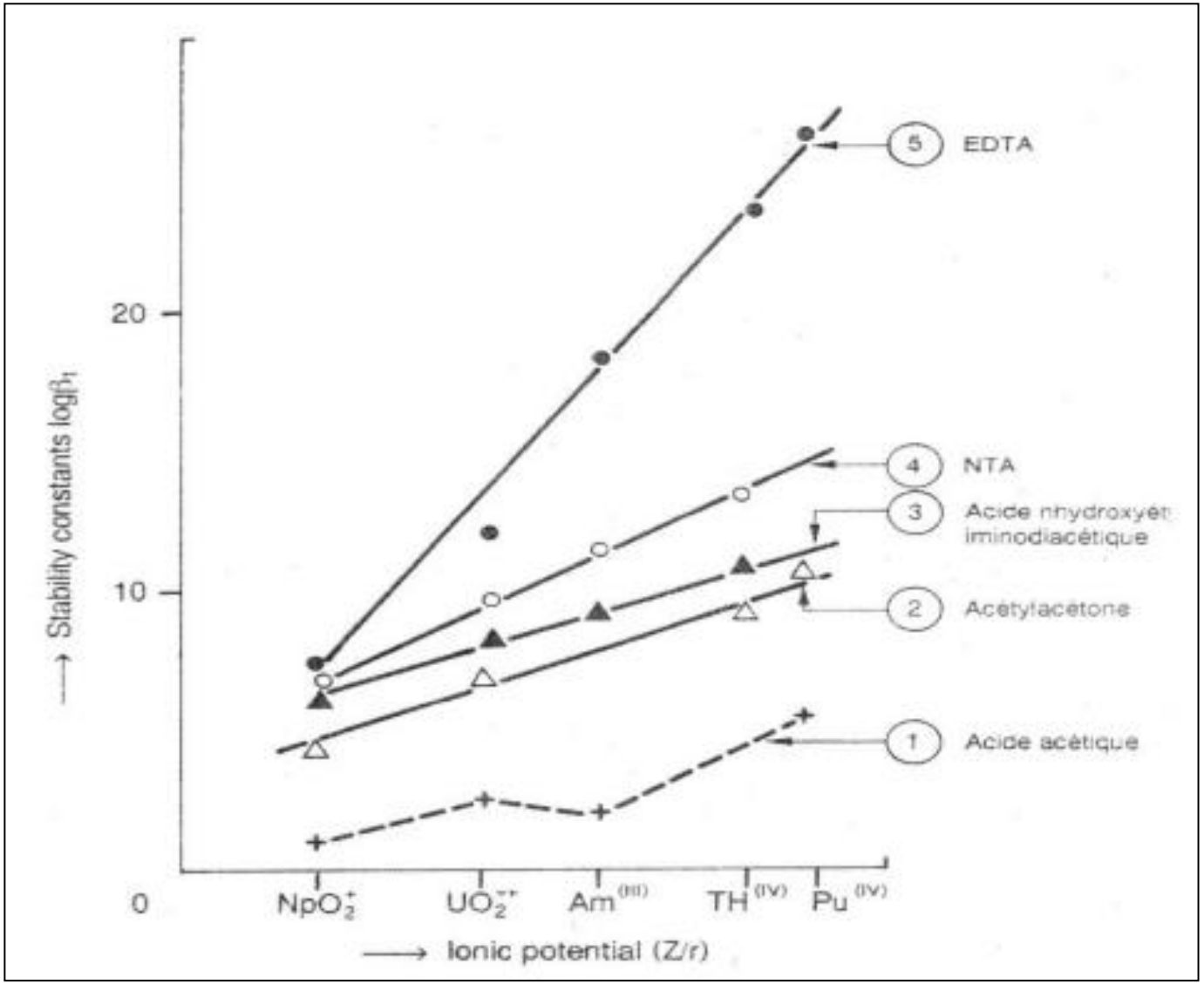
General law for complexation of An in aqueous solution

For the same actinide, the complexation increase with:

$$M^{4+} > M^{3+} > MO_2^{2+} > MO_2^{+}$$

For the same oxidation state, the complexation increase with Z (**atomic number**) according to ionic potential (z/r)

But steric constraint modify this order !



Carbonate complexes of An(V and VI): An = U, Np, Pu and Am

1) Acido-basicity:

2) Not Redox:

$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow CO_3^{2-} + 2H^+$

3) **Complexation**: mono/bidendate, no steric constraint

$UO_2^{2+} + CO_3^{2-} \Leftrightarrow \underline{UO_2CO_3}$

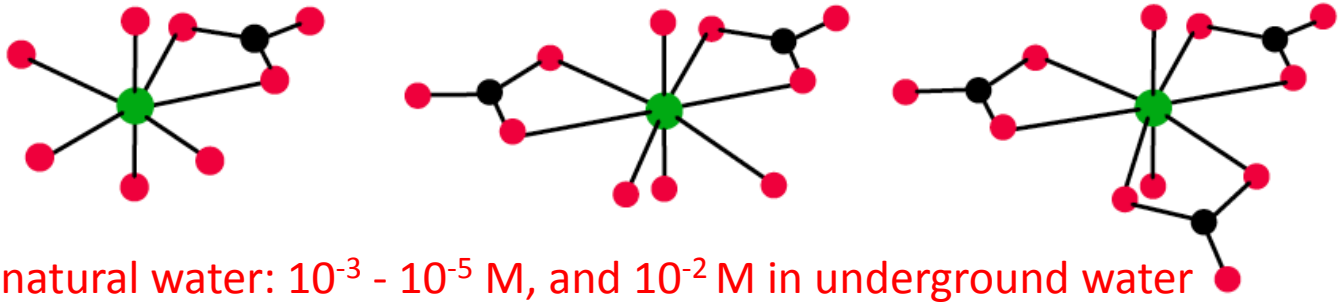
$UO_2CO_3 + CO_3^{2-} + 2\ M^+ \text{ (or } M^{2+}) \Leftrightarrow \underline{M_2UO_2(CO_3)_2}$

$UO_2(CO_3)_2^{2-} + CO_3^{2-} + 4\ M^+ \text{ (or } 2M^{2+}) \Leftrightarrow \underline{M_4UO_2(CO_3)_3}$

AUPuC (RNR fuel)

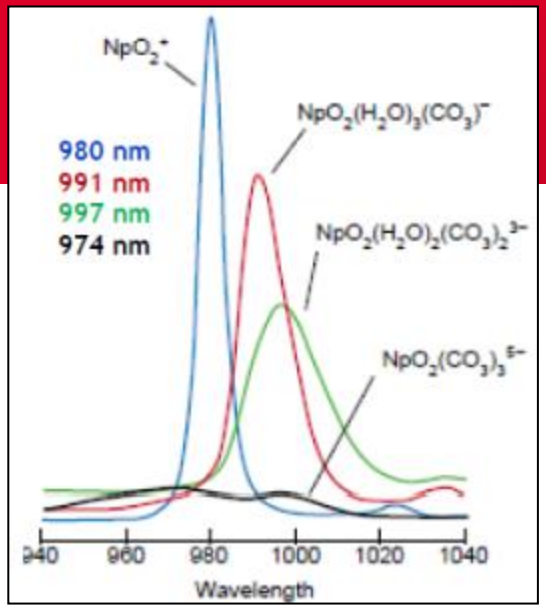
Conversion at 600^{0}C under N_2/H_2 atm. of $(NH_4)_4(U\text{-}Pu)O_2(CO_3)_3$ To $(U\text{-}Pu)O_2$

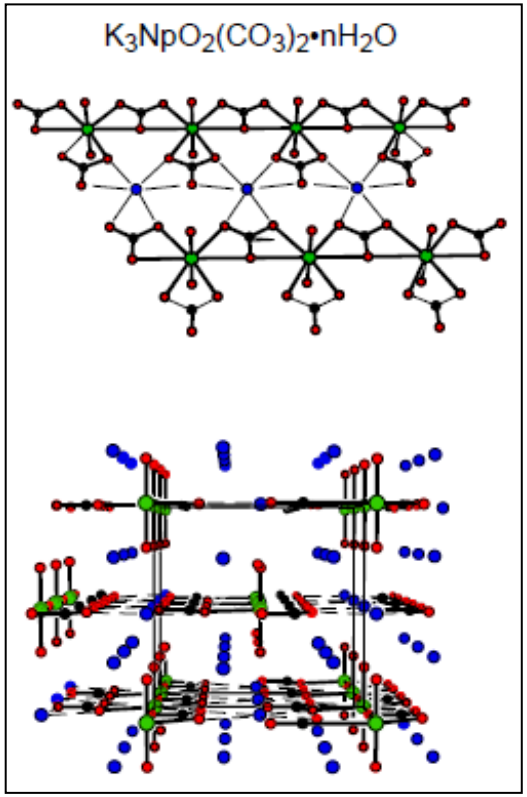
(a) $AnO_2(CO_3)^{m-2}$ (b) $AnO_2(CO_3)_2^{m-4}$ (c) $AnO_2(CO_3)_3^{m-6}$

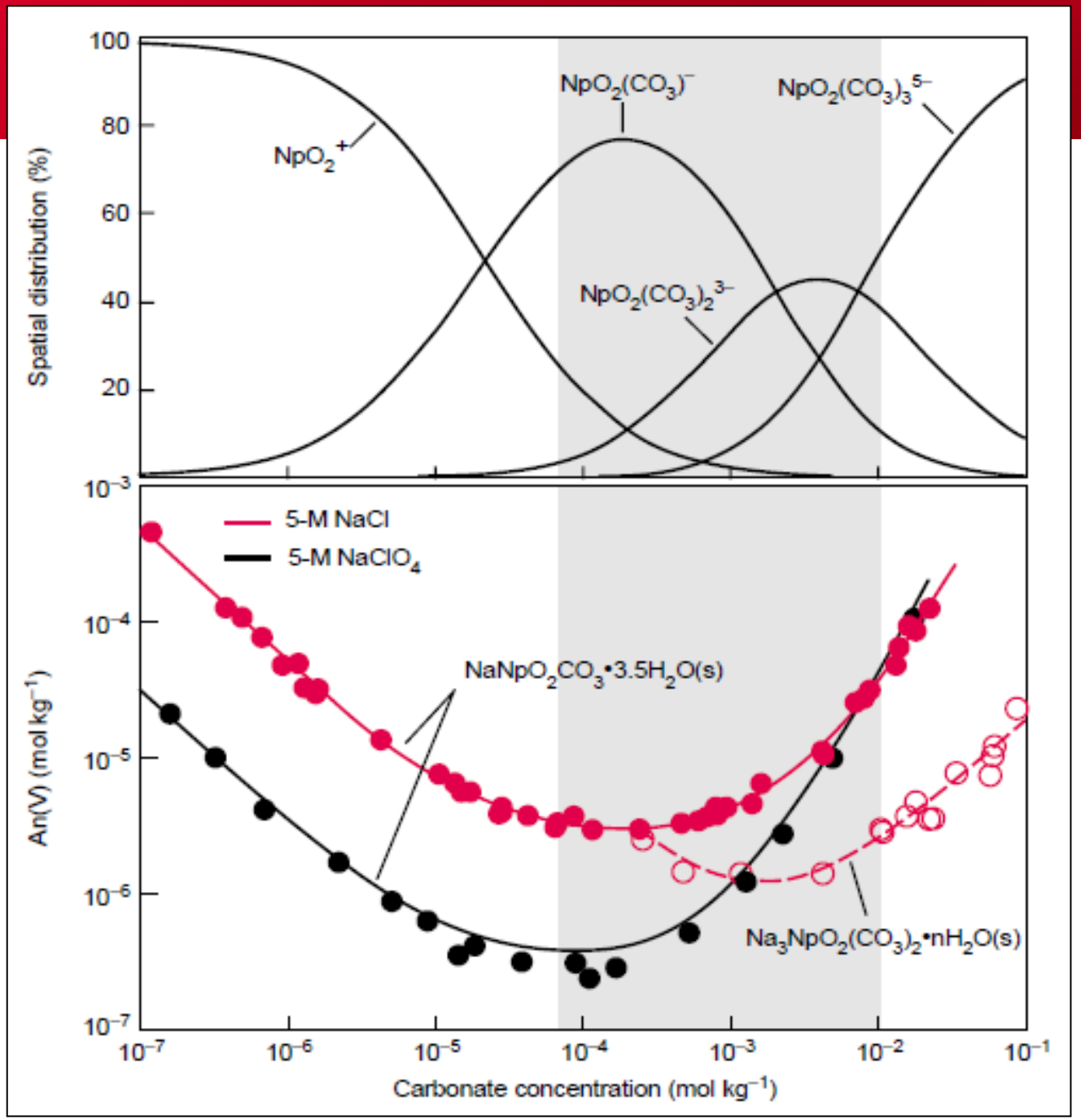


Concentration in natural water: 10^{-3} - 10^{-5} M, and 10^{-2} M in underground water

$AnO_2(CO_3)$, $CaAnO_2(CO_3)_2$ and $Ca_2AnO_2(CO_3)_3$ compounds are expected

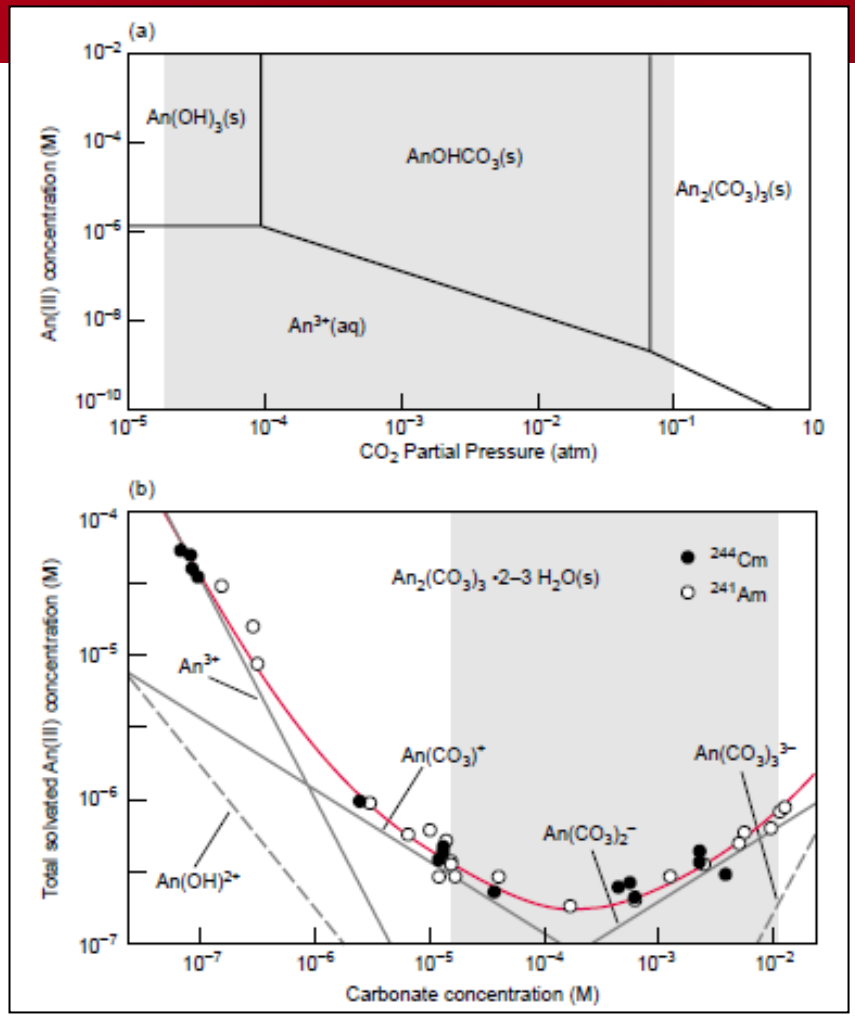

NpO_2^+
$NpO_2(H_2O)_3(CO_3)^-$
$NpO_2(H_2O)_2(CO_3)_2^{3-}$
$NpO_2(CO_3)_3^{5-}$
980 nm
991 nm
997 nm
974 nm
940
960
980
1000
1020
1040
Wavelength


$K_3NpO_2(CO_3)_2 \cdot nH_2O$


Spatial distribution (%)
100
80
60
40
20
NpO_2^+
$NpO_2(CO_3)^-$
$NpO_2(CO_3)_2^{3-}$
$NpO_2(CO_3)_3^{5-}$
An(V) (mol kg^{-1})
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
5-M NaCl
5-M $NaClO_4$
$NaNpO_2CO_3 \cdot 3.5H_2O(s)$
$Na_3NpO_2(CO_3)_2 \cdot nH_2O(s)$
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Carbonate concentration (mol kg^{-1})

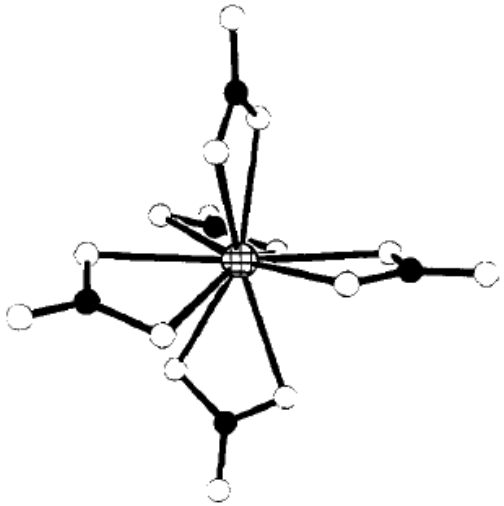
Carbonate complexes of An(III and IV): An = Np, Pu and Am

- Bidentate mode and bridger
- Soluble and unsoluble form ($Am_2(CO_3)_3.nH_2O$, $NaAm(CO_3)_2.nH_2O$, …)
- Competition between OH^- and CO_3^{2-} ($An(OH)(CO_3)$ for An(III) and $An(OH)_{2m}(CO_3)_n$ for An(IV))
- Limit complexes better known than intermediate forms



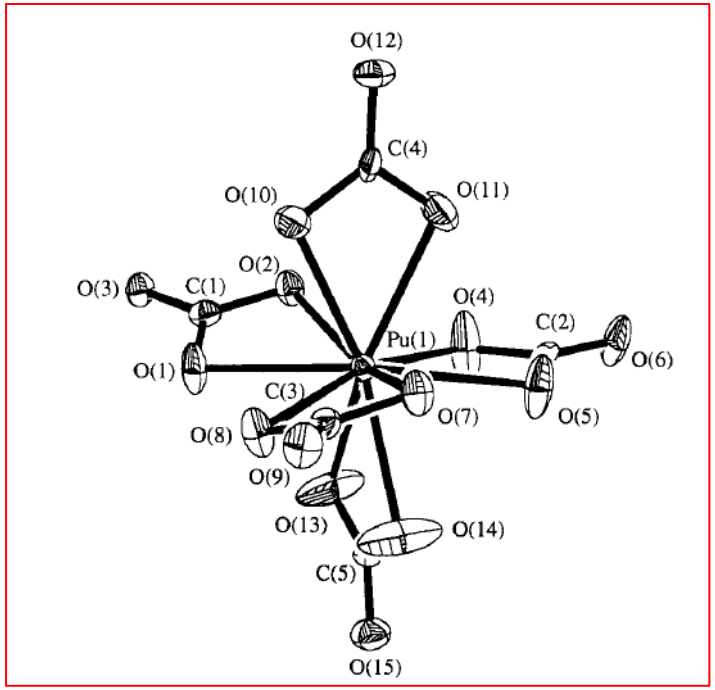
reaction	I	log K
	Thorium(IV)	
$Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}$	1.0[a]	26.2(±0.2)
	2.5[a]	26.3(±0.2)
	3.0	32.3
$ThO_2(s) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}$	3.0	39.64(±0.4)
$ThO_2(s) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3(CO_3)^-$	3.0	6.78(±0.3)
	Uranium(IV)	
$U^{4+} + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$	0	34.0(±0.9)
	3.0	69.86(±0.55)
$U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$	0	−1.12(±0.22)
	Neptunium(IV)	
$Np^{4+} + 3CO_3^{2-} \rightleftharpoons Np(CO_3)_3^{2-}$	0.3	37.1(±1.2)
$Np^{4+} + 4CO_3^{2-} \rightleftharpoons Np(CO_3)_4^{4-}$	0.3	41.1(±1.4)
$Np^{4+} + 4OH^- + 2CO_3^{2-} \rightleftharpoons Np(OH)_4(CO_3)_2^{4-}$	0.1	53.07(±0.44)
	Plutonium(IV)	
$Pu^{4+} + CO_3^{2-} \rightleftharpoons Pu(CO_3)^{2+}$	0.3	17.0(±0.7)
$Pu^{4+} + 2CO_3^{2-} \rightleftharpoons Pu(CO_3)_2$	0.3	29.9(±0.96)
$Pu^{4+} + 3CO_3^{2-} \rightleftharpoons Pu(CO_3)_3^{2-}$	0.3	39.1(±0.82)
$Pu^{4+} + 4CO_3^{2-} \rightleftharpoons Pu(CO_3)_4^{4-}$	0.3	42.9(±0.75)
$Pu^{4+} + 5CO_3^{2-} \rightleftharpoons Pu(CO_3)_5^{6-}$	0.3	44.5(±0.77)
$Pu^{4+} + 2CO_3^{2-} + 4OH^- \rightleftharpoons Pu(OH)_4(CO_3)_2^{4-}$	≈0.1	46.4(±0.7)

Coordination sphere

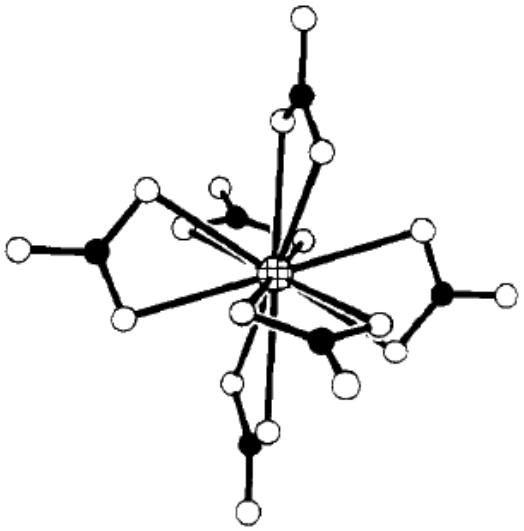


$[C(NH_2)_3]_6[Th(CO_3)_5]$

Hexagonal bipyramid



$[Na_6Pu(CO_3)_5]_2.Na_2CO_3.33H_2O$



$Na_6BaTh(CO_3)_6.6H_2O$

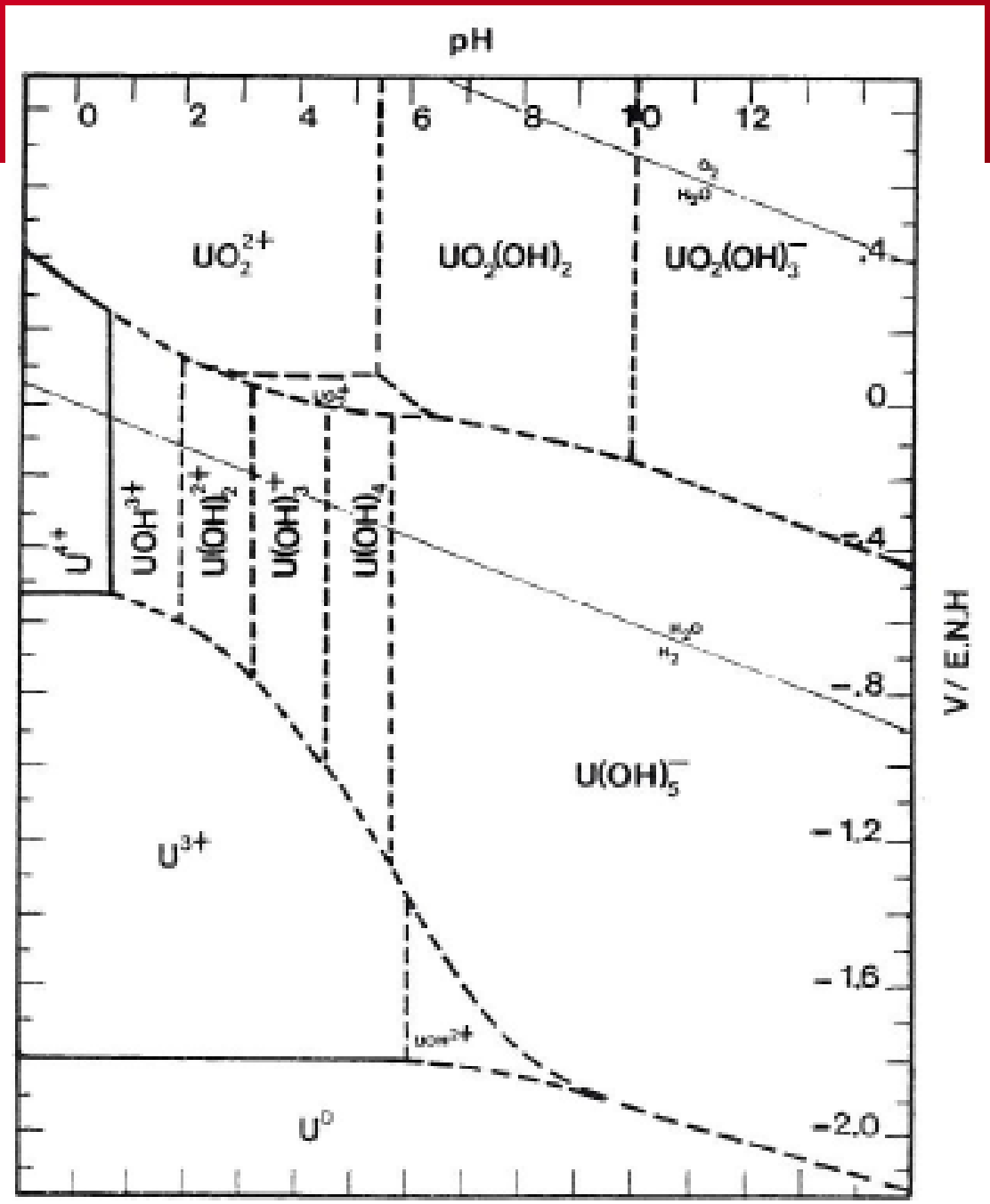
Icosahedron

Tuliokite $Na_6BaTh(CO_3)_6.6H_2O$, has been discovered in the Khibinski region, Russia, in 1990

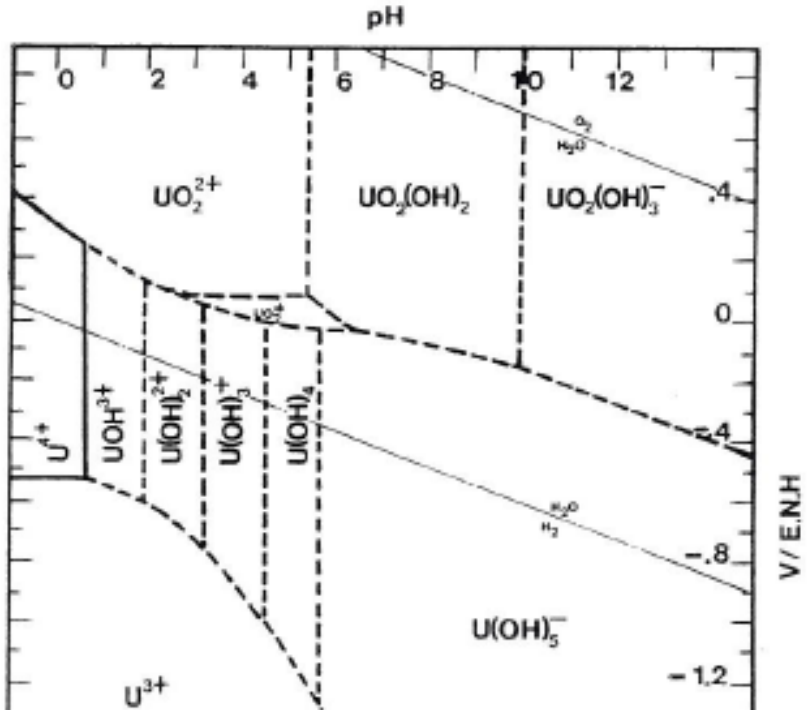
Pourbaix diagram: the case of U(IV) (0<pH<4)

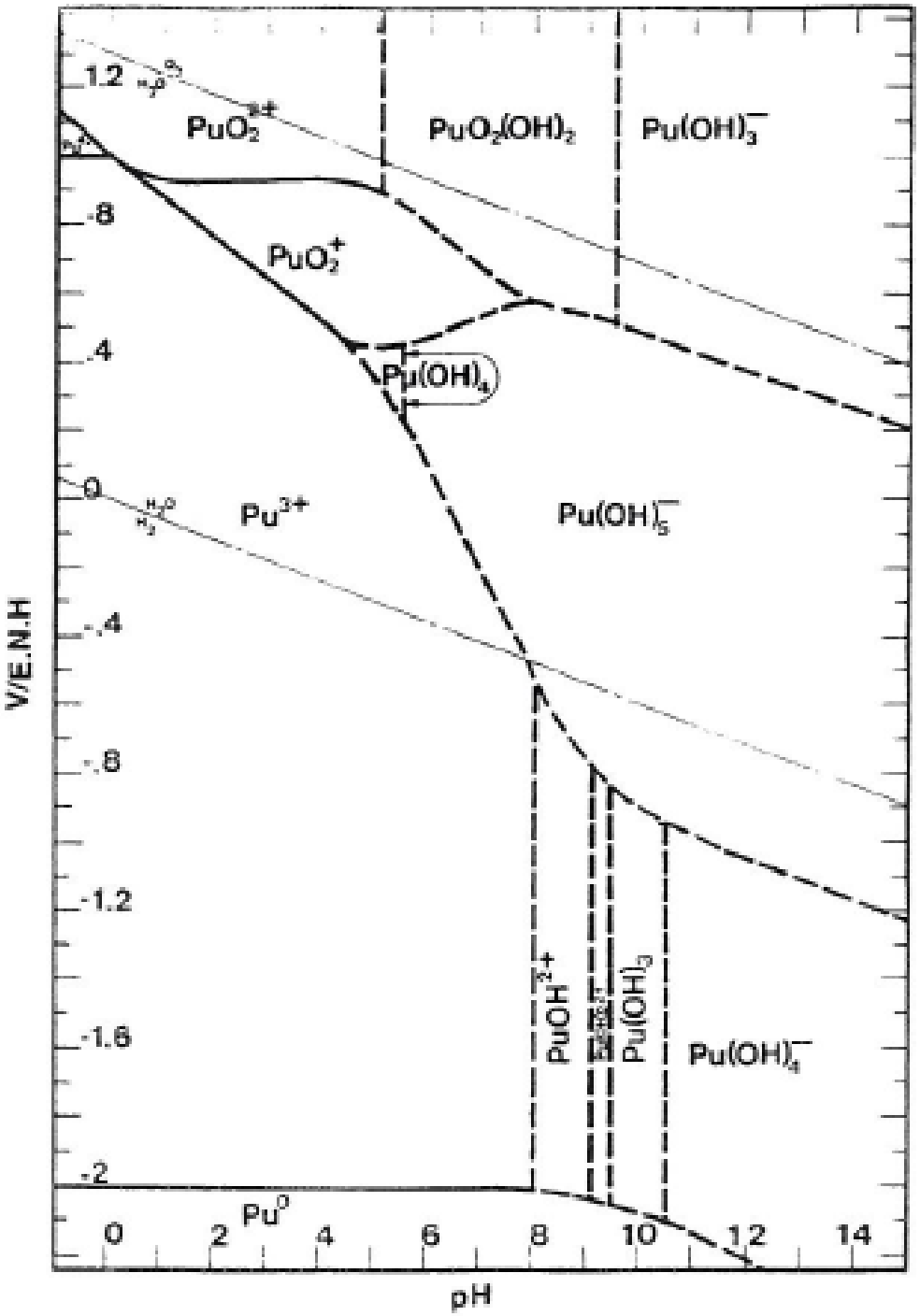
$U^{4+} + H_2O \Leftrightarrow UOH^{3+} + H^+$	$\log Q_{11} = -1{,}16$ (**pH = 1.16**)
$U^{3+} \Leftrightarrow U^{4+} + e$	E= **-0.607**+ 0.0591 $\log[U^{4+}] / [U^{3+}]$
$UO_2^+ \Leftrightarrow UO_2^{2+} + e$	E= **0.052** + 0.0591 $\log[UO_2^{2+}] / [UO_2^+]$
$U^{4+} + 2H_2O \Leftrightarrow UO_2^+ + 4H^+ + e$	E= **0.612 – 0.2364pH** + 0.0591 $\log[UO_2^+] / [U^{4+}]$
$U^{3+} + H_2O \Leftrightarrow U(OH)^{3+} + H^+ + e$	E= **-0.538 – 0.0591pH** + 0.0591 $\log[U(OH)^{3+}] / [U^{3+}]$
⑤$UOH^{3+} + H_2O \Leftrightarrow UO_2^+ + 3H^+ + e$	E= **0.546 – 0.1773pH** + 0.0591 $\log[UO_2^+] / [UOH^{3+}]$
⑥$U^{4+} + 2H_2O \Leftrightarrow UO_2^{2+} + 4H^+ + 2e$	E= **0.333 – 0.1182pH** + 0.0295 $\log[UO_2^{2+}] / [U^{4+}]$
⑦$UOH^{3+} + H_2O \Leftrightarrow UO_2^{2+} + 3H^+ + 2e$	E= **0.299 – 0.0886pH** + 0.0295 $\log[UO_2^{2+}] / [UOH^{3+}]$

E – pH Uranium

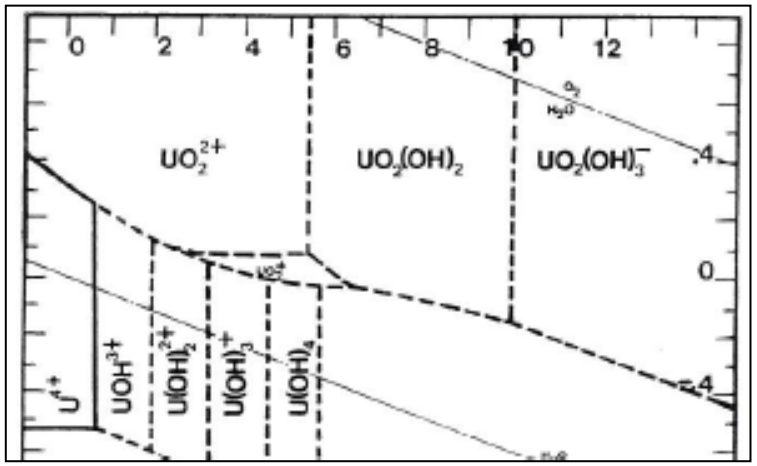

pH
0
2
4
6
8
10
12
UO_2^{2+}
$UO_2(OH)_2$
$UO_2(OH)_3^-$
U^{4+}
UOH^{3+}
$U(OH)_2^{2+}$
$U(OH)_3^+$
$U(OH)_4$
$U(OH)_5^-$
U^{3+}
U^0
.4
0
-.4
-.8
-1.2
-1.6
-2.0
V/E.N.H

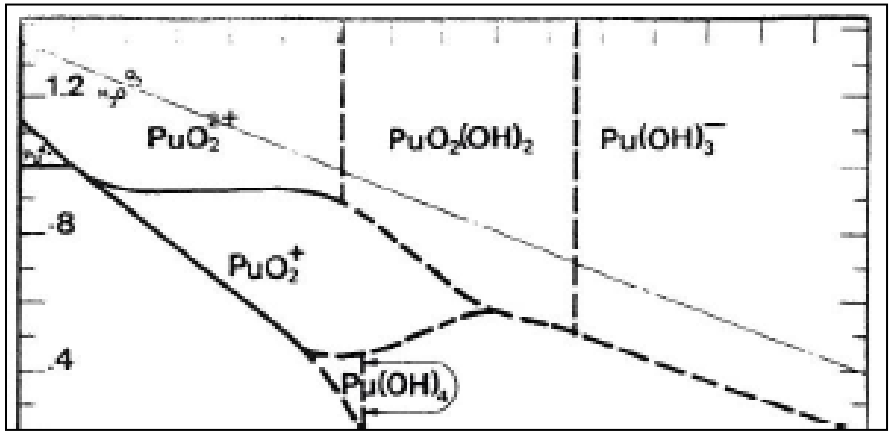
E – pH Plutonium

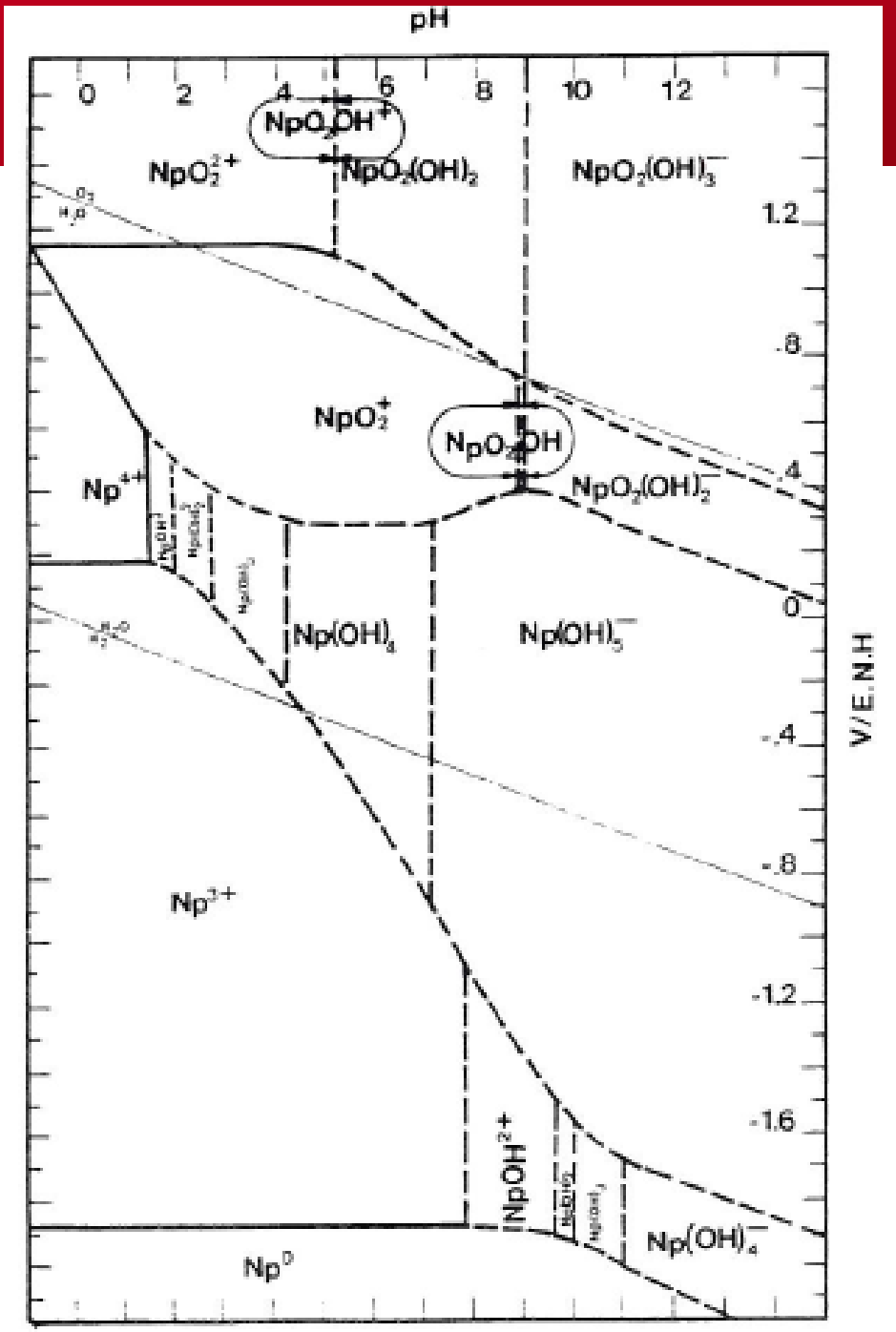




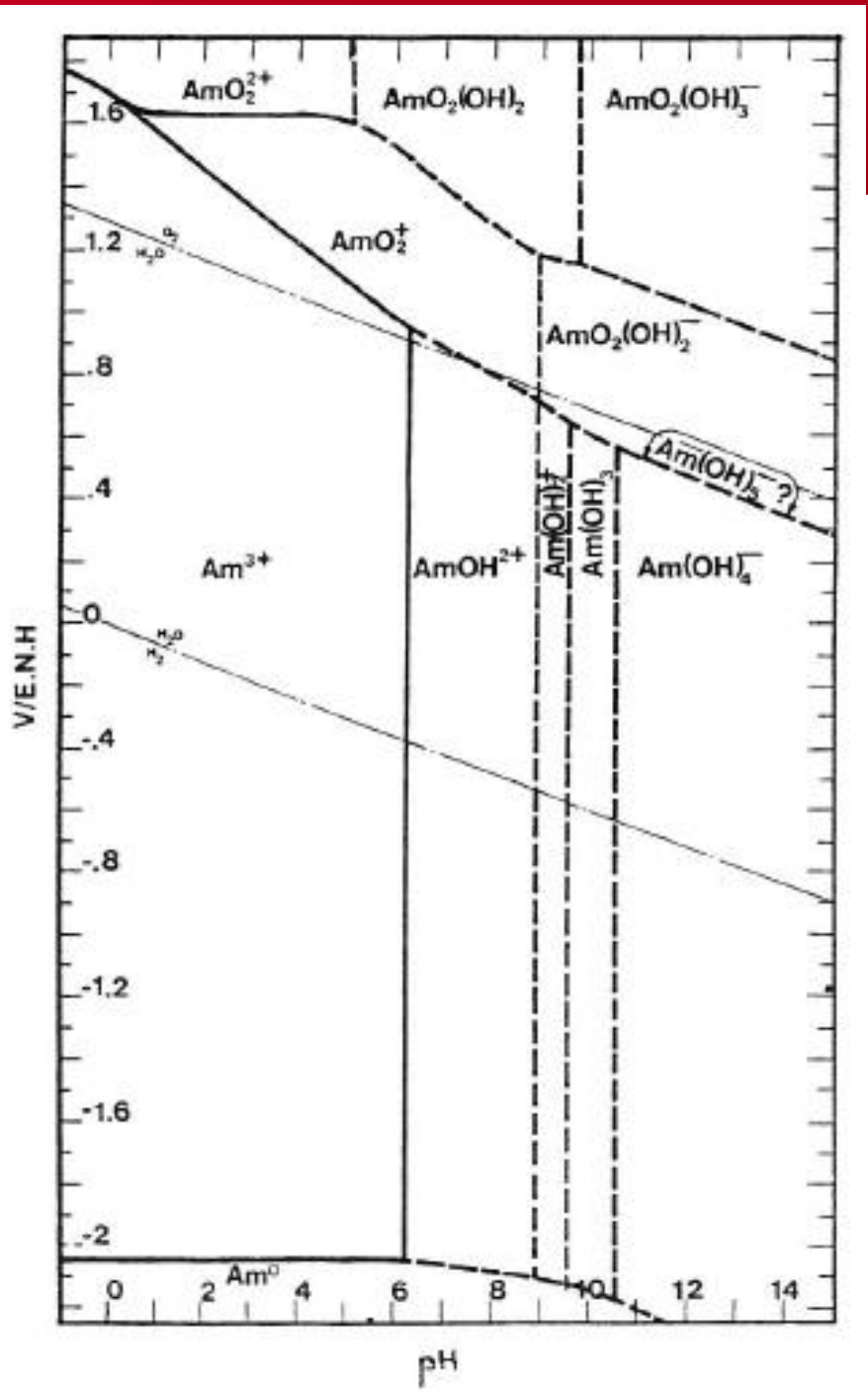
E – pH Neptunium







E – pH Americium



Gas phase chemistry of actinide

Liquid media

- Solvation (hydration)
- Redox behaviour
- Hydrolysis
- Complexation

Solid compounds

- Coordination chemistry

Gas phase

- ElectroSpray Ionisation Mass Spectroscopy (ESI MS)

DE LA RECHERCHE À L'INDUSTRIE

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Plutonium chemistry and other actinides in aqueous solutions

Part 2b

Biphasic System

Ph. MOISY

CEA/DEN/DMRC ; Marcoule

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FROM RESEARCH TO INDUSTRY
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Actinide behaviour in aqueous media with diphasic system

Solid / Liquid Separation

- Precipitation
- Co-precipitation

Liquid / Liquid Extraction

- Neutral complexes
- Ionic species (cation and anion complexes)

Ionic exchange on solid support

- Cationic exchange
- Anionic exchange

Solide/Liquid distibution

Coprecipitation

- Very useful for heavy actinides (at trace scale):

Coprecipitation of ^{256}Md with LaF_3 ⟶ Md^{3+}

Coprecipitation of ^{256}Md with $BaSO_4$ ($Eu^{II}SO_4$) in presence of Cr(II) ⟶ Md^{2+}

- Interesting for decontamination and for liquid waste treatment: $Fe(OH)_3$, ($Fe(OH)_2$, $Fe(OH)_3$), …

Precipitation

- Very useful for actinide dioxide conversion: thermal decomposition of neutral compounds (under air or controled atmopsphere)

$An^{III}_2(C_2O_4)_3.10\ H_2O$, $An^{IV}(C_2O_4)_2.6\ H_2O$, …

$An(O_2)_2$, $An^{VI}O_2(O_2)$, …

$M^{I}_{(1+2x)}.An^{V}O_2(CO_3)_{(1+x)}$, $An^{VI}O_2(CO_3)$, …

Two phases distibution: liquid/liquid system

Interest

- Fundamental research of Actinide behaviour in aqueous media
- Reprocessing of Nuclear Fuel

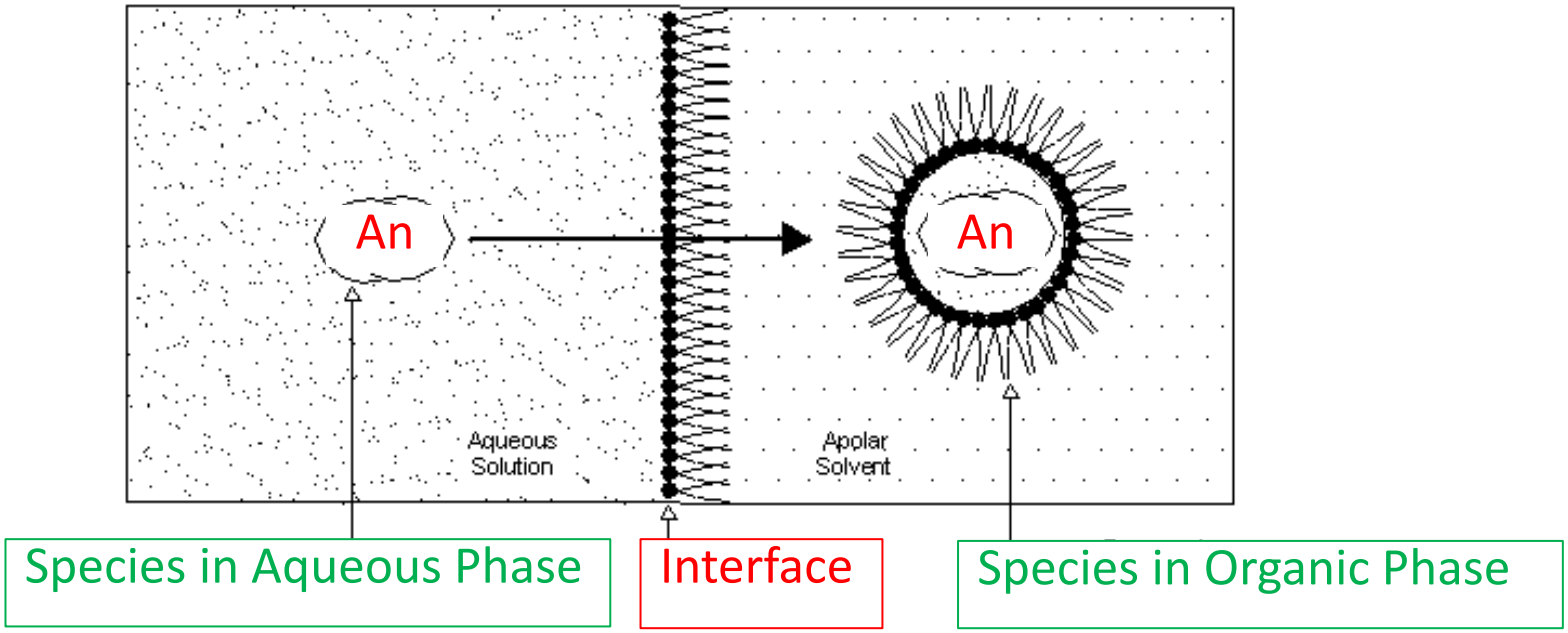
General consideration: « One aqueous phase and One organic phase »

- Good affinity between An and extractant with hard donnor as oxygen and nitrogen (Pearson model)
- An extractant is a ligand (complexant) only soluble in organic phase
- Competition between cation and acidity for extractant
- Reactivity (extractibility) of An: high for An^{4+} ; An^{3+} ; AnO_2^{2+} but low for AnO_2^{+}
- Mainly electrostatic interaction but also covalent bonding (selectivity)
- Competition between extraction (ligand soluble in organic phase) and complexation in aqueous media

Liquid/Liquid extraction: supramolecular organisation of organic phase

- « Organic chain » ⟶ Lipohily (solubility in organic phase « apolar tail » and immiscibility in aqueous phase)

- « Polar head » ⟶ Actinide interaction (water, mineral acid, …)



- Extraction of water and mineral acid: micellisation in organic phase (reversed micelles)

- Interfacial structure ?