Thermodynamic Stabilities of $MO_{2+x}(s)$ (M = U, Np, Pu and Am), Pourbaix diagrams.

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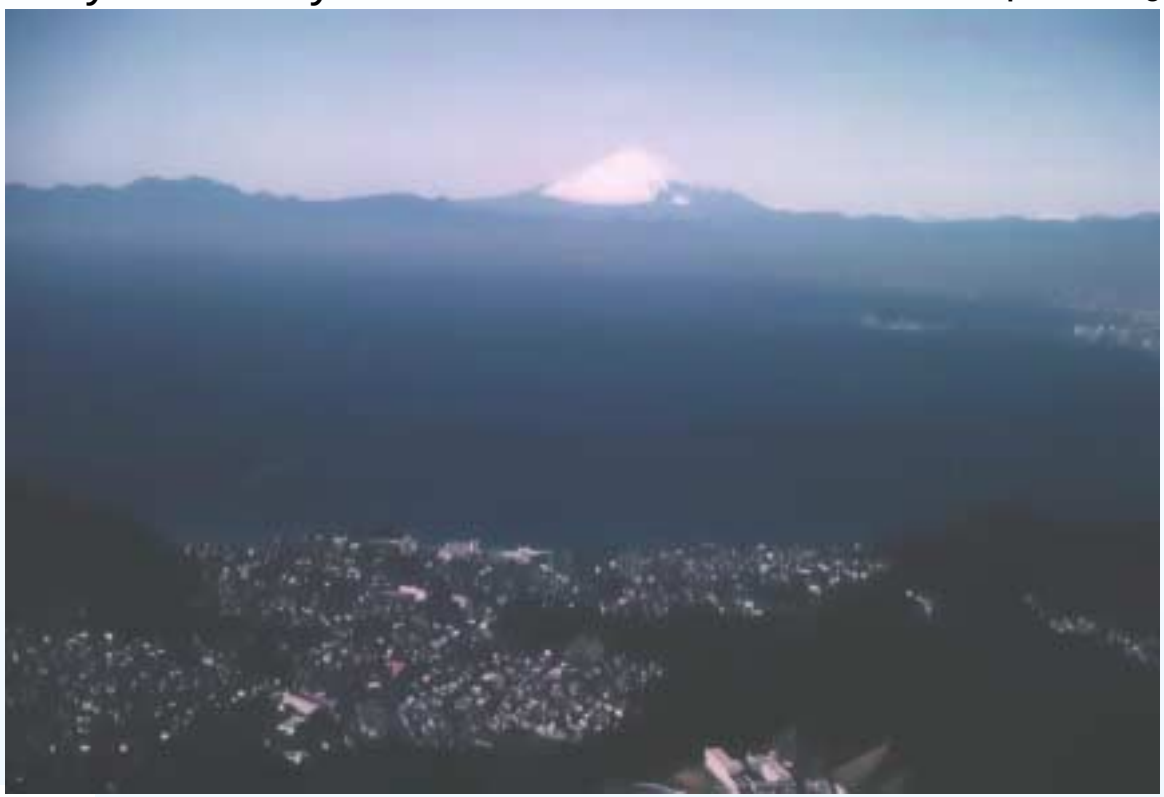


Overview

Thermodynamic data — **P.Vitorge, H.Capdevila**

MO_2(am,hyd) — **H.Capdevila, P.Vitorge**

MO_{2+x} — **P.Vitorge**

2+x=2.25 $\quad U_4O_9(s) + 14H^+ \rightarrow 3U^{4+} + UO_2^{2+} + 7H_2O$

2+x=2.33 $\quad U_3O_7(s) + 10H^+ \rightarrow 2U^{4+} + UO_2^{2+} + 5H_2O$

2+x=2.67 $\quad U_3O_8(s) + 8H^+ \rightarrow U^{4+} + 2UO_2^{2+} + 4H_2O$

Analogies for non-redox reactions

Ionic strength corrections

$E°(M(VII)/M(VI))$, M = Np, Pu, Am

$E°(AmO_2^{2+}/AmO_2^{+})$, $E°(AmO_2^{+}/Am^{3+})$, $E°(Am^{4+}/Am^{3+})$

Pourbaix and solubility diagrams — **P.Vitorge**

Testing published equations for solid solutions — M.-H.Fauré, P.Vitorge

Equations for solid solutions — S.Maillard, P.Vitorge, M.-H.Fauré

$$0 = d\Delta_r G = \left(\sum \mu_i \nu_i\right) d\xi + \left(\sum \mu_i \frac{d\nu_i}{dx}\right) \xi dx$$

P.Vitorge, H.Capdevila, S.Maillard, M.-H.Fauré Note CEA to be published.

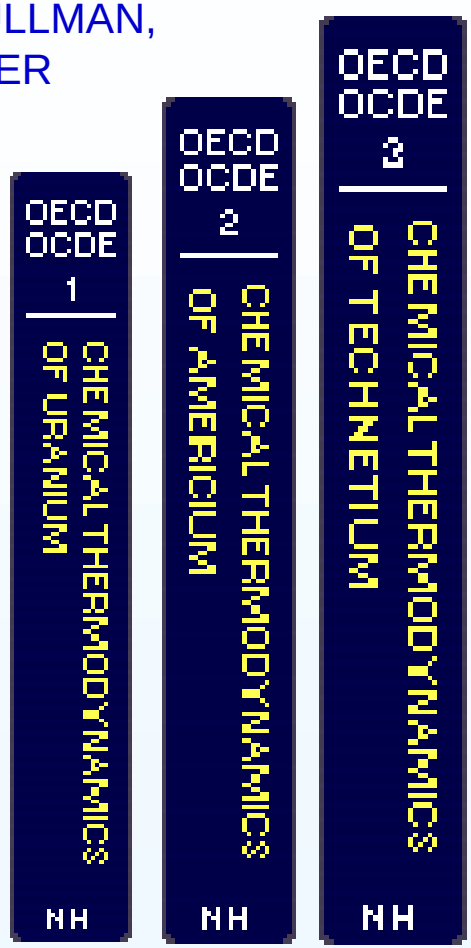
Thermodynamic data

NEA-TDB review Edited by OECD Nuclear Energy Agency, Data Bank, Elsevier (2001)

CHEMICAL THERMODYNAMICS OF NEPTUNIUM & PLUTONIUM

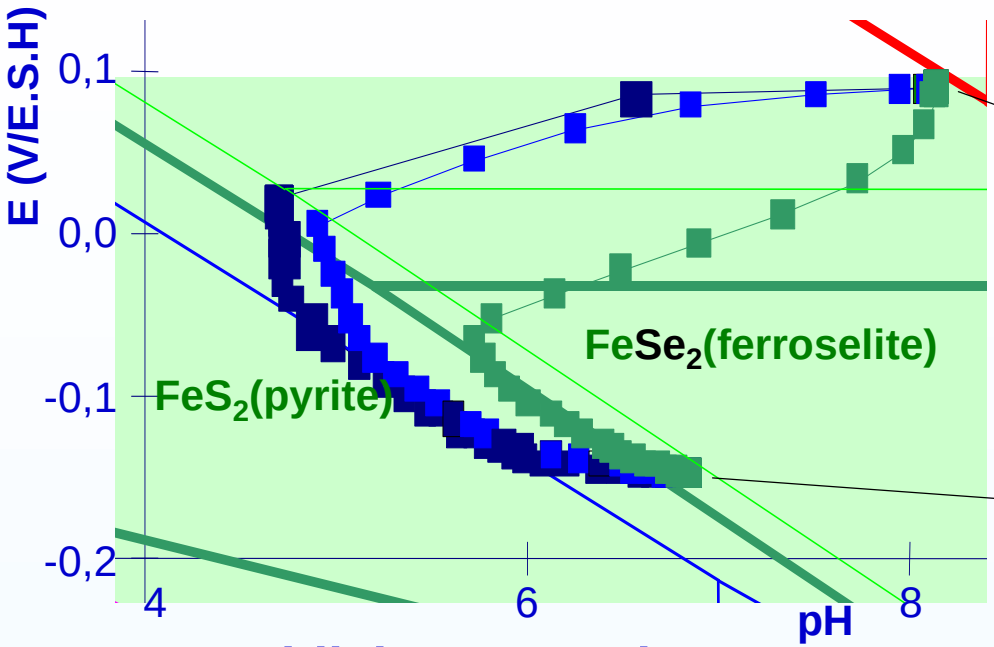
Robert LEMIRE (Chairman)
Jean FUGER, Heino NITSCHE, Paul POTTER,
Malcolm RAND, Jan RYDBERG, Kastriot SPAHIU,
James SULLIVAN, William J. ULLMAN,
Pierre VITORGE, Hans WANNER

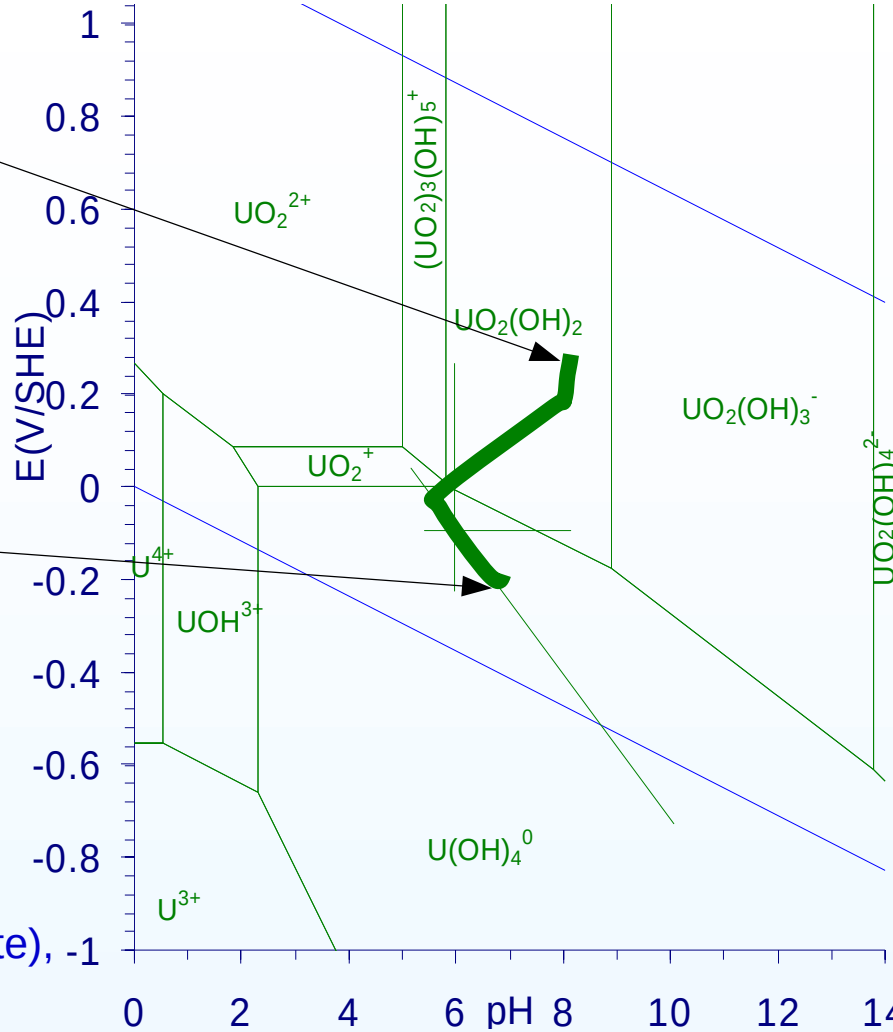
Validated data



Relevant redox and pH conditions in groundwaters

Marie-Hélène Fauré





Oxidising groundwaters on an Uranium ore (Wyoming, Texas)

Fields observations at the redox boundary

oxidising side :

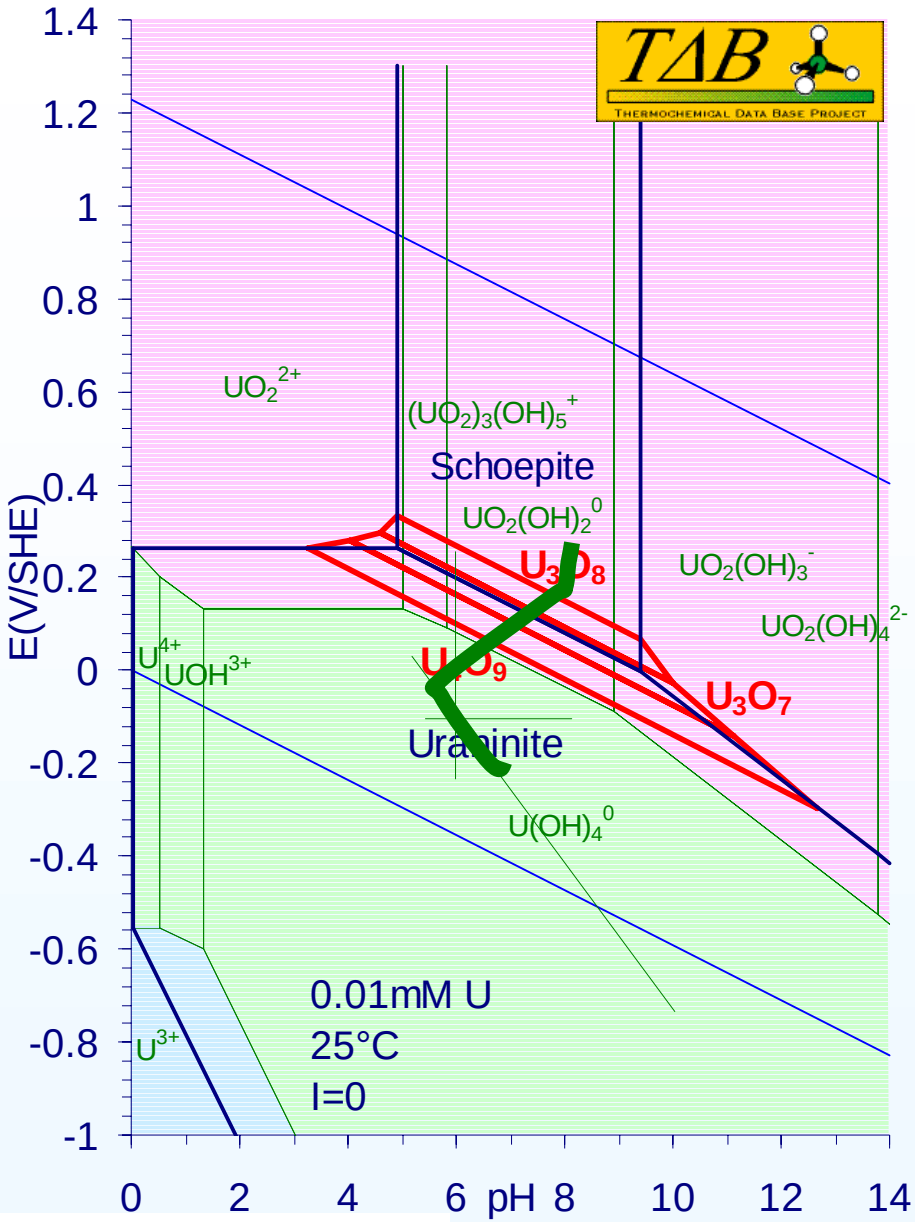
Se(s), ferroselite, **FeOOH(goethite)** et Fe_2O_3(hematite),

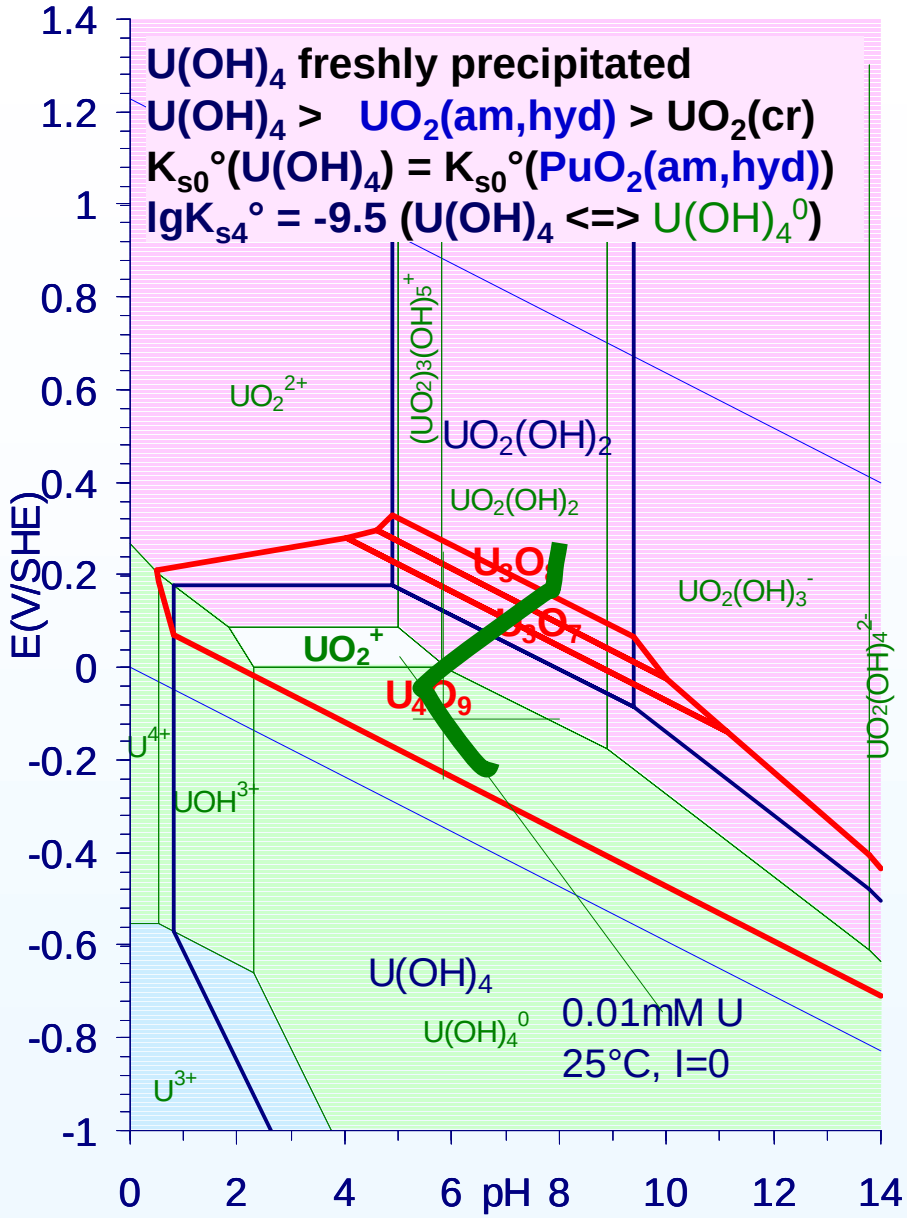
reducing side :

Se(s), ferroselite, pyrite.

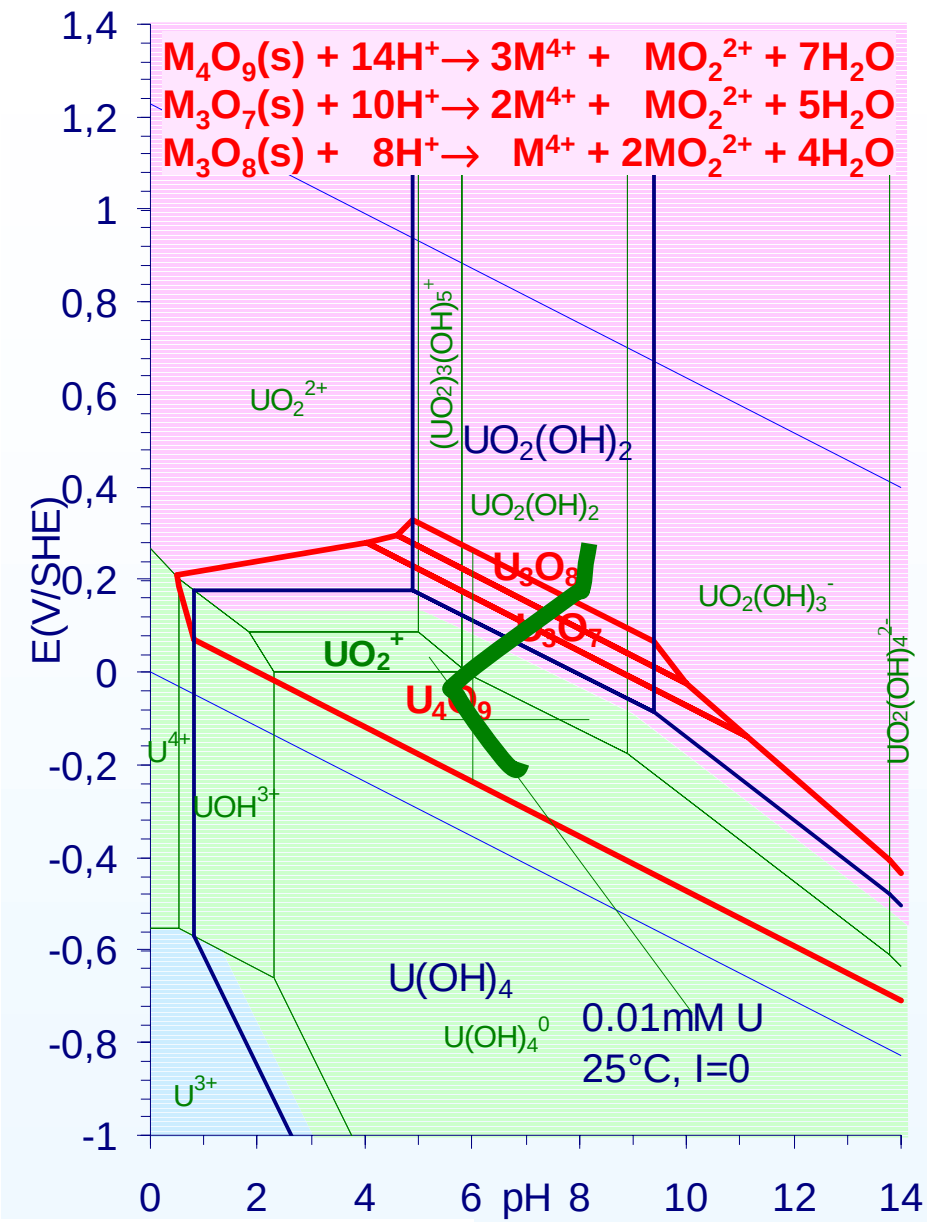
Simulations with the IMPACT code

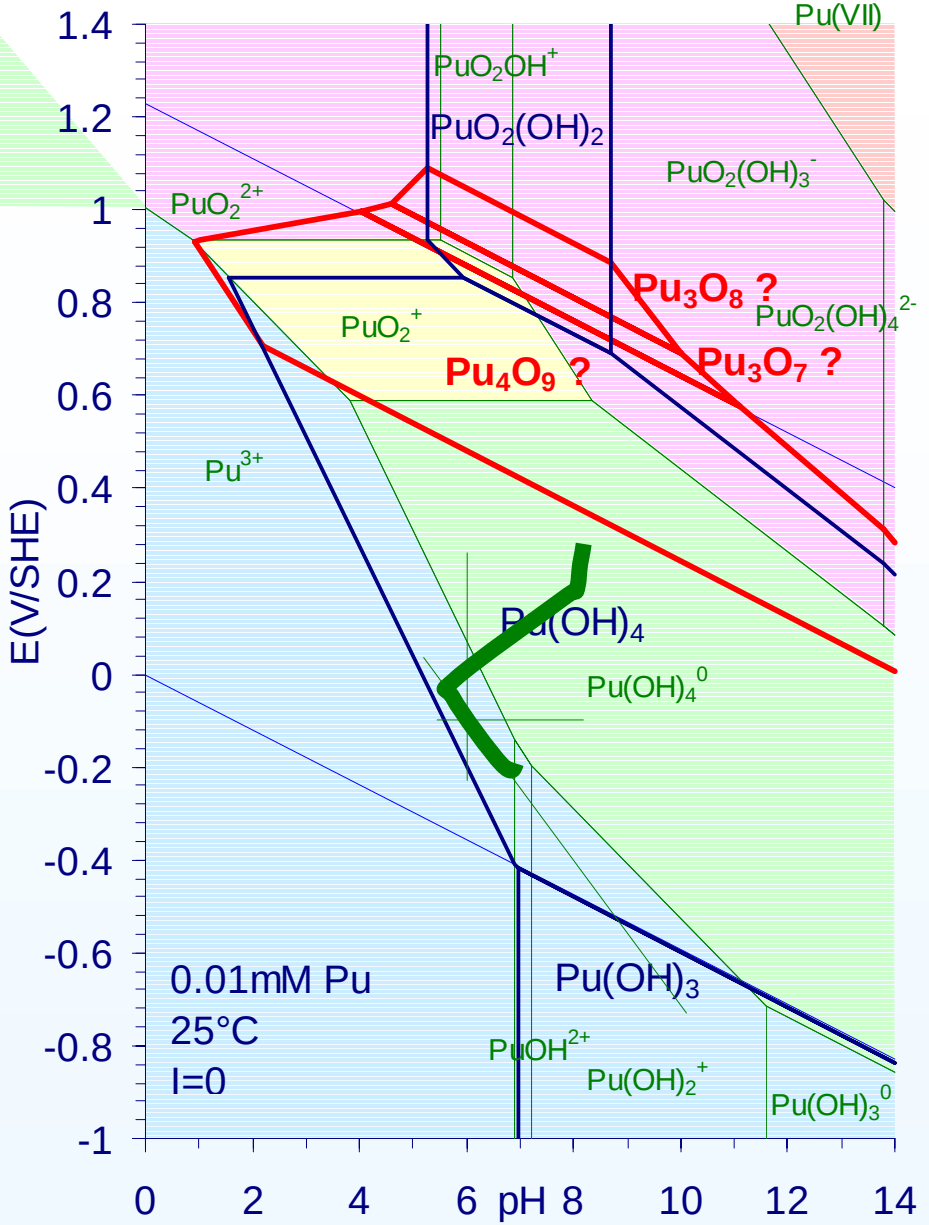
Pourbaix diagrams of Uranium: comparison of thermodynamic data



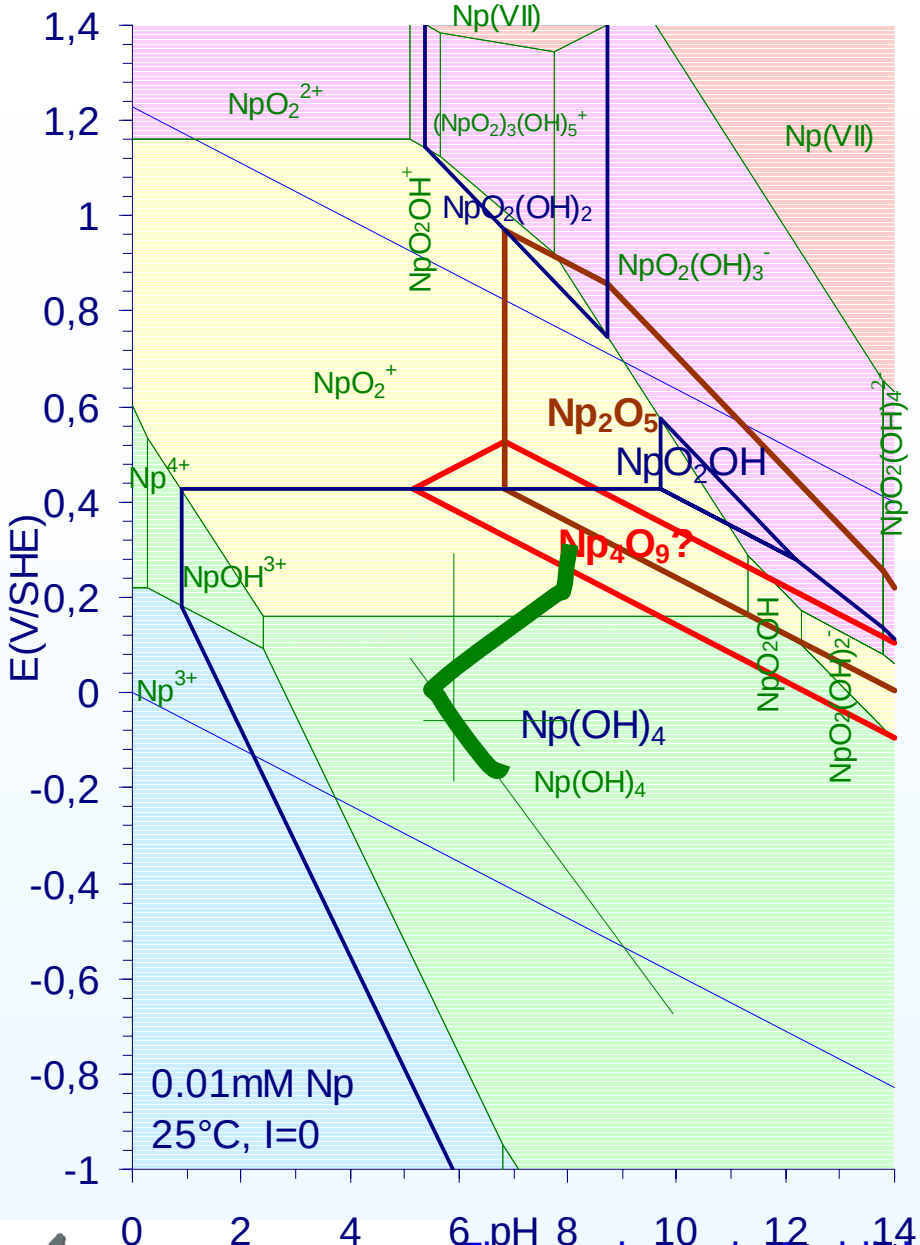


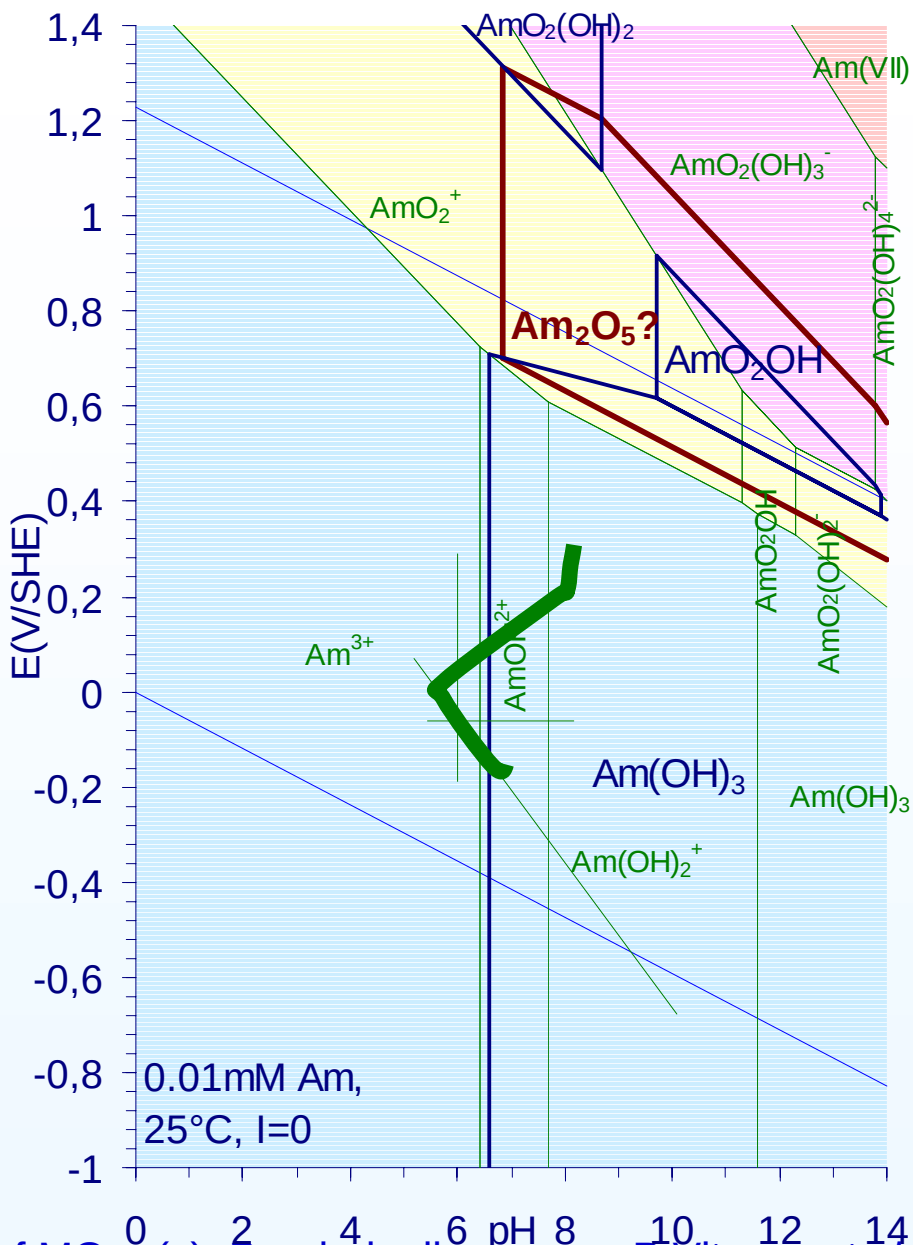
Using the stability of UO_{2+x} for estimating the stability of PuO_{2+x}: TDB data



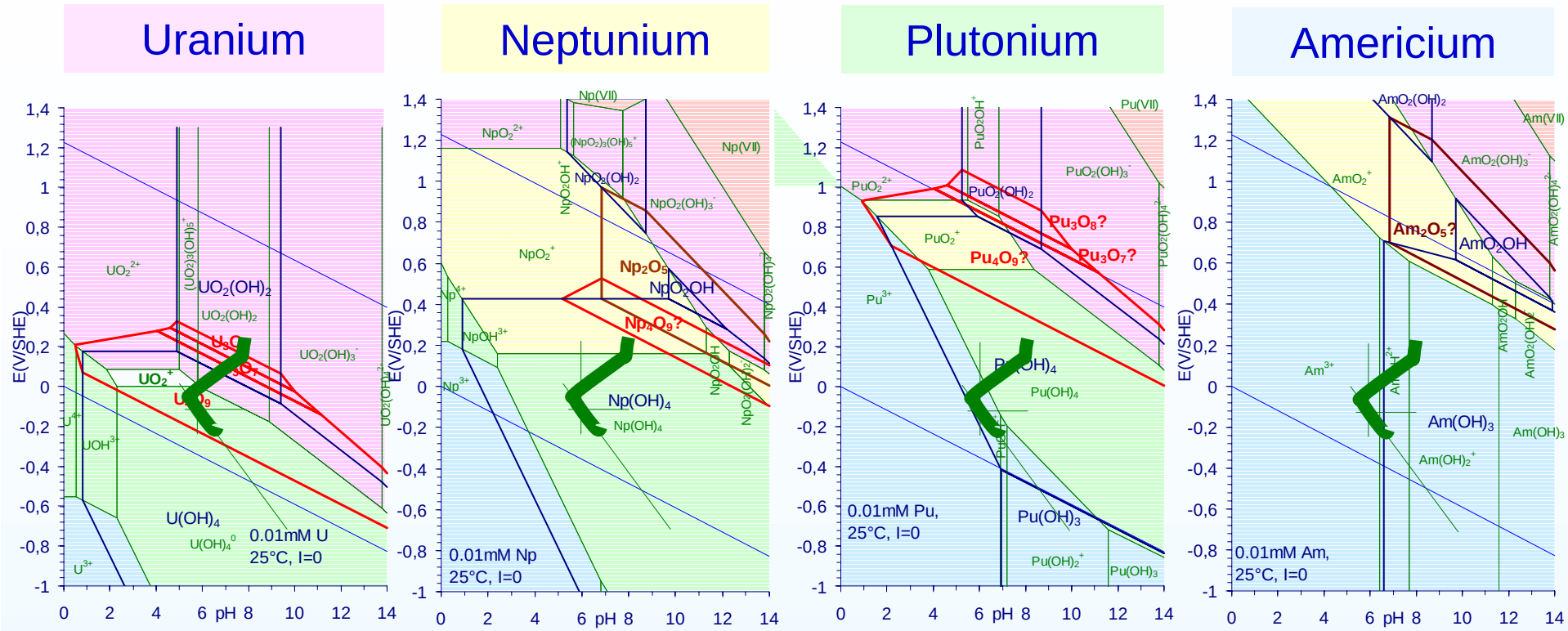


Pourbaix diagrams of Neptunium and Americium

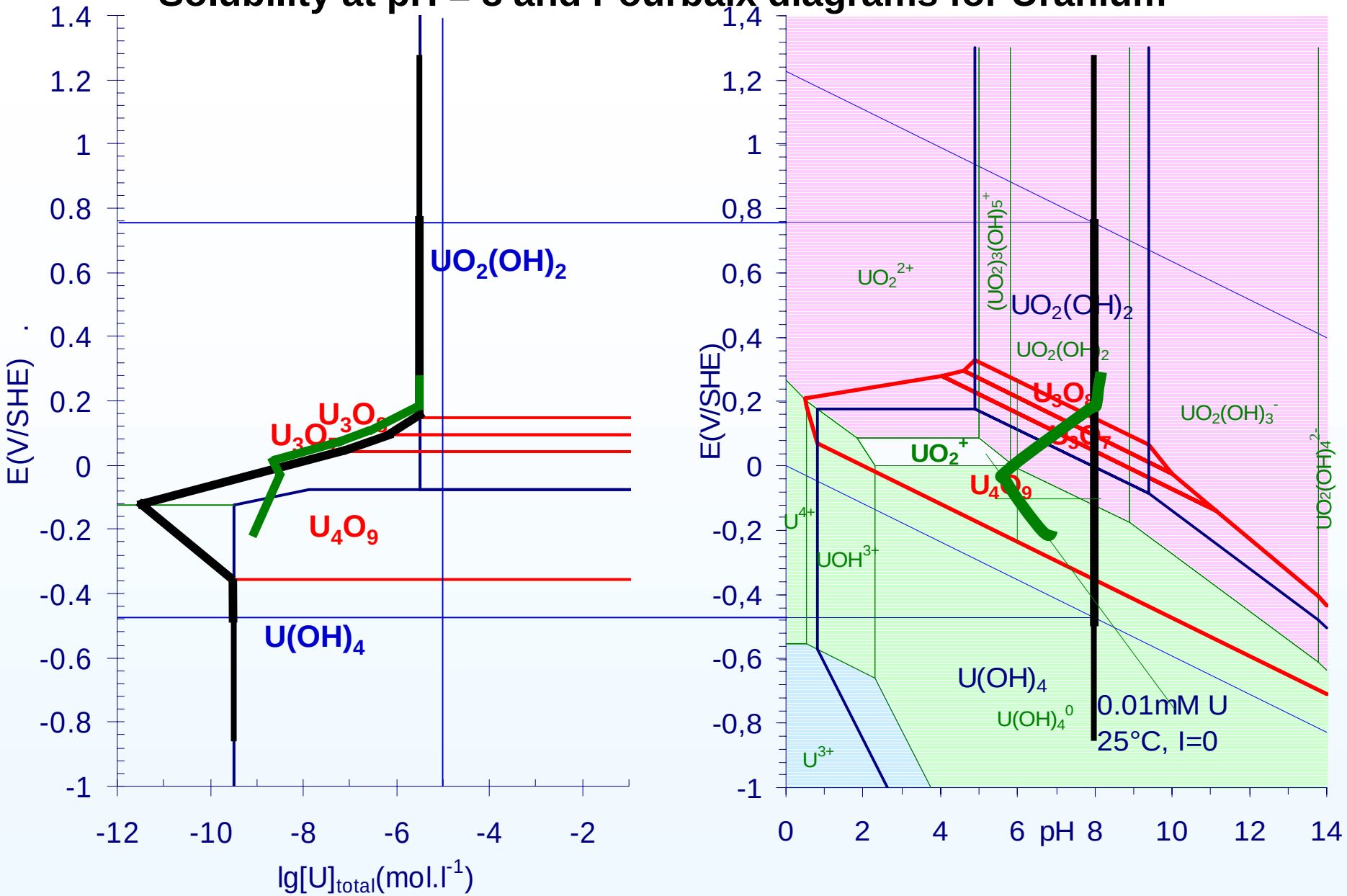




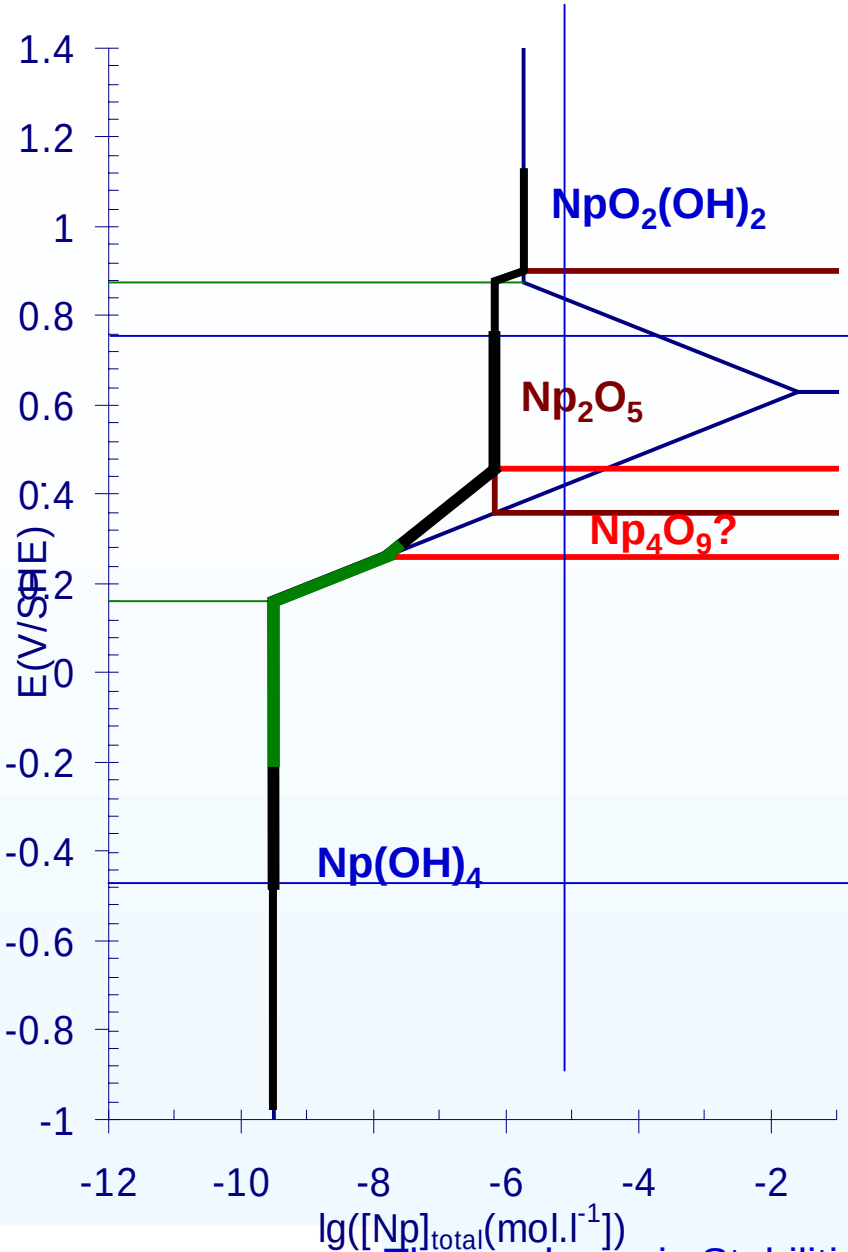
Pourbaix diagrams of Uranium, Neptunium Plutonium and Americium

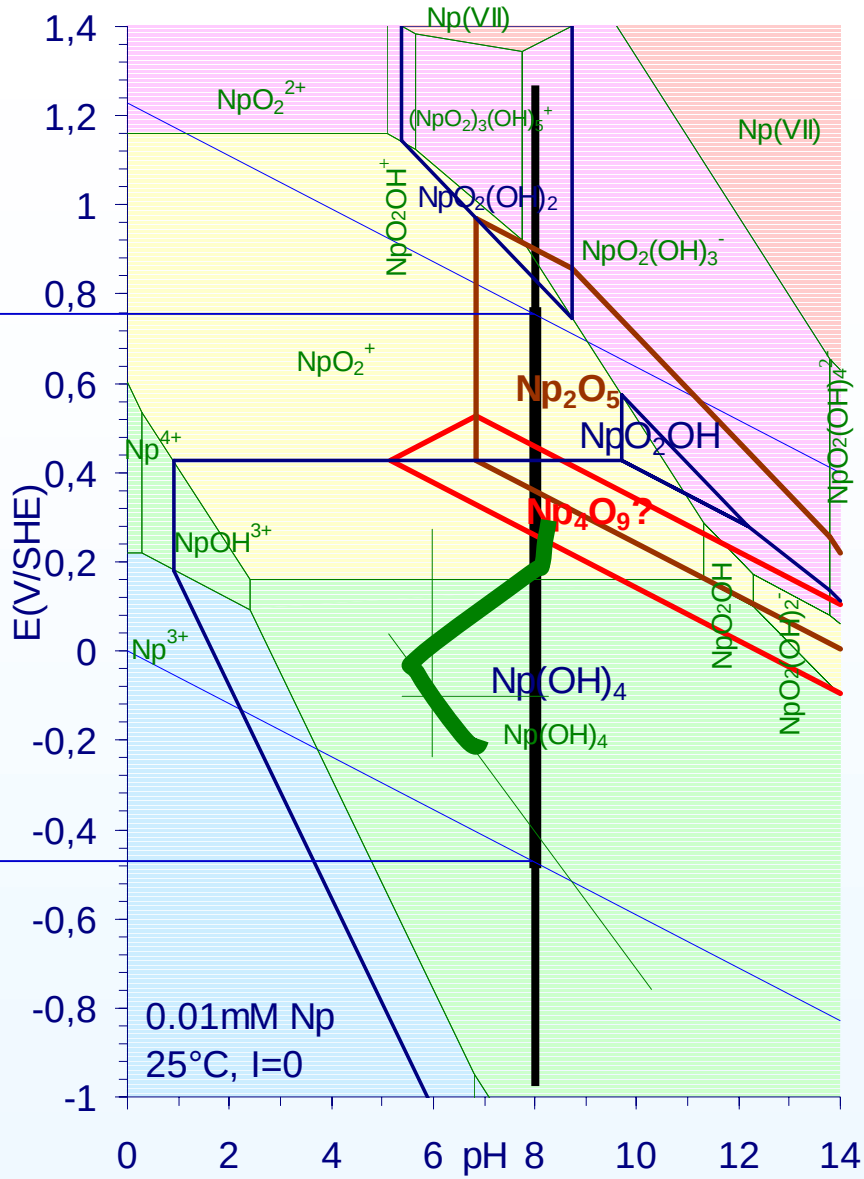


Solubility at pH = 8 and Pourbaix diagrams for Uranium

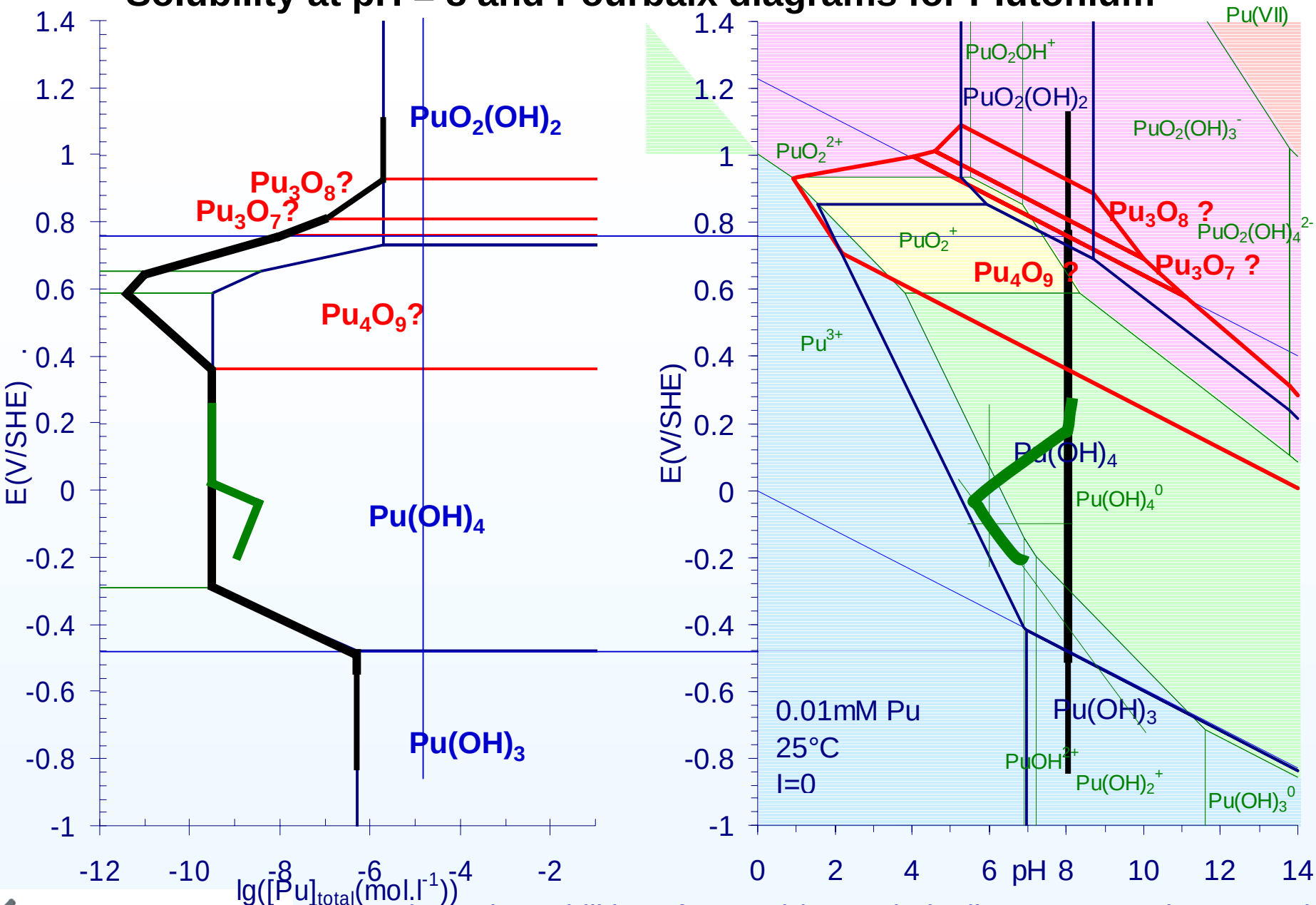


Solubility at pH = 8 and Pourbaix diagrams for Neptunium

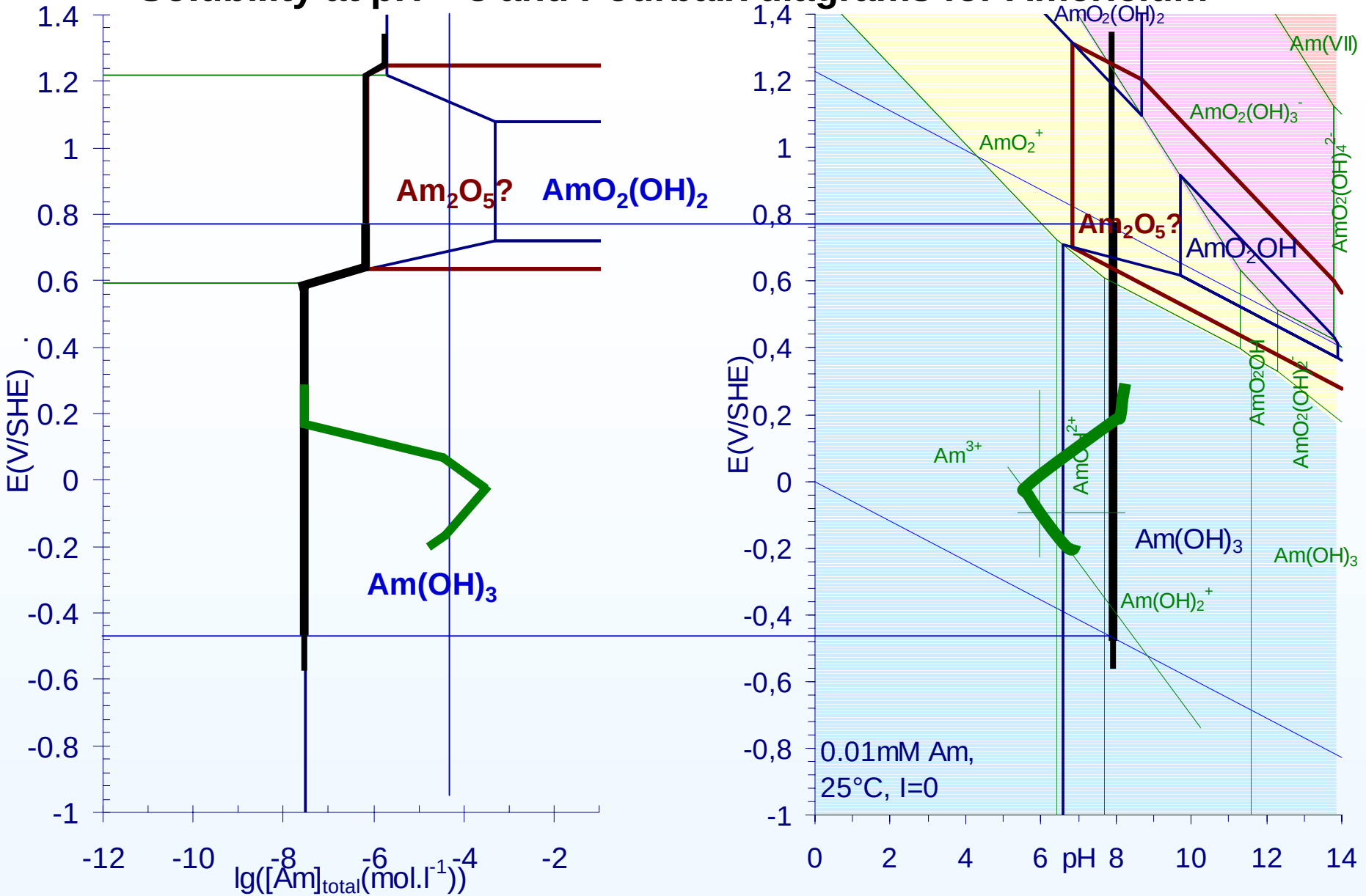




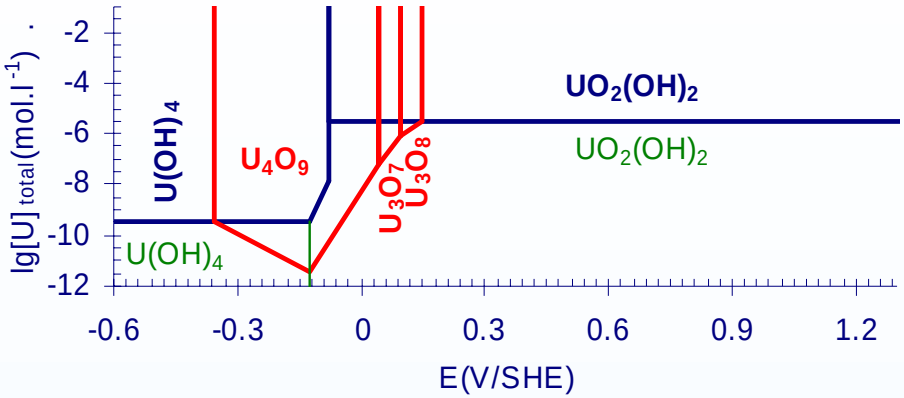
Solubility at pH = 8 and Pourbaix diagrams for Plutonium

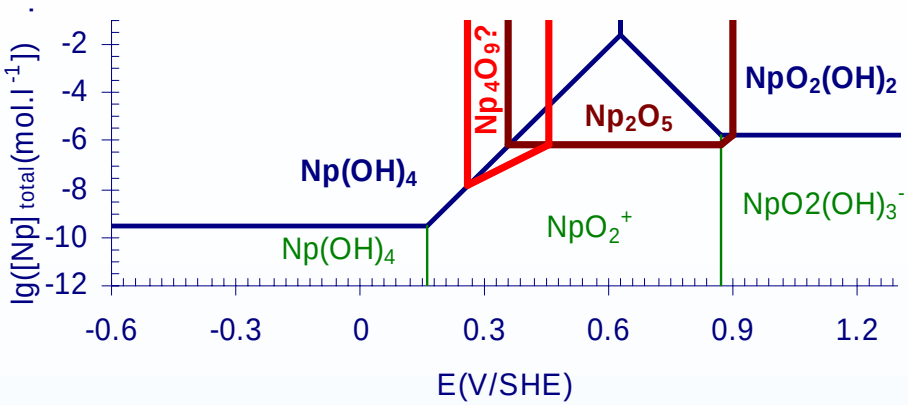


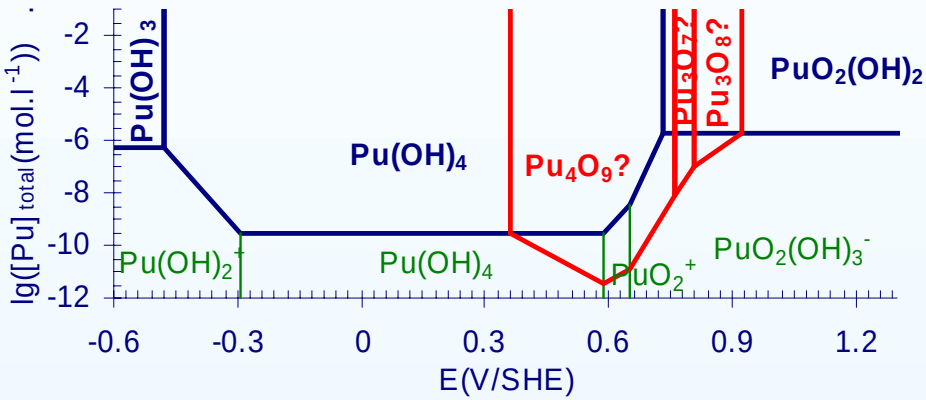
Solubility at pH = 8 and Pourbaix diagrams for Americium

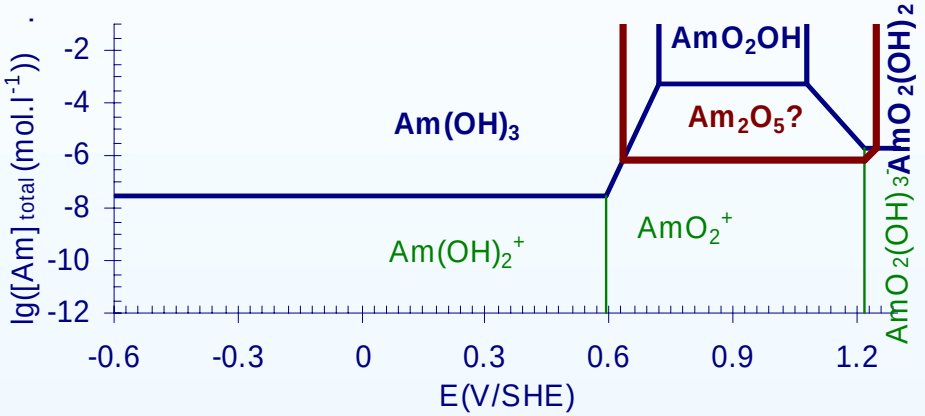


Solubilities of Uranium, Neptunium Plutonium and Americium at pH = 8









Conclusions

- **Thermodynamic data are available** for predicting Actinide speciations in Groundwaters
- However validations and **new experimental measurements of good quality are still needed** (we typically had to use analogies)
- The type of **a priori modelling** exercises presented here is also a tool for **sensitivity analysis**, and to decide which new measurements are needed
- Typically: **MO_{2+x}** stabilities
  only **important for M = U in groundwaters**
  however retention of trace concentrations of Pu in spent fuel matrix (not only MOX) important for spent fuel corrosion in wet conditions (interim storage)
  theoretical description of solid solution?

Thermodynamic data

Precipitation in groundwaters:

$M(OH)_4(am) \rightarrow MO_2(am,hyd) \rightarrow MO_2(cr)$?

Analogies for **non-redox reactions** to estimate the stabilities of **MO_{2+x}**

$$UO_{2+x} + 2(2-x)\,H^+ \rightarrow x\,UO_2^{2+} + (1-x)\,U^{4+} + (2-x)\,H_2O$$

$$x\,UO_2^{2+} + x(2\,e^- + 4\,H^+ - 2\,H_2O) \rightarrow U^{4+}$$

$$U^{4+} + 4OH^- \rightarrow U(OH)_4$$

$$UO_{2+x} + 2x\,e^- + 2\,H^+ + (2-x)\,H_2O \rightarrow U(OH)_4$$

2+x=2.25	$U_4O_9(s) + 14\,H^+ \rightarrow 3\,U^{4+} + UO_2^{2+} + 7\,H_2O$
2+x=2.33	$U_3O_7(s) + 10\,H^+ \rightarrow 2\,U^{4+} + UO_2^{2+} + 5\,H_2O$
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Another hypothesis (i.e another redox characterisation inside the solid)

$M_4O_9(s) + 10\,H^+ \rightarrow 2\,M^{4+} + 2\,MO_2^+ + 5\,H_2O$???