



# 1. Actinide Chemistry



Thermodynamic Data for radionuclide speciation (solubility or migration).

DESD / SESD

**Coupling sorption and complexation with Np(V) transport**

Christine André (1997 Thesis ) Pierre Vitorge, Marie-Hélène Fauré (Michel Sardin LSGC CNRS)

**Speciation in carbonate media from solubility.**

Pierre Vitorge, Christian Dautel (1984 -1998), TDB-AEN-OCDE (2000)

....Stability of possible solid ideal solution  $\text{Na}_{(2-y)}(\text{NpO}_2)_y\text{CO}_3$

P.Vitorge (1999)

....Ligand Competition in solid phase (Am speciation).

P.Vitorge (1992), TDB-AEN-OCDE (1999)

**Pu and Np redox reactions in non complexing solutions.**

P.Vitorge *et al.*, TDB-AEN-OCDE (1987, 1989, 1990, 1992, 1994, 1995, 1998, 1999, 2000) and thesis

....Ionic strength corrections ( $\gamma$ ) : standard state.

Piotr Robouch (1987), Chantal Riglet (1989), Hélène Capdevila (1992)

.... Temperature and ionic strength corrections ( $\Delta G^{\text{ex}}$ ,  $\Delta H^{\text{ex}}$ ,  $\Delta S^{\text{ex}}$ )

H.Capdevila (1992), Eric Giffaut (1995)

**Disproportionation and solubility of  $\text{Pu}^{4+}$**

H.Capdevila, P.Vitorge (1992, 1995, 1999)

**Study of the limiting carbonate complexe of Pu(IV) by using solubility and EXAFS**

D.Rai, N. Hess, A.Felmy, D.Moore (PNNL USA), M.Yui (JNFCDI Japan), P.Vitorge (CEA France), 1999

**Ab initio calculation and molecular modelling for hard cations**

Michel Masella (PostDoc) P.Vitorge

DIRECTION DU CYCLE DU COMBUSTIBLE

L'ATOME, DE LA RECHERCHE A L'INDUSTRIE

Pierre Vitorge.CONTACT.pierre.vitorge(at)cea.fr.

Conseil Scientifique et Technique - audition des 27 et 28 octobre 1999

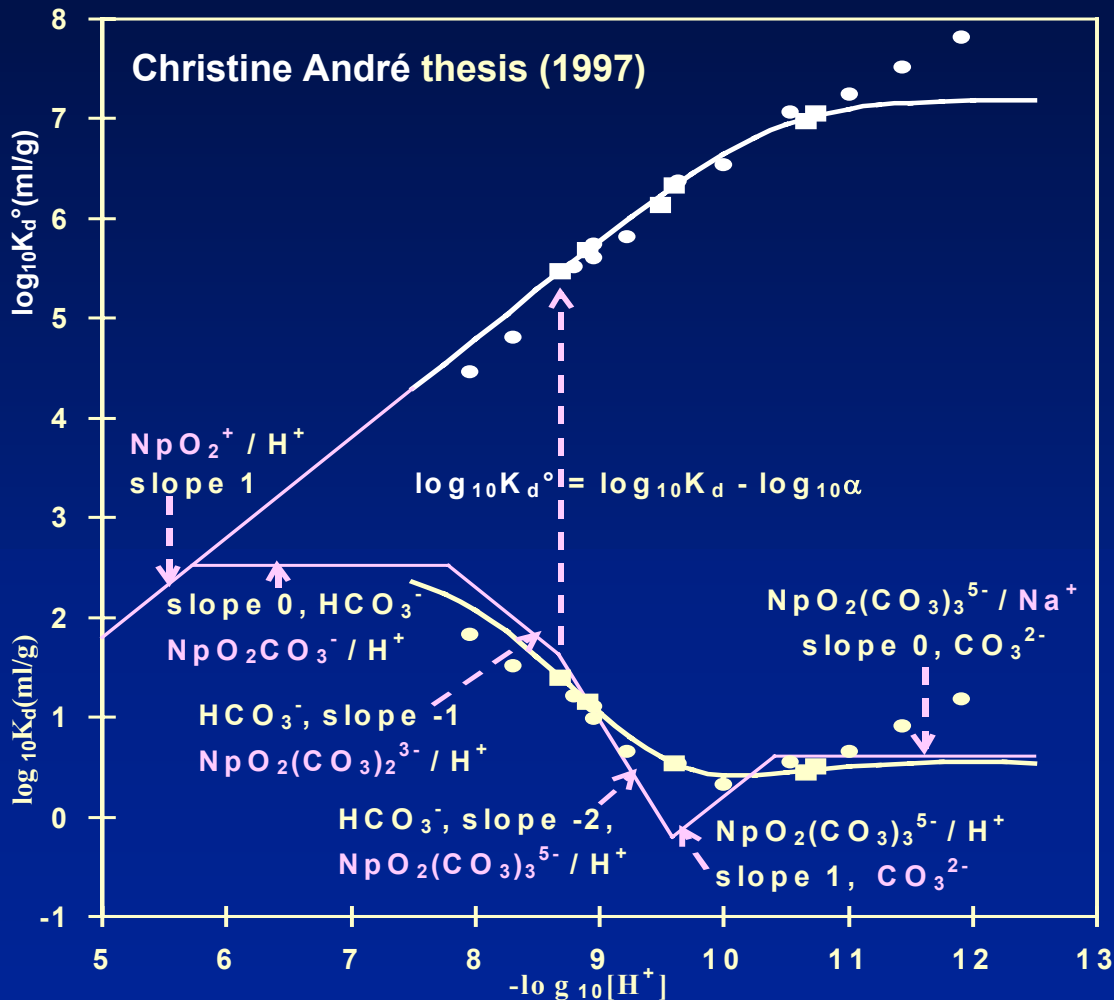


## 2. Chromatography with sorption on a clayey sand (NpO<sub>2</sub><sup>+</sup>/H<sup>+</sup> ionic exchange) and CO<sub>3</sub><sup>2-</sup> complexes

M.Sardin (LSGC CNRS ENSIC Nancy) P.Vitorge, M.-H.Fauré (CEA Saclay)



DESD / SESD



**Coupling**  
sorption and complexation,  
with Np(V) transport

Np(V) is eluted with 1M Na<sup>+</sup>,  
0.2M(HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup>), ClO<sub>4</sub><sup>-</sup> solutions

Partition coefficient,  $K_d$ , is obtained  
from chromatographic data.

$K_d^\circ$  is NpO<sub>2</sub><sup>+</sup> partition coefficient, as  
obtained by correcting  $K_d$  for  
complexation coefficient,  $\alpha$ , as  
calculated from complexing constants  
measured independently (by  
solubility)).

Linear variations of  $\log_{10} K_d^\circ$  vs  
 $\log_{10} [CO_3^{2-}]$  with slope 1 evidence  
H<sup>+</sup>/NpO<sub>2</sub><sup>+</sup> ionic exchange.



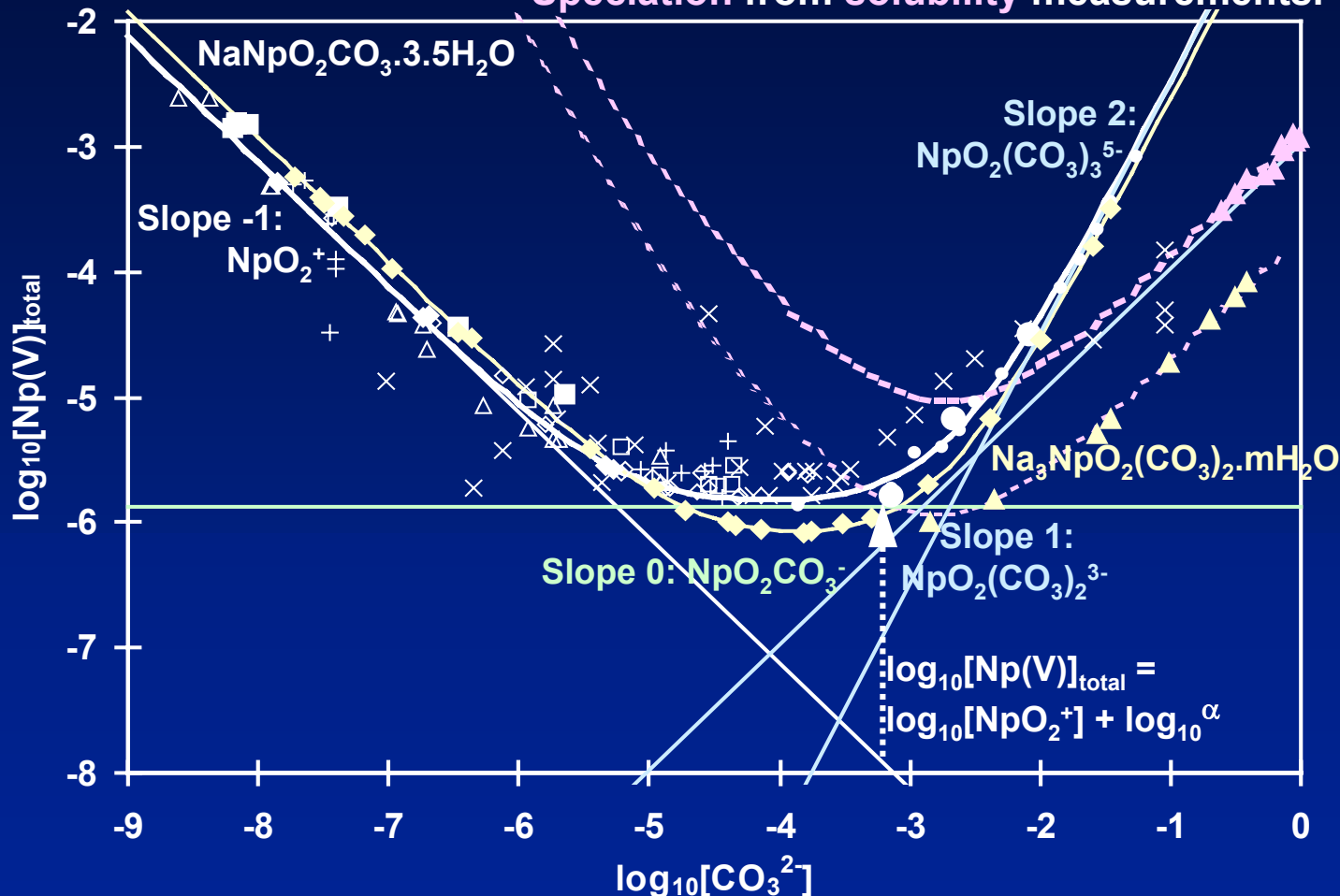
### 3. Np(V) Solubility in 3M Na<sup>+</sup> (ClO<sub>4</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>) solutions



DESD / SESD

Pierre Vitorge, Christian Dautel (1984, 1985, 1986, 1991, 1998),  
TDB-AEN-OCDE (2000), Simakin (1977), Kim *et al.* (1991, 1994, 1995)

Speciation from solubility measurements.



Solid Characterisation (X ray diffraction) after equilibrium achievement (dissolution and précipitation)

Control of activity coefficients and junction potential

Mass action law is valid for ideal system (Slope -1 for  $\text{NpO}_2^{++}$ ): solid phase (constant activity), and in solution (constant activity coefficient)

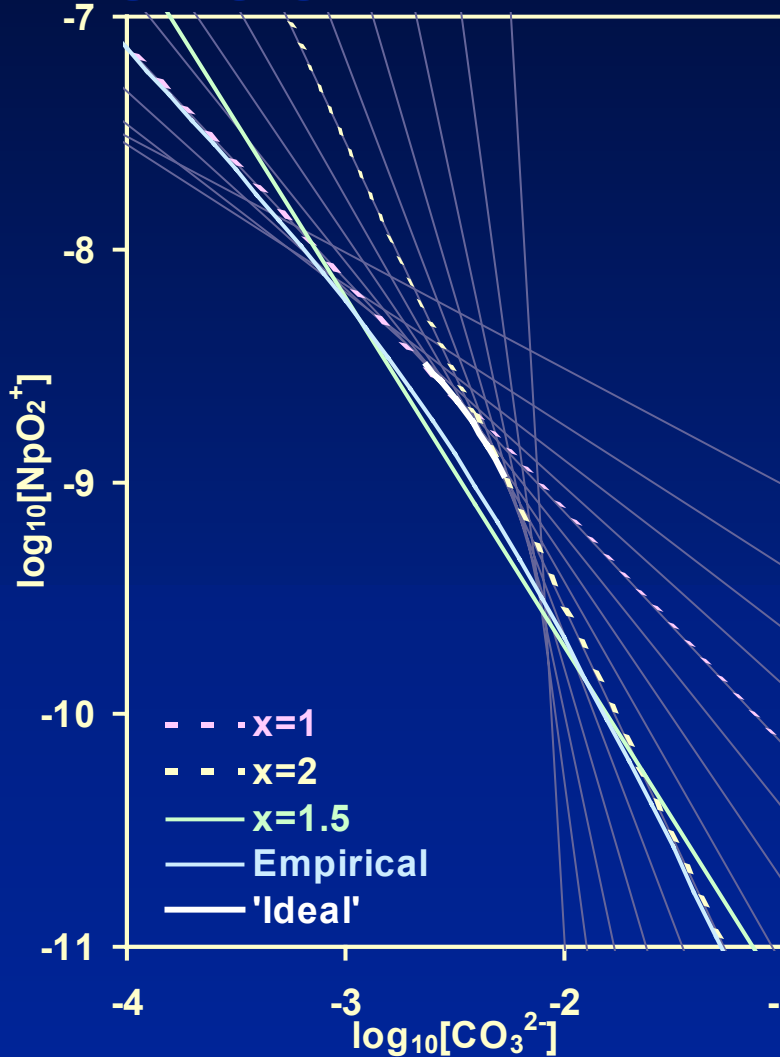
Slow solid transformation (equilibrium for  $\log_{10}[\text{CO}_3^{2-}] = -2.4$ ):





Pierre Vitorge (Mol 1999)

DESD / SESD



$$K_{s1} = [\text{Na}^+] [\text{NpO}_2^+] [\text{CO}_3^{2-}], \quad K_{s2} = [\text{Na}^+]^3 [\text{NpO}_2^+] [\text{CO}_3^{2-}]$$

$$K_{s1.5} = [\text{Na}^+]^2 [\text{NpO}_2^+] [\text{CO}_3^{2-}]^{1.5}, \quad v K_{s1} = [\text{Na}^+] [\text{NpO}_2^+] [\text{CO}_3^{2-}]$$

$$(1-v) K_{s2} = [\text{Na}^+]^3 [\text{NpO}_2^+] [\text{CO}_3^{2-}]$$

$$\frac{1}{v} = 1 + [\text{Na}^+]^2 [\text{CO}_3^{2-}] \frac{K_{s1}}{K_{s2}}$$

$$K_y = \frac{\chi_{\text{Na}}^{2-y} \chi_{\text{NpO}_2}^y \chi_{\text{CO}_3}}{[\text{Na}^+]^{2-y} [\text{NpO}_2^+]^y [\text{CO}_3^{2-}]}$$

$$K_y = K_1^{2-y} K_2^{y-1} \quad (\text{voir Michard 1989})$$

$$D = \frac{\chi_{\text{Na}} [\text{Na}^+]}{\chi_{\text{NpO}_2} [\text{NpO}_2^+]} = \frac{K_2}{K_1}$$

$$\left( \frac{\partial [\text{NpO}_2^+]}{\partial x} \right)_{[\text{Na}^+], [\text{CO}_3^{2-}]} = 0, \quad \text{où } x = \frac{1}{y}$$

$$\left( \frac{\partial \ln [\text{NpO}_2^+]}{\partial \ln [\text{CO}_3^{2-}]} \right)_{[\text{Na}^+]} = -x$$

$$\chi_{\text{Na}} = (2-y) \chi_{\text{CO}_3}$$

$$\chi_{\text{NpO}_2} = y \chi_{\text{CO}_3}$$

$$\chi_{\text{CO}_3} = \frac{1}{3}$$

$$K_1 = \frac{1}{9K_{s1}}$$

$$K_2 = \frac{0.1443}{\sqrt{K_{s2}}}$$

Hypothesis:  $\mu_{\bar{X}} = \mu_{\bar{X}}^0 + RT \ln \chi_X$  for  $X = \text{Na}^+, \text{NpO}_2^+$  et  $\text{CO}_3^{2-}$

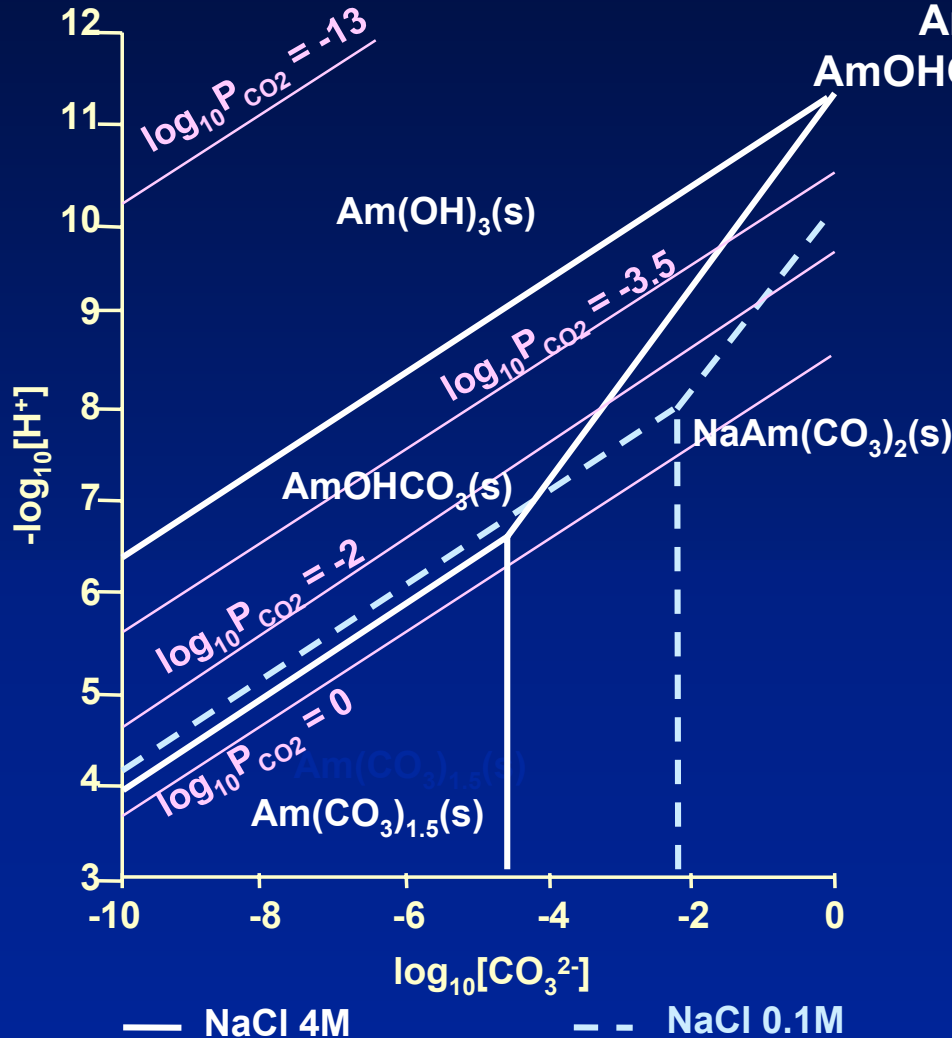


# 5. Stability for CO<sub>3</sub><sup>2-</sup> - OH<sup>-</sup> - Am(III) solids



Pierre Vitorge (1992). Piotr Robouch thesis (1987),  
Eric Giffaut's thesis (1994), TDB-AEN-OCDE (1995)

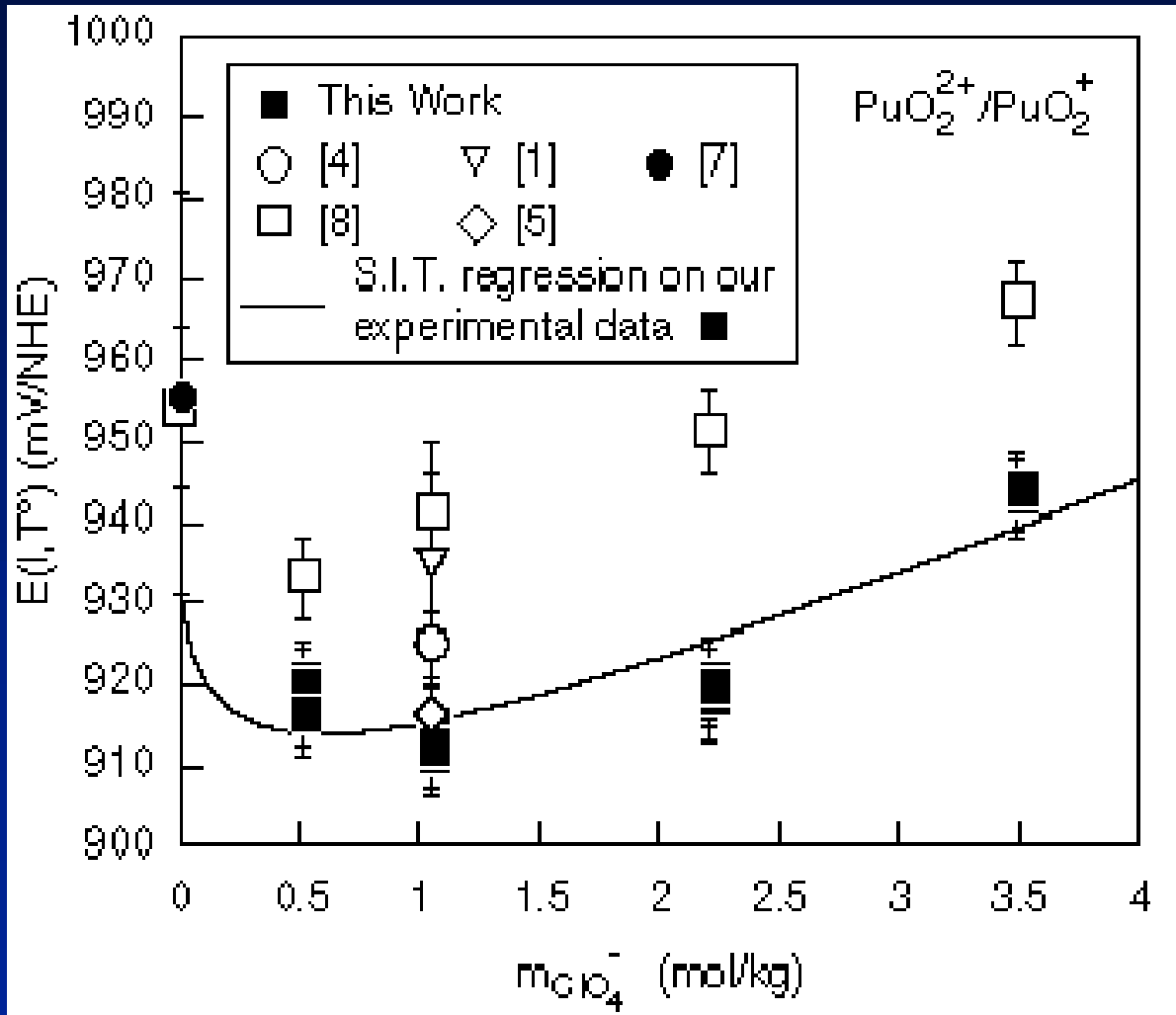
DESD / SESD



CO<sub>2</sub> partial pressure (P<sub>CO2</sub>, atm) is the key parameter.

Speciation cannot be elucidated only from measurements equilibrated with air, or with a single solid phase: this explains incorrect published interpretations (Kim *et al.*, and others) now reinterpreted (Piotr Robouch's thesis 1987, TDB 1995).





Pu and Np redox equilibria in non complexing solutions

$E$  = normal potential for  $\text{PuO}_2^{2+}/\text{PuO}_2^+$  couple measured in  $(\text{H}^+, \text{Na}^+)\text{ClO}_4$  media

$$\Delta_r G = -F E^\circ = -RT \ln K$$

$$\log_{10} K_T(I) = \log_{10} K_T(0) - \Delta \epsilon_T m(\text{ClO}_4^-) - 3 D_T(I_m)$$

$$D_T(I_m) = \frac{a_T \sqrt{I_m}}{1 + b_T \sqrt{I_m}}$$

$I_m$  = ionic strength (mol.kg)



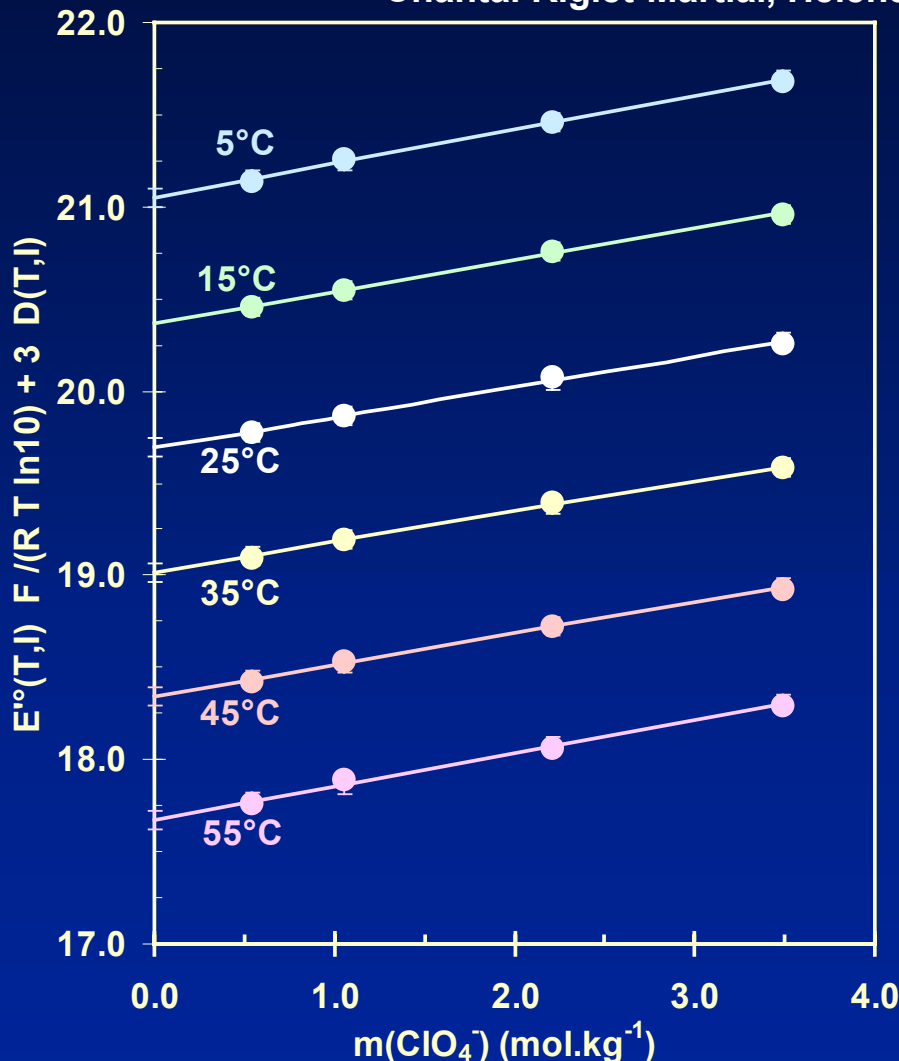


# 7. Ionic strength and temperature influences on $E(\text{NpO}_2^{2+}/\text{NpO}_2^+)$



DESD / SESD

Hélène Capdevila (thesis (1992),  
Hélène Capdevila, Pierre Vitorge (1995, 1998), TDB-AEN-OCDE (2000)  
Chantal Riglet-Martial, Hélène Capdevila, Pierre Vitorge (not published)



### Pu and Np redox equilibria in non complexing solutions

$E^\circ$  = Normal potential of  $\text{NpO}_2^{2+}/\text{NpO}_2^+$  measured in  $(\text{H}^+, \text{Na}^+)\text{ClO}_4$  media

$$\Delta_r G = - F E^\circ = - R T \ln K$$

$$\log_{10} K_T(I) = \log_{10} K_T(0) - 3 D_T(I) - \Delta \varepsilon_T m(\text{ClO}_4^-)$$

$$D_T(I_m) = \frac{a_T \sqrt{I_m}}{1 + b_T \sqrt{I_m}}$$

$I_m$  = ionic strength (mol.kg<sup>-1</sup>)

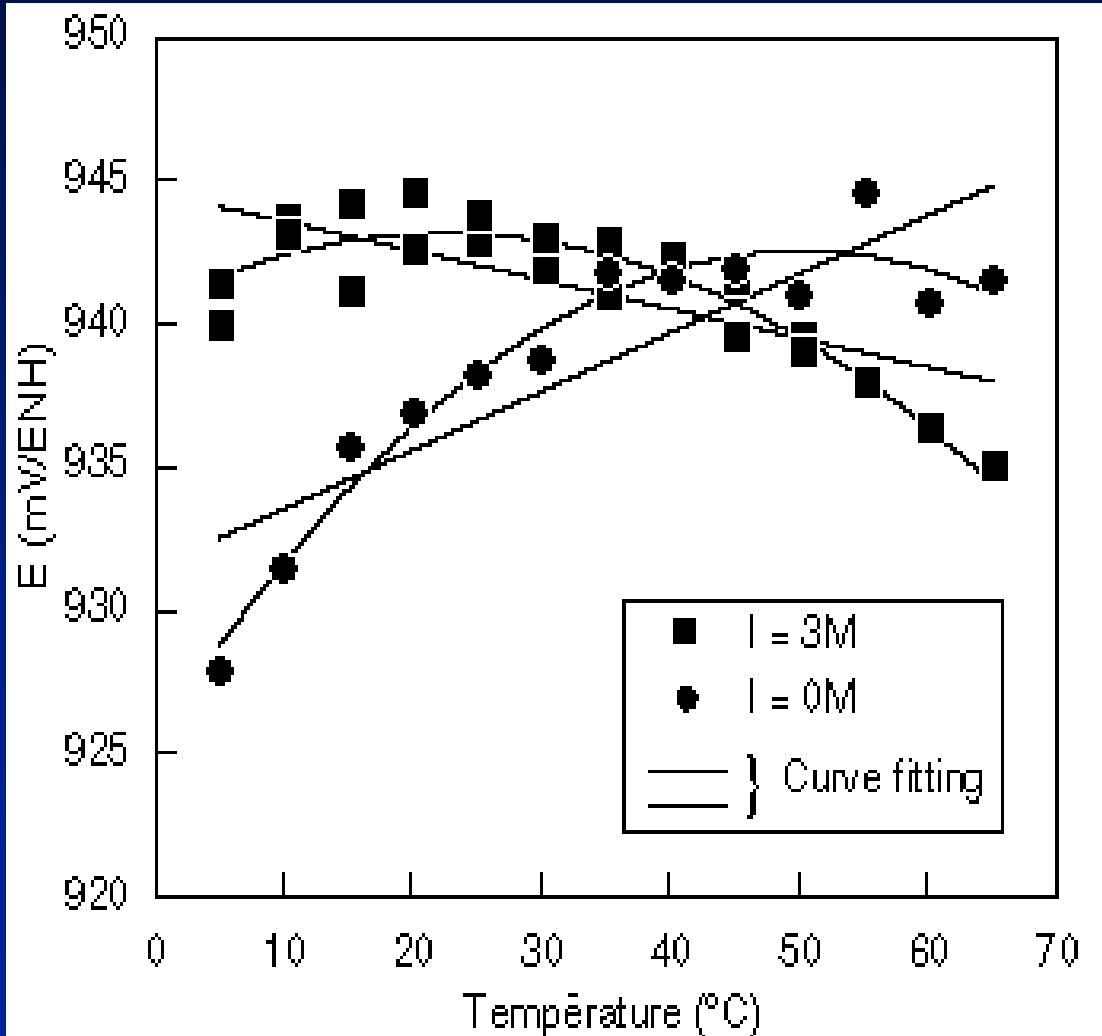


8. Ionic strength and temperature influences on  $E(\text{PuO}_2^{2+}/\text{PuO}_2^+)$ :  
 $\Delta_r S$  estimation



DESD / SESD

Hélène Capdevila, Pierre Vitorge (1995)



Pu and Np redox equilibria  
in non complexing solutions

$E$  = Normal potential of  $\text{PuO}_2^{2+}/\text{PuO}_2^+$   
measured in  $(\text{H}^+, \text{Na}^+)\text{ClO}_4$  media

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad X' = \left(\frac{\partial X}{\partial T}\right)_P$$

$$\Delta_r S_T(I) = \Delta_r S_T(0) + R \ln 10 [-3(D_T(I) + T D'_T(I)) - (\Delta \varepsilon_T + T \Delta \varepsilon'_T) m(\text{ClO}_4^-)]$$

$$\Delta_r G = -F E^\circ = -R T \ln K$$

$$\log_{10} K_T(I) = \log_{10} K_T(0) - 3 D_T(I) - \Delta \varepsilon_T m(\text{ClO}_4^-)$$

$$D_T(I_m) = \frac{a_T \sqrt{I_m}}{1 + b_T \sqrt{I_m}}$$

$I_m$  = ionic strength ( $\text{mol.kg}^{-1}$ )

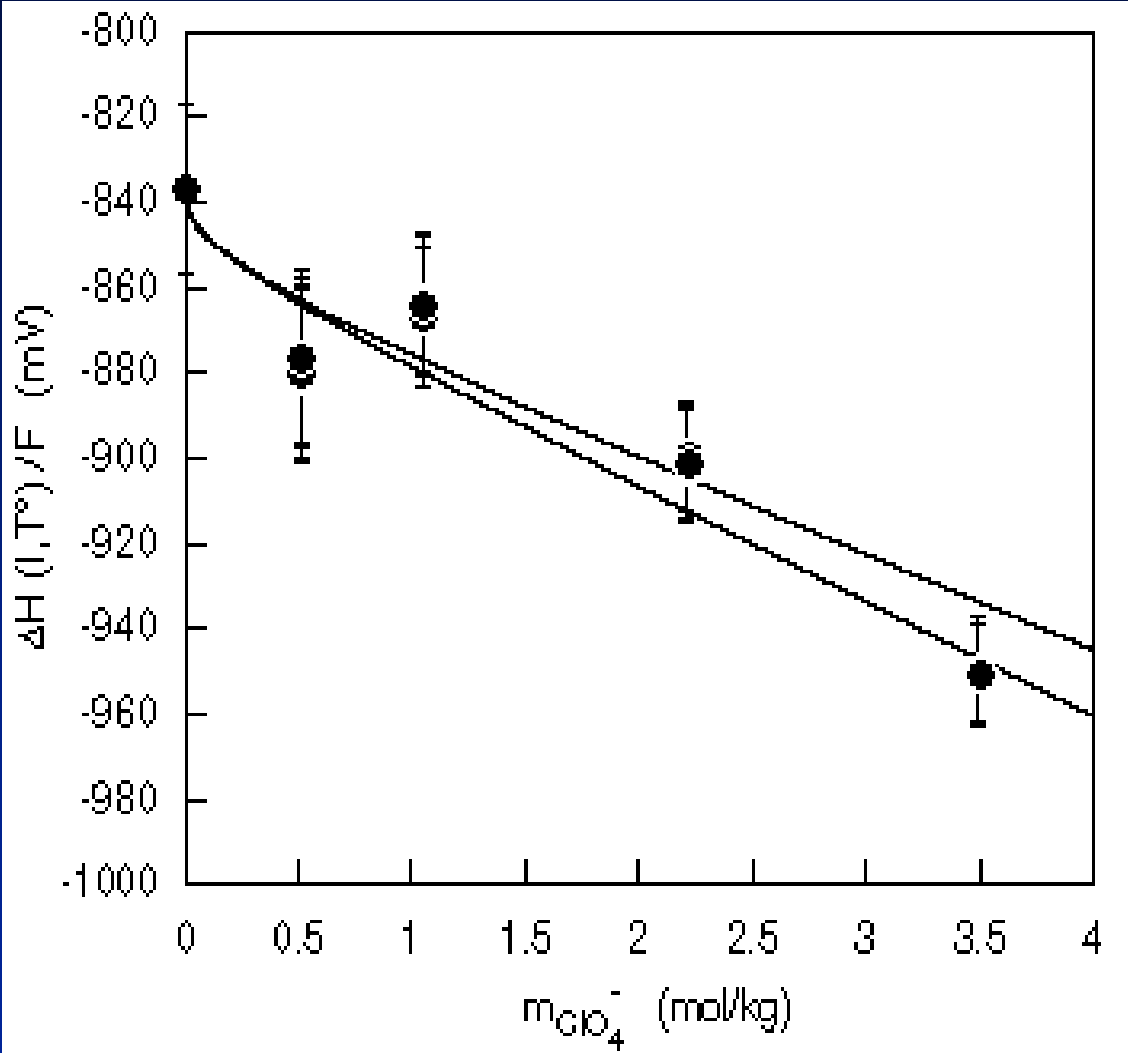


9. Ionic strength and temperature influences on  $E(\text{PuO}_2^{2+}/\text{PuO}_2^+)$ :  
 $\Delta_r H$  estimation



Hélène Capdevila, Pierre Vitorge (1995)

DESD / SESD



Pu and Np redox equilibria  
in non complexing solutions

$E$  = Normal potential of  $\text{PuO}_2^{2+}/\text{PuO}_2^+$   
measured in  $(\text{H}^+, \text{Na}^+)\text{ClO}_4$  media

$$\Delta_r H = -R \left( \frac{\partial \ln K}{\partial 1/T} \right)_P \quad X' = \left( \frac{\partial X}{\partial T} \right)$$

$$\Delta_r H_T(l) = \Delta_r H_T(0) + R T^2 \ln 10 [-3 D'_T(l) - \Delta \varepsilon'_T] m(\text{ClO}_4^-)$$

$$\Delta_r G = -F E^\circ = -R T \ln K$$

$$\log_{10} K_T(l) = \log_{10} K_T(0) - 3 D_T(l) - \Delta \varepsilon_T m(\text{ClO}_4^-)$$

$$D_T(l_m) = \frac{a_T \sqrt{l_m}}{1 + b_T \sqrt{l_m}}$$

$l_m$  = ionic strength ( $\text{mol} \cdot \text{kg}^{-1}$ )





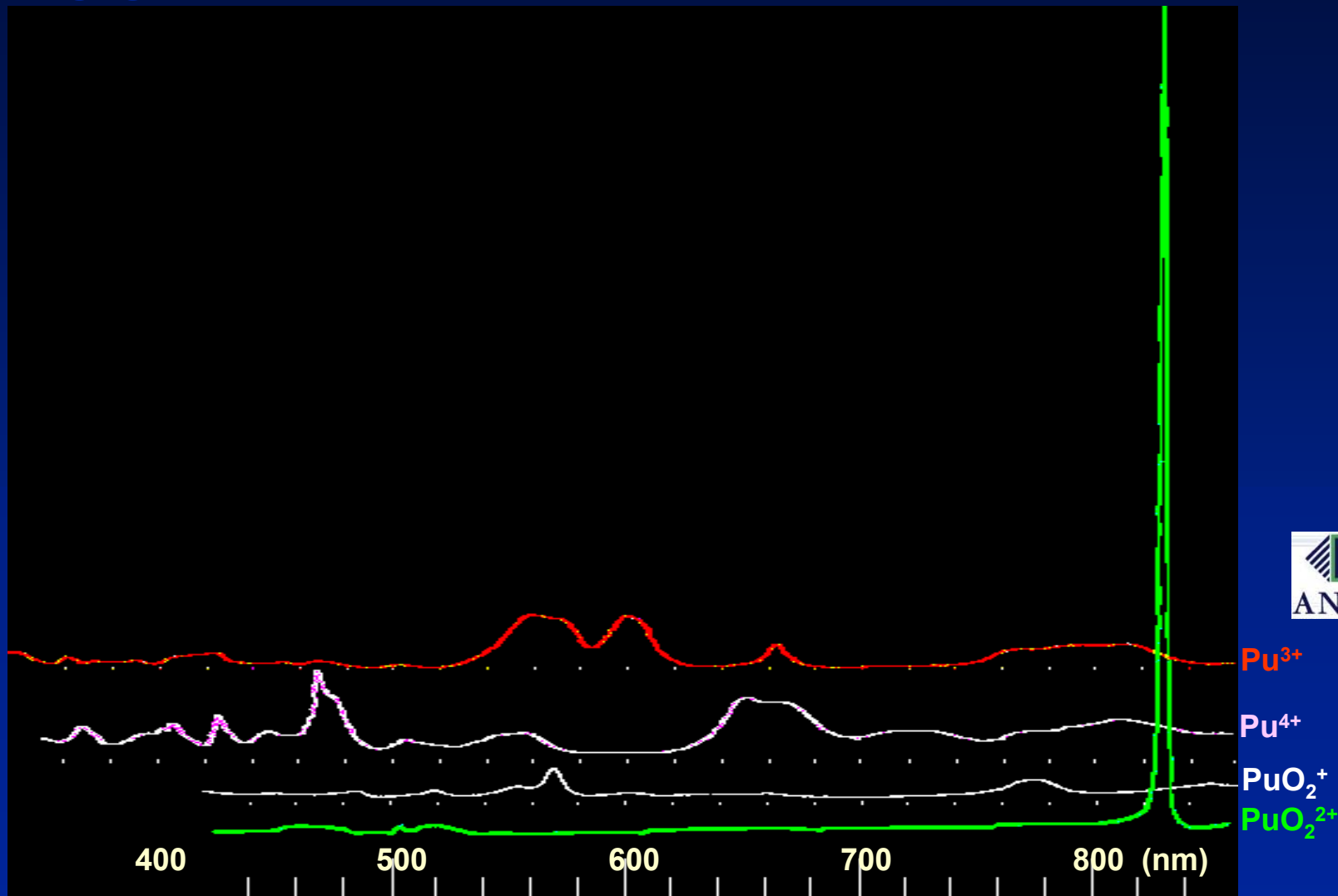
# 10. Spectrophotometric titrations of $\text{Pu}^{3+}$ , $\text{Pu}^{4+}$ and $\text{PuO}_2^{2+}$ , or $\text{Pu}^{3+}$ , $\text{PuO}_2^+$ et $\text{PuO}_2^{2+}$ in 1 or 0,1M $\text{HClO}_4$ solution.



Hélène Capdevila (thèse (1992), Hélène Capdevila, Pierre Vitorge (1995, 1998)

DESD / SESD

Pu disproportionation and solubility in non complexing solutions





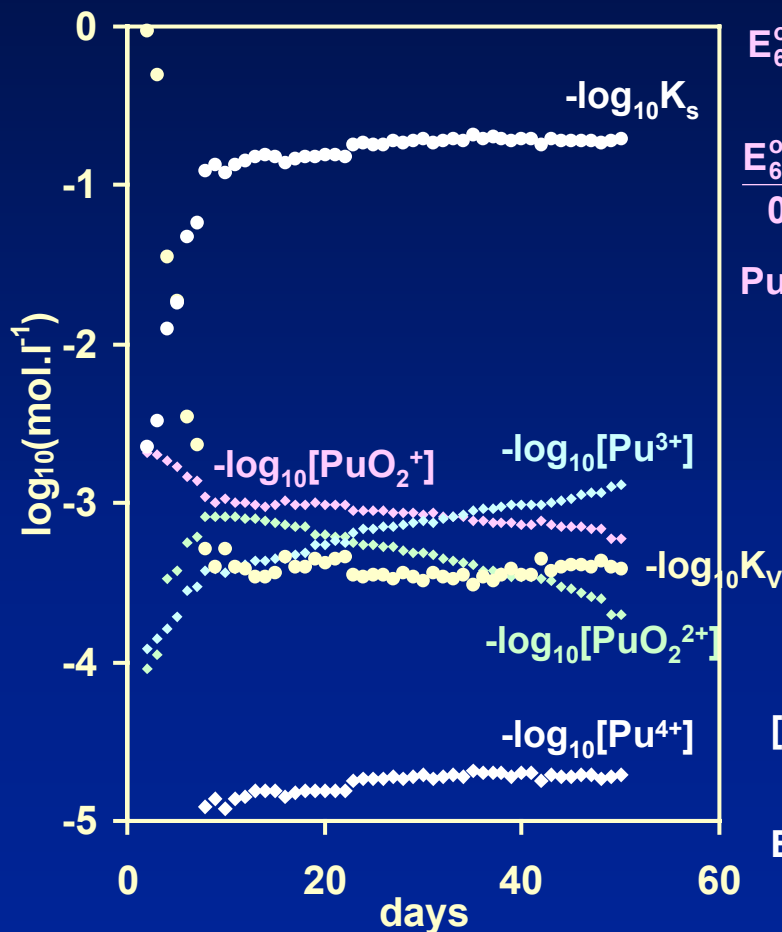
# 11. Measurements of solubility product $K_s$ for $\text{PuO}_2(\text{am,hyd})$ , and disproportionation constant $K_v$ for $\text{PuO}_2^+$



Hélène Capdevila (thèse 1992), Hélène Capdevila, Pierre Vitorge (1995, 1998)

## DESD / SESD Pu disproportionation and solubility in non complexing solutions

Methodology equivalent to  $\text{Pu}^{4+}$ -specific electrode: possible formation of  $\text{PuOH}^{3+}$  or any other  $\text{Pu}^{4+}$  complex, does not interfere with this determination of  $[\text{Pu}^{4+}]$ .



$E_{6/5}^o$  et  $E_{4/3}^o$  are measured independently by cyclic voltametry

$$\frac{E_{6/5}^o - E_{4/3}^o}{0.05916} - \log_{10} K_s = \log_{10} \frac{[\text{PuO}_2^+][\text{H}^+]^4}{[\text{Pu}^{3+}][\text{PuO}_2^{2+}]} = 10^{-0.64 \pm 0.03}$$



$$K_v = \frac{[\text{PuO}_2^{2+}]^2 [\text{Pu}^{3+}]}{[\text{PuO}_2^+]^3 [\text{H}^+]^4} = 10^{3.44 \pm 0.08}$$

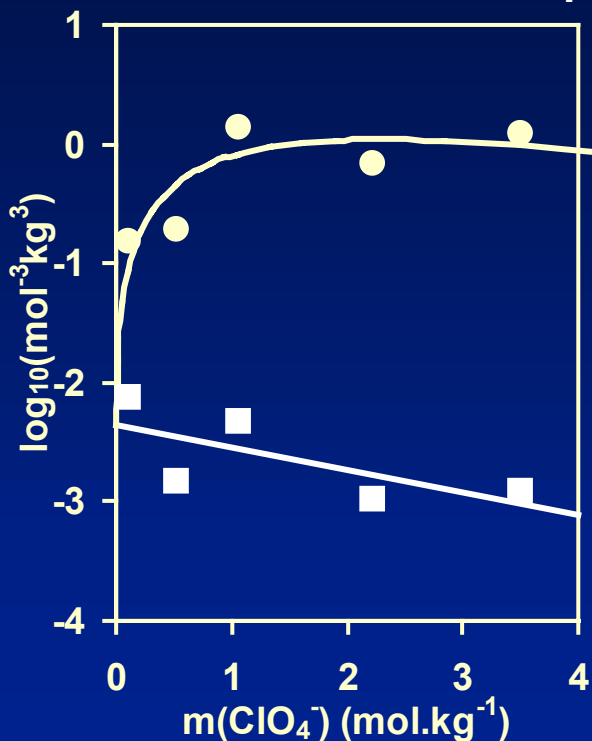
$$[\text{Pu}^{4+}] = [\text{Pu}^{3+}] 10^{\frac{E - E_{4/3}^o}{0.05916}} = 10^{-4.72 \pm 0.03}, \quad K_s = \frac{[\text{Pu}^{4+}]}{[\text{H}^+]^4} = 10^{-0.72 \pm 0.03}$$

$$E = E_{6/5}^o + 0.05916 \log_{10} \frac{[\text{PuO}_2^{2+}]}{[\text{PuO}_2^+]} = 0.902 \pm 0.009$$





## Pu disproportionation and solubility in non complexing solution



$$\log_{10} K_s \quad K_s = \frac{[\text{Pu}^{4+}]}{[\text{H}^+]^4}$$

 Solubility product extrapolation to  $I=0$  (standard state)

$$\log K_s + 12 \frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} = \log K_s^0 - \Delta\varepsilon \quad m_{\text{ClO}_4^-}, \quad I_m = \text{ionic strength (mol.kg}^{-1}\text{)}$$

Fitted values :

$$\log K_s^0 = -2.26 \pm 0.44$$

$$\Delta\varepsilon = 0.27 \pm 0.23$$

$$\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) = 0.89 \pm 0.27$$

$$\text{known value : } 0.82 \pm 0.06$$

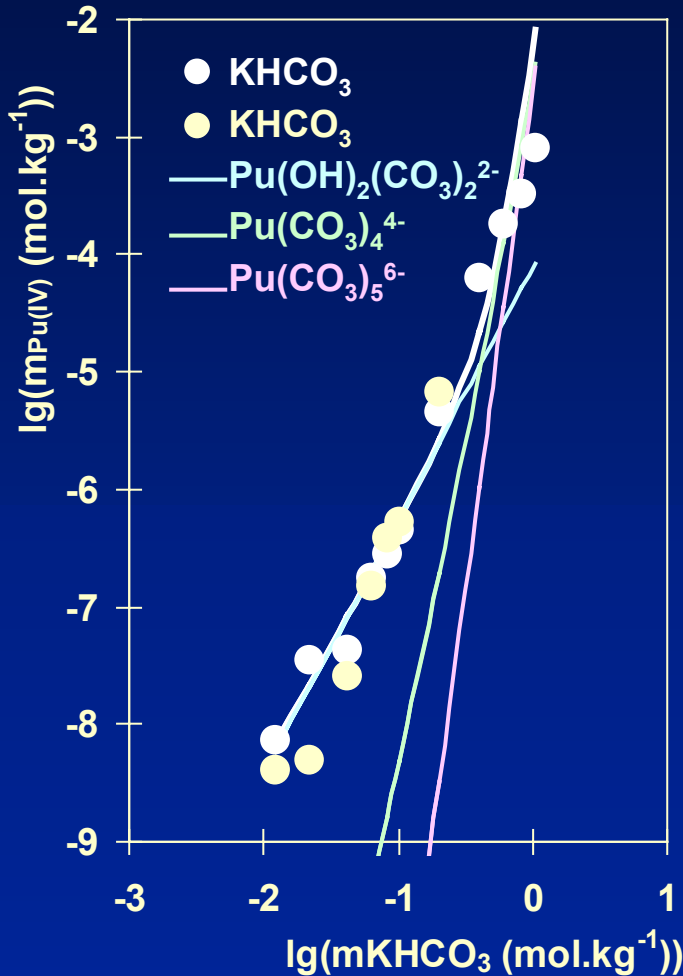


# 13. Pu(IV) solubility in KHCO<sub>3</sub> aqueous solutions



DESD / SESD

Dhanpat Rai, Nancy Hess, Andrew Felmy, Dean Moore,  
Pacific Northwest National Laboratory, Richland, Washington USA  
Mizaku Yui, Japan Nuclear Fuel Cycle Development Institute, Tokai, Japan  
Pierre Vitorge, CEA Saclay DCC/DESD/SESD, France (1999)



## Solubility and EXAFS studies of the Pu(IV) limiting complex



Pu(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> stability is deduced from solubility in K<sub>2</sub>CO<sub>3</sub> aqueous solutions

Pu(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> → Pu(CO<sub>3</sub>)<sub>4</sub><sup>4-</sup> + CO<sub>3</sub><sup>2-</sup> equilibrium constant is measured independently by spectrophotometry (1992 Capdevila; 1996 Capdevila, Vitorge, Giffaut, Delmau)

Pu(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> improved the fit; but it is not enough to validate the interpretation,

conclusion:

- separate I from complexation (is it possible here?)
- EXAFS
- inter-actinide comparison
- other techniques: spectrophotometry, redox

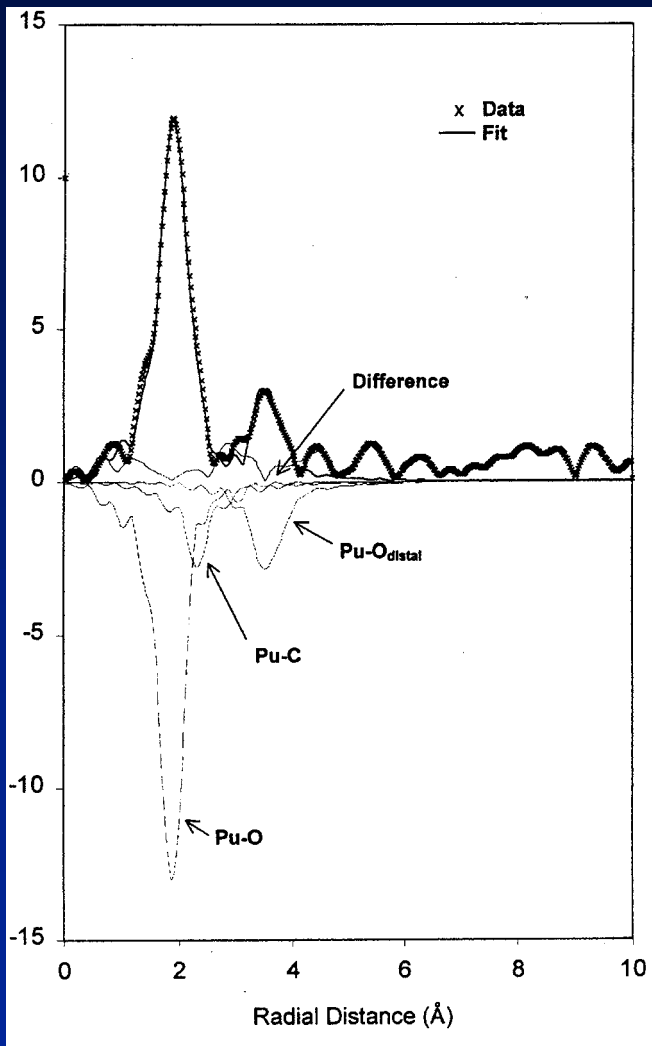


# 14. Fourier transformed of $\text{Pu}(\text{CO}_3)_5^{6-}$ EXAFS spectrum



DESD / SESD

Solubility and EXAFS studies of the Pu(IV) limiting complex



Dhanpat Rai, Nancy Hess, Andrew Felmy, Dean Moore,  
Pacific Northwest National Laboratory, Richland, Washington U  
Mizaku Yui, Japan Nuclear Fuel Cycle Development Institute,  
Tokai, Japan  
Pierre Vitorge, CEA Saclay DCC/DESD/SESD, France  
(1999)

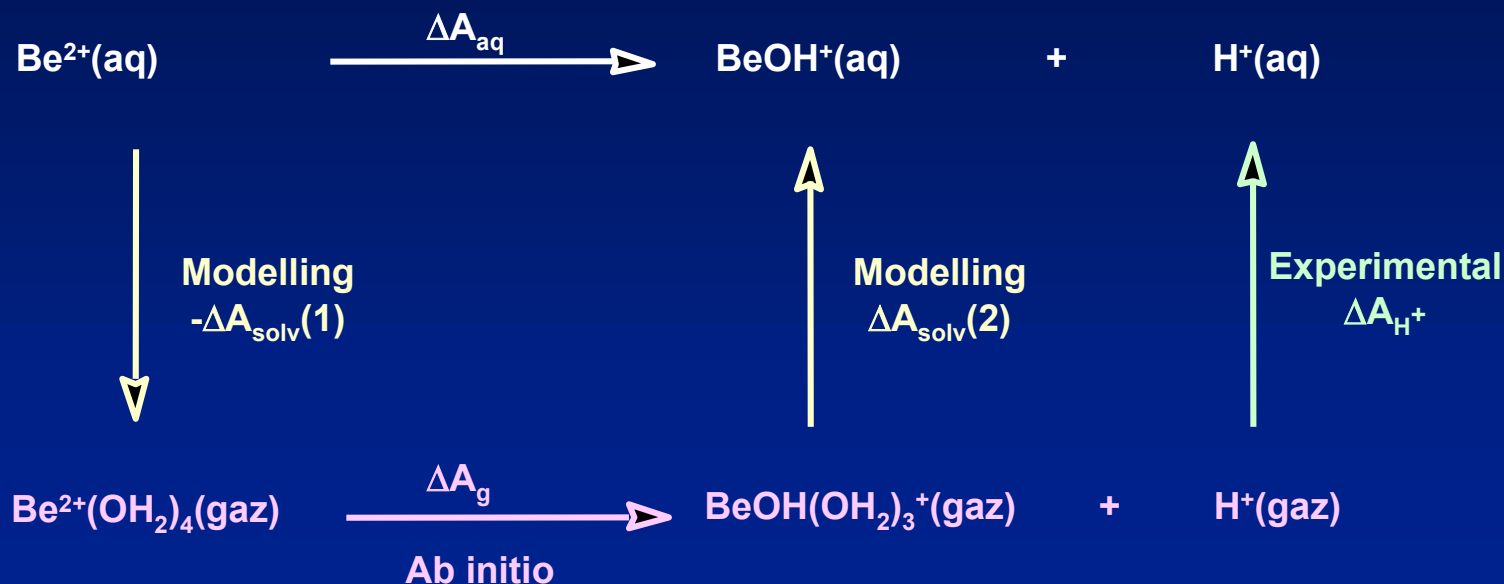


DESD / SESD

Michel Masella, Pierre Vitorge,  
collaboration with Philippe Millié (CEA Saclay DSM)  
and Jeanine Tortajada (CNRS: UMR 8587, Evry University and CEA)



Applications of theoretical chemistry:  
Ab-initio calculations and molecular modelling for hard cations



$$\Delta A_{\text{aq}} = -\Delta A_{\text{solv}}(1) + \Delta A_{\text{g}} + \Delta A_{\text{solv}}(2) + \Delta A_{\text{H}^+}$$





DESD / SESD

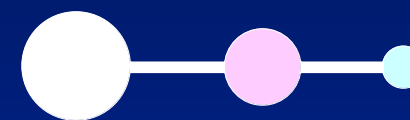
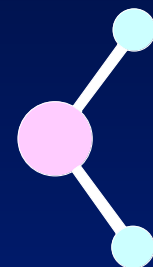
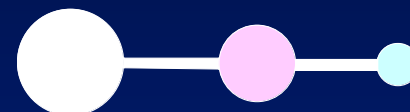
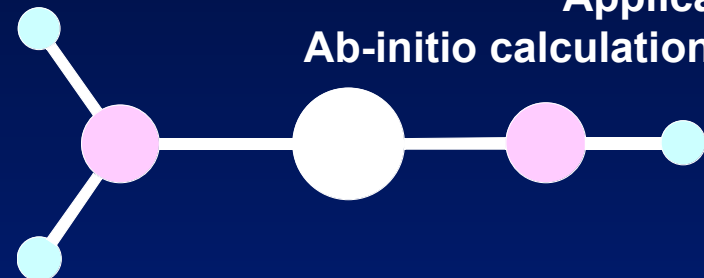
# 16. Molécules $\text{Be}^{2+} - \text{OH}^- - \text{H}_2\text{O}$



Michel Masella, Pierre Vitorge,  
collaboration with Philippe Millié (CEA Saclay DSM)  
and Jeanine Tortajada (CNRS: UMR 8587, Evry University and CEA)

## Applications of theoretical chemistry:

### Ab-initio calculations and molecular modelling for hard cations



1,58 Å  
1,57 Å  
1,57 Å

1,36 Å  
1,35 Å  
1,35 Å

1,34 Å  
1,33 Å

1,52 Å  
1,53 Å

### Bonding energies for $\text{Be}^{2+} + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{BeOHOH}_2^+$

-588.42 kcal/mol MP2 / 6-31+G(d,p)  
-593.57 kcal/mol CISD / 6-31+G(d,p)  
-590.33 kcal/mol MP2 / 6-311+G(2df,2p)

-528.47 kcal/mol MP2 / 6-31+G(d,p)  
-529.61 kcal/mol MP2 / 6-311+G(2df,2p)





DESD / SESD

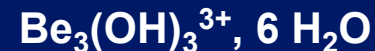
# 17. Structures for hydrated et hydrolysed ions



Michel Masella, Pierre Vitorge,  
collaboration with Philippe Millié (CEA Saclay DSM)  
and Jeanine Tortajada (CNRS: UMR 8587, Evry University and CEA)

Applications of theoretical  
chemistry:

Ab-initio calculations and molecular  
modelling for hard cations



Bonding energies for

