



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 (1992)

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

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

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 (γ) : standard state.

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

.... Temperature and ionic strength corrections (ΔG^{ex} , ΔH^{ex} , ΔS^{ex})

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

Disproportionation and solubility of Pu^{4+}

H.Capdevila, P.Vitorge (1992, 1995, 1998)

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), 1998

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

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

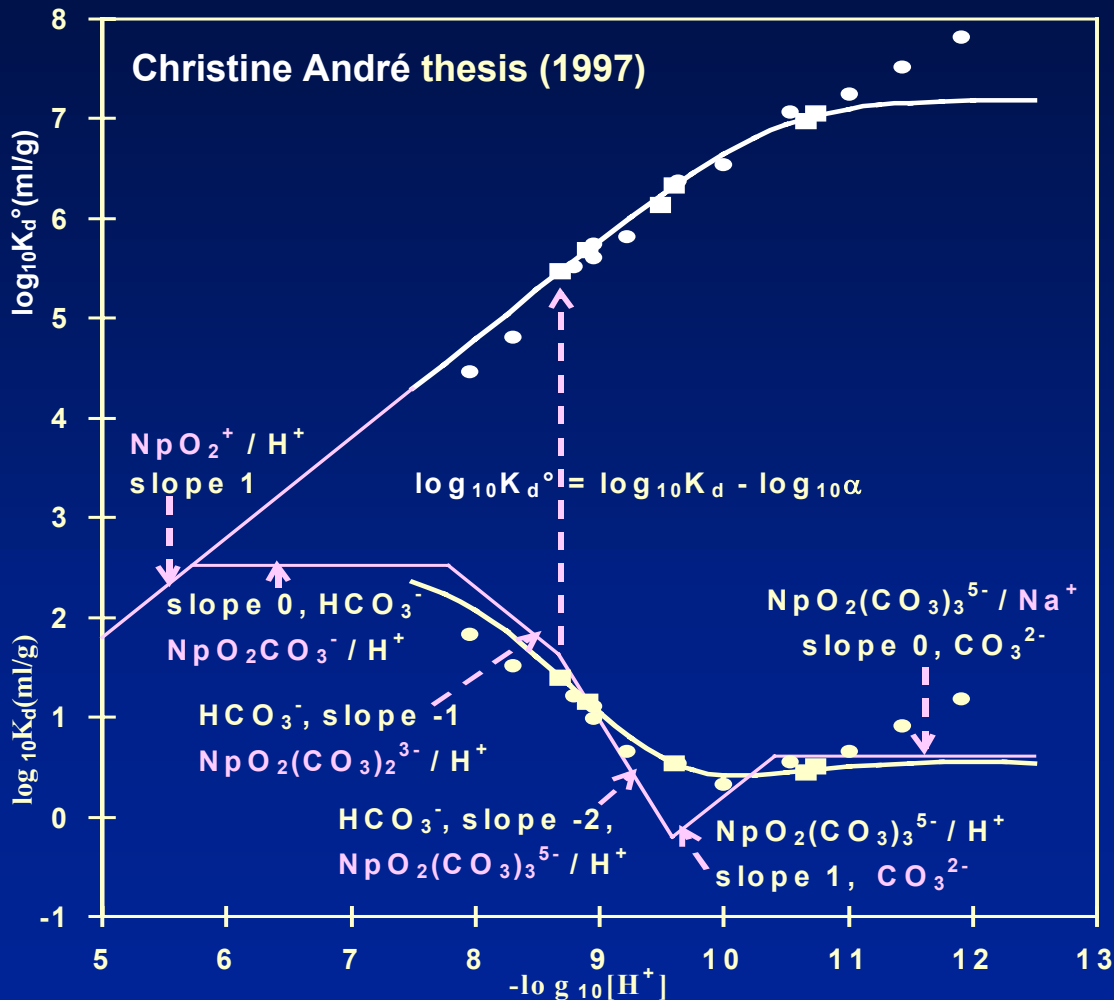


2. Chromatography with sorption on a clayey sand (NpO₂⁺/H⁺ ionic exchange) and CO₃²⁻ complexes

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



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Coupling
sorption and complexation,
with Np(V) transport

Np(V) is eluted with 1M Na⁺,
0.2M(HCO₃⁻ + CO₃²⁻), ClO₄⁻ solutions

Partition coefficient, K_d , is obtained
from chromatographic data.

K_d° is NpO₂⁺ partition coefficient, as
obtained by correcting K_d for
complexation coefficient, α , 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⁺/NpO₂⁺ ionic exchange.



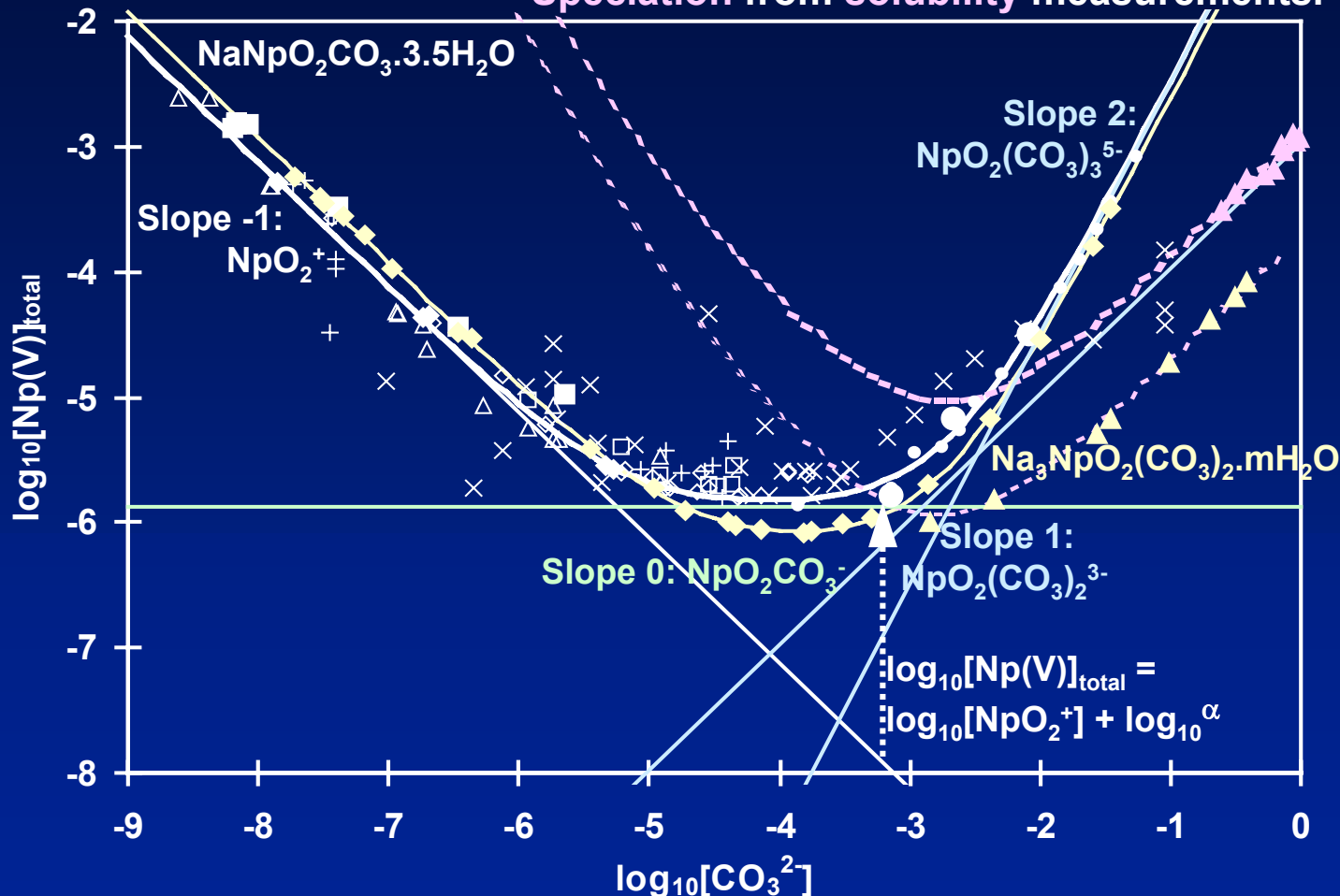
3. Np(V) Solubility in 3M Na⁺ (ClO₄⁻, CO₃²⁻, HCO₃⁻) solutions



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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 NpO_2^{++}): solid phase (constant activity), and in solution (constant activity coefficient)

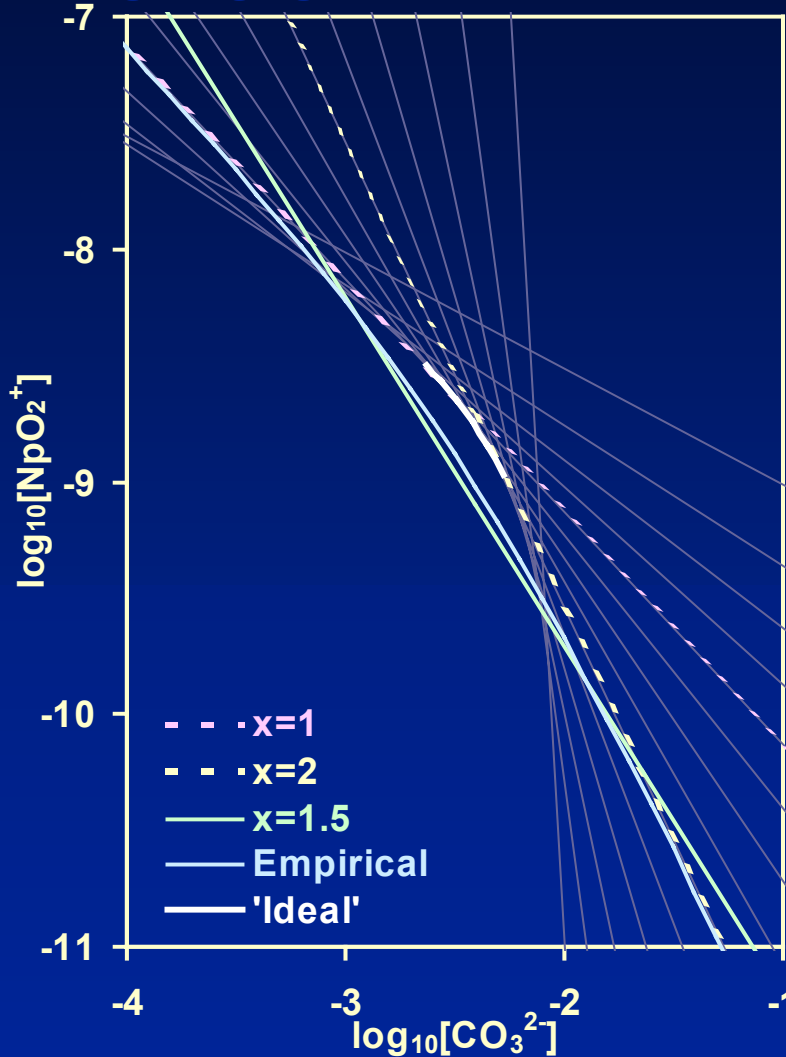
Slow solid transformation (equilibrium for $\log_{10}[\text{CO}_3^{2-}] = -2.4$):





Pierre Vitorge (Mol 1999)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Hypothesis: $\mu_{\bar{X}} = \mu_{\bar{X}}^0 + RT \ln \chi_X$ for $X = \text{Na}^+, \text{NpO}_2^+$ et CO_3^{2-}

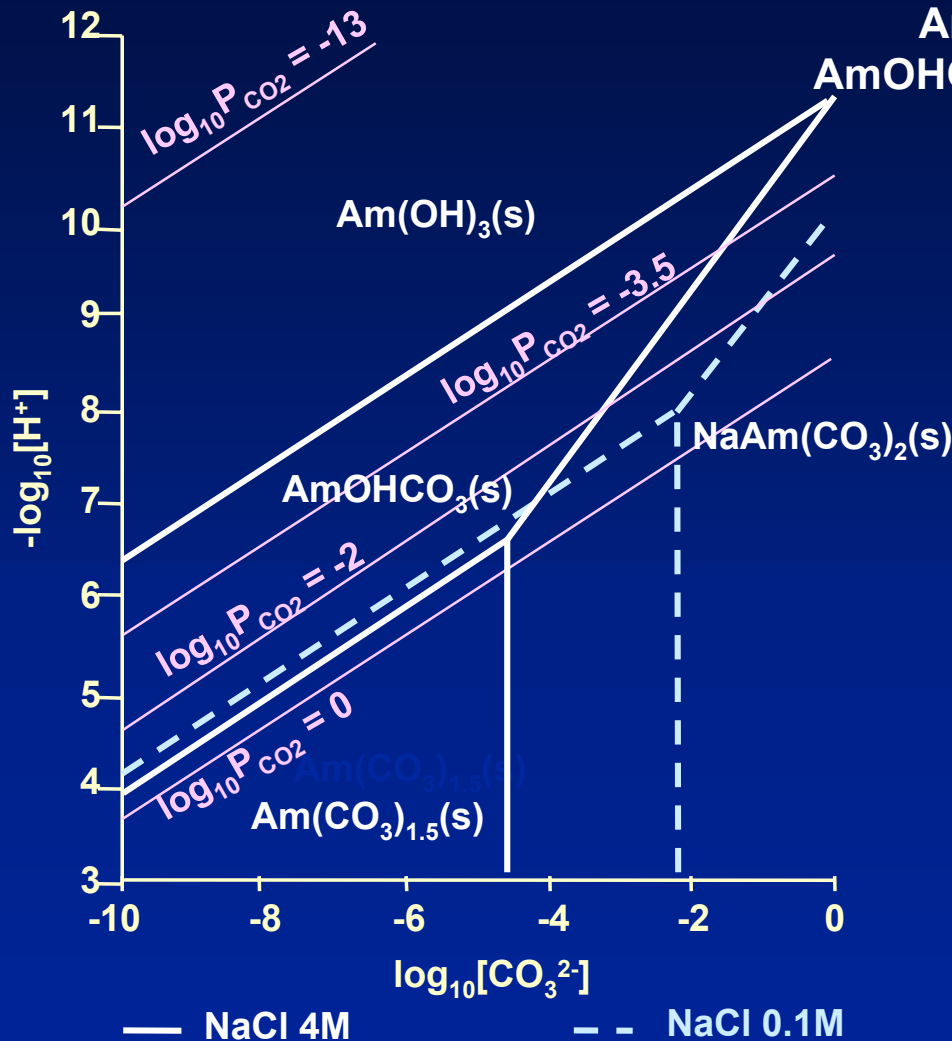


5. Stability for CO₃²⁻ - OH⁻ - Am(III) solids



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

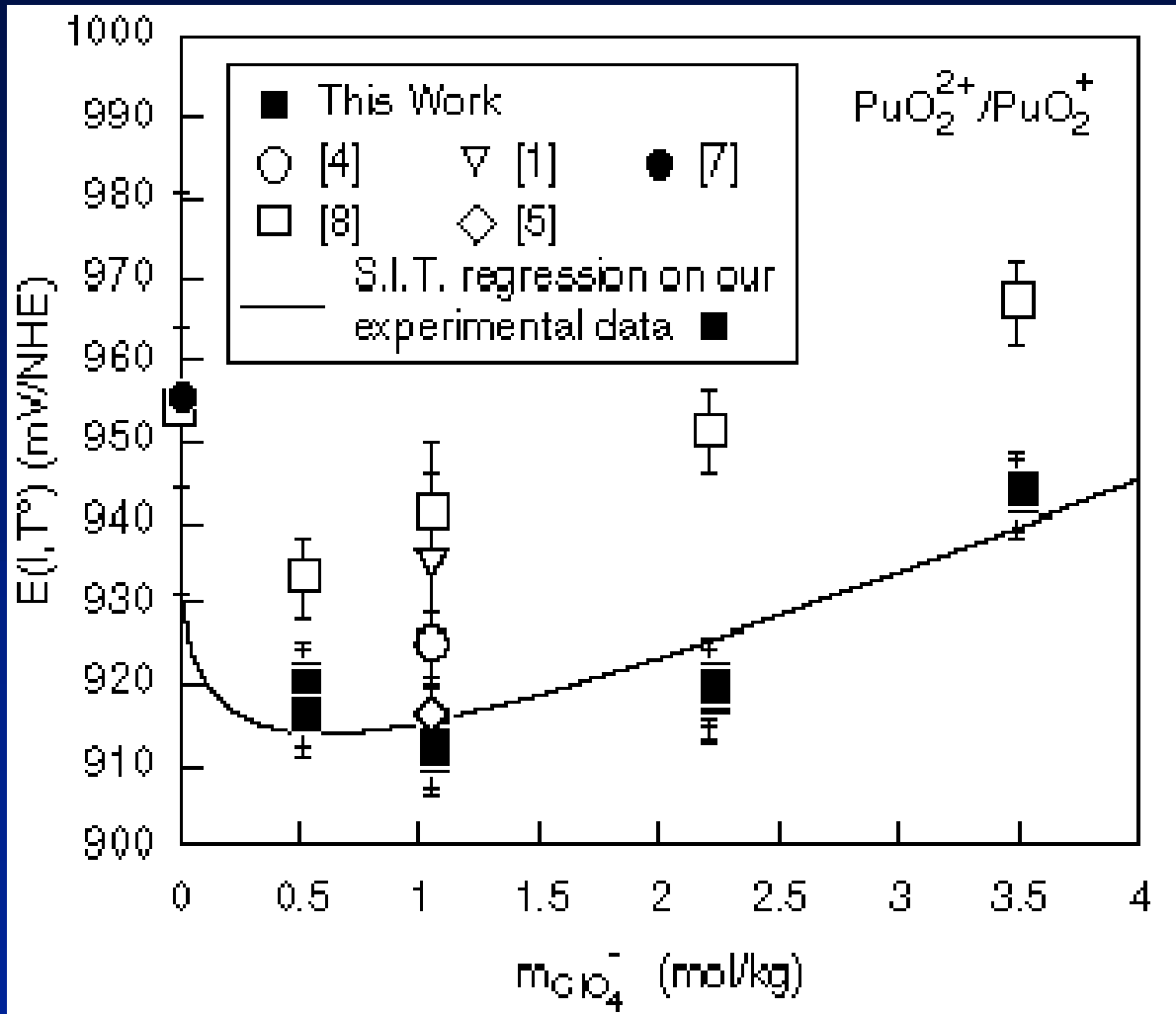
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CO₂ partial pressure (P_{CO_2} , atm) is the key parameter.

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 PuO₂²⁺/PuO₂⁺ couple measured in (H⁺, Na⁺)ClO₄ media

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

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

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

I_m = ionic strength (mol.kg⁻¹)

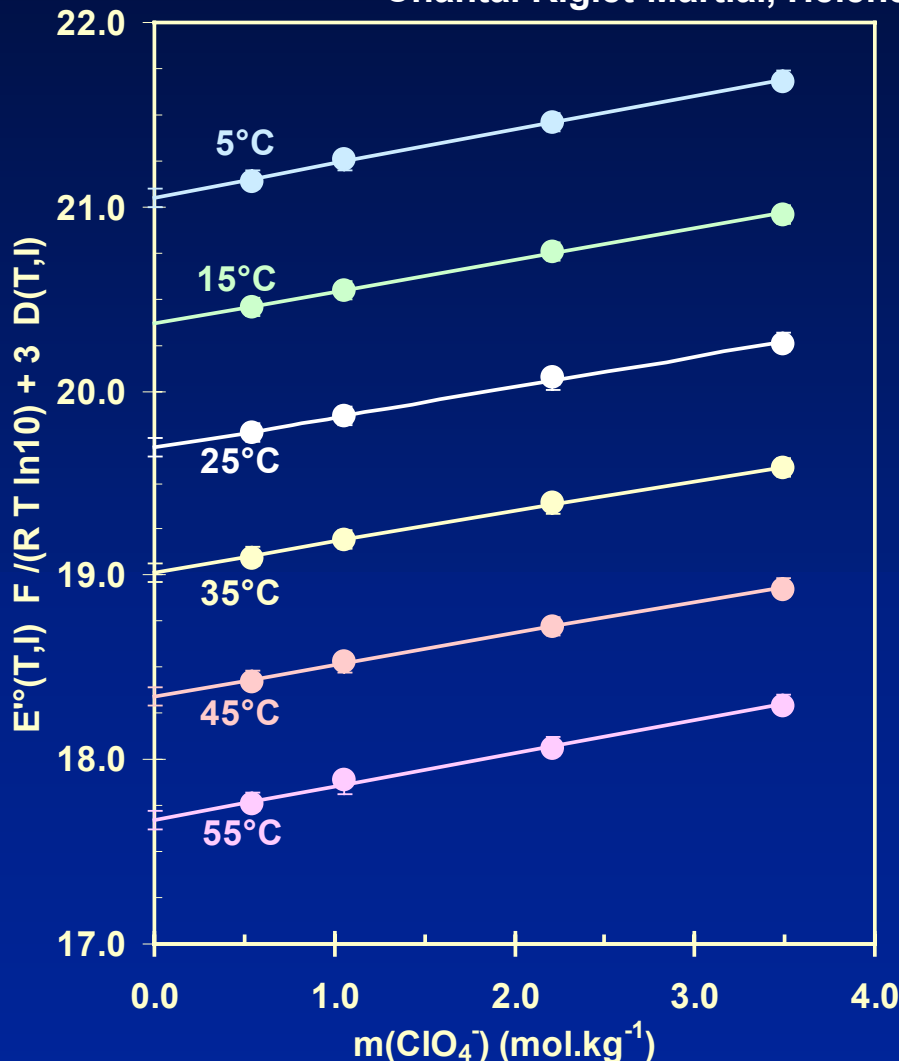


7. Ionic strength and temperature influences on E(NpO₂²⁺/NpO₂⁺)



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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° = Normal potential of NpO₂²⁺/NpO₂⁺ measured in (H⁺,Na⁺)ClO₄ 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⁻¹)

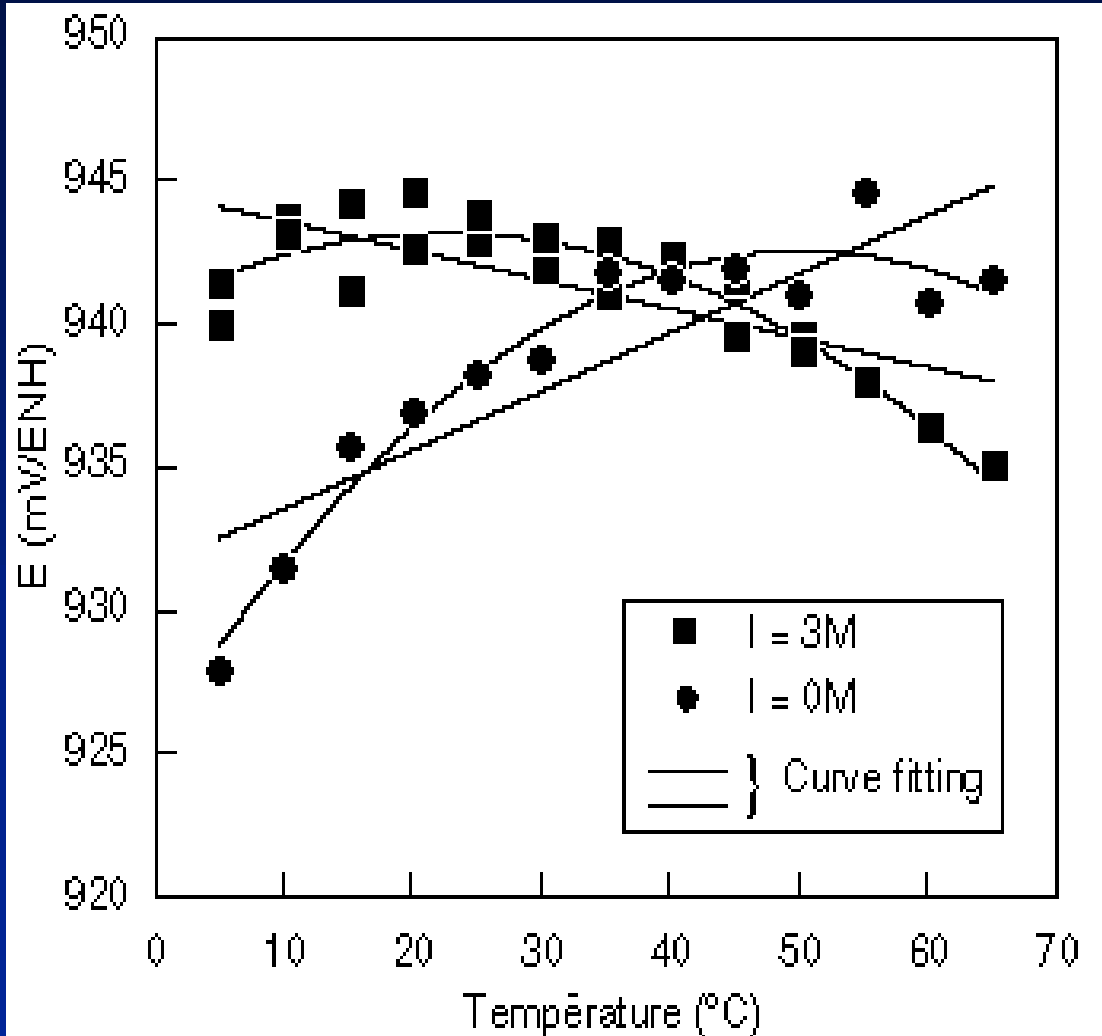


8. Ionic strength and temperature influences on $E(\text{PuO}_2^{2+}/\text{PuO}_2^+)$:
 $\Delta_r S$ estimation



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 (mol.kg^{-1})

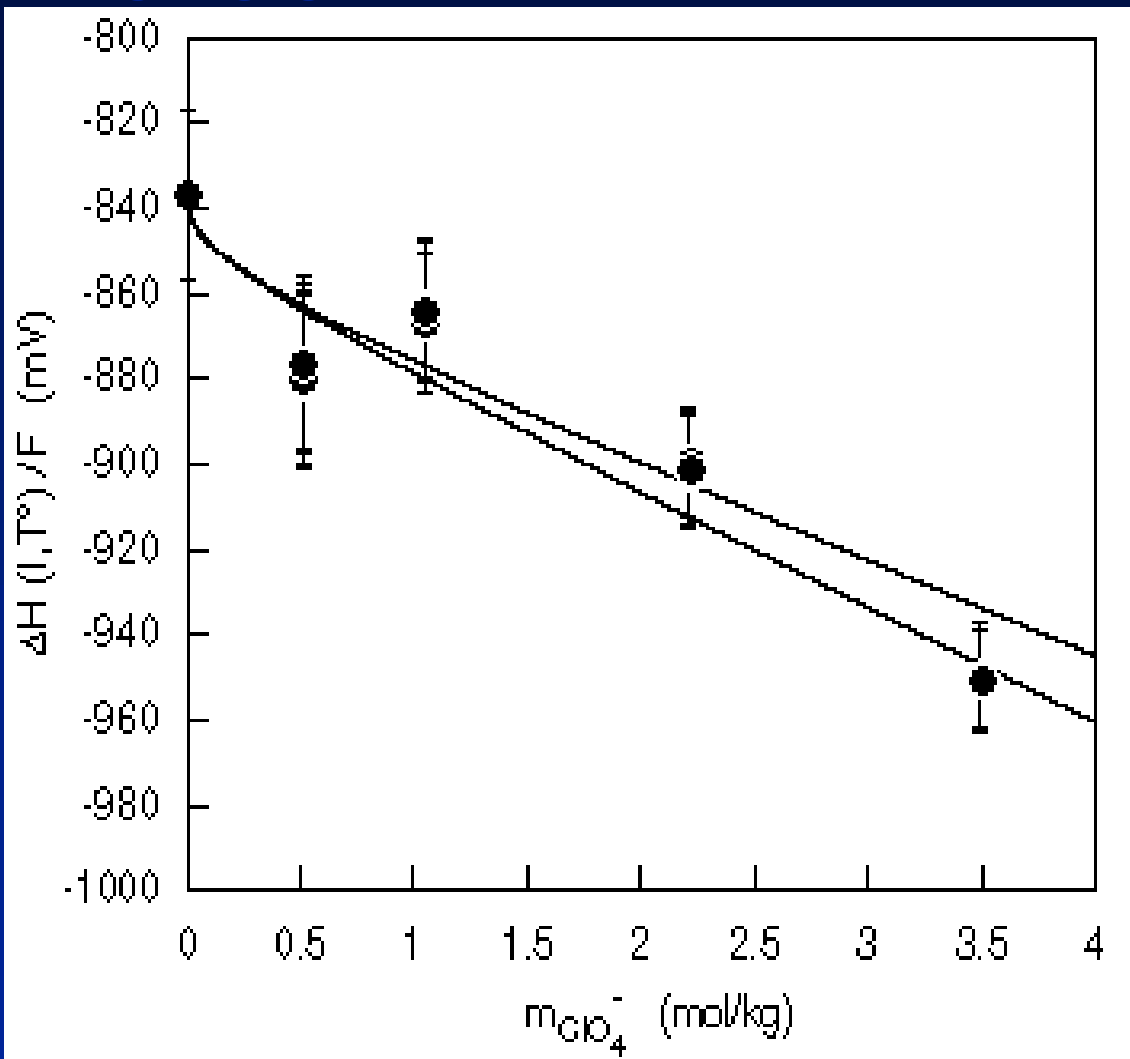


9. Ionic strength and temperature influences on $E(\text{PuO}_2^{2+}/\text{PuO}_2^+)$:
 $\Delta_r H$ estimation



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 ($\text{mol} \cdot \text{kg}^{-1}$)





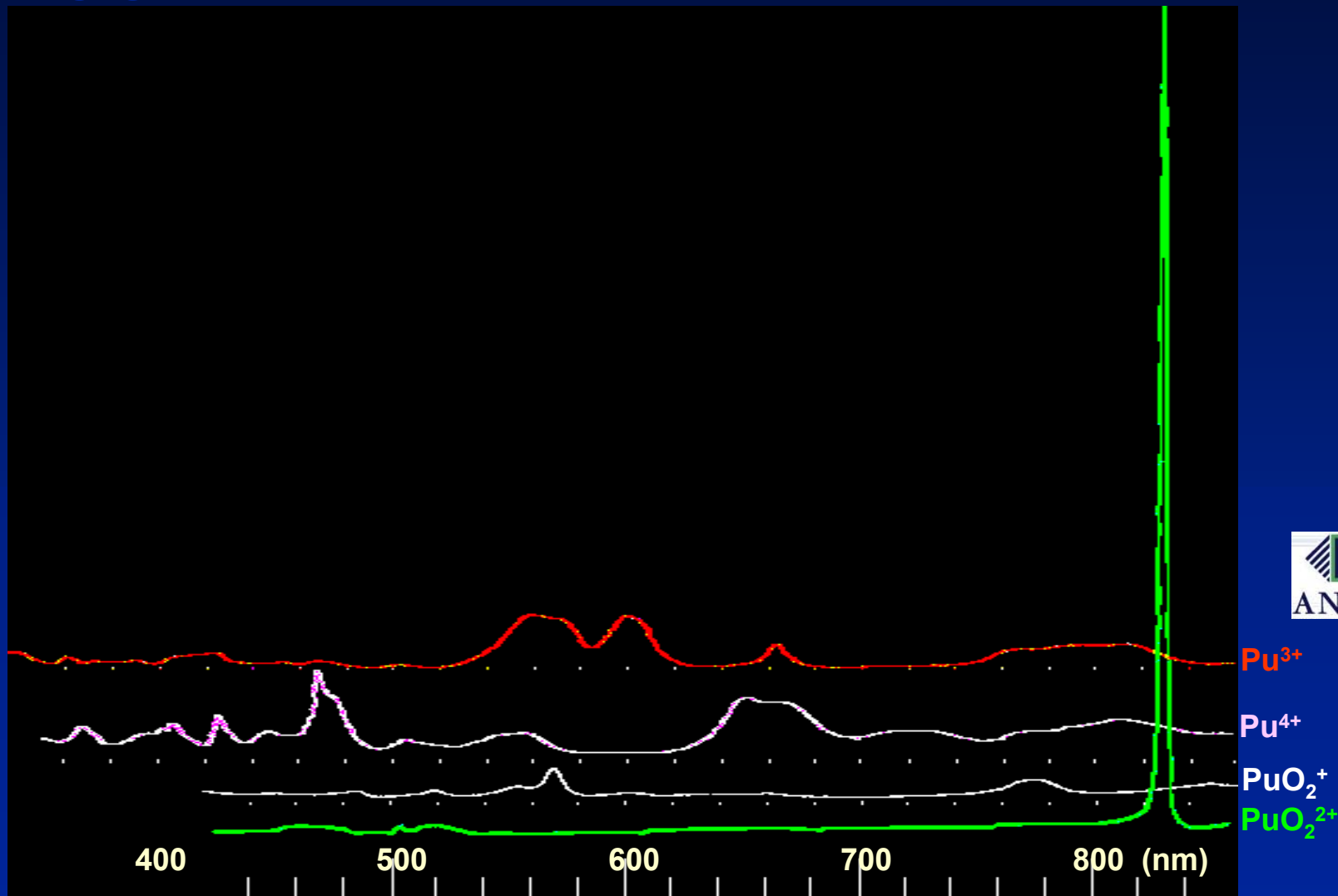
10. Spectrophotometric titrations of Pu^{3+} , Pu^{4+} and PuO_2^{2+} , or Pu^{3+} , PuO_2^+ et PuO_2^{2+} in 1 or 0,1M HClO_4 solution.



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

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Pu disproportionation and solubility in non complexing solutions





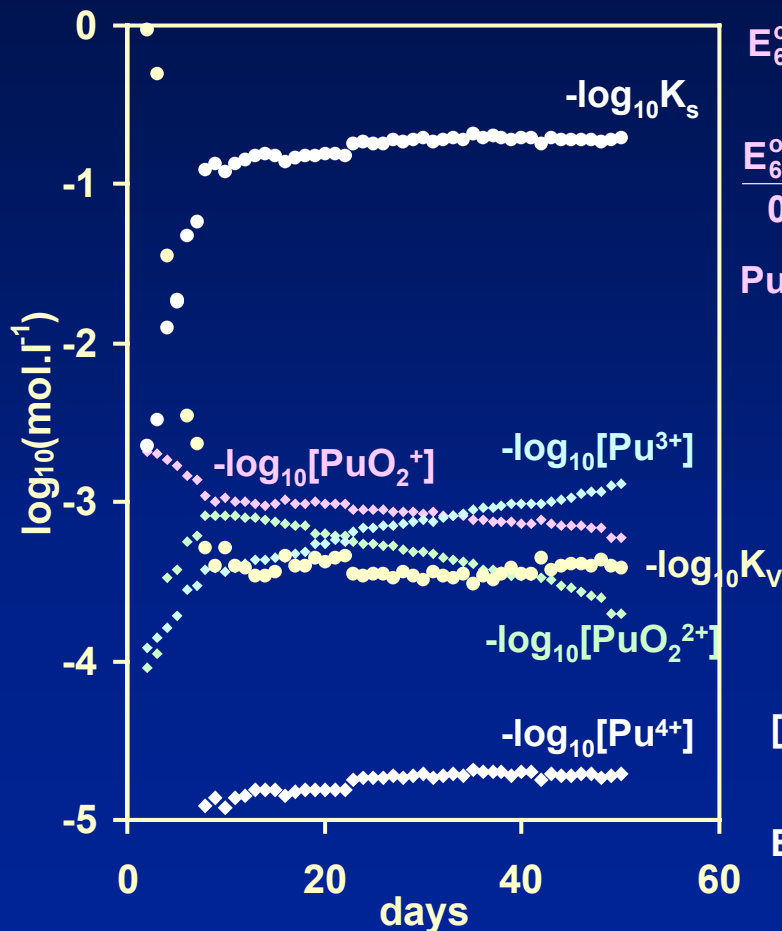
11. Measurements of solubility product K_s for $\text{PuO}_2(\text{am,hyd})$, and disproportionation constant K_v for PuO_2^+



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

DESD / SESD Pu disproportionation and solubility in non complexing solutions

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



$E_{6/5}^0$ et $E_{4/3}^0$ are measured independently by cyclic voltametry

$$\frac{E_{6/5}^0 - E_{4/3}^0}{0.05916} - \log_{10} K_s = \log_{10} \frac{[\text{PuO}_2^+][\text{H}^+]^4}{[\text{Pu}^{3+}][\text{PuO}_2^{2+}]} = 10^{-0.64 \pm 0.03}$$



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

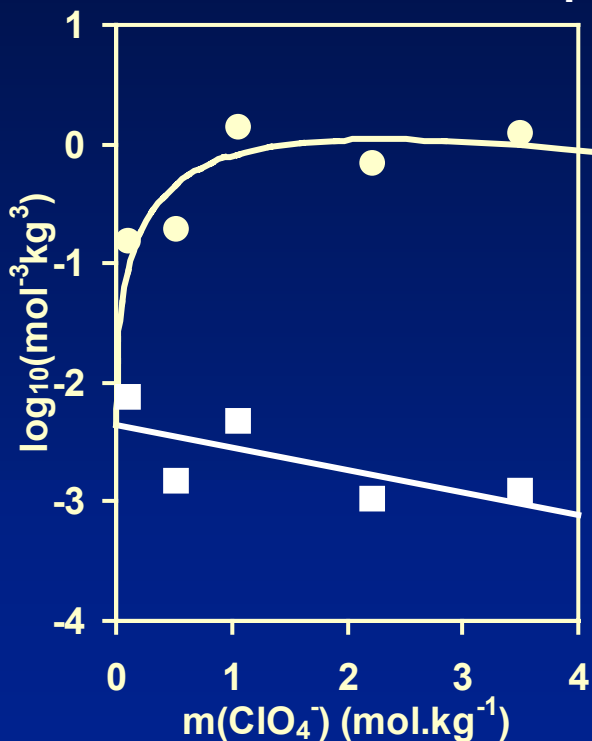
$$[\text{Pu}^{4+}] = [\text{Pu}^{3+}] 10^{\frac{E - E_{4/3}^0}{0.05916}} = 10^{-4.72 \pm 0.03}, \quad K_s = \frac{[\text{Pu}^{4+}]}{[\text{H}^+]^4} = 10^{-0.72 \pm 0.03}$$

$$E = E_{6/5}^0 + 0.05916 \log_{10} \frac{[\text{PuO}_2^{2+}]}{[\text{PuO}_2^+]} = 0.902 \pm 0.009$$





Pu disproportionation and solubility in non complexing solution


 $\log_{10} K_s$

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

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

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

Fitted values :

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

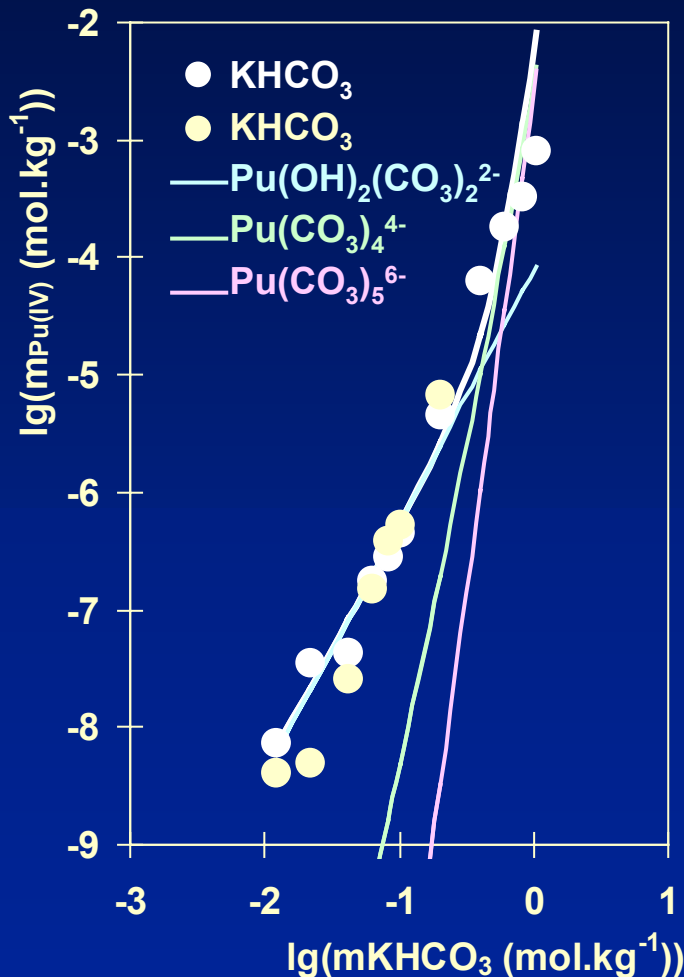
$$\Delta \epsilon = 0.27 \pm 0.23$$

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

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



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



$\text{Pu}(\text{CO}_3)_5^{6-}$ stability is deduced from solubility in K_2CO_3 aqueous solutions

$\text{Pu}(\text{CO}_3)_5^{6-} \rightarrow \text{Pu}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-}$ equilibrium constant is measured independently by spectrophotometry (1992 Capdevila; 1996 Capdevila, Vitorge, Giffaut, Delmau)

$\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ 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

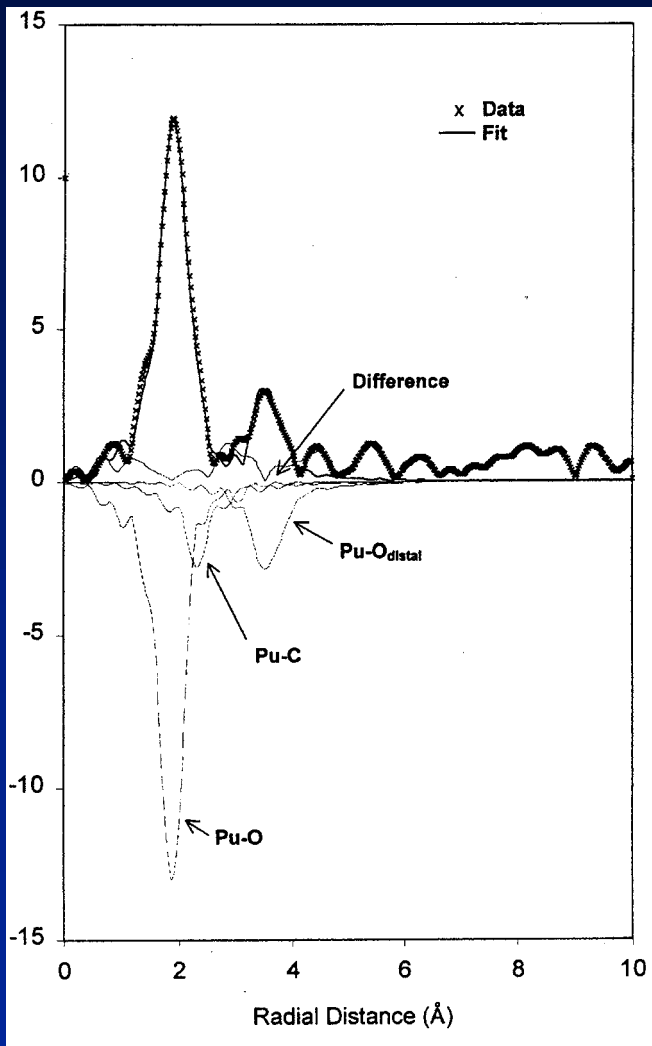


14. Fourier transformed of $\text{Pu}(\text{CO}_3)_5^{6-}$ EXAFS spectrum



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)

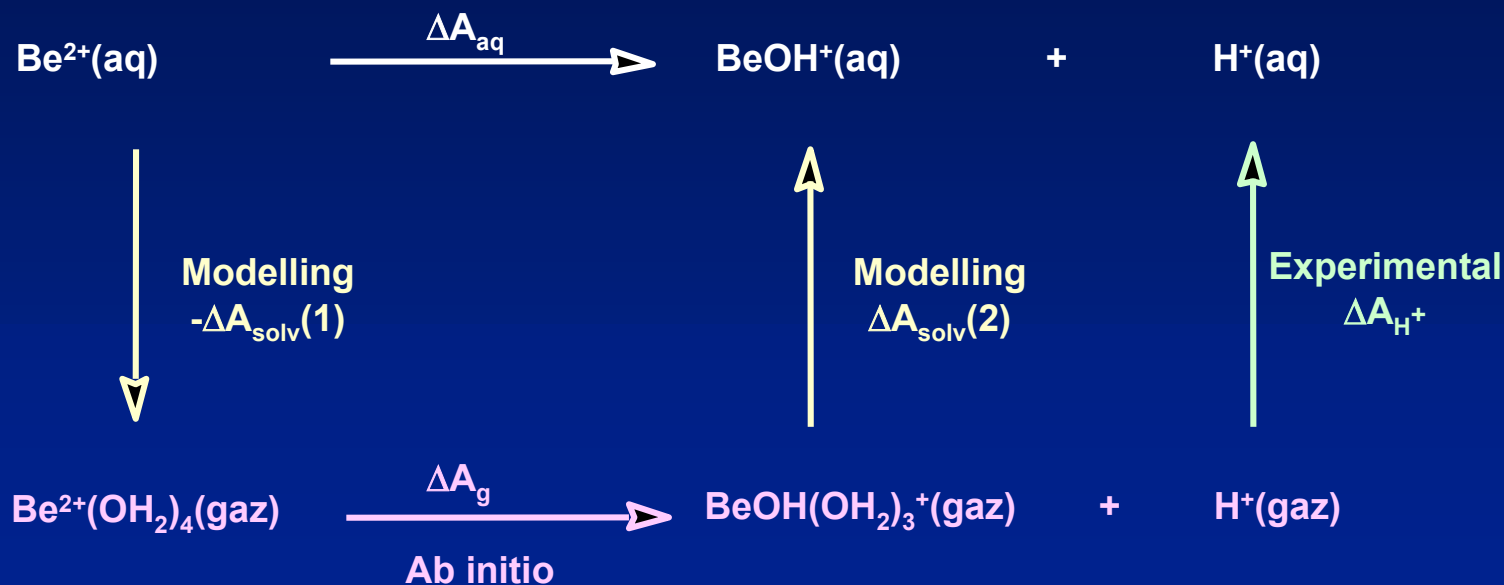


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Michel Masella, Pierre Vitorge,
collaboration with Philippe Millié (CEA Saclay DSM)
and Jeanine Tortajada (CNRS: UMR 8587, Evry University and CEA)



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



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





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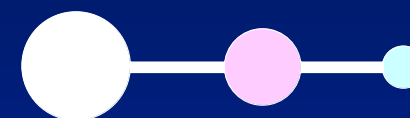
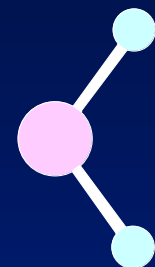
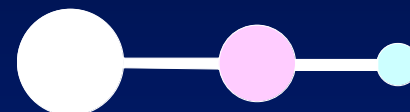
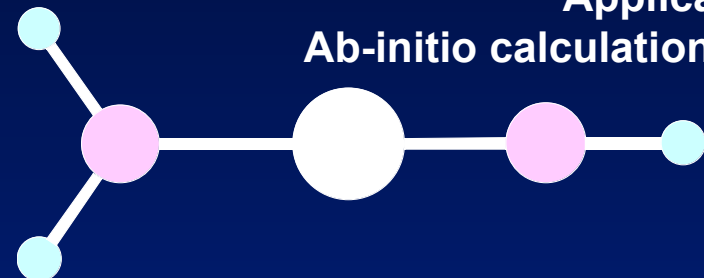
16. Molécules $\text{Be}^{2+} - \text{OH}^- - \text{H}_2\text{O}$



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)





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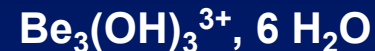
17. Structures for hydrated et hydrolysed ions



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
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Bonding energies for

