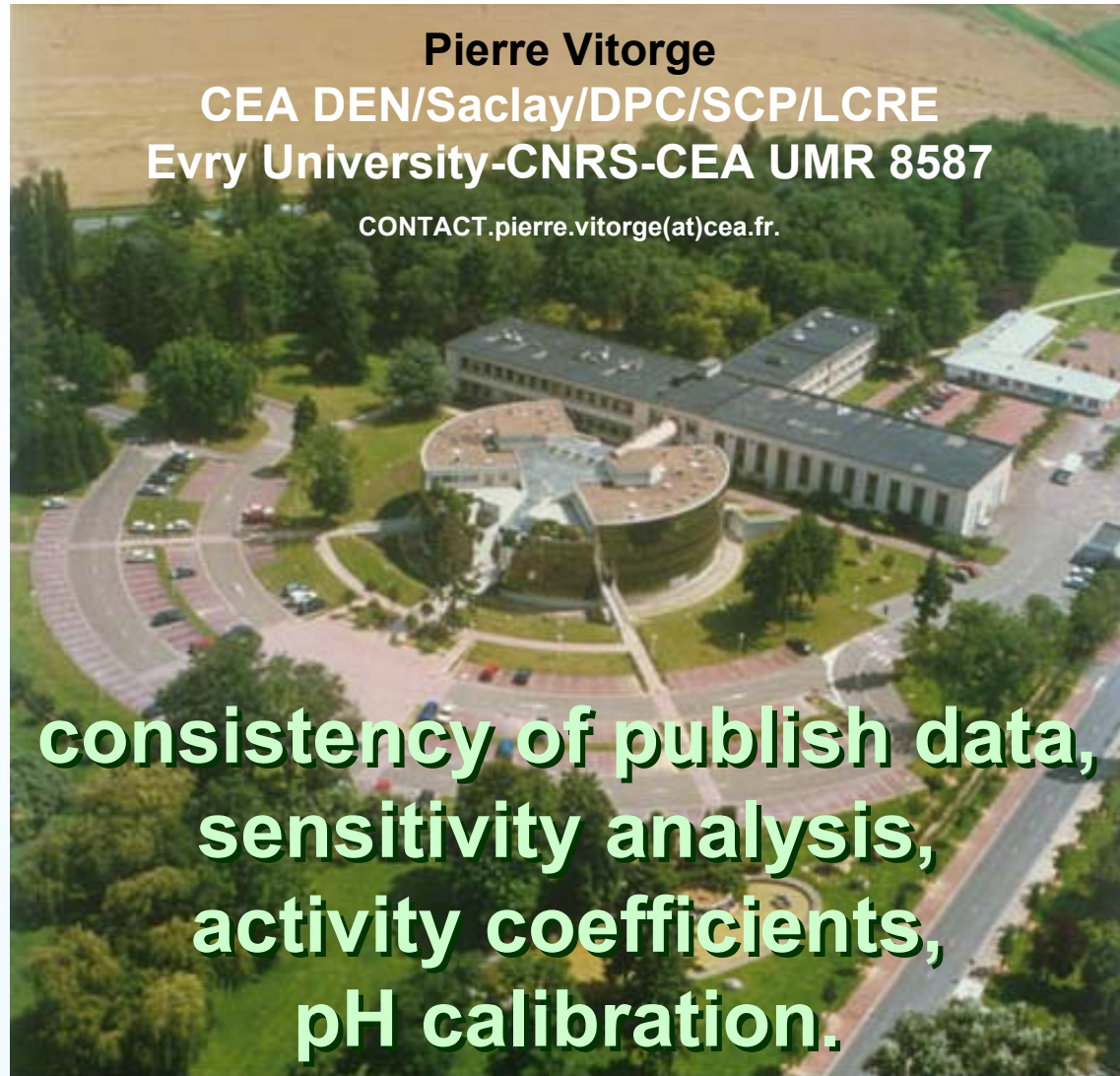


Back-experience from an initial TDB workgroup



Pierre Vitorge
CEA DEN/Saclay/DPC/SCP/LCRE
Evry University-CNRS-CEA UMR 8587
CONTACT.pierre.vitorge(at)cea.fr.

**consistency of publish data,
sensitivity analysis,
activity coefficients,
pH calibration.**

TDB = Thermodynamic Data Base (NEA-OECD)

CEA

Journée d'information CETAMA, SEMINAIRE SPECIATION,
11 décembre 2001 INSTN-Saclay

What should be in the data base?

Pierre Vitorge

For example numbers for modelling
speciation,
solubilities,
partition coefficients...
while direct experimental results are too specific.

This need agreement on the scientific bases of the models,
typically thermodynamic modelling of speciation, solubility, sorption, interaction
between organics and cations...

**consistency of publish data,
sensitivity analysis,
activity coefficients,
pH calibration.**

CEA

Journée d'information CETAMA, SEMINAIRE SPECIATION,
11 décembre 2001 INSTN-Saclay

Thèses :

Chimie des actinides

Transport (Collaboration ENSIC)

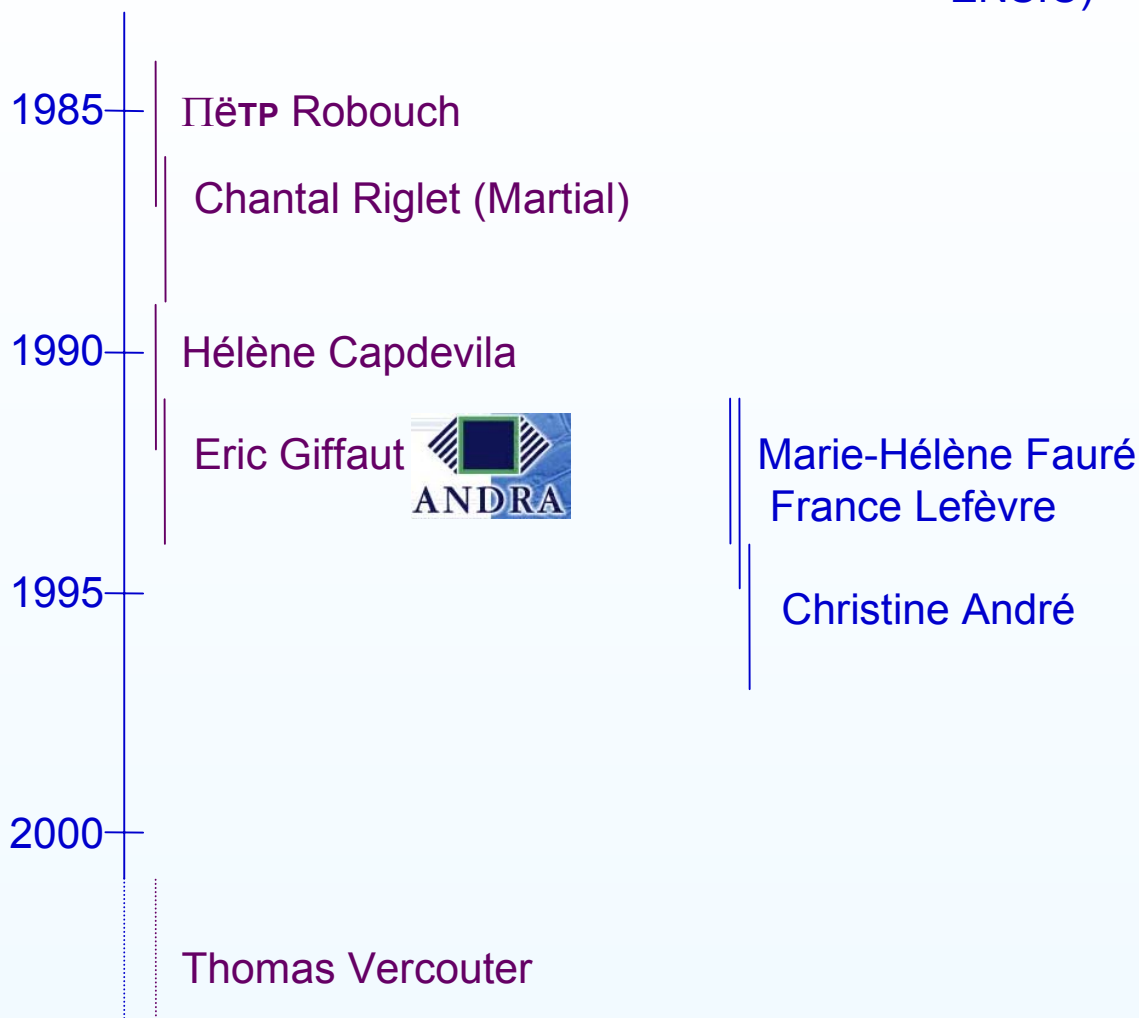
Activités au CEA (Fontenay-aux-Roses), Grenoble, Saclay, Cadarache :

chimie, (actinides, produits de fission, colloïdes)
sorption,
corrosion

transport
(solutions analytiques,
IMPACT,
CASTEM,
modèles opérationnels)

thermo-hydro-mécanique

intégration



Consistency of publish data

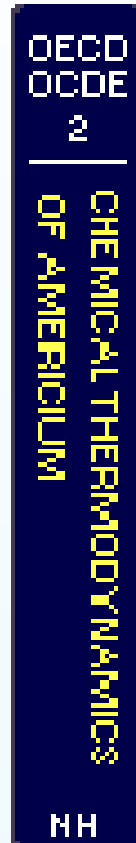
NEA-TDB review Edited by OECD Nuclear Energy Agency, Data Bank, Elsevier (2001)

CHEMICAL THERMODYNAMICS OF NEPTUNIUM & PLUTONIUM

Robert LEMIRE (Chairman)

Jean FUGER, Heino NITSCHKE, Paul POTTER,
Malcolm RAND, Jan RYDBERG, Kastriot SPAHIU,
James SULLIVAN, William J. ULLMAN,
Pierre VITORGE, Hans WANNER

Validated data



pH calibration

Pierre Vitorge, Ingmar Grenthe,
Piotr Robouch, Chantal Riglet (Martial),
Hélène Capdevila, Eric Giffaut

Prendre en compte **potentiel de jonction (E_j)** et **coefficients d'activité (γ)** :

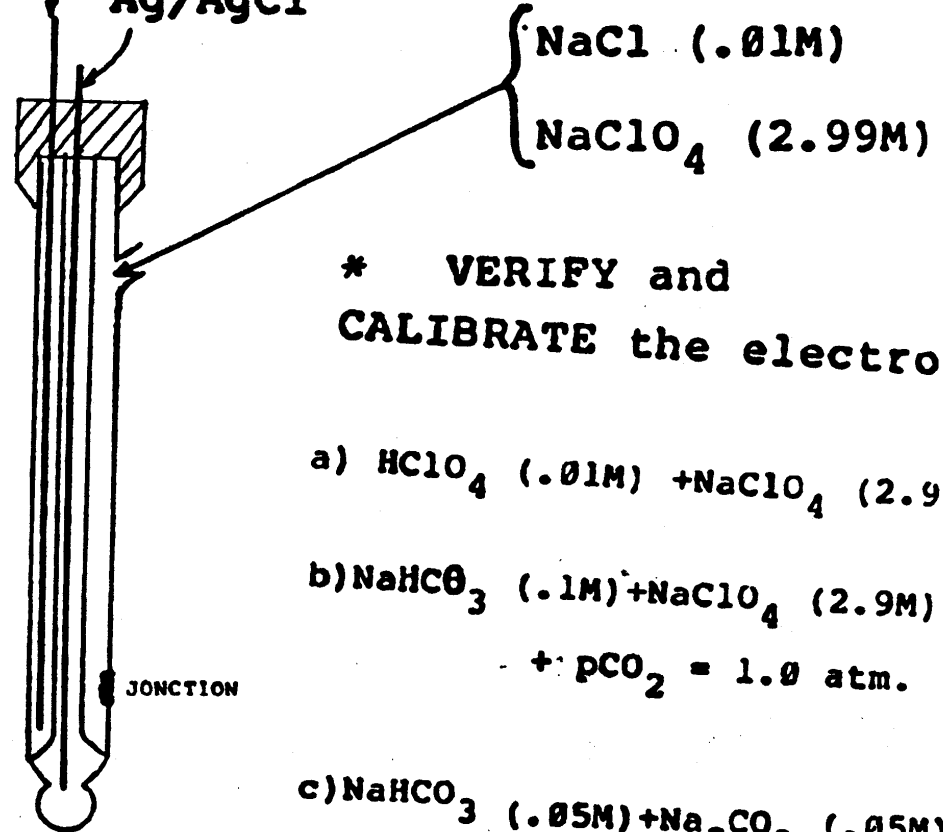
même E_j pour étalonnage et mesure (si possible $E_j = 0$),

γ : les mesurer, les calculer ou les maintenir constants grâce à une force ionique (I) élevée .

Quand $I = \text{constante}$ la loi d'action de masse est "vérifiée pour les concentrations" (système idéal); mais il faut **extrapoler à $I = 0$** (état standard) pour **comparer les données publiées** (on utilise les γ).

pH measurement

REFERENCE
ELECTRODE
Ag/AgCl



* **VERIFY and CALIBRATE** the electrode

a) HClO_4 (.01M) + NaClO_4 (2.99M)

b) NaHCO_3 (.1M) + NaClO_4 (2.9M)
+ $p\text{CO}_2 = 1.0$ atm.

c) NaHCO_3 (.05M) + Na_2CO_3 (.05M)
+ NaClO_4 (2.85M)

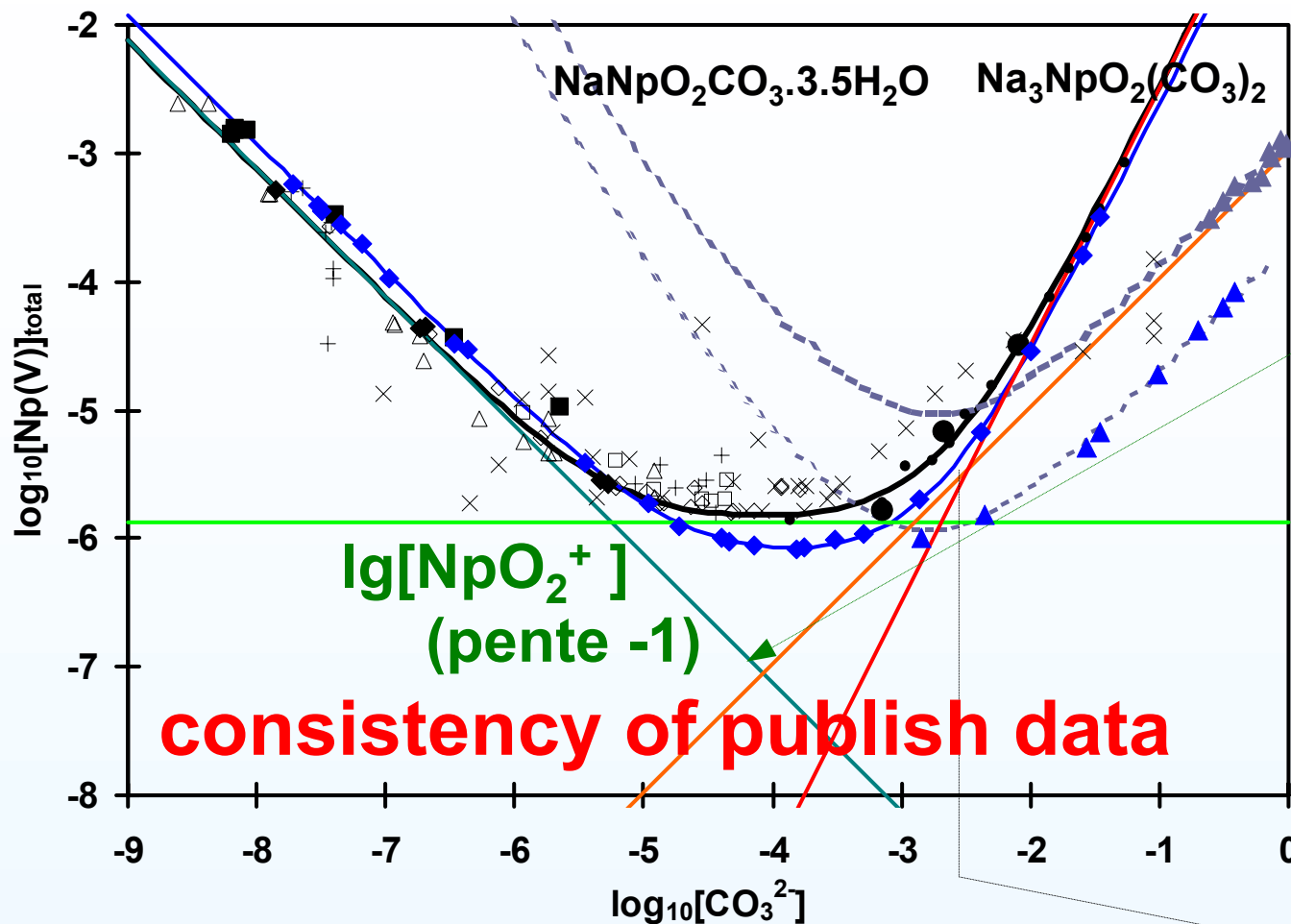
GLASS
ELECTRODE



Solubilité de Np(V) en solution 3M Na⁺ (CO₃²⁻, HCO₃⁻, ClO₄⁻)

Pierre Vitorge, Christian Dautel (1984, 1985, 1986, 1991, 1998, 2000)

Simakin (1977), Kim *et al.* (1991, 1994, 1995)



Détermination de speciation par mesure de solubilité.

La loi d'action de masse

"s'applique en concentration"

à tout système idéal : dans le solide (activité constante) et en solution (coef. d'activité constants)



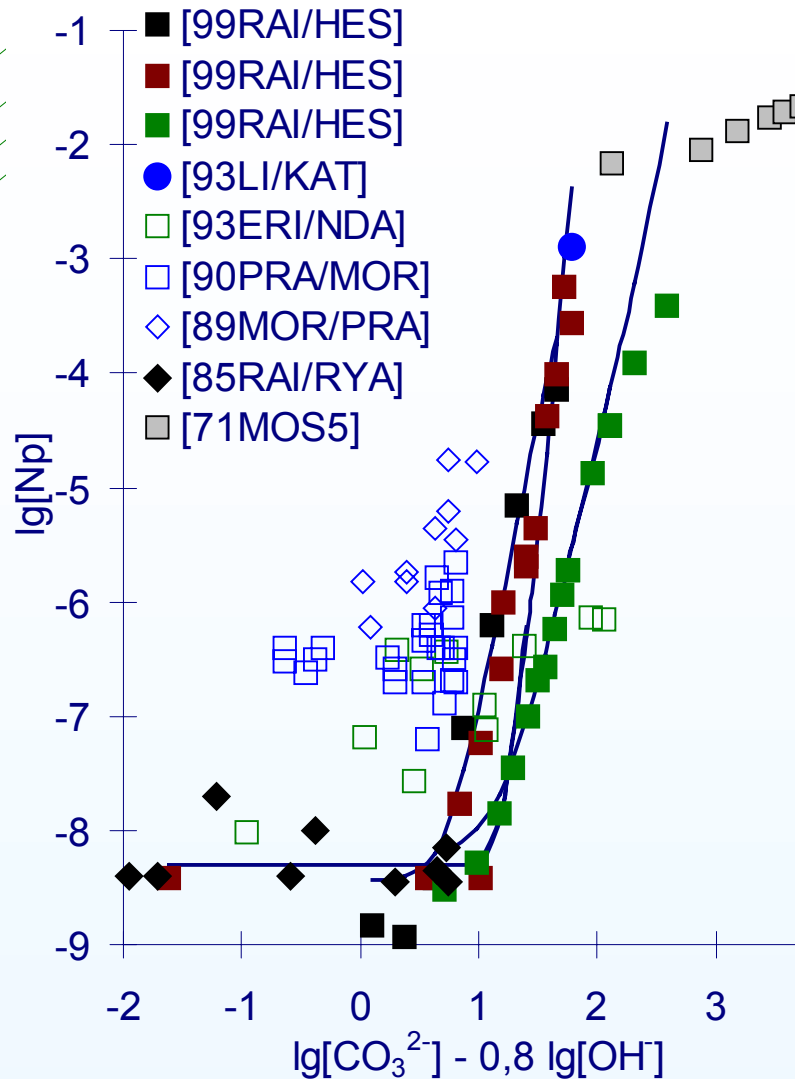
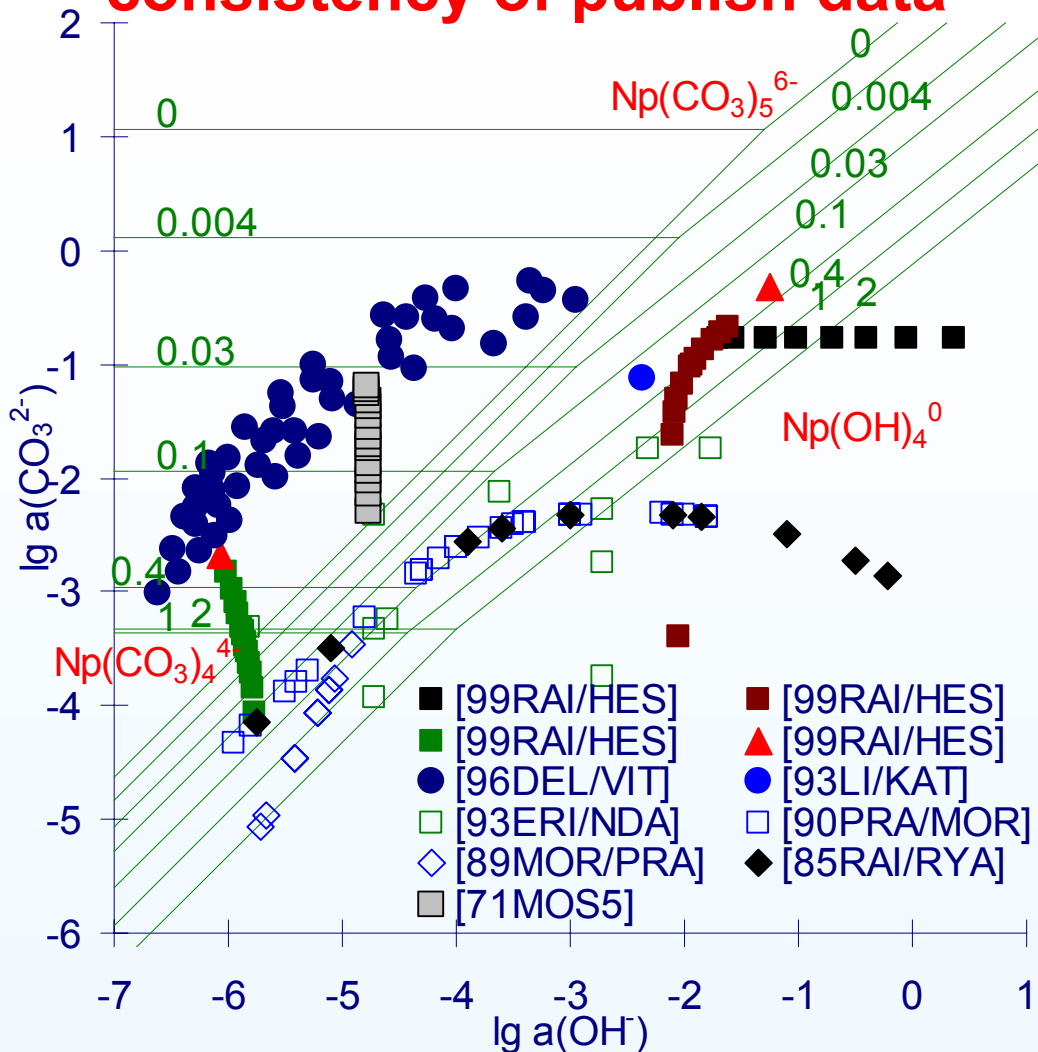
Chaque solide évolue. Lente transformation (à l'équilibre pour $\log_{10}[\text{CO}_3^{2-}] = -2.4$) :

$$\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O} + 2\text{Na}^+ \rightarrow \text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot m\text{H}_2\text{O} + 2\text{CO}_3^{2-} + (3.5-m)\text{H}_2\text{O}$$

Bibliographie critique sur Np(IV) en milieux $\text{HCO}_3^-/\text{CO}_3^{2-}$

Pierre Vitorge

consistency of publish data



sensitivity analysis



Speciation de Pu(IV) par spectrophotométrie d'absorption

Hélène Capdevila, Pierre Vitorge (1994)

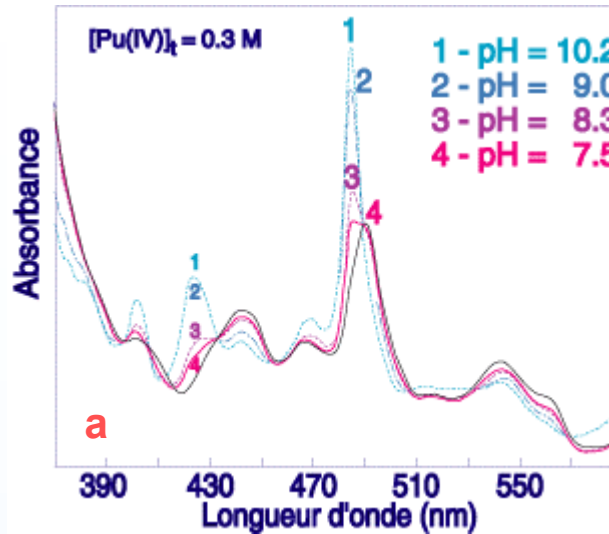
Des solutions de Pu(IV) en milieu Na_2CO_3 concentré sont dosées par $\text{CO}_2(\text{gaz})$.

a spectres

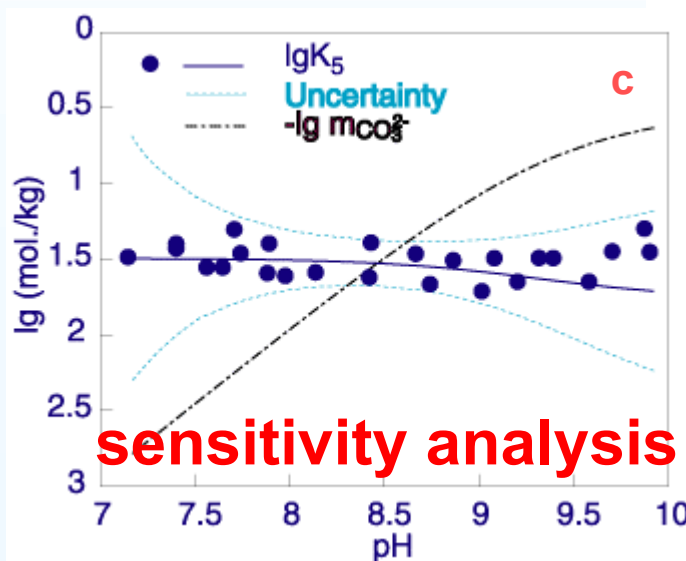
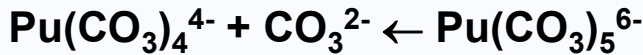
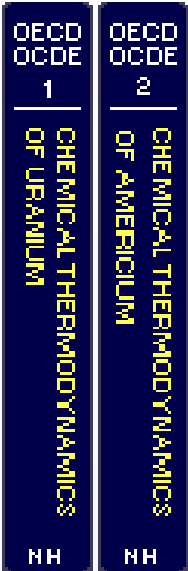
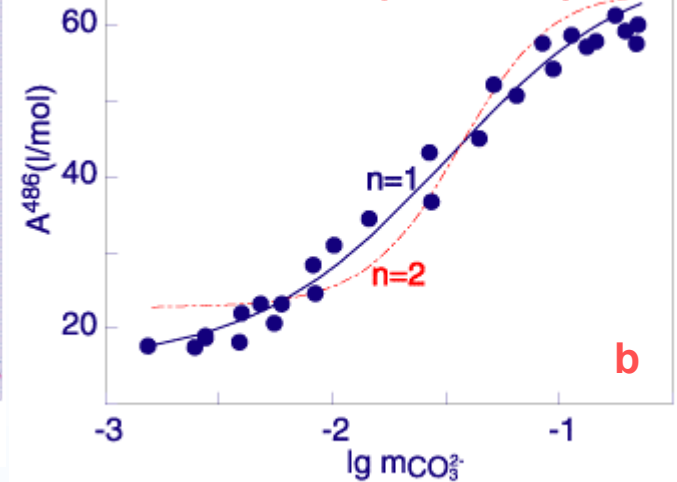
b échange de 1 CO_3^{2-}

c pas d'échange d' OH^-

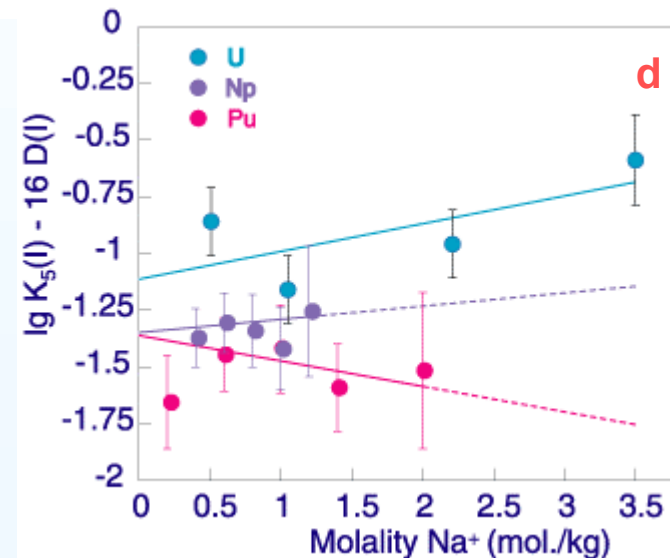
d extrapolation à $I=0$



sensitivity analysis

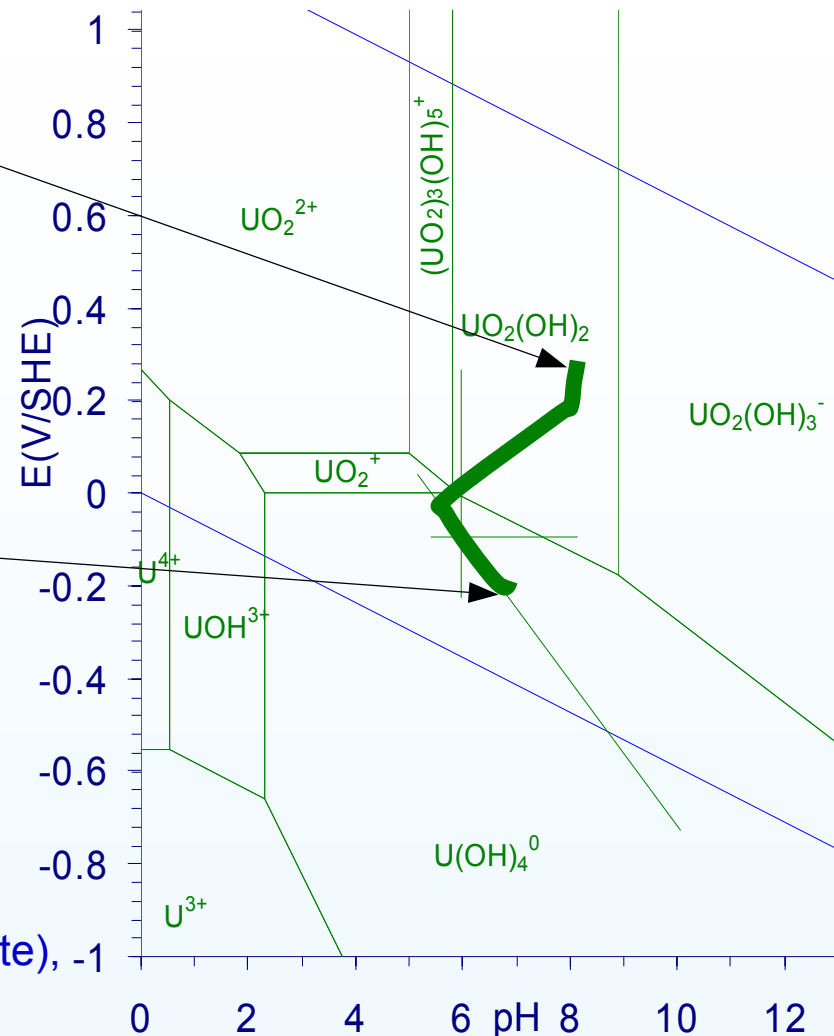
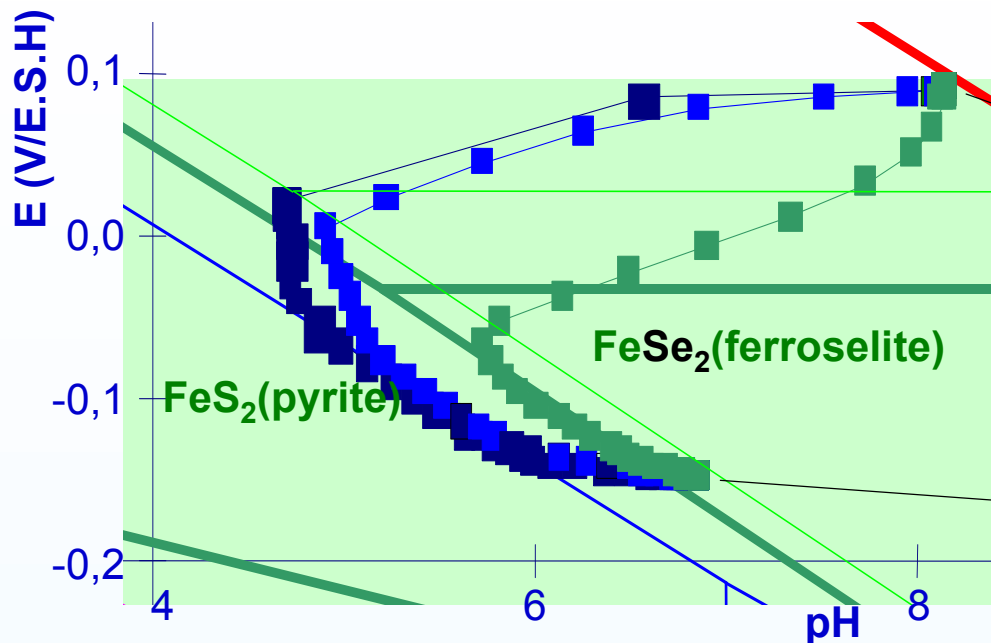


sensitivity analysis



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 :

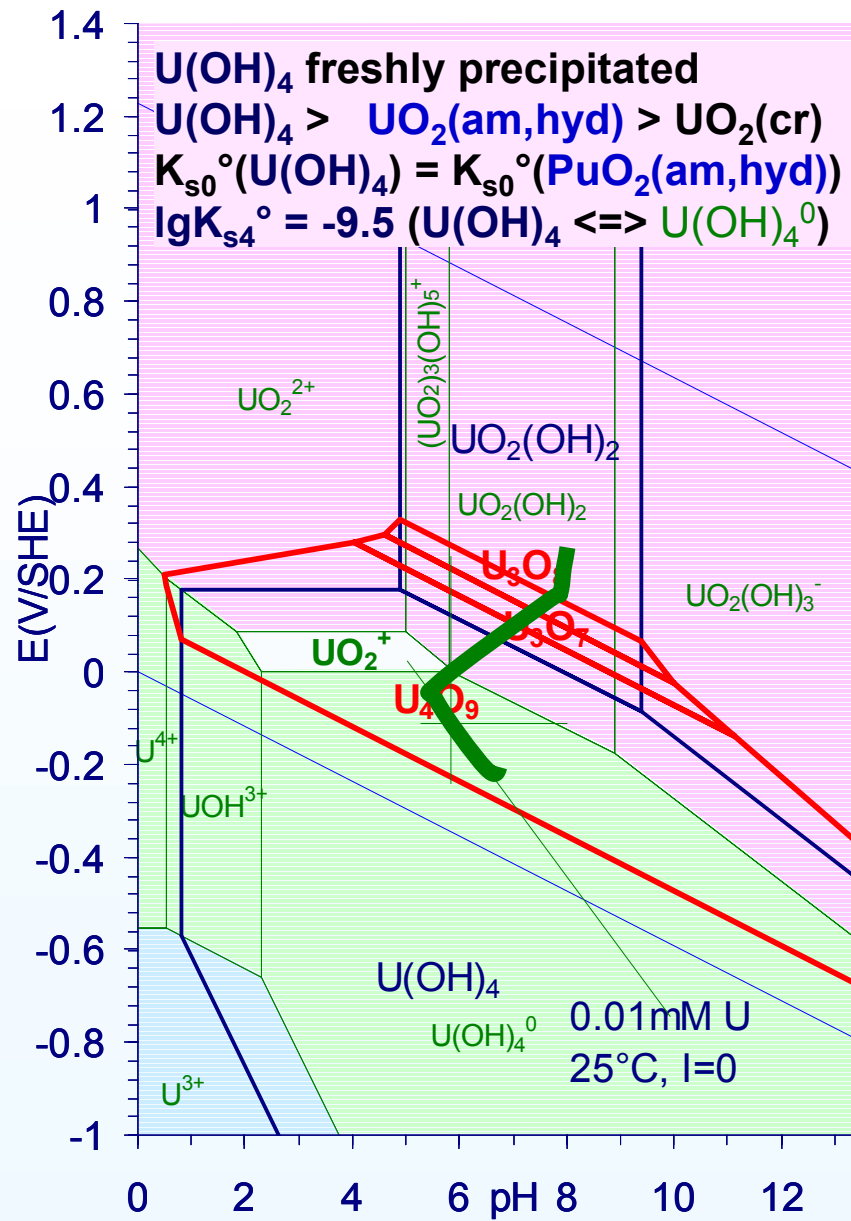
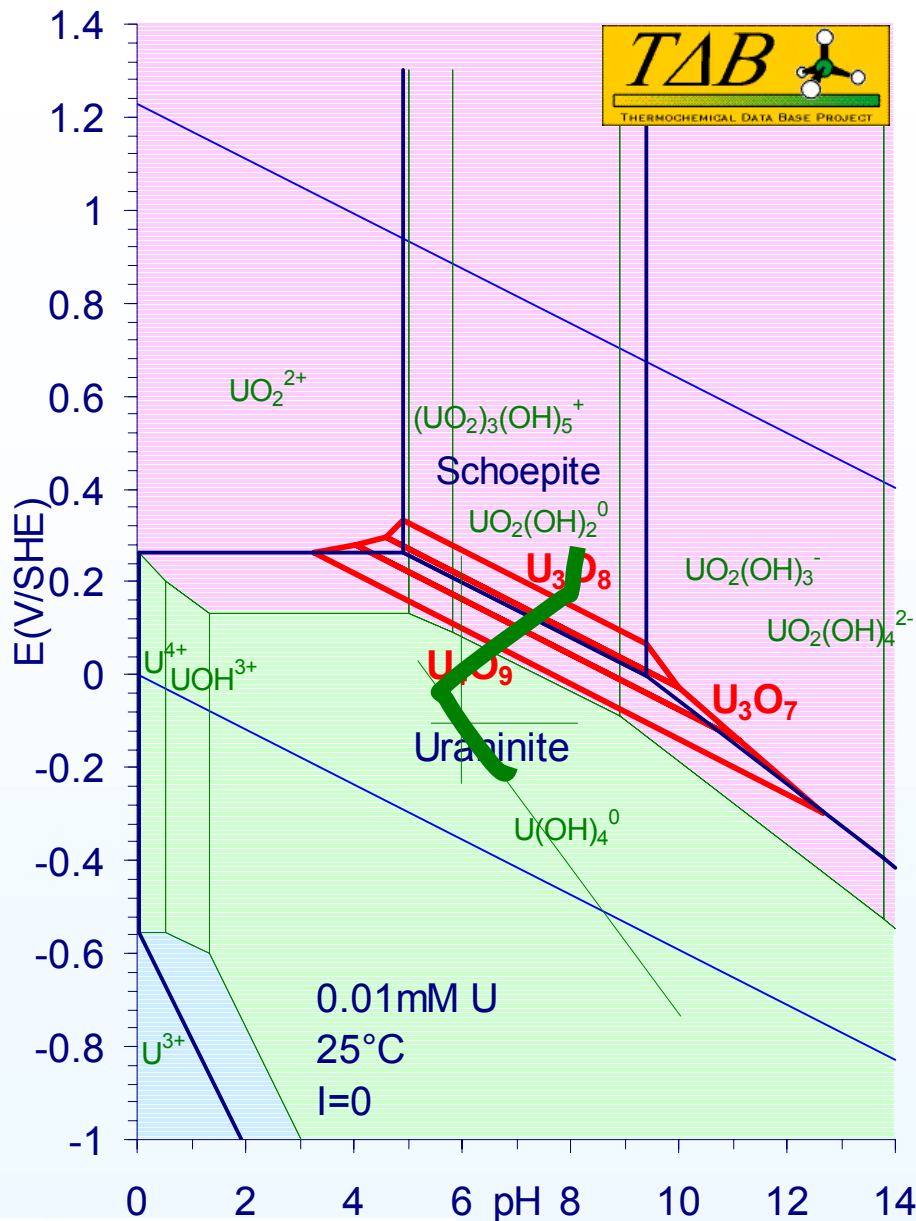
Se(s), ferroselite, **FeOOH(goethite)** et Fe₂O₃(hematite), -

reducing side :

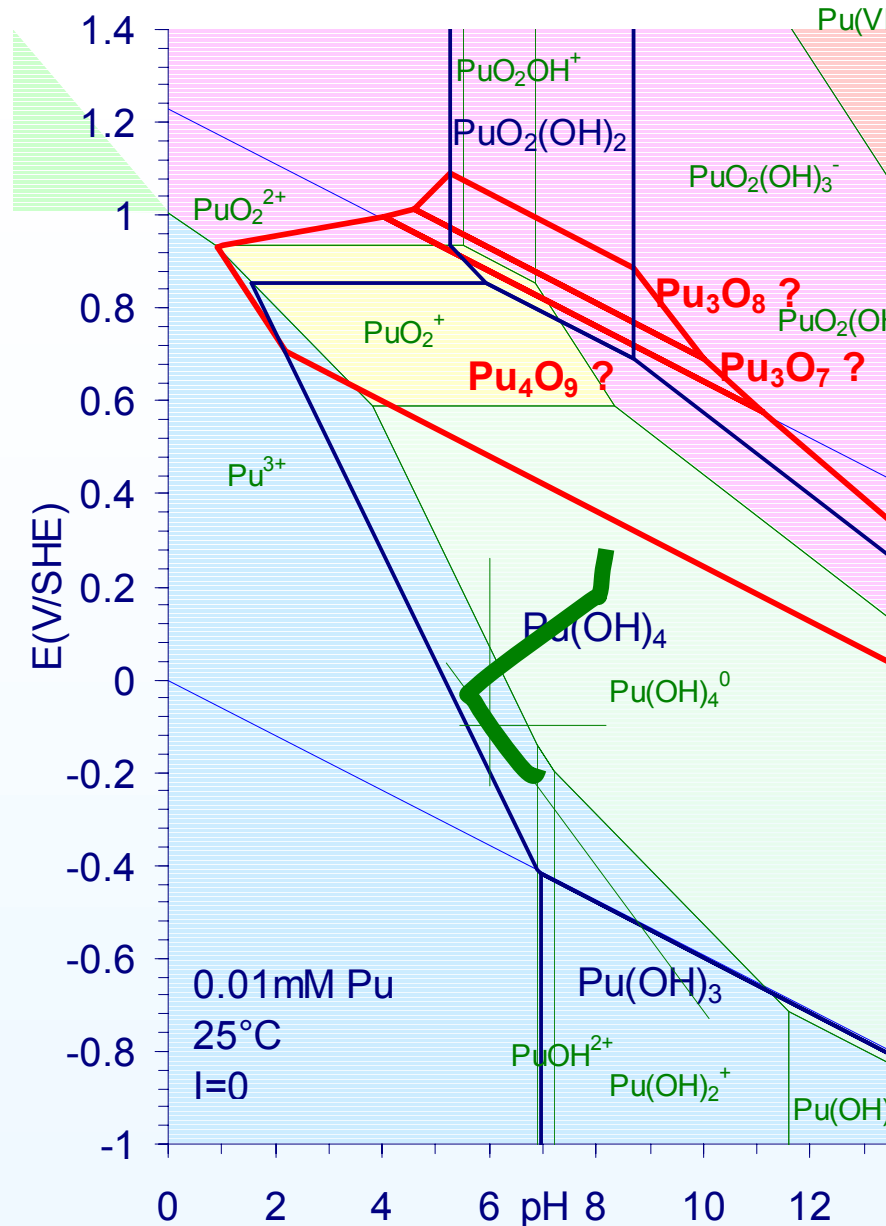
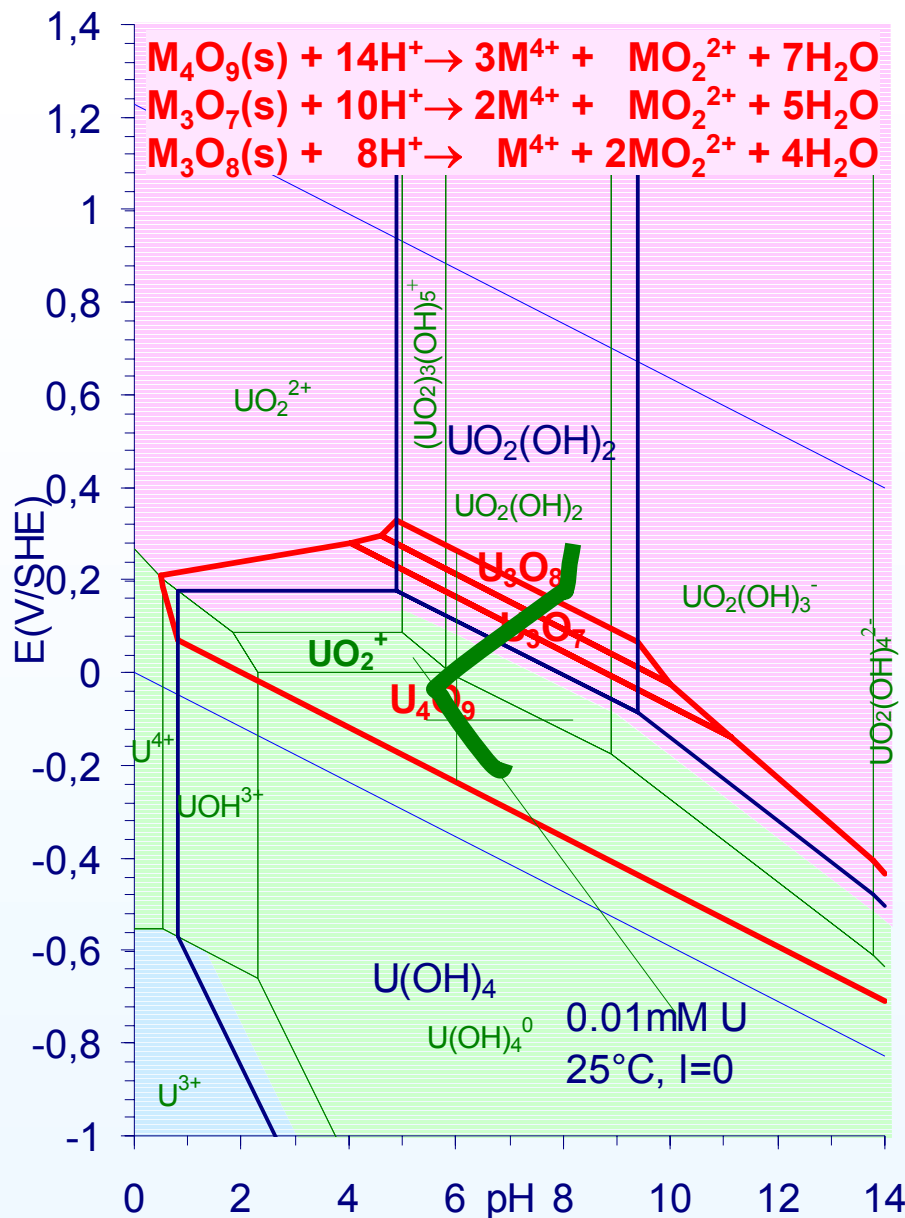
Se(s), ferroselite, pyrite.

Simulations with the IMPACT code

Pourbaix diagrams of Uranium: comparison of thermodynamic data

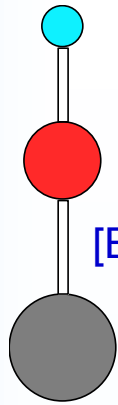


Using the stability of UO_{2+x} for estimating the stability of PuO_{2+x} : TDB data

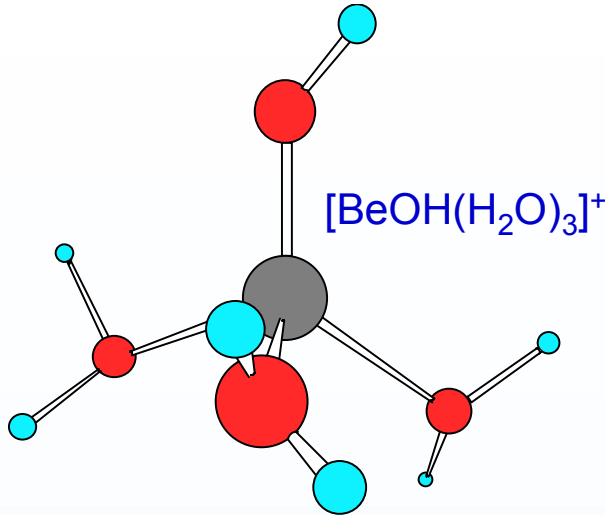


Calcul ab initio de $[M_p(OH)_q(H_2O)_n]^{z_p-q}$

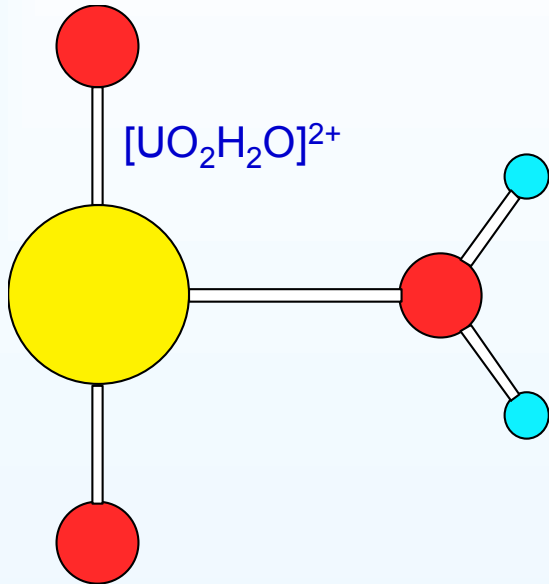
Michel Masella, Pierre Vitorge (2000)



$[BeOH]^+$

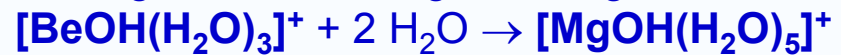


$[BeOH(H_2O)_3]^+$



$[UO_2H_2O]^{2+}$

Résultats : géométrie, charges, énergies de réactions



$$H_2O(g) \rightarrow H_2O(l) \quad \Delta_r H(25^\circ C) = -44,00_4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r G(25^\circ C) = -8,55_8 \text{ kJ}\cdot\text{mol}^{-1}$$

Niveaux de calcul pour Li^+ , Na^+ , Be^{2+} , Mg^{2+} :

HF, B3LYP et MP2 / 6-31+G(d,p) et 6-311+G(2df,2p)

Collaborations :

J.Tortajada (UMR 8587),

J.-P. Dognon et Ph.Millié (CEA Saclay DSM/DRECAM/SPAM)

Pour UO_2^{2+} : C.Marsden (IRSAMC Toulouse)