



From Ions to Colloids Without Gel Transition

SPECIATION OF IONS: REDOX AND VALENCY

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IUPAC definitions



• **Speciation analysis** is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample.

• The **speciation** of an element is the distribution of an element amongst defined chemical species in a system.

• The **chemical species** are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.

• In case that it is not possible to determine the concentration of the different individual chemical species that sum up the total concentration of an element in a given matrix, that means it is impossible to determine the speciation, it is a useful practice to do **fractionation** instead.

• Fractionation is the process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties.

D.M. Templeton, F. Ariese, R. Cornelis, L.-G. Danielsson, H. Muntau, H.P. van Leeuwen, R. Lobinski, IUPAC Guidelines for Terms Related to Speciation of Trace Elements, Pure Appl. Chem., 72/8 (2000) 1453-1470.



Speciation information

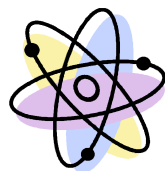


- isotopic composition
- Electronic and oxidation states
- Inorganic compounds and complexes
- Organic complexes
- Organometallic complexes
- Macromolecular compounds and complexes



Outline : actinide chemistry in aqueous solution

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● General considerations

- Electronic configurations
- Oxidation states
- Hydration
- Interactions (HSAB principle)

● Redox properties

- Redox equilibria
- SHE definition
- Pourbaix diagrams



● Hydrolysis and complexation

- Thermodynamic constants
- Chemical analogies
- Inner- and outer-sphere complexes



● Medium effects

- Activity coefficient models
- Application of the SIT formula

● Temperature dependence

- Enthalpy, entropy and heat capacity of reactions
- Approximations



● Speciation calculation

- Sillen diagrams
- Solubility / colloid formation



● References





General considerations



The ground electronic configurations of Ln and An



La	$[\text{Xe}]5d^16s^2$	Ac	$[\text{Rn}]6d^17s^2$
Ce	$[\text{Xe}]4f^15d^16s^2$	Th	$[\text{Rn}]6d^27s^2$
Pr	$[\text{Xe}]4f^36s^2$	Pa	$[\text{Rn}]5f^26d^17s^2$
Nd	$[\text{Xe}]4f^46s^2$	U	$[\text{Rn}]5f^36d^17s^2$
Pm	$[\text{Xe}]4f^56s^2$	Np	$[\text{Rn}]5f^46d^17s^2$
Sm	$[\text{Xe}]4f^66s^2$	Pu	$[\text{Rn}]5f^67s^2$
Eu	$[\text{Xe}]4f^76s^2$	Am	$[\text{Rn}]5f^77s^2$
Gd	$[\text{Xe}]4f^75d^16s^2$	Cm	$[\text{Rn}]5f^76d^17s^2$
Tb	$[\text{Xe}]4f^96s^2$	Bk	$[\text{Rn}]5f^97s^2$
Dy	$[\text{Xe}]4f^{10}6s^2$	Cf	$[\text{Rn}]5f^{10}7s^2$
Ho	$[\text{Xe}]4f^{11}6s^2$	Es	$[\text{Rn}]5f^{11}7s^2$
Er	$[\text{Xe}]4f^{12}6s^2$	Fm	$[\text{Rn}]5f^{12}7s^2$
Tm	$[\text{Xe}]4f^{13}6s^2$	Md	$[\text{Rn}]5f^{13}7s^2$
Yb	$[\text{Xe}]4f^{14}6s^2$	No	$[\text{Rn}]5f^{14}7s^2$
Lu	$[\text{Xe}]4f^{14}5d^16s^2$	Lr	$[\text{Rn}]5f^{14}6d^17s^2$



Possible oxidation states

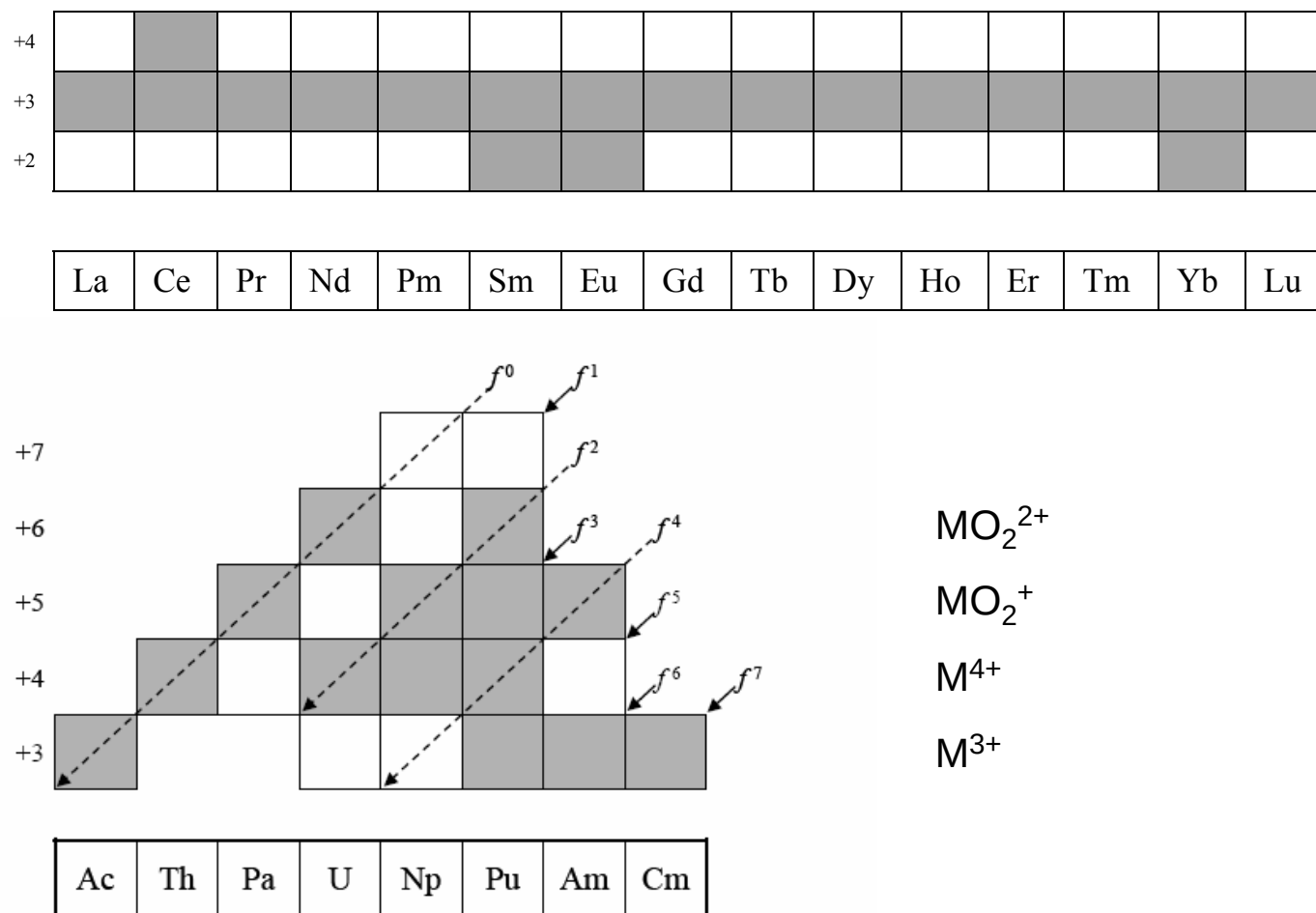
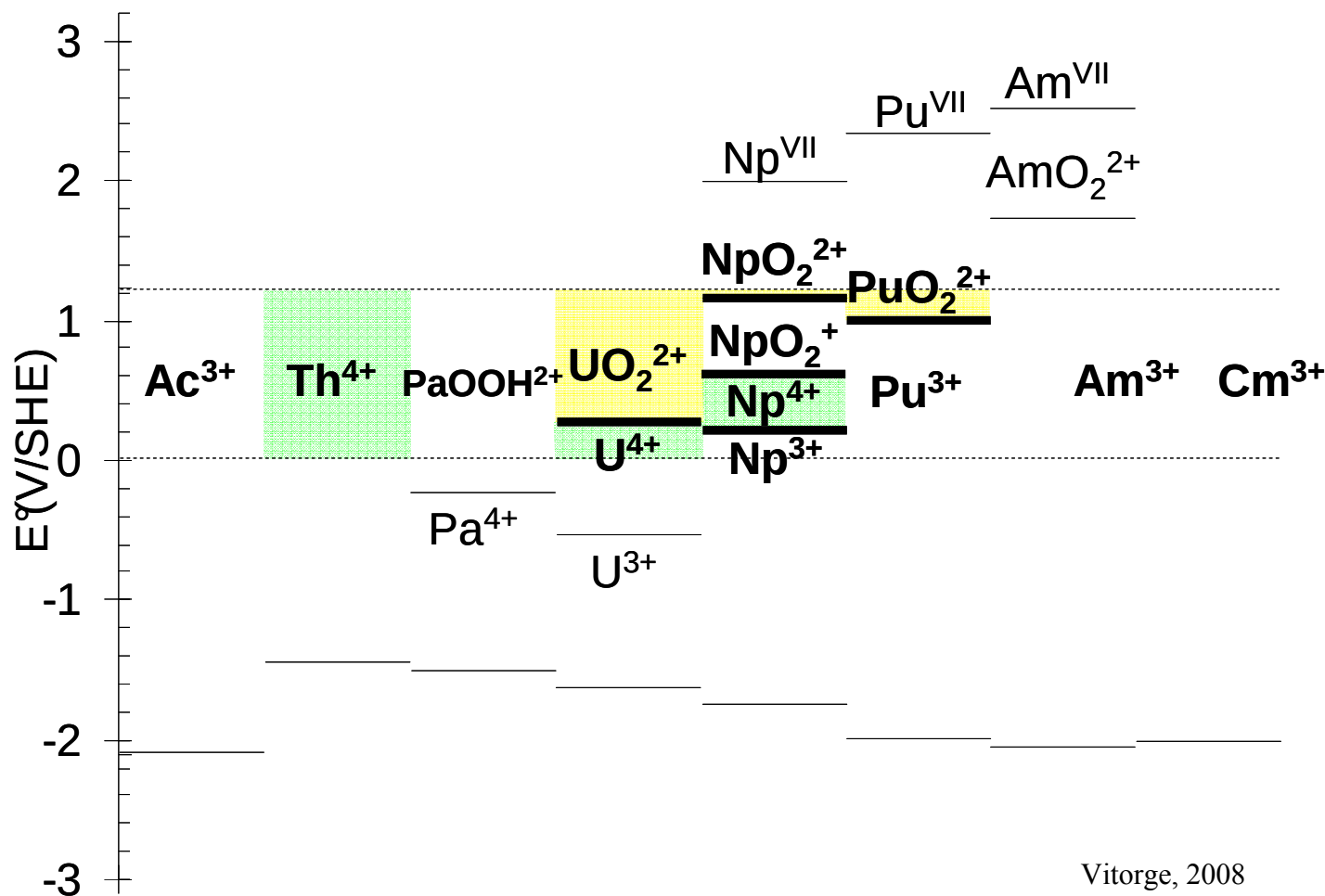


Fig. 2.1 Oxidation states of the light actinide elements and their electron configuration (f electrons).

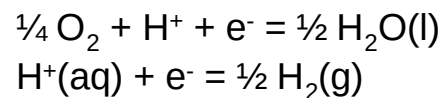


Stable oxidation states of actinides in aqueous solution



Vitorge, 2008

----- Water limits



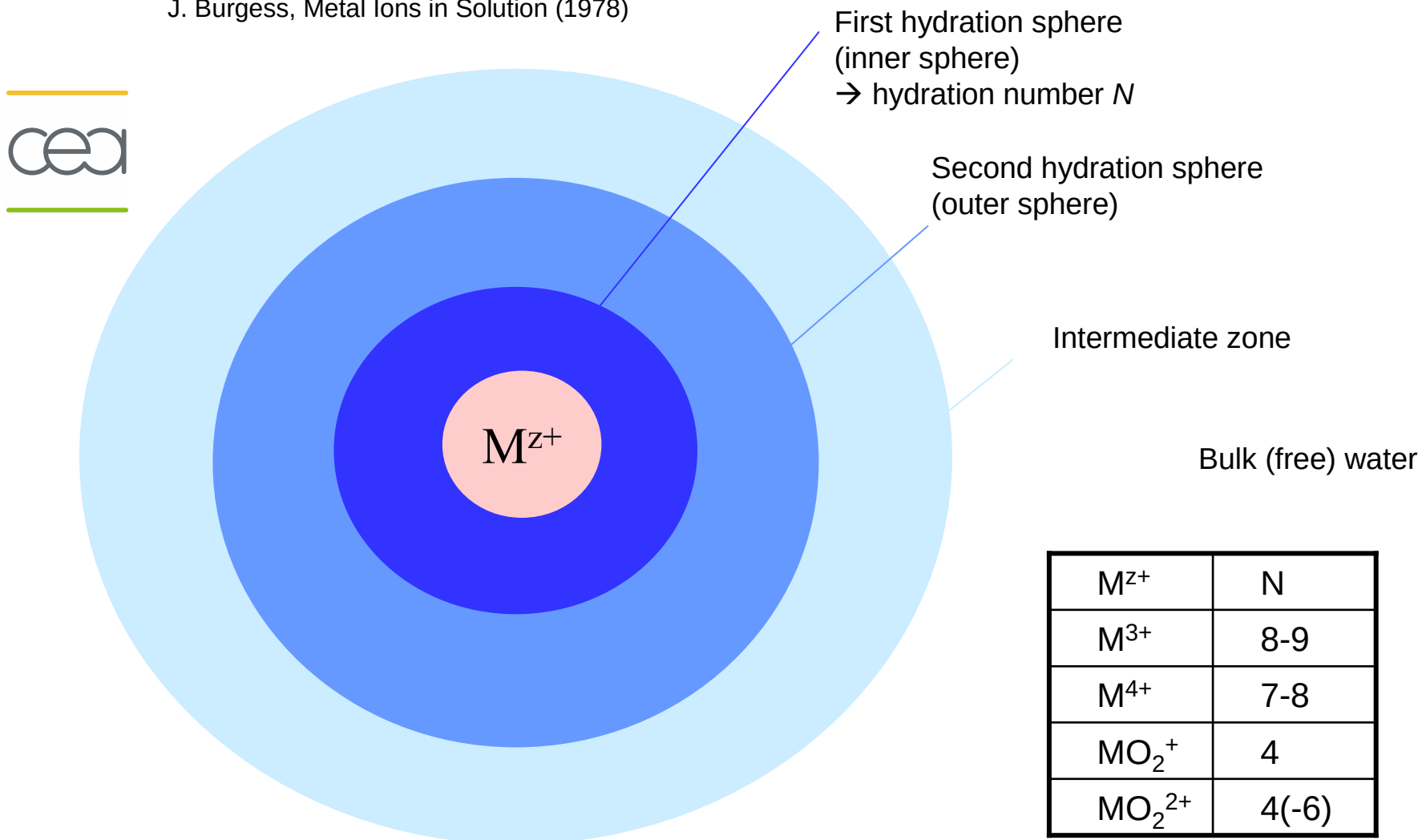
$$E^\circ = 1.23 \text{ V/SHE}$$

$$E^\circ = 0 \text{ V/SHE}$$



Hydration of An and Ln ions: sphere model

J. Burgess, Metal Ions in Solution (1978)

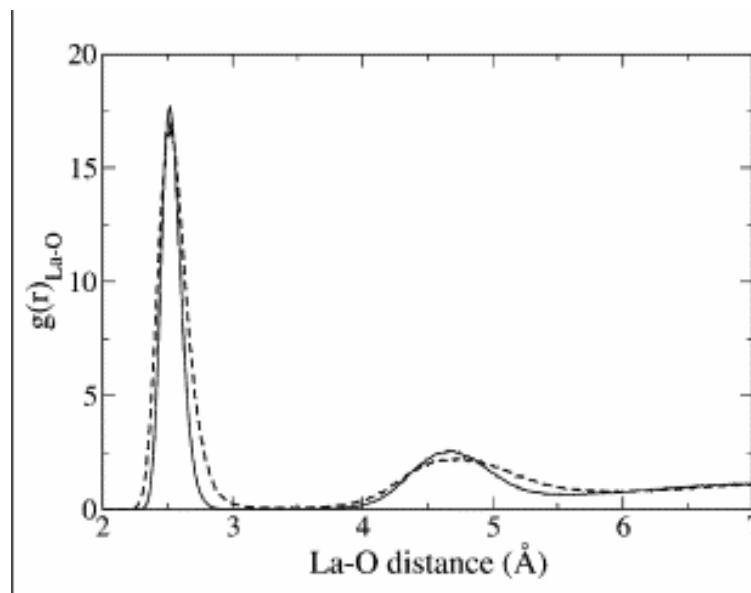
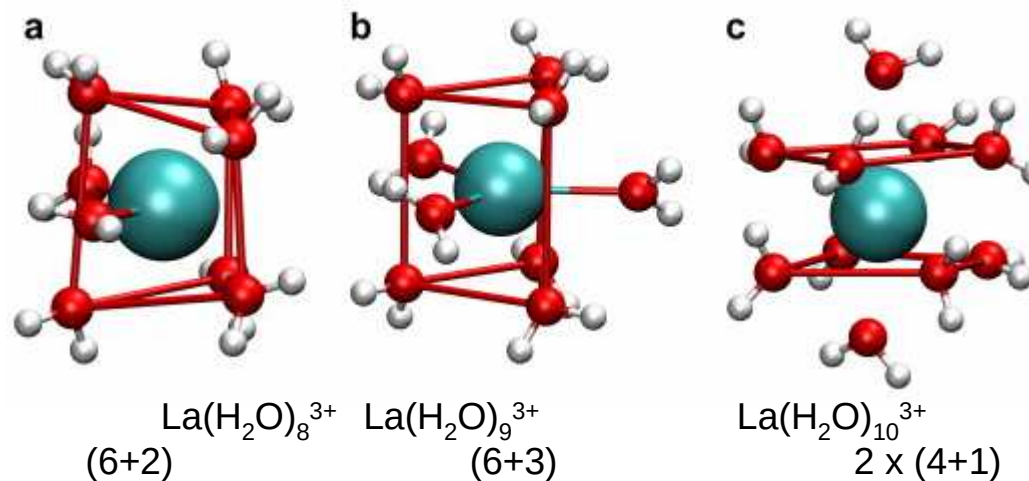


Choppin, Marine Chem., 99, 83-92, 2006



Structures of aquo trications

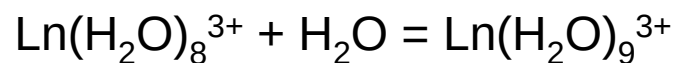
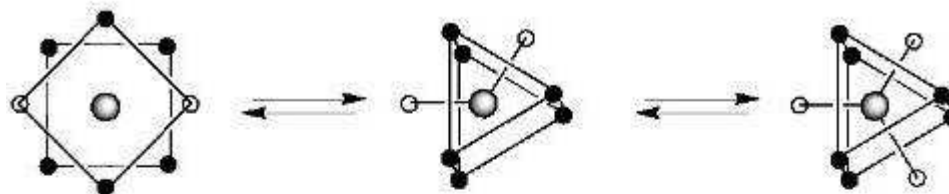
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Duvail, Spezia, Cartailier, Vitorge,
Chem. Phys. Letters, 2008



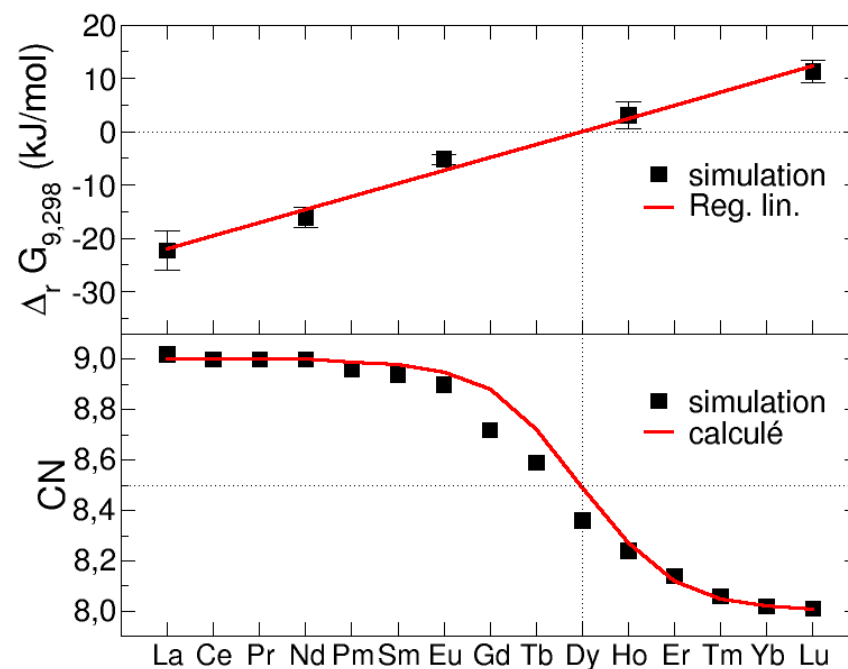
Gibbs energy of water exchange, hydration numbers



$$\Delta_r G_{j,T} = - R T \ln K_{j,T}$$

$$K_{8 \rightarrow 9} = \frac{[\text{Ln}(\text{H}_2\text{O})_9^{3+}]}{[\text{Ln}(\text{H}_2\text{O})_8^{3+}]} = \frac{n_9}{n_8}$$

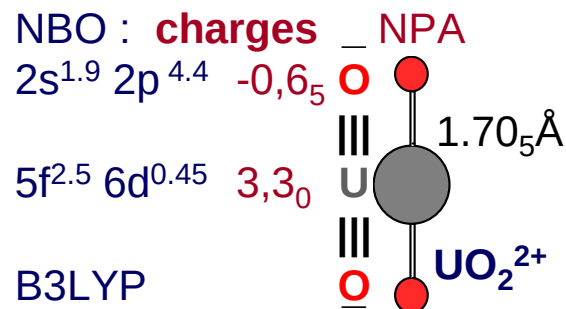
$$\text{CN} = 9 - \frac{1}{1 + K_{8 \rightarrow 9}}$$



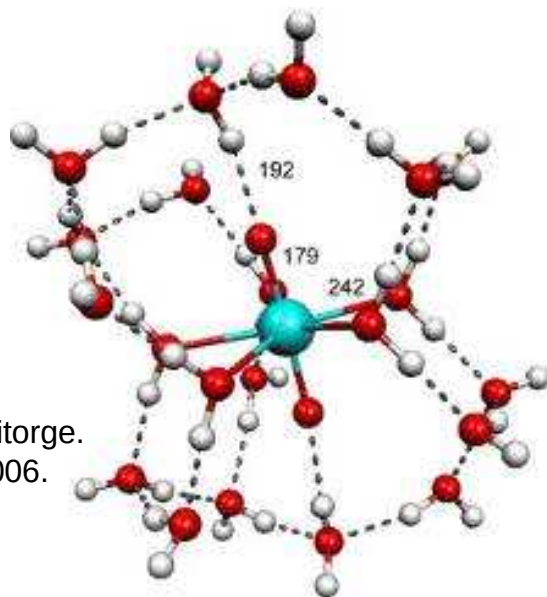
Molecular dynamic [Duvail, 2008]



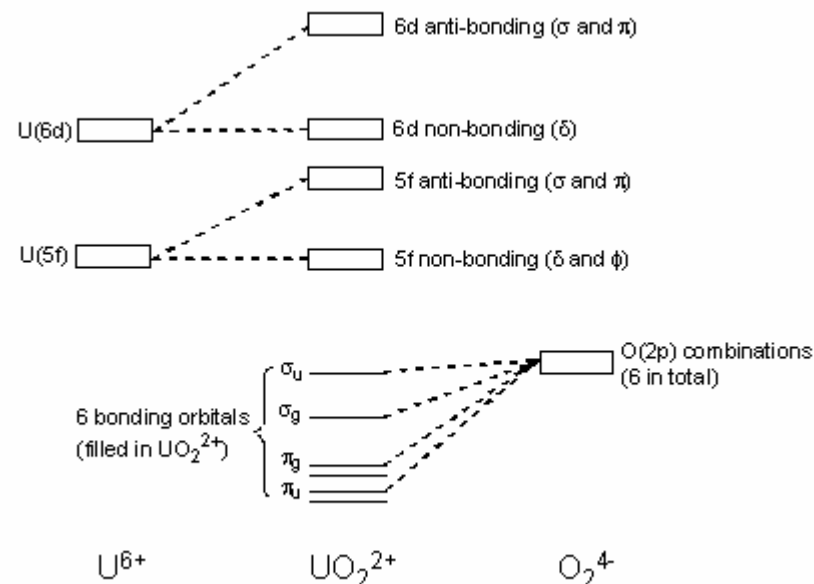
Structure of actinyl ions



DFT calculations by P.Vitorge and C.Marsden



Siboulet, Marsden, Vitorge.
Chemical Physics, 2006.



Kaltsoyannis

www.chem.helsinki.fi/~sundholm/winterschool/lecture_notes_2007/

$\text{M}^{\text{VI}}\text{O}_2^{2+}$ and $\text{M}^{\text{V}}\text{O}_2^{+}$ are stable
for $\text{M} = \text{U}, \text{Np}, \text{Pu}, \text{Am}$, but not Pa



Solvation in non-aqueous solutions



● Solvent properties

- Dielectric constant
- Donor / Acceptor numbers

● Investigations of the first solvation sphere

- Preferential solvation
DMSO, DMF > water > alcohols > acetone, acetonitrile, dioxanne
- Mixtures water/methanol, water/DMSO, water/DMF



Hard-Soft Acids and Bases (HSAB)

- The HSAB principle (Pearson) to predict metal-ligand interactions



	Lewis Acid	Lewis Base
Hard	Difficult to oxidize Weak polarizability Small size High oxidation state High charge density of acceptor sites <u>Ex:</u> Ln/An cations, Ca^{2+} , Zn^{2+} , Ba^{2+} ,...	Difficult to reduce Weak polarizability Small size High pKa value High charge density of donor sites <u>Ex:</u> F^- , oxygen functions,...
Soft	Easy to oxidize Strong polarizability Big size Small charge density of acceptor sites	Easy to reduce Strong polarizability Big size Small charge density of donor sites <u>Ex:</u> nitrogen functions,...

- *The hard acids more strongly interact with hard bases,
the soft acids with soft bases.*
- Hard-hard interactions → mostly ionic
Soft-soft interactions → mostly covalent



● Ln and An cations are considered hard Lewis acids

- Many coordination numbers and symmetries
- Steric and electrostatic effects
 - ✚ Similar charge and size → chemical analogues
- Small influence of valence orbitals
- But high positive charges can promote charge transfer (= covalent binding)
Ex: UF_6 , UO_2^{2+}

● An^{3+} is slightly softer than Ln^{3+} because the 5f electrons are more delocalized than 4f electrons (shielding effect)

- Selective separation $\text{Ln}^{3+}/\text{An}^{3+}$ using soft ligands
 - ✚ No more chemical analogues!
- Effect of the electronic structure
 - ✚ Pa(V) would not be stable in the form PaO_2^+ , but rather in protonated forms, PaO(OH)^{2+} or Pa(OH)_4^+ [Siboulet, New J. Chem., 2008]

Last lines of the periodic table

5 O	³⁷ Rb	³⁸ Sr	³⁹ Y	⁴⁰ Zr	⁴¹ Nb	⁴² Mo	⁴³ Tc	⁴⁴ Ru	⁴⁵ Rh	⁴⁶ Pd	⁴⁷ Ag	⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te	⁵³ I	⁵⁴ Xe
6 P	⁵⁵ Cs	⁵⁶ Ba	⁵⁷ La	⁷² Hf	⁷³ Ta	⁷⁴ W	⁷⁵ Re	⁷⁶ Os	⁷⁷ Ir	⁷⁸ Pt	⁷⁹ Au	⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po	⁸⁵ At	⁸⁶ Rn
7 Q	⁸⁷ Fr	⁸⁸ Ra	⁸⁹ Ac	¹⁰⁴ Rf	¹⁰⁵ Db	¹⁰⁶ Sg	¹⁰⁷ Bh	¹⁰⁸ Hs	¹⁰⁹ Mt	¹¹⁰ Ds	¹¹¹ Rg	¹¹² ?		¹¹⁴ ?		¹¹⁶ ?		

Highest oxidation number for each element = number of its group

In each d or f series

slight decrease of the ionic radii

hardness slightly increases

From one line (of d or f series) to the next line

the valence electrons are better shielded (from the nucleus) by the core electrons

softness slightly increases

higher oxidation states are stable.

Relativistic effects

contraction of the first s (and p) orbital : increasing their shielding effect on f (and d) ones

spin orbit coupling



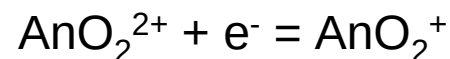
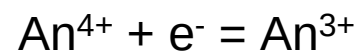


Redox properties



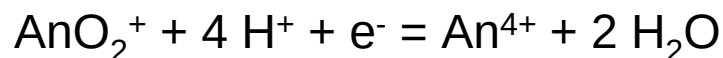
Redox equilibria for actinides

● An(IV)/An(III) and An(VI)/An(IV)



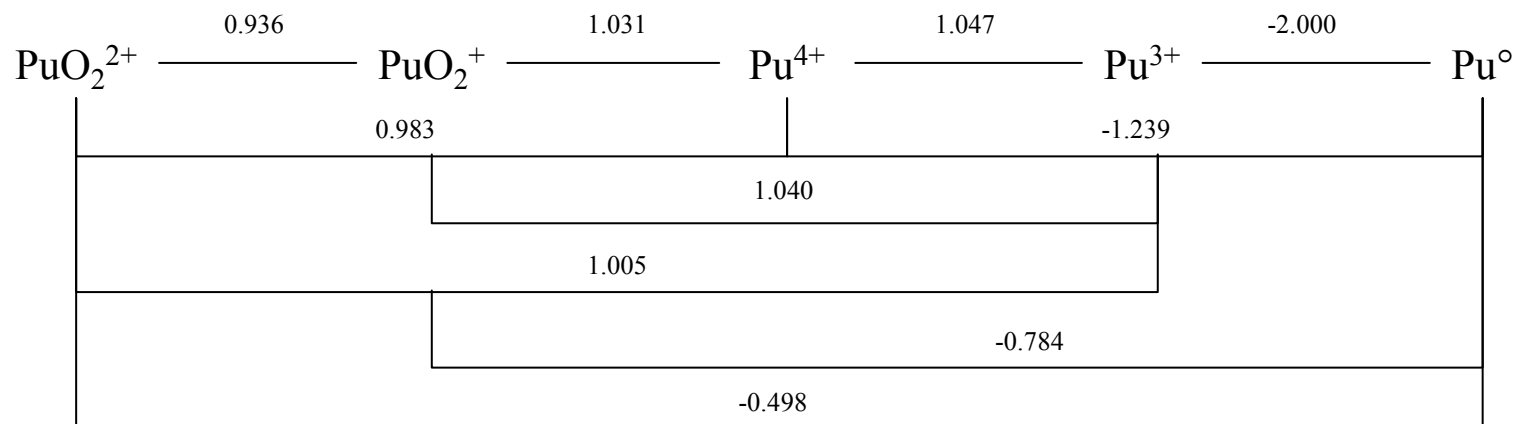
- pH independent
- Reversible (fast) reactions

● An(V)/An(IV)



- pH dependent (decomposition of the actinyl ion)
- Irreversible (slow) reaction

● Example: standard potentials (I=0, 25°C) for plutonium (in V/SHE)



Lemire et al, NEA-TDB, 2001.



Redox definitions

• Standard electrode potential

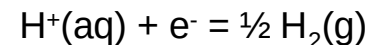


$$E^\circ = - \Delta_r G^\circ / (n F) \\ = (RT/nF) \ln K^\circ \quad \text{where} \quad K^\circ = a_{\text{red}} / (a_{\text{ox}} a_{e^-})$$

• Redox potential

$$E = E^\circ_{\text{ox/red}} - (RT/nF) \sum \nu_i \ln a_i \quad \text{where } \nu_i \text{ and } a_i \text{ are the stoichiometric coefficient and the activity of the species } i \text{ in the reduction reaction}$$

• Standard Hydrogen Electrode (SHE)



$$E_h = E_h^\circ_{\text{H}^+/\text{H}_2(\text{g})} + (RT/F) \ln (a_{\text{H}^+} / \sqrt{f_{\text{H}_2}})$$

SHE convention

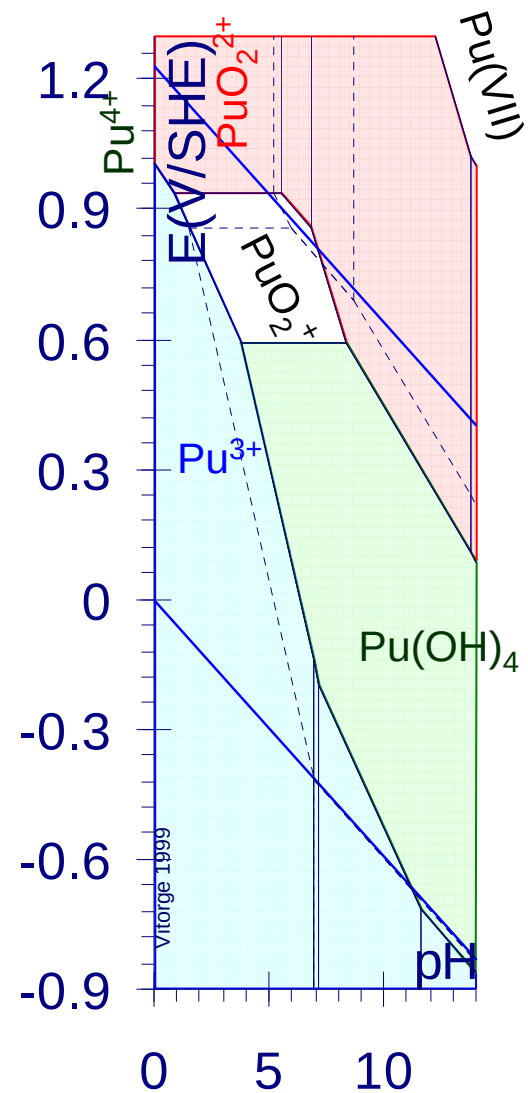
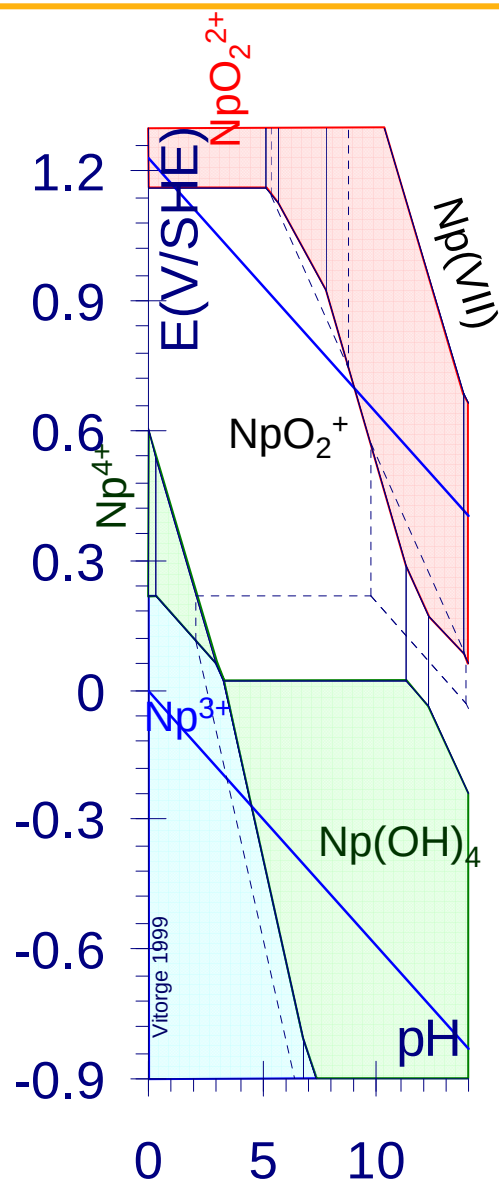
- $E^\circ_{\text{H}^+/\text{H}_2(\text{g})} = 0$
- $f_{\text{H}_2} = 1$ (unit fugacity, ideal gas at 0.1 MPa)
- $a_{\text{H}^+} = 1$ (unit activity, ideal solution at 1 mol/kg_{solvant})
- E_h (and equivalently a_{e^-}) is relative to the SHE

• Hence, $E_h = - (RT/F) \ln a_{e^-}$

- Electron activity : $pe = -\log_{10} a_{e^-}$ (analogy to $pH = -\log_{10} a_{\text{H}^+}$)
- a_{e^-} is not the concentration of the solvated electron [$e^-(\text{aq})$]
- $RT \ln(10)/F = 59.16 \text{ mV}$ and $pe = 16.9 E_h$ at 25°C



Pourbaix diagrams ($I = 0$, 25°C)



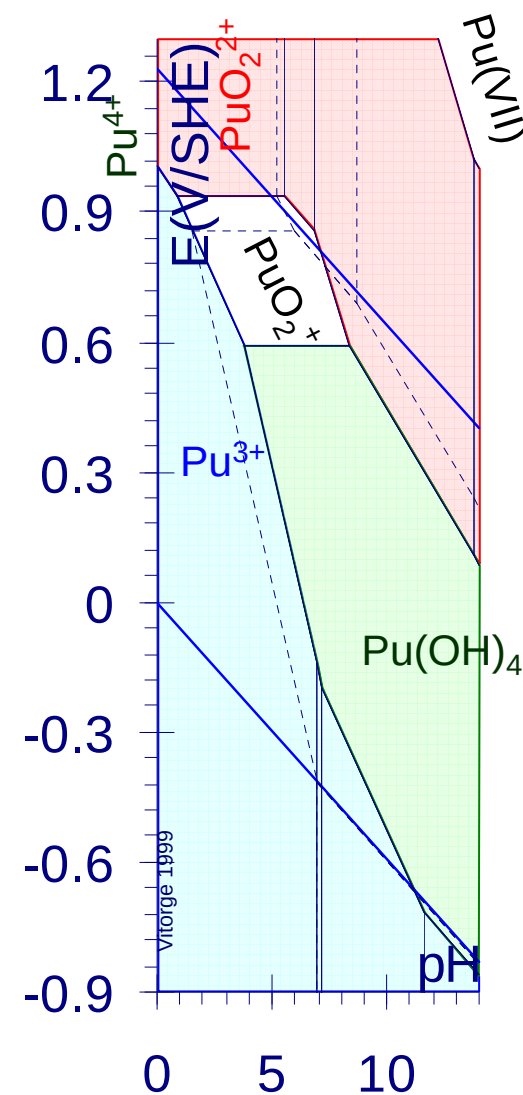
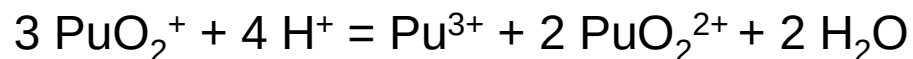
Disproportionation



Some oxidation states are not stable in solution
When they are formed,
they (more or less rapidly) disproportionate

Examples:

Pu(IV) and Pu(V) in acidic solution (<1M)





Hydrolysis and complexation



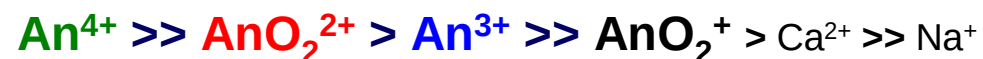
Hydrolysis



- Positive charges **polarize** water molecules

→ hydrolysis of cations

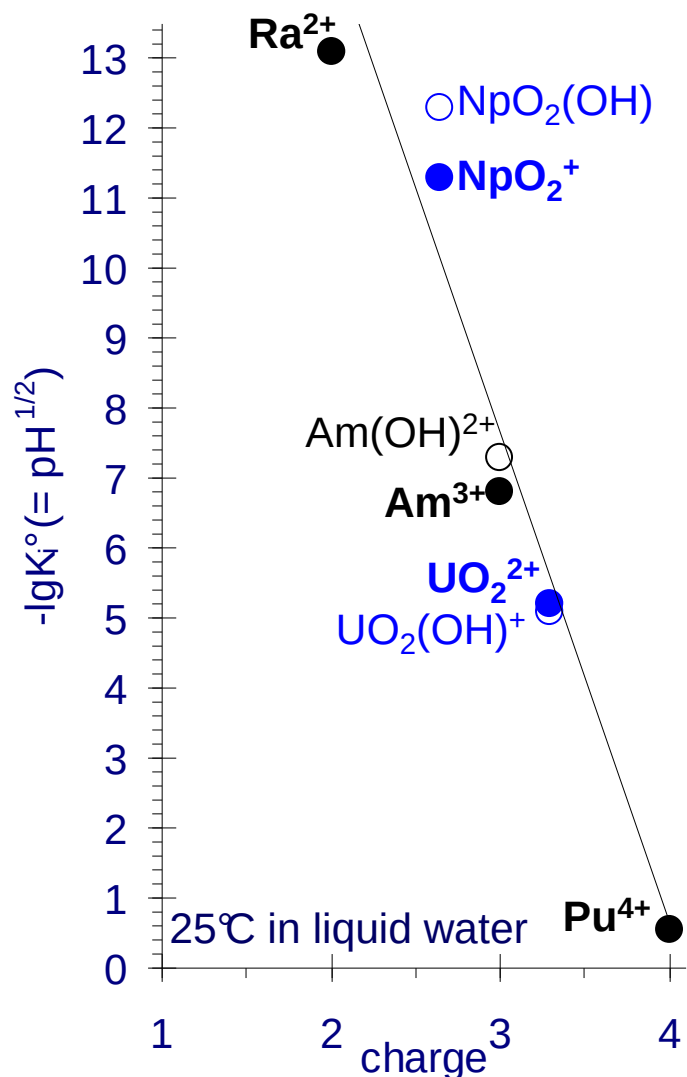
- Most usual order for the stabilities of An hydroxides:



Charge localised on the metal



Correlation between hydrolysis constants and charges



$$^*K_i^0 = \frac{|\text{M}(\text{OH})_{i-1}^{z+1-i}|}{|\text{M}(\text{OH})_i^{z-i}| |\text{H}^+|}$$

for $i = 1$ or 2 , $|X|$ is X activity

$\text{M}^{z+} = \text{Ra}^{2+}, \text{Am}^{3+}, \text{Pu}^{4+},$
 $\text{NpO}_2^+ \text{ or } \text{UO}_2^{2+}.$

$$\Delta_r G_{m,i}^\circ = -R T \ln(^*K_i^0)$$

$$R T \ln(10) = 5.71 \text{ kJ.mol}^{-1} \text{ at } 25^\circ\text{C}$$

The hydrolysis constants are correlated to the metal ion charge, and increase

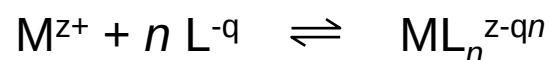
- with the charge (of the metal ion)
- with the atomic number for the An(III) and An(IV) ions

Charge is the atomic charge of the metal ion



Complexation

Equilibrium reactions



$$\beta_n^\circ = \frac{|ML_n^{z-qn}|}{|M^{z+}| |L^{-q}|^n}$$

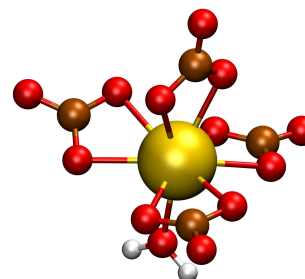
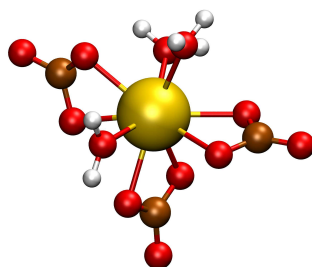


$$pK_a$$



Preferential interactions

- inorganic ligands: CO_3^{2-} , SO_4^{2-} , $SiO(OH)_3^-$, $H_2PO_4^{2-}$, F^- , ...
- organic ligands with COO^- and OH functional groups (oxygen donors), or with aliphatic and aromatic nitrogen groups (nitrogen donors)
- Geometrical constraints

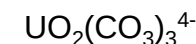
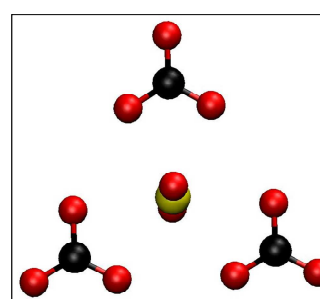
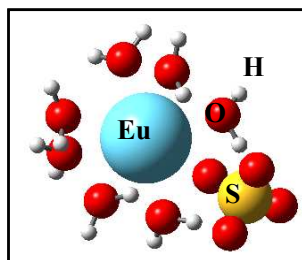


Coordination



● Inner-sphere complexes = direct contact between the metal ion and the ligand

- inorganic ligands: CO_3^{2-} , SO_4^{2-} , $\text{SiO}(\text{OH})_3^-$, $\text{H}_2\text{PO}_4^{2-}$, F^- , ...
- most carboxylate groups
- monodentate / multidentate



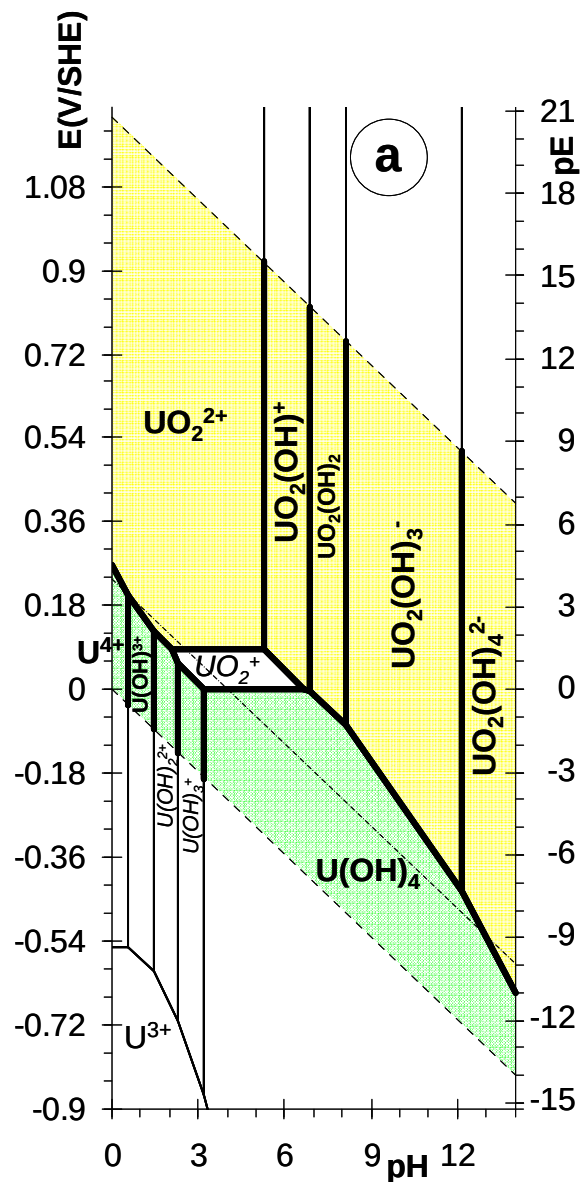
● Outer-sphere complexes = one bridging solvent molecule

- inorganic ligands: Cl^- , Br^- , I^- , ClO_4^- , ...

● Binding to softer atoms (N, S, ...) occurs via chelate formation where interactions with oxygen donors play a major role

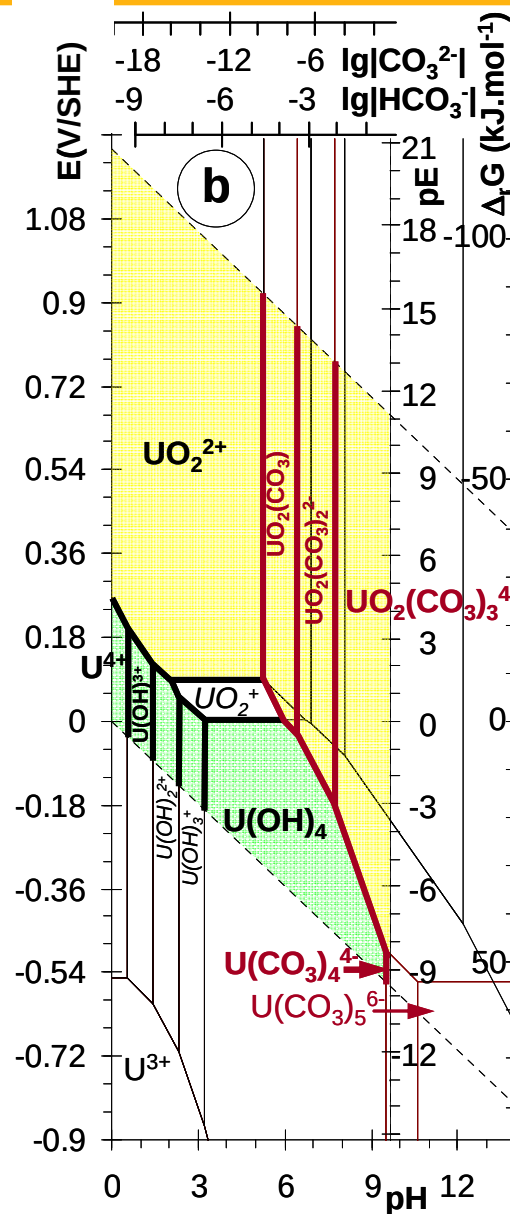


Effect of hydrolysis and complexation on Eh°



(b) $P_{\text{CO}_2} = 0.01 \text{ atm}$

$[U]_{\text{total}} < 10^{-9.5} \text{ M}$
(no polynuclear complexes, no precipitates)



Chemical analogies

The basic rule for analogy between f-block cations

- In the same oxidation state

→ Pu / Am / Cm(III)

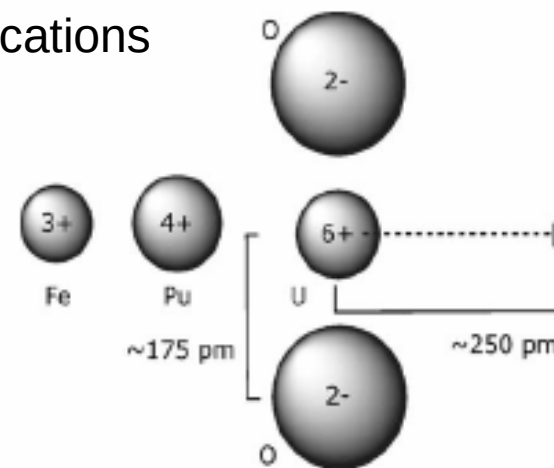
→ U / Pu / Th(IV)

- With similar ratio charge over ionic radius

→ An(III) / Ln(III)

→ Fe(III) / Pu(IV)

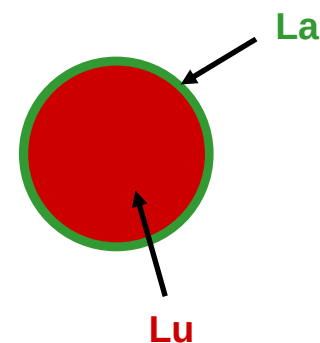
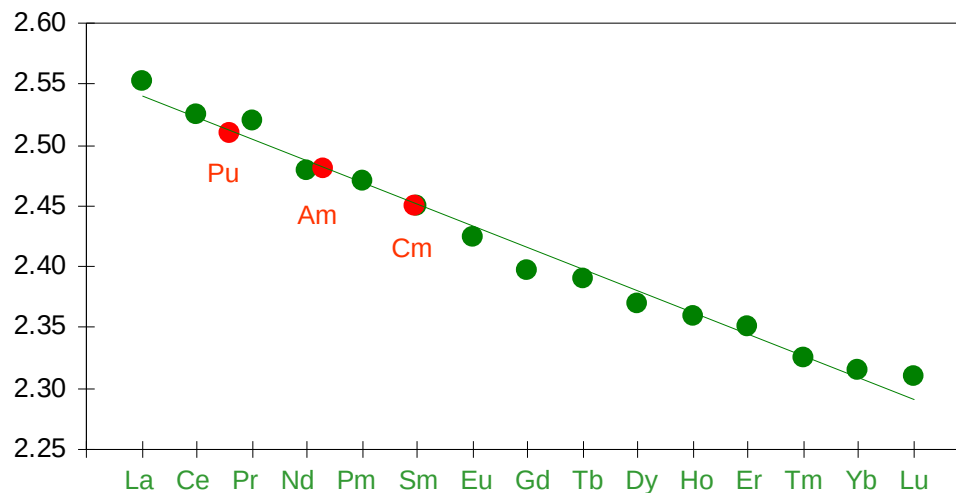
• LANTHANIDES	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
+ ACTINIDES	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Scheme 1.

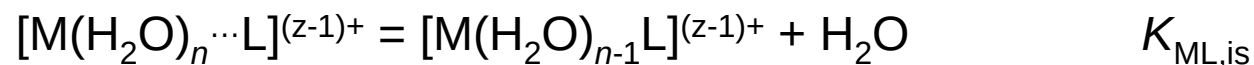
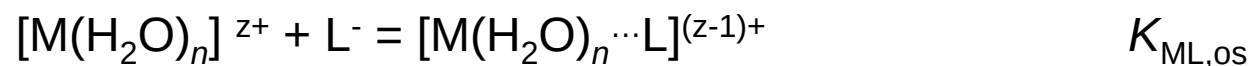
Van Horn and Huang, Coordination Chemistry Reviews 250 (2006) 765–775.

d_{Ln-OH_2} (Å) (determined by EXAFS)



Inner- and outer-sphere complexation

● Eigen-Wilkins mechanism

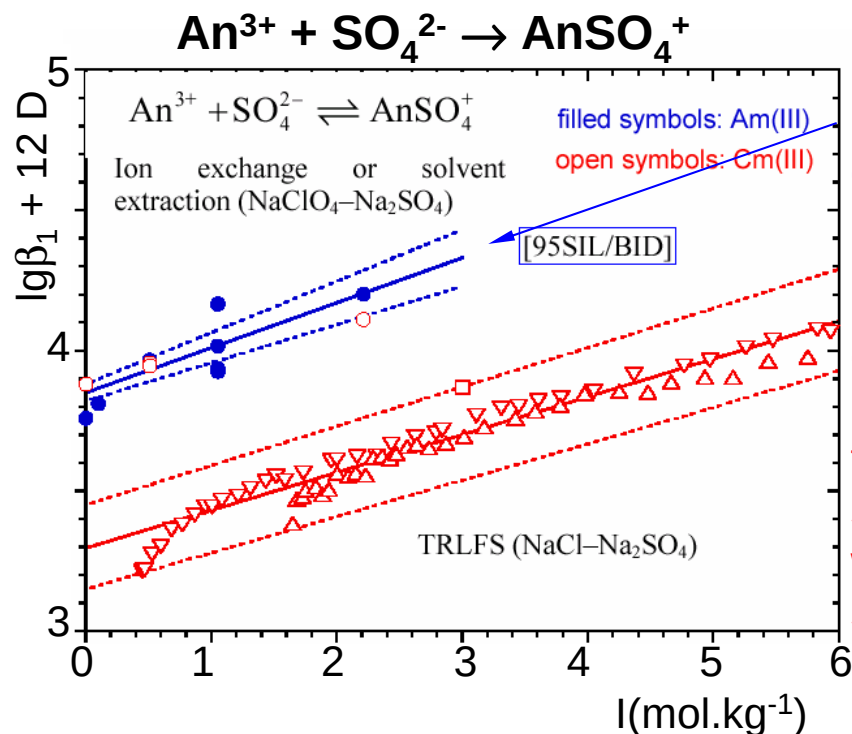


$$K_{ML} = K_{ML,os} K_{ML,is}$$

■ Which K do we usually measure?



Sulfate complexes of M^{3+}



NEA 1995¹ Ion exchange or solvent extraction ($NaClO_4-Na_2SO_4$)

NEA 2003² from **TRLF** ($NaCl-Na_2SO_4$) data³

Inconsistency had been explained as follows: Spectroscopy would measure the stability of only **inner sphere complexes**, while other techniques would measure the stability of **in+outer sphere complexes**.

¹R.Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, I. Puigdomenech. *Chemical thermodynamics of Am*. NEA Paris (France) 1995

²R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D.A. Palmer, I. Grenthe, M.H. Rand. *Update on the chemical thermodynamics of U, Np, Pu, Am and Tc*, Elsevier, Amsterdam, 2003

³P. Paviet, T. Fanghänel *et al.*, *Radiochim. Acta*, 74, 99-103 (1996) and V. Neck, T. Fanghänel *et al.*, Report, 1-108 (1998)

⁴T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)



Spectrophotometry is sensitive to inner- and outer-sphere complexations



$$M_i L_j^{iz-jy (in)} = M_i L_j^{iz-jy (out)} + \delta n H_2O \quad k_{i,j} = \frac{\beta_{i,j}^{(out)}}{\beta_{i,j}^{(in)}}$$

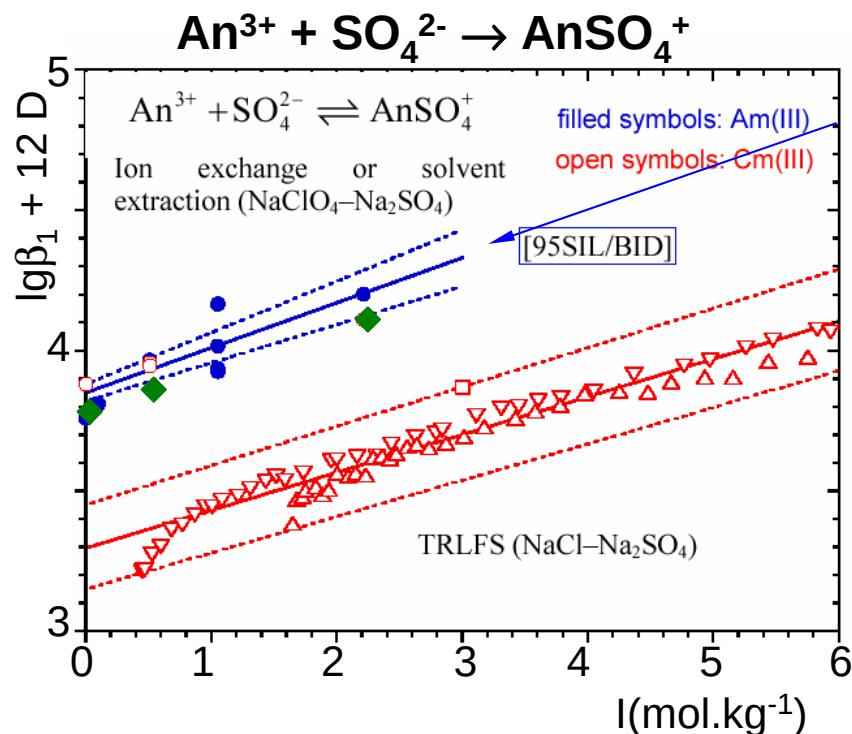
$$\left\{ \begin{array}{l} [M]_{TOTAL} = \sum_{i,j} [M_i L_j^{iz-jy(in)}] + [M_i L_j^{iz-jy(out)}] = \sum_{i,j} \beta_{i,j}^{(tot)} [M^{z+}]^i [L^{y-}]^j \\ I = \sum_{i,j} \epsilon_{i,j}^{(in)} [M_i L_j^{iz-jy(in)}] + \epsilon_{i,j}^{(out)} [M_i L_j^{iz-jy(out)}] = \sum_{i,j} \beta_{i,j}^{(tot)} \epsilon_{i,j}^{(tot)} [M^{z+}]^i [L^{y-}]^j \end{array} \right.$$

where

$$\left\{ \begin{array}{l} \beta_{i,j}^{(tot)} = \frac{[M_i L_j^{iz-jy(in)}] + [M_i L_j^{iz-jy(out)}]}{[M^{z+}]^i [L^{y-}]^j} = \beta_{i,j}^{(in)} + \beta_{i,j}^{(out)} \\ \epsilon_{i,j}^{(tot)} = \frac{\beta_{i,j}^{(in)} \epsilon_{i,j}^{(in)}}{\beta_{i,j}^{(tot)}} + \frac{\beta_{i,j}^{(out)} \epsilon_{i,j}^{(out)}}{\beta_{i,j}^{(tot)}} = \frac{\epsilon_{i,j}^{(in)}}{1 + k_{i,j}} + \frac{\epsilon_{i,j}^{(out)}}{1 + \frac{1}{k_{i,j}}} \end{array} \right.$$



Sulfate complexes of M^{3+}



NEA 1995¹ Ion exchange or solvent extraction ($\text{NaClO}_4\text{-Na}_2\text{SO}_4$)

NEA 2003² from **TRLF** ($\text{NaCl-Na}_2\text{SO}_4$) data³

TRLFS study for analogous Eu ($\text{NaClO}_4\text{-Na}_2\text{SO}_4$)⁴ rather confirms NEA 1995 selection

¹R.Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, I. Puigdomenech. *Chemical thermodynamics of Am*. NEA Paris (France) 1995

²R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D.A. Palmer, I. Grenthe, M.H. Rand. *Update on the chemical thermodynamics of U, Np, Pu, Am and Tc*, Elsevier, Amsterdam, 2003

³P. Paviet, T. Fanghänel et al., *Radiochim. Acta*, 74, 99-103 (1996) and V. Neck, T. Fanghänel et al., Report, 1-108 (1998)

⁴T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)



Estimation of the outer sphere complex formation constant

- The Fuoss equation [Fuoss, 1958]



$$K_{os} = \frac{4000\pi N_A r^3}{3} \exp\left(-\frac{U}{RT}\right)$$

- U is the Debye-Hückel interaction potential and r is the distance between the two reactants M and L

- U is given by [Margerum et al., 1978; Wilkins, 1991]

$$U = \frac{N_A z_M z_L e^3}{4\pi\epsilon\epsilon_0} \left(\frac{1}{r} - \frac{\kappa}{1 + \kappa r} \right)$$

- κ is the inverse Debye length, which mainly depends on the ionic strength

$$\kappa^{-1} = \frac{1}{\sqrt{8\pi\lambda_B N_A I}}$$

λ_B is the Bjerrum length of the medium

for water at 25°C, $\lambda_B \sim 0.7$ nm then $\kappa^{-1} \sim 1$ nm for $I=0.1\text{mol/dm}^3$; $\kappa^{-1} \sim 0.3$ nm for $I=1\text{mol/dm}^3$;





Medium effects



Thermodynamics of solution

Gibbs energy $G(T,P,n_i)$ of a uniform system



$$G = \sum_i n_i \mu_i$$

n_i : nb of moles of the i constituent
 μ_i : chemical potential of the i constituent

In solution, μ_i is described with the activity a_i of the ion i

$$\mu_i = \mu_i^\circ + RT \ln \left(\frac{a_i}{a_i^\circ} \right) \quad \text{standard activity } a_i^\circ = 1$$

Standard state

- electrolytes : a hypothetical solution at 1 mol kg⁻¹ ($m^\circ = 1$)
When the molality $m \rightarrow 0$, $(a_i / m_i) \rightarrow 1$
We define the activity coefficient

$$\gamma_i = \frac{a_i m^\circ}{m_i}$$

→ Deviation from ideality

- a state physically accessible



Activity coefficient models

$$\text{Deviation from ideality} \quad \gamma_i = \frac{a_i m^\circ}{m_i}$$



Specific
interactions

Debye-Hückel ($\gamma_{\pm}$)

Davies

Brønsted-Guggenheim-Scatchard (SIT)

Pitzer

...

Increasing
number of
parameters

1E-4 1E-3 0.01 0.1 1 10

Force ionique (mol/kg)

Physical
description

Binding Mean Spherical Approximation (BIMSA)

Advantages of the Specific Ion interaction Theory (SIT) :

- restricted number of parameters, usually 1 single ($\Delta\epsilon$) per chemical equilibrium
- only pair interactions between cation – anion
- formula much used in coordination chemistry for aqueous solution (NEA-TDB)

See Grenthe and Puigdomènech, MODELLING IN AQUATIC CHEMISTRY, OECD Publications, 1997, 724 pp.



Deviation to ideality : application of the SIT formula



$$^*\beta_n^\circ = \underbrace{\frac{\gamma_{\text{Am}(\text{OH})_n^{3-n}} \gamma_{\text{H}^+}^n}{\gamma_{\text{Am}^{3+}}}}_{\text{}} \times \underbrace{\frac{[\text{Am}(\text{OH})_n^{3-n}][\text{H}^+]^n}{[\text{Am}^{3+}]}}_{^*\beta_n}$$

SIT

$$\lg \gamma_i = -z_i^2 D(I_m) + \sum_j \varepsilon_{i,j} m_j$$

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

$$D(I_m) = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}}$$

- Can be maintained constant for constant I_m (ionic medium)
- SIT formula, valid for $0 < I_m < \sim 4 \text{ mol kg}^{-1}$

$$\lg ^*\beta_n(I_m) - \Delta z^2 D(I_m) - n \lg a_{\text{H}_2\text{O}} = \lg ^*\beta_n^\circ - \Delta \varepsilon m$$

- $\Delta \varepsilon$ can be determined from $\varepsilon_{i,j}$ (experimental measurements of mean activity coefficients, of osmotic coefficients, of equilibrium constants, or from correlations, etc)
- or directly, even if $\Delta \varepsilon m$ is often $\leq$ to the uncertainty on $\lg ^*\beta_n$



Activity coefficient using the SIT formula



$$\Delta Z^2 = 3^2 - 4^2 = -7$$



$$\lg K_{\text{Pu}^{4+}/\text{Pu}^{3+}} + 7 D = \lg K^{\circ}_{\text{Pu}^{4+}/\text{Pu}^{3+}} - \Delta \varepsilon_{\text{Pu}^{4+}/\text{Pu}^{3+}} m_{\text{ClO}_4^-}$$

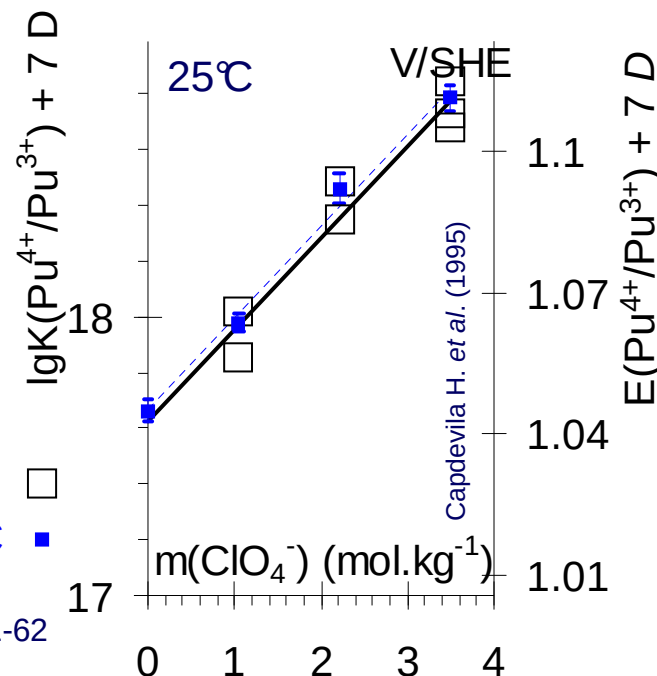
$\Delta \varepsilon$ appears to be constant, which validates SIT Formula

$$\Delta_r G^{\circ} = -R T \ln K_{\text{Pu}^{4+}/\text{Pu}^{3+}} = -F E_{\text{Pu}^{4+}/\text{Pu}^{3+}}$$

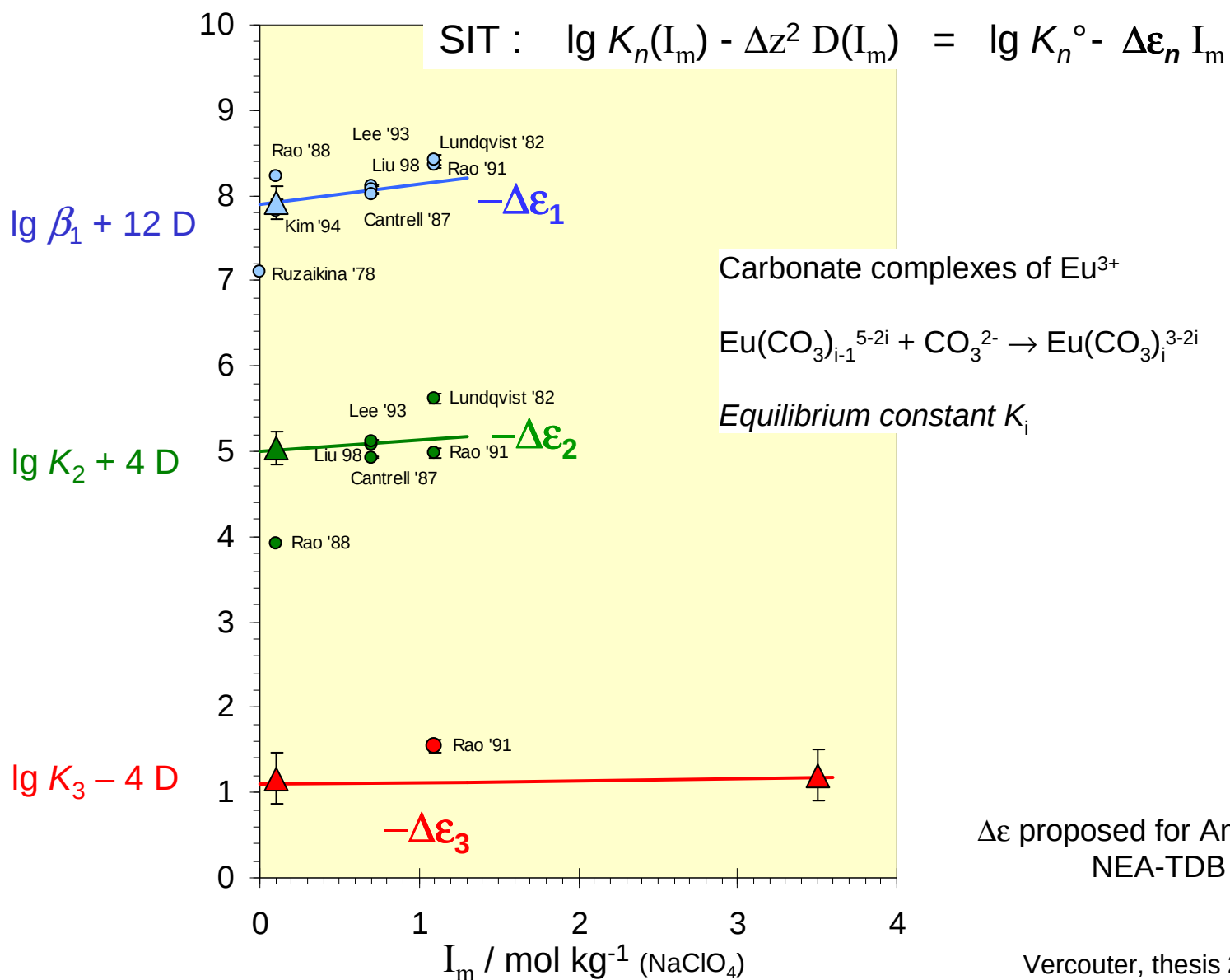
R is the molar gas constant,
 F the Faraday constant

measured at 25°C □
 interpolated at 25°C from data at 5 to 65°C ■

Capdevila H., Vitorge P. (1995) Radiochim. Acta 68(1), 51-62
 . & CEA-N-2762 (1994)



Extrapolation to $I_m = 0$





Temperature dependence



Thermodynamic properties

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$



$$\Delta_r G^\circ(T, P) = \Delta_r G^\circ(T^\circ, P^\circ) - (T - T^\circ)\Delta_r S^\circ(T^\circ, P^\circ) + \int_{T^\circ}^T \Delta_r C_p^\circ dT - T \int_{T^\circ}^T \frac{\Delta_r C_p^\circ}{T} dT + \int_{P^\circ}^P \Delta_r V^\circ dP$$

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

- Integration for $\Delta_r C_p^\circ = \text{constant}$, and at constant P

$$\lg K(T) = \lg K(T^\circ) - \underbrace{\frac{\Delta_r H(T^\circ)}{R \ln(10) T^\circ} \left(\frac{T^\circ}{T} - 1 \right)}_{1^{\text{st}} \text{ order}} + \underbrace{\frac{\Delta_r C_p}{R \ln(10)} \left(\frac{T^\circ}{T} - 1 + \ln \frac{T}{T^\circ} \right)}_{2^{\text{nd}} \text{ order}}$$

- Approximations:

- Van't Hoff ($\Delta_r H^\circ = \text{constant}$)
- evaluation of $\Delta_r C_p^\circ$ with parameterized equations ($C_p^\circ = f(T)$)
- revised HKF model for aqueous species (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock et al., 1992).



Estimation methods



● Isoelectric reactions

- total amount of positive charges is the same for reactants and for products
- idem for the negative charges



YES

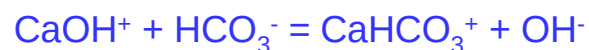


NO

- $\Delta_r C_p^\circ$ is small thus considered constant with T
- $\Delta_r H^\circ = \text{constant}$ is valid for T < 473 K

● Isocoulombic reactions

- The individual charges of each aqueous species balance out between the reactants and the products



YES

- $\Delta_r C_p^\circ$ is almost zero
- $\Delta_r H^\circ = \text{constant}$ is even better justified

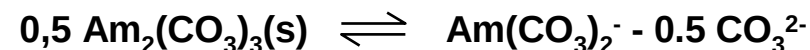
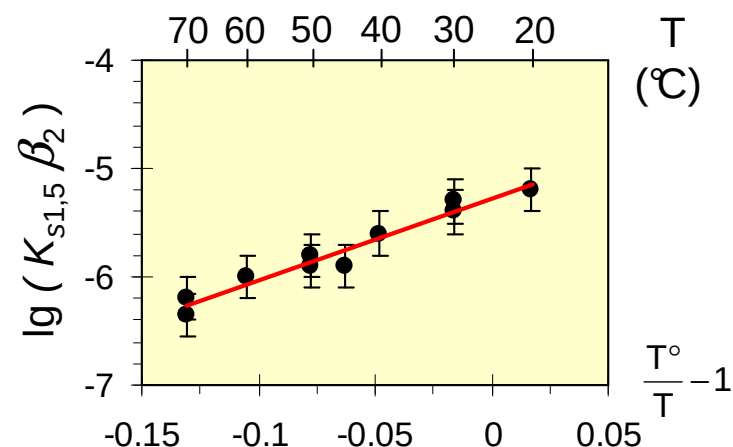
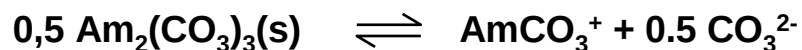
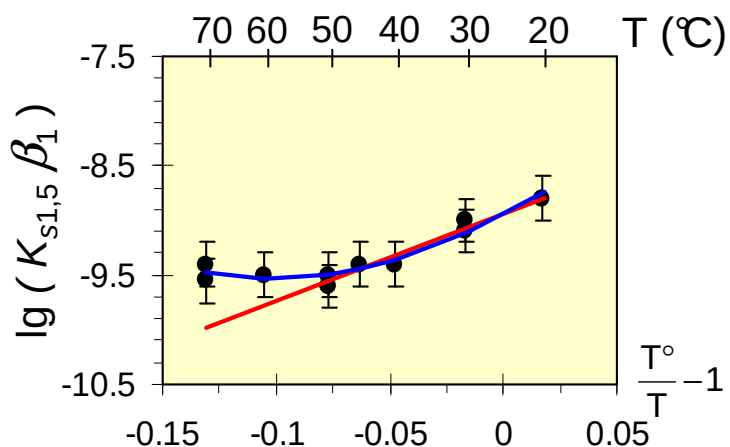
See Grenthe and Puigdomènech, MODELLING IN AQUATIC CHEMISTRY, OECD Publications, 1997, 724 pp.



Temperature dependence of dissolution reactions of $\text{Am}_2(\text{CO}_3)_3(\text{s})$



$$\lg K(T) = \lg K(T^\circ) - \underbrace{\frac{\Delta_r H(T^\circ)}{R \ln(10) T^\circ} \left(\frac{T^\circ}{T} - 1 \right)}_{1^{\text{st}} \text{ order}} + \underbrace{\frac{\Delta_r C_p}{R \ln(10)} \left(\frac{T^\circ}{T} - 1 + \ln \frac{T}{T^\circ} \right)}_{2^{\text{nd}} \text{ order}}$$



isoelectric reaction

$\Delta_r H$ and $\Delta_r C_p$ / $\Delta_r H$



Vercouter et al., *Inorg. Chem.* (2005)

What drives complexation



$$\Delta_r H^\circ = \Delta_r H_{\text{dehydration}}^\circ + \Delta_r H_{\text{binding}}^\circ$$

- In many cases, $\Delta_r H_{\text{dehydration}}^\circ > 0$ (unfavourable)
 $\Delta_r H_{\text{binding}}^\circ < 0$ (favourable)

$$\Delta_r S^\circ = \sum \Delta_r S_{\text{translation}}^\circ + \Delta_r S_{\text{vibration}}^\circ + \Delta_r S_{\text{rotation}}^\circ + \Delta_r S_{\text{conformation}}^\circ + \dots$$

- The different contributions are hardly determined

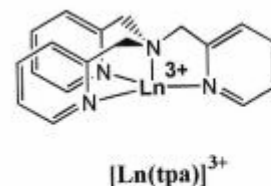
$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

- The reaction is either driven by the enthalpy or the entropy

The formation reaction of $\text{Ln}(\text{tpa})^{3+}$ is exothermic with a low entropy of reaction,

whereas the formation reaction of $\text{Ln}(\text{tpaam})^{3+}$ is highly endothermic with a highly positive entropy

Finally the complexation constants are quite similar!



Bravard et al. *Dalton Transaction*, **2004**, 2012-2018



Speciation calculation



Sillen diagrams

- Calculated speciation with a set of thermodynamic data ($I=0$, 25°C)



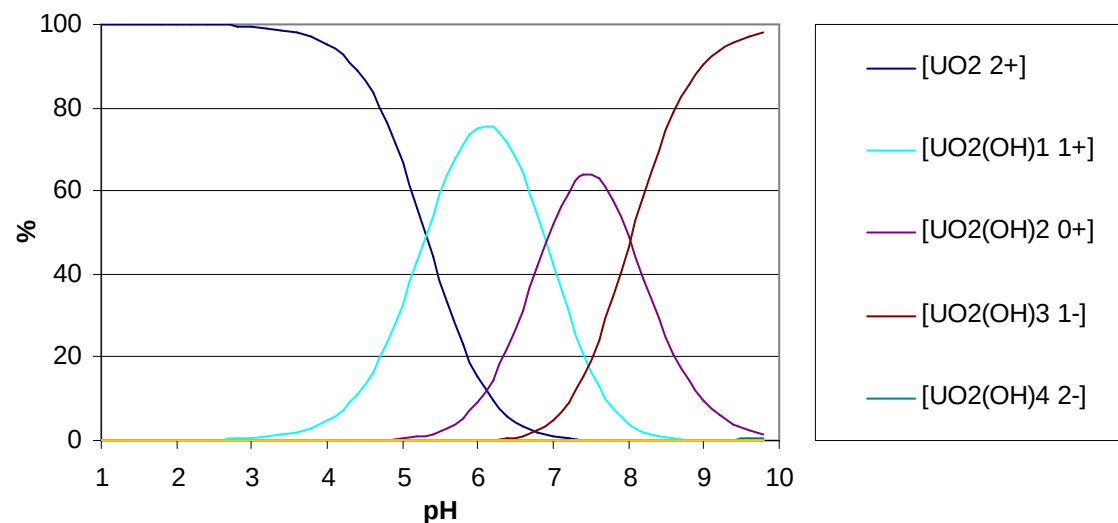
- For N species

- (N-1) equilibria of complex formation (= (N-1) laws of mass action)
- 1 equation for the mass balance
- ➔ the N values of species concentrations can be calculated analytically

- U(VI) hydrolysis

[U(VI)] = 10^{-9} mol/L

$I = 0$, 25°C



Sillen diagrams

- If polynuclear complexes can form, there is no analytical solution

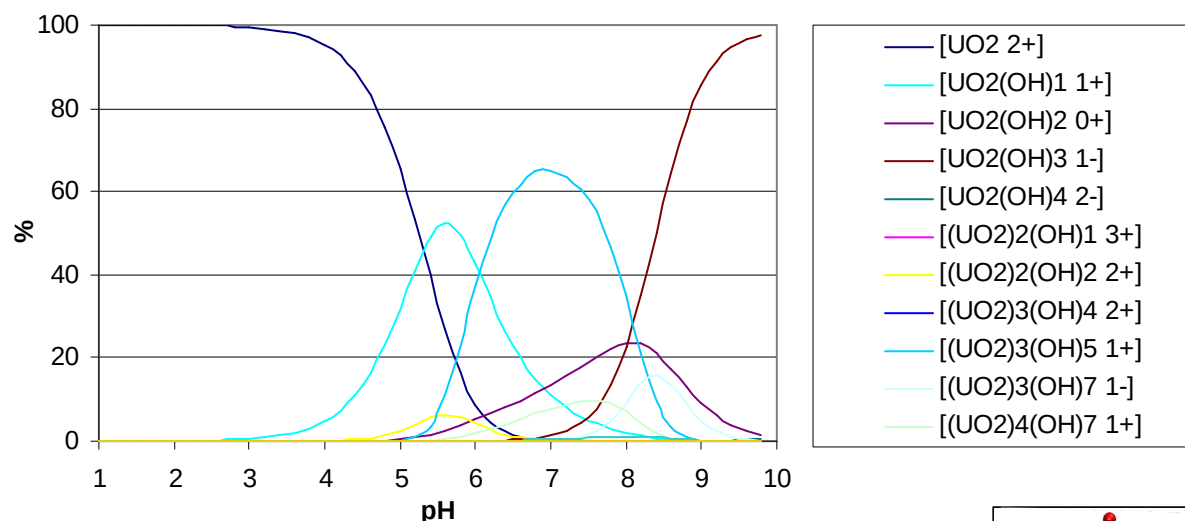
→ Numerical solution (speciation codes)



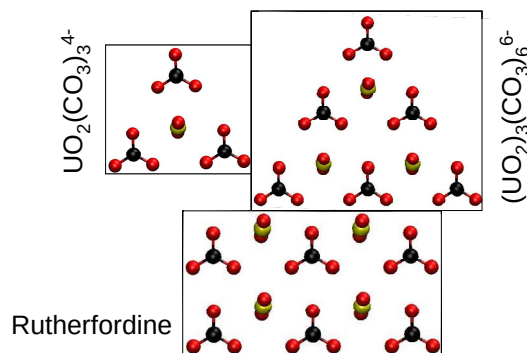
- At higher [U(VI)], $(\text{UO}_2)_3(\text{OH})_5^+$ predominates for pH 6-8

[U(VI)] = 10^{-6} mol/L

I = 0, 25°C



- Increasing the metal concentration may favour polynuclear species until precipitation occurs



Vitorge et al., (2008)



Contrast between U(VI) and Pu(VI) chemistry



- Potentiometry and IR spectroscopy



- However, polynuclear complexes are usually observable close to the solubility limits, and consequently difficult to identify,...

- ... except when they are strongly stabilised (particular geometries of $(\text{UO}_2)_3(\text{OH})_5^+$, etc...)

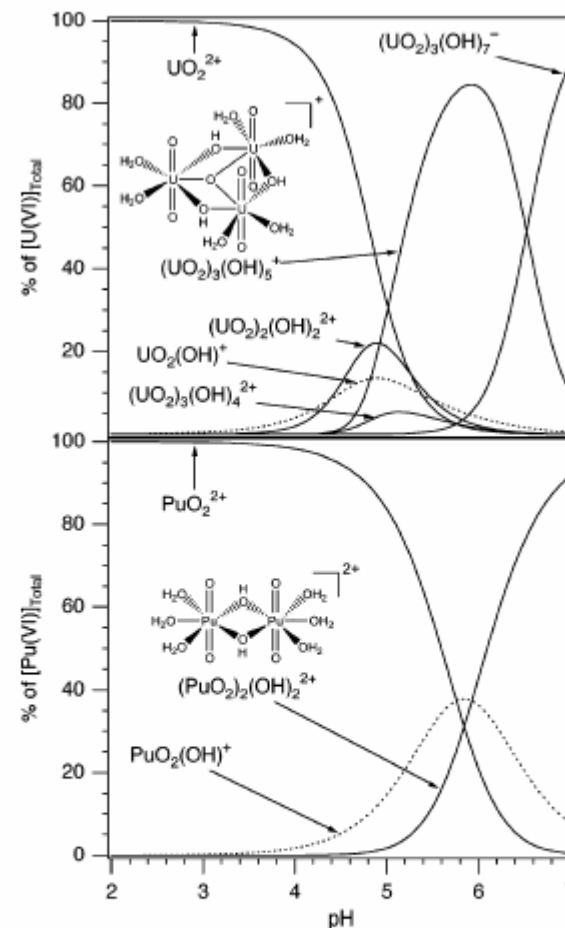


Figure 5. Calculated speciation diagrams for 0.10 mM U(VI) and Pu(VI). The U(VI) diagram is generated using literature constants for U(VI) hydrolysis in 0.10 M NaNO_3 (ref 27). The Pu(VI) diagram is generated using the values for the first monomeric and dimeric hydrolysis constants determined for Pu in 0.10 M NaNO_3 . The monomeric first hydrolysis species of each actinide are accentuated with dotted lines. The known structure of the predominant $(\text{UO}_2)_3(\text{OH})_5^+$ species and the proposed structure of $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ are shown.



Reilly, and Neu, Inorg. Chem. **2006**, 45, 1839-1846

Solubility and colloid formation



- Tetravalent actinides have a high tendency toward polynucleation and colloid formation
- The solubility of the PuO_2 solid phase strongly depends on the redox conditions, the pH, and the possible formation of colloidal particles

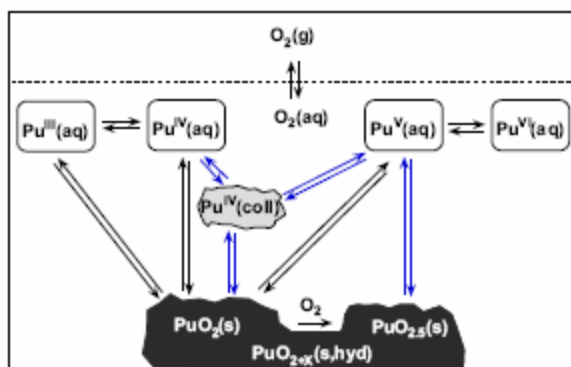
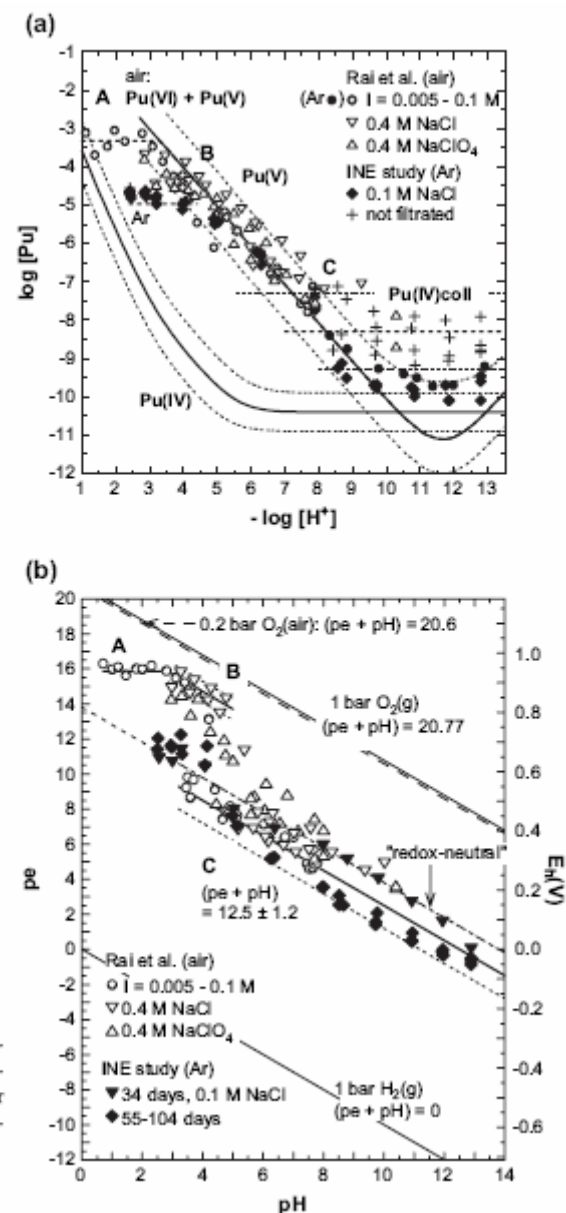


Fig. 7. Solid-liquid and redox equilibria of plutonium under reducing conditions, in redox-neutral solutions and in the presence of oxygen.

Fig. 6. (a) Solubility of $\text{PuO}_{2+x}(\text{s,hyd})$ at 20–25 °C; Pu concentration measured after ultrafiltration and without removal of Pu(IV) colloids/polymers (crosses); comparison of data measured under air (open symbols) [13–15] and under Ar (filled symbols) [9,10]. (b) Simultaneously measured redox potentials (analogous symbols).



Neck et al., C.R. Chimie 2006



References

J. Burgess, Metal ions in Solution, E. Horwood Ed., Chichester, 1978



Modelling in Aquatic Chemistry, I. Grenthe and I. Puigdomènech (Eds.), OECD Publications, 1997, 724 pp.

The Chemistry of the Actinide and Transactinide Elements, 3rd ed.; L.R. Morss, N.M. Edelstein, J. Fuger, J.J. Katz (Eds.), 2006. (in 5 volumes)

