

# Actinide chemistry in aqueous solutions for waste disposal and environmental studies

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# Actinide chemistry in aqueous solutions for waste disposal and environmental studies



**Introduction.** For the management of radioactive wastes, Equilibrium Speciation is studied in aqueous solutions: Chemistry of Actinides and other Radionuclides (critical reviewing and measuring thermodynamic data), also thermodynamics, methodologies...

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## Mass Action Law

in Nature

in Laboratory (measuring equilibrium constants and stoichiometries)

...for Solid Solutions ...and Ionic Exchange Equilibria

## Activity coefficients

SIT (and Pitzer) Formula = extended Debye and Hückel Formula

= Boltzmann – Poisson Calculus ...as for Surface Complexation Formula

## Consistency

of thermochemical data

between different scientific fields, *i.e.* reference states ...e<sup>-</sup> notation

## Ab initio calculations

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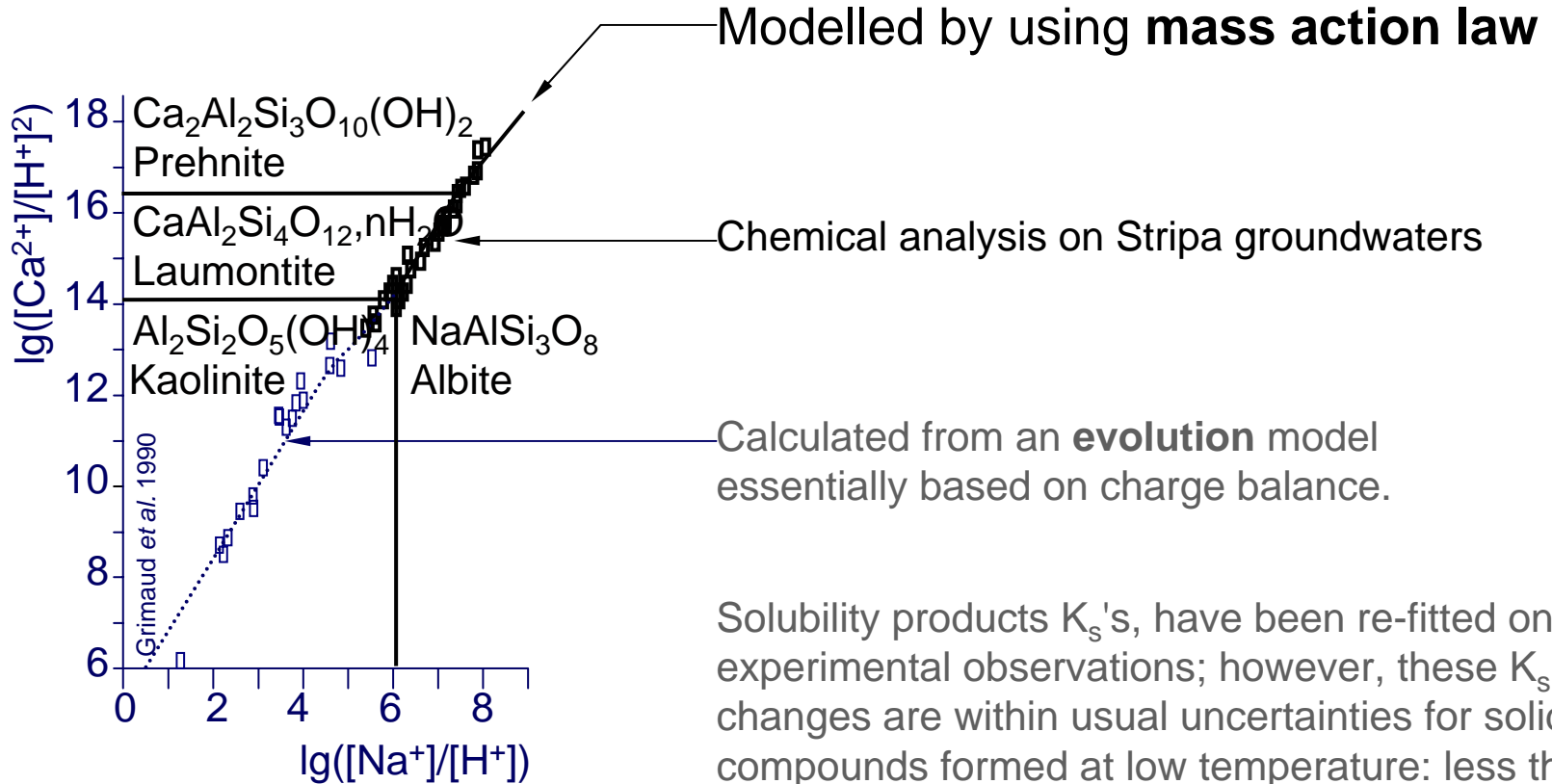
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Ab initio calculations

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# Equilibration of Stripa groundwaters with minerals



Grimaud D., Beaucaire C., Michard G. (1990) Applied Geochemistry, Vol.5, 515-525



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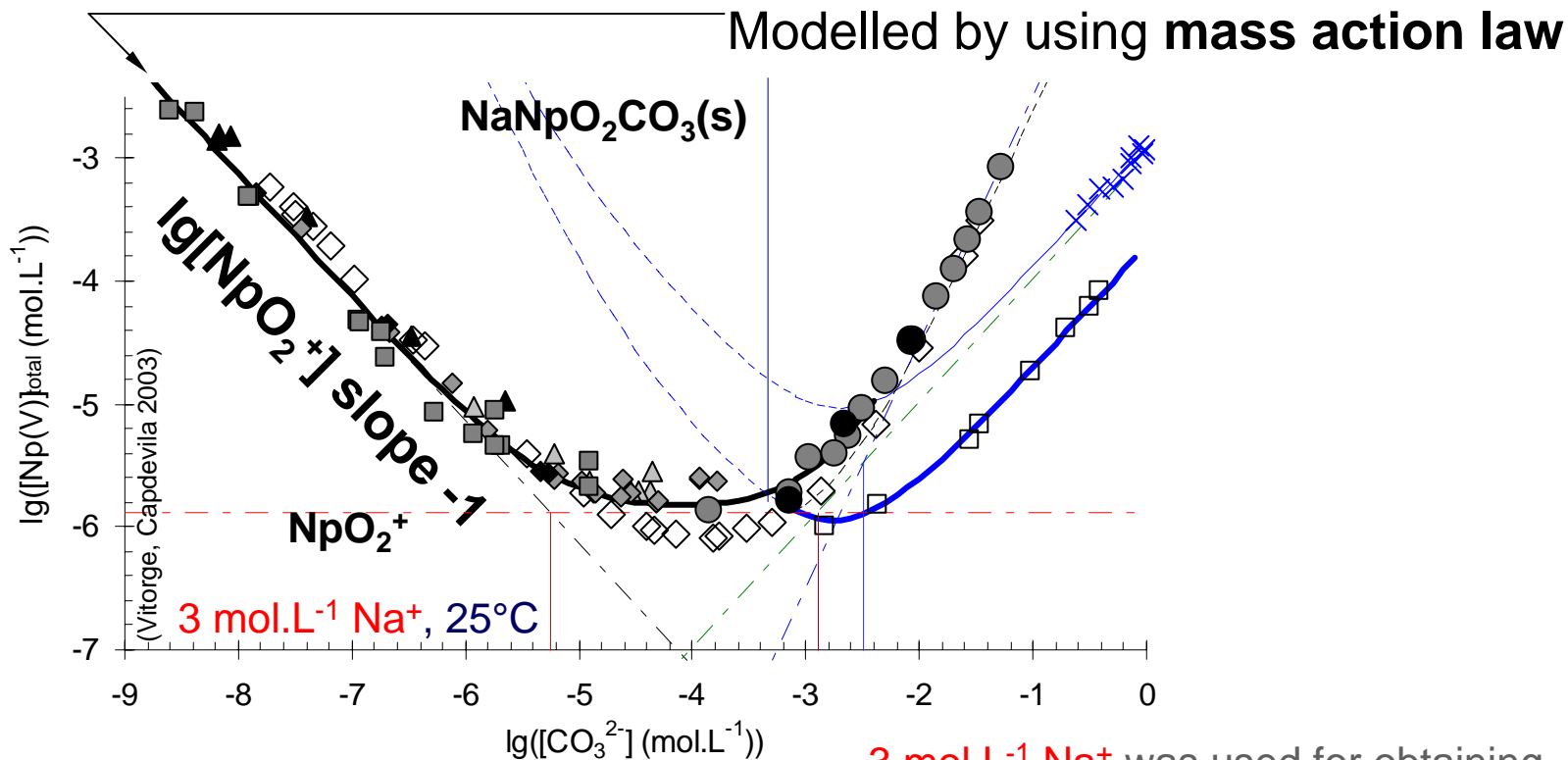
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# Np(V) solubility in $\text{CO}_3^{2-} / \text{HCO}_3^- / \text{CO}_2$ aqueous solutions

## Solubility product



$$K_s = [\text{Na}^+] [\text{NpO}_2^+] [\text{CO}_3^{2-}]$$

$$\text{lg}[\text{NpO}_2^+] = -\text{lg}[\text{CO}_3^{2-}] + \text{Constant}$$

$$\text{Constant} = \text{lg } K_s + \text{lg}[\text{Na}^+]$$

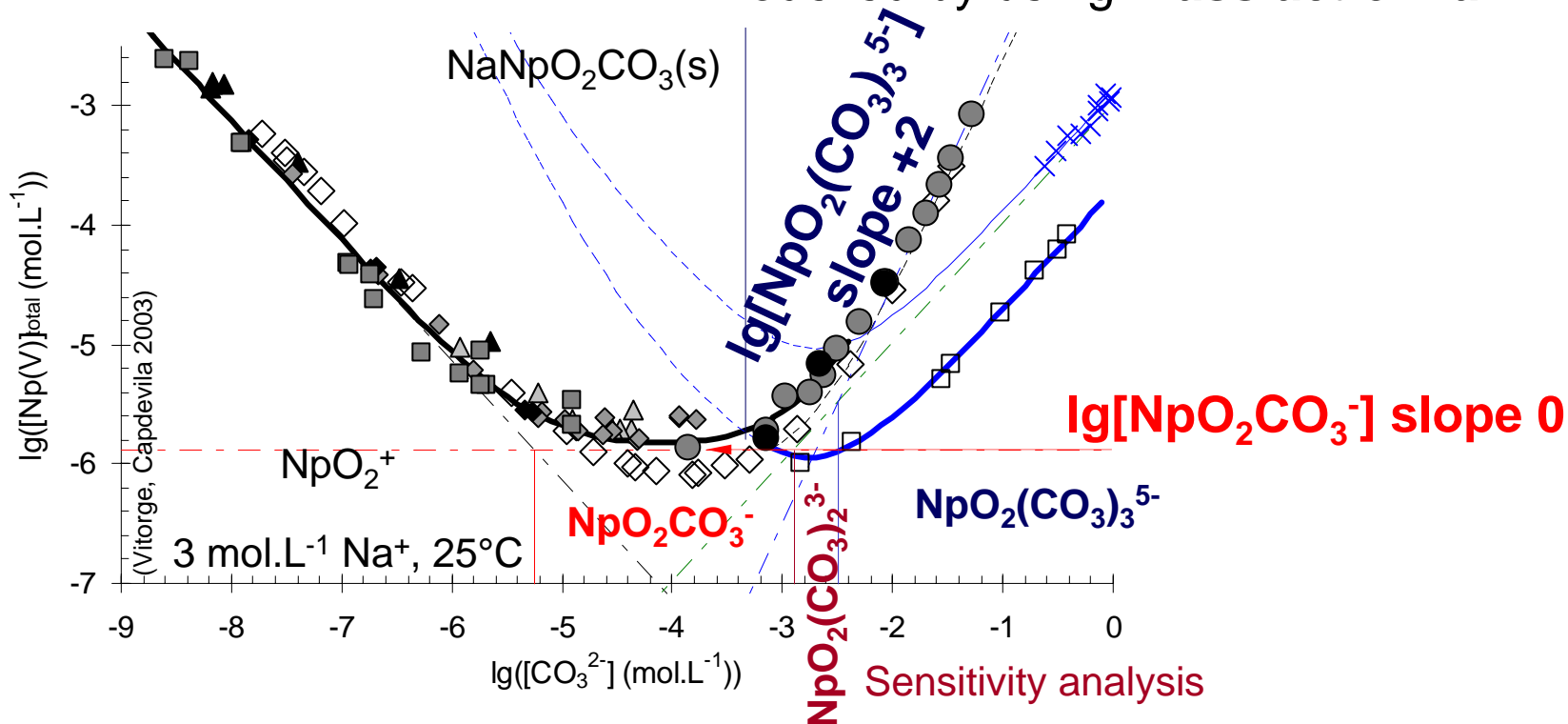
$3 \text{ mol.L}^{-1} \text{ Na}^+$  was used for obtaining **constant activity coefficients**  $\gamma$ , in the aqueous phase. This makes the **system ideal** and allows **slope and sensitivity analysis**.

Vitorge P., Capdevila H. (1998) CEA-R-5793. Vitorge P., Capdevila H (2003). Radiochim. Acta 91, 623–631.

# Np(V) solubility in $\text{CO}_3^{2-} / \text{HCO}_3^- / \text{CO}_2$ aqueous solutions

## Complexing constants

Modelled by using mass action law



$$K_{si} = [\text{Na}^+] [\text{NpO}_2(\text{CO}_3)_i^{1-2i}] [\text{CO}_3^{2-}]^{1-i} = K_s \beta_i \quad \beta_i = \frac{[\text{NpO}_2(\text{CO}_3)_i^{1-2i}]}{[\text{NpO}_2^+] [\text{CO}_3^{2-}]^{1-i}}$$

$$\lg[\text{NpO}_2(\text{CO}_3)_i^{1-2i}] = (1-i)\lg[\text{CO}_3^{2-}] + \text{Constant}$$

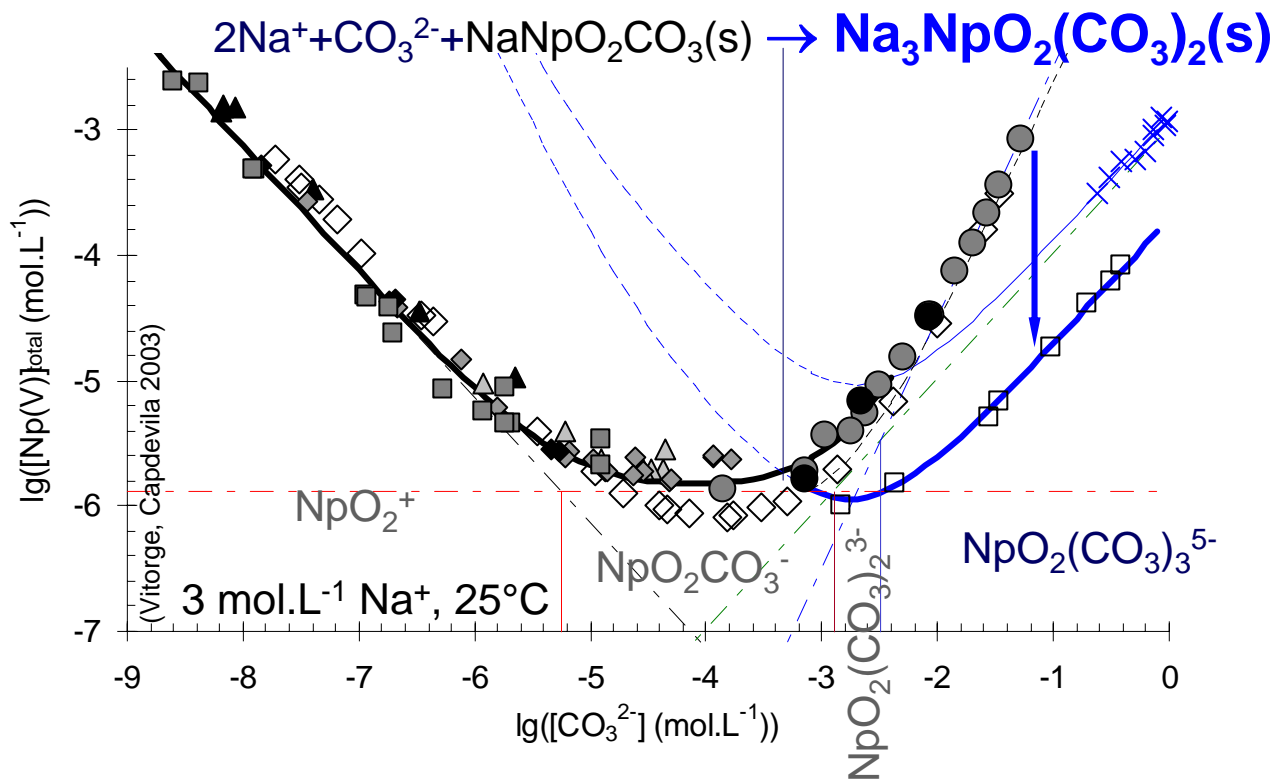
$$\text{Constant} = \lg K_{si} + \lg[\text{Na}^+]$$



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# Np(V) solubility in $\text{CO}_3^{2-}$ / $\text{HCO}_3^-$ / $\text{CO}_2$ aqueous solutions

## Precipitation of a new solid phase



**Other stoichiometries** of compounds have been proposed in literature<sup>1</sup> for Na/NpO<sub>2</sub>

<sup>1</sup>Volkov, Y.F., Visyashcheva, G.I., Tomilin, S.V., Spiryaov, V.T., Kapshukov, I.I., Rykov, A.G. Sov. Radiochem., 21, 5 (1979) 583-590. Transl. Radiokhim., 21, 5 (1979) 673-681.

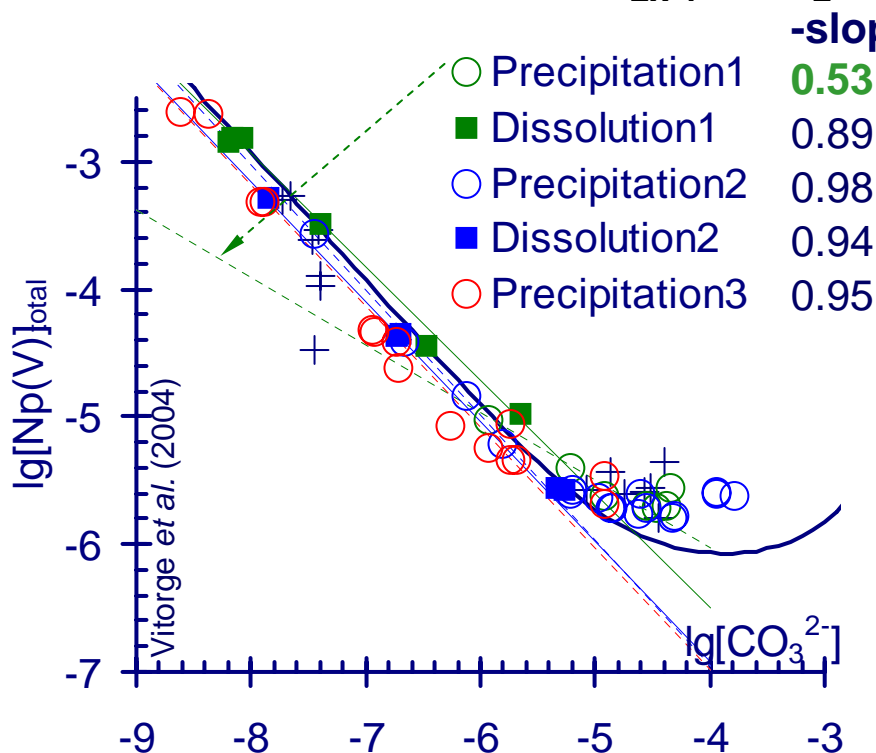
Vitorge PIAEA-SR-104/25. Sofia, Bulgarie (6-10 février 1984).

Vitorge P., Capdevila H., CEA-R-5793 (1998)



# Np(V) solubility in $\text{CO}_3^{2-} / \text{HCO}_3^- / \text{CO}_2$ aqueous solutions

## Evidence of $\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x$ Solid Solution?



**$x = -0.53$  for initial precipitation**  
 should certainly be attributed to kinetics; however, other stoichiometries for  $\text{Na}/\text{NpO}_2$  have been proposed in literature<sup>1</sup> based on X-ray diffraction and ionic exchange studies:  
 $\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x(\text{s})?$   
*i.e. a solid solution?...*

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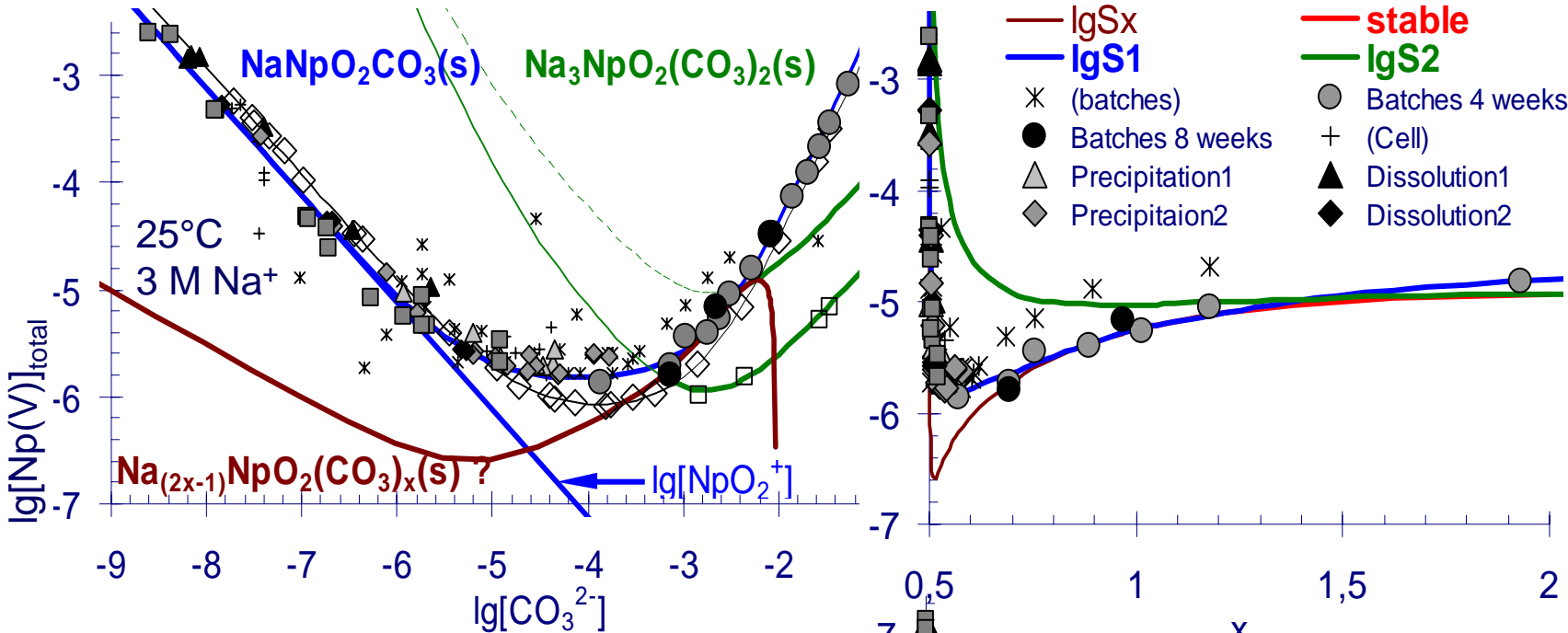
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Ab initio calculations

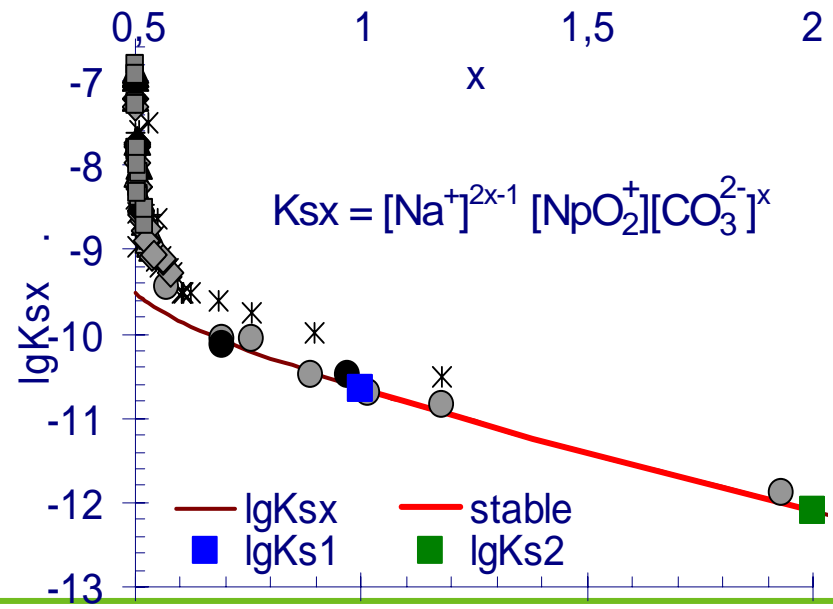
# No clear evidence of any $\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x$ ideal solid solution.



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While X-ray studies suggest the formation of a solid solution; this is not reflected in solubility measurements...despite this is not evidenced in classical graphical representations.



## Is Mass Action Law valid for Solid Solutions?

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# Thermodynamics of solid solutions as published in text books



Example:  $\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x$

or equivalently  $\text{Na}_{2(1-y)}(\text{NpO}_2)_{2y}\text{CO}_3$  where  $y = 1/(2x)$

the amount of  $\text{CO}_3^{2-}$  is the amount of solid matrix  
while  $\text{Na}^+/\text{NpO}_2^+$  cations are exchanged

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## Dissolution Reaction



## Ionic Exchange Reaction



Mass Action Law for Reaction(2):

$$D = \frac{[\text{Na}^+(\text{s})] [\text{NpO}_2^+(\text{aq})]}{[\text{Na}^+(\text{aq})] [\text{NpO}_2^+(\text{s})]} = \frac{2(1-y)[\text{NpO}_2^+(\text{aq})]}{2y [\text{Na}^+(\text{aq})]}$$

$D = K_{s1} / K_{s0}$  is obtained by linear combinations of chemical potentials  
where  $K_{sy} = [\text{Na}^+(\text{aq})]^{2(1-y)} [\text{NpO}_2^+(\text{aq})]^{2y} [\text{CO}_3^{2-}(\text{aq})]$   
are the solubility product of the endmembers for  $y = 0$  or  $1$

Similarly  $K_{sy} = K_{s0}^{1-y} K_{s1}^y (1-x)^{b(1-y)} x^{cy}$

which is **only similar to** Mass Action Law for Reaction(1)

# Thermodynamics of solid solutions

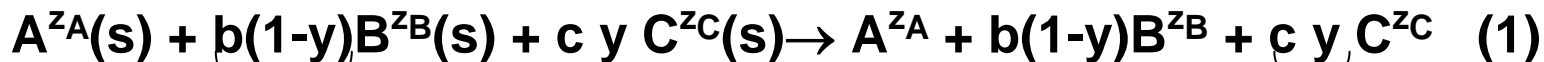
## a reaction with 2 advancement variables

Advancement variable for Reaction 1 at constant  $y$  ( $n_X$  = number of mole for

Species X):  $(dn_X)_y = v_X (dn_{A^{zA}})_y$   $v_A = 1$ ,  $v_B = b(1-y)$ ,  $v_C = c y$ ,  $v_{X(s)} = -v_X$

$$b = -z_A/z_B, c = -z_A/z_C, \mathbf{AB}_{b(1-y)}\mathbf{C}_{cy}(\mathbf{s}) = A^{zA}(\mathbf{s}) + b(1-y)B^{zB}(\mathbf{s}) + c y C^{zC}(\mathbf{s})$$

Dissolution Reaction



It appears that:  $\frac{dv_X}{dy} = v'_X$  are the stoichiometric coefficients for Reaction 2:

$$v'_A = 0 \quad v'_B = b, \quad v'_C = c, \quad v_{X(s)} = -v_X$$

Ionic Exchange Reaction



$$dn_X = d(v_X n_{A^{zA}}) = v_X (dn_{A^{zA}})_y$$

$$0 = \sum_X (\mu_X dn_X) = \left( \sum_X (\mu_X v_X) \right) (dn_{A^{zA}})_y$$

+

$$n_{A^{zA}} v'_X dy$$

+

$$n_{A^{zA}} \left( \sum_X (\mu_X v'_X) \right) dy$$

$$\frac{[A^{zA}] [B^{zB}]^{b(1-y)} [C^{zC}]^{cy}}{(1-y)^{b(1-y)} y^{cy}} = K_{s0}^{1-y} K_{s1}^y \text{ and}$$

$$\frac{(1-y)^b [C^{zC}]^c}{[B^{zB}]^b y^c} = \frac{K_{s1}}{K_{s0}}$$

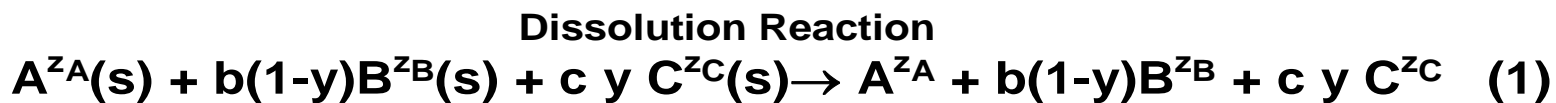
$$0 < y < 1$$



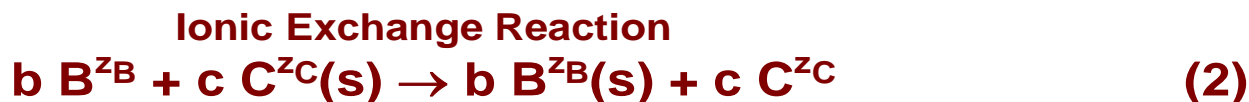
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# Thermodynamics of solid solutions

## Dissolution Reaction ↔ Ionic Exchange Reaction



Differentiating:  $\frac{dv_x}{dy} = v'_x$       Integral calculus:  $v_x = \int v'_x dy$



$K_{ex} = \frac{K_{s1}}{K_{s0}}$ , where  $K_{ex}$  is the equilibrium constant for a **ionic exchange equilibrium**.



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# H<sup>+</sup> / NpO<sub>2</sub><sup>+</sup> ionic exchange on a clayey sand

Should it be considered as part of a (surface) solid solution?

$K_d$  is Np(V) partition coefficient between a clayey sand and an aqueous solution.

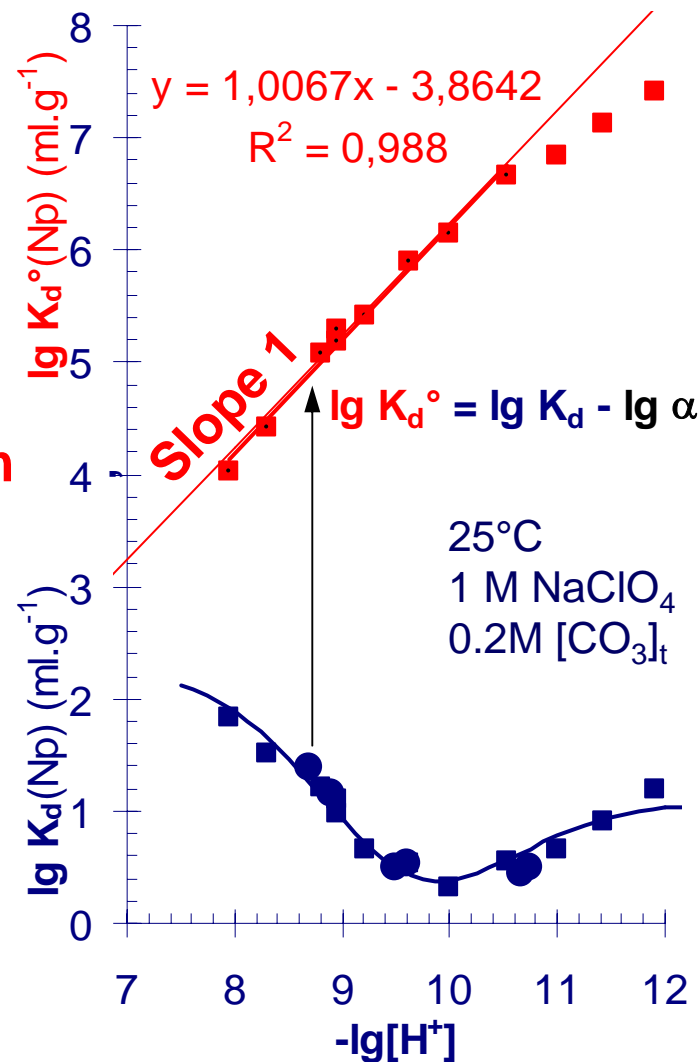
$K_d^\circ$  is NpO<sub>2</sub><sup>+</sup> partition coefficient.

$\alpha = [\text{NpO}_2]_t / [\text{NpO}_2^+]$   
is calculated from complexing constants

**Slope 1**  
**evidences Ionic Exchange Equilibrium**  
**NpO<sub>2</sub><sup>+</sup>(aq) + H<sup>+</sup>(s) → NpO<sub>2</sub><sup>+</sup>(s) + H<sup>+</sup>(aq)**

$$K_{\text{ex}} = \frac{[\text{NpO}_2^+(\text{s})][\text{H}^+(\text{aq})]}{[\text{NpO}_2^+(\text{aq})][\text{H}^+(\text{s})]} = K_d \frac{[\text{H}^+(\text{aq})]}{[\text{H}^+(\text{s})]} \approx K_d \frac{[\text{H}^+(\text{aq})]}{\text{CEC}}$$

$$K_{\text{ex}} = \frac{K_{s1}}{K_{s0}} ?$$



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Ab initio calculations

# Activity coefficients

using SIT formula at 25°C for Reaction  $\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$

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

$$D = \frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} \text{ at } 25^\circ\text{C}$$

Equilibrium constant K is constant in a given ideal system, typically a solution of high and constant ionic strength I.

here  $m_{\text{ClO}_4^-} = I_m$ ,

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

Reference state  $K^\circ = K(I \rightarrow 0)$



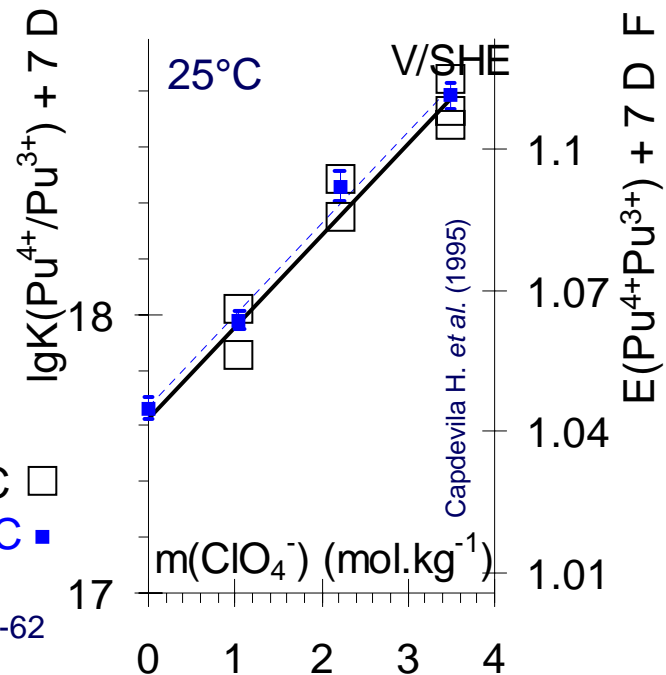
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$\Delta\varepsilon$  appears to be constant, which validates SIT Formula

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

R is the molar gas constant,

F the Faraday constant



measured at 25°C  $\square$

interpolated at 25°C from data at 5 to 65°C  $\blacksquare$

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

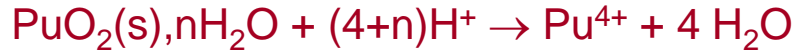
# Activity coefficients

## SIT formula at 25°C for the highly charged species Pu<sup>4+</sup>

$$\lg \gamma_i = -z_i^2 D + \varepsilon_{i,j} m_j, \quad (j = \text{ClO}_4^- \text{ or } \text{Na}^+)$$

$$\Delta_r \lg \gamma = -\Delta_r z^2 D + \Delta_r \varepsilon m$$

$$\Delta_r \lg \gamma_i + \Delta_r z_i^2 D = \Delta_r \varepsilon_{i,j} m_j \quad ?$$



$$\Delta \varepsilon_{\text{PuO}_2(\text{s})} = \varepsilon_{\text{Pu}^{4+}, \text{ClO}_4^-} + (4+n) a_{\text{H}_2\text{O}}/m - 4 \varepsilon_{\text{H}^+, \text{ClO}_4^-}$$



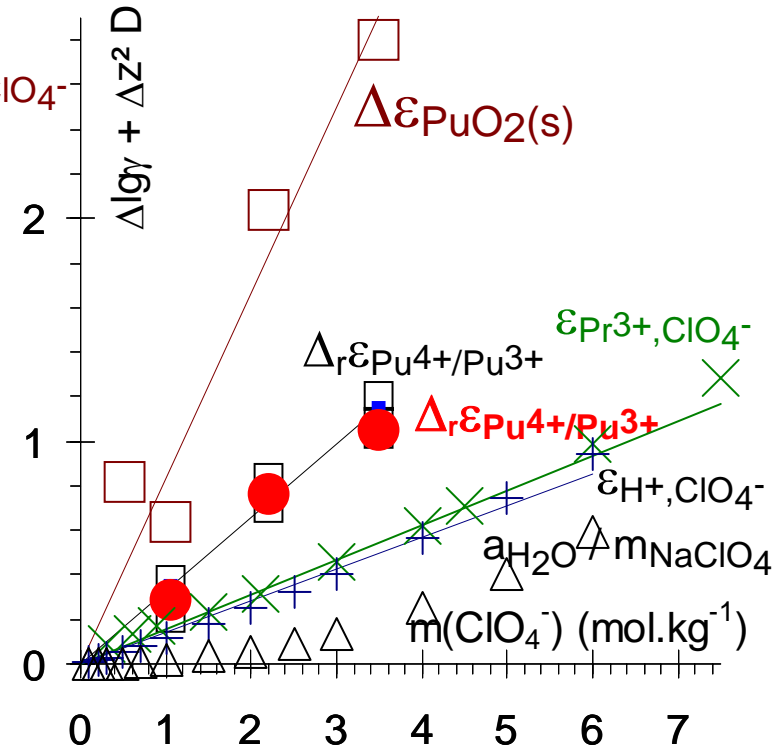
$$\Delta_r \varepsilon_{\text{Pu}^{4+}/\text{Pu}^{3+}} = \varepsilon_{\text{Pu}^{3+}, \text{ClO}_4^-} - \varepsilon_{\text{Pu}^{4+}, \text{ClO}_4^-}$$

**Checking by using Thermodynamic Cycle**

$$\Delta_r \varepsilon_{\text{Pu}^{4+}/\text{Pu}^{3+}} = \varepsilon_{\text{Pu}^{3+}} - \Delta \varepsilon_{\text{PuO}_2} - 4 \varepsilon_{\text{H}^+} \dots$$

Auxiliary data from isopiestic measurements

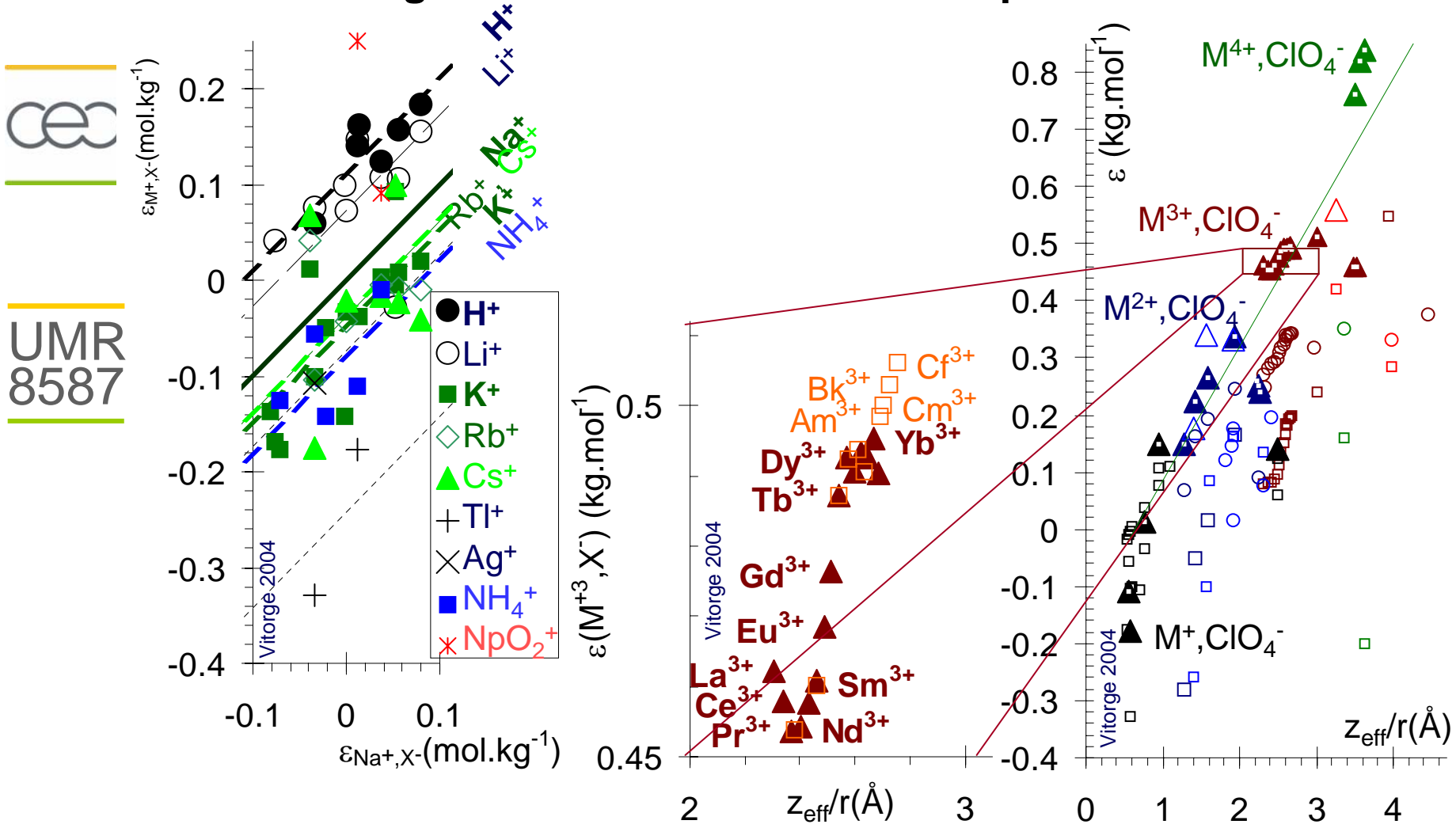
$$\varepsilon_{\text{Pr}^{3+}, \text{ClO}_4^-} \approx \varepsilon_{\text{Pu}^{3+}, \text{ClO}_4^-}$$



Capdevila H., Vitorge P. Radiochim. Acta 82, 11-16 (1998)

# Activity coefficients

Estimating numerical values for SIT empirical coefficients  $\varepsilon$ .



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# Activity coefficients at 25°C: conclusion

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**SIT Formula accounts for experimental data to surprisingly high ionic strength, even for highly charged species.**

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However, this might very well be fortuitous; several linear effects might very well be empirically included in Ion Pair term  $\varepsilon$ .

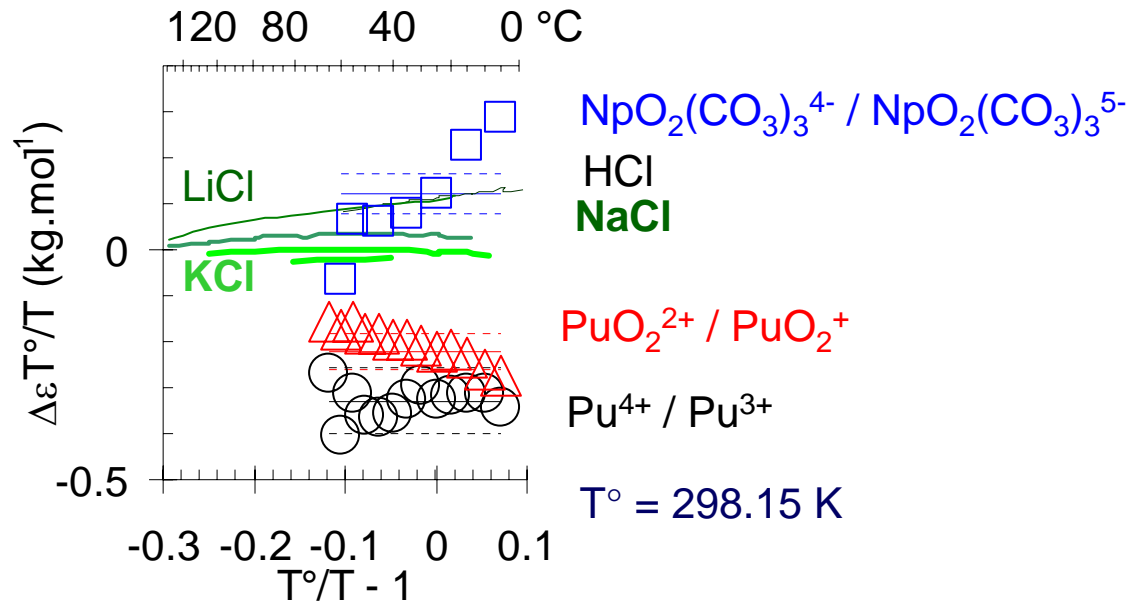
It is interesting to check whether SIT formula is also consistent with **temperature influence**, since it was proposed by using Statistical Physics as a result of temperature effect (disorder) and interactions (order).

# Activity coefficients

temperature Influence on  $\varepsilon$ , the ion pair coefficient of SIT formula.



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It appears that

**in several cases,  $(\varepsilon / T)$  does not depend on temperature,  $T$ .**

Despite this corresponds to the model used to obtain SIT Formula, this was not specially expected.

As a consequence **the values of the activity coefficients, can be extrapolated from their values known at typically 25°C, i.e. without any new fitted parameter.**



# Activity coefficients

## comparison of SIT and Surface Complexation Formula.

### SIT Formula

$\Psi_{total}$

-

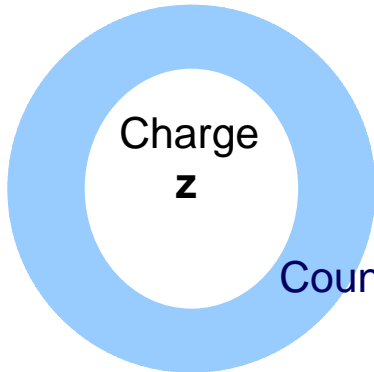
$\Psi_{Coulomb}$

=

$\Psi_{excess}$

Debye-Hückel Formula  
+ steric exclusion  
+ ion pair interactions

$\Psi$  = electrostatic potential



The model are different, however, are the physical phenomena actually different?

Debye distance = constant / (ionic strength)<sup>1/2</sup>

Charges

z  
z  
z  
z

Double layer

### Surface Complexation Formula

$\Psi_{total}$

Gouy and Chapman Formula  
+ supplementary layer(s)



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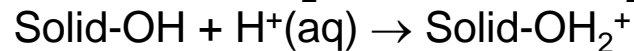
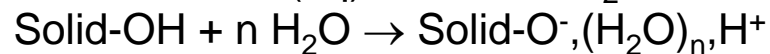
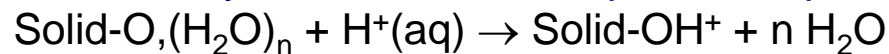
Ab initio calculations

# Surface chemistry:

## Sorption

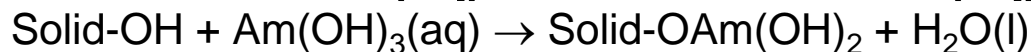
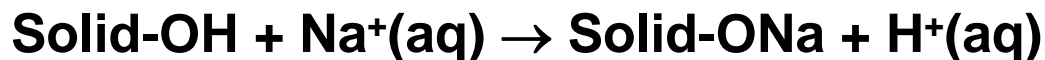


The surfaces of compounds are ionised, when in contact with water for typically oxides, hydroxides, silicate, apatite compounds:



➡ This is at the origin of the **surface charges** (and double layer)

➡ and **ionic exchanges** typically



modeled by using **Surface Complexation Formula** or **Mass Action Law** for ideal neutral phases

➡ What about **solid compounds that do not contain oxygen atoms**?

Are other surface anions protonated / hydrated / hydrolysed?

Conversely is the surface of the solid merely oxidised?

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# Consistency of thermochemical data

## Critical reviewing

➔ Comparing raw experimental data

➔ Reinterpreting, sensitivity analysis, consistency

➔ **Consistency = using a single chemical model (*i.e.* set of chemical species) for all published data on a given chemical system** *see Nuclear Division Conference "Actinide Carbonate Complexes"*

➔ **Correcting systematic errors as typically in calibrations (activity coefficients, junction potentials)**

➔ **Extrapolating to zero ionic strength**

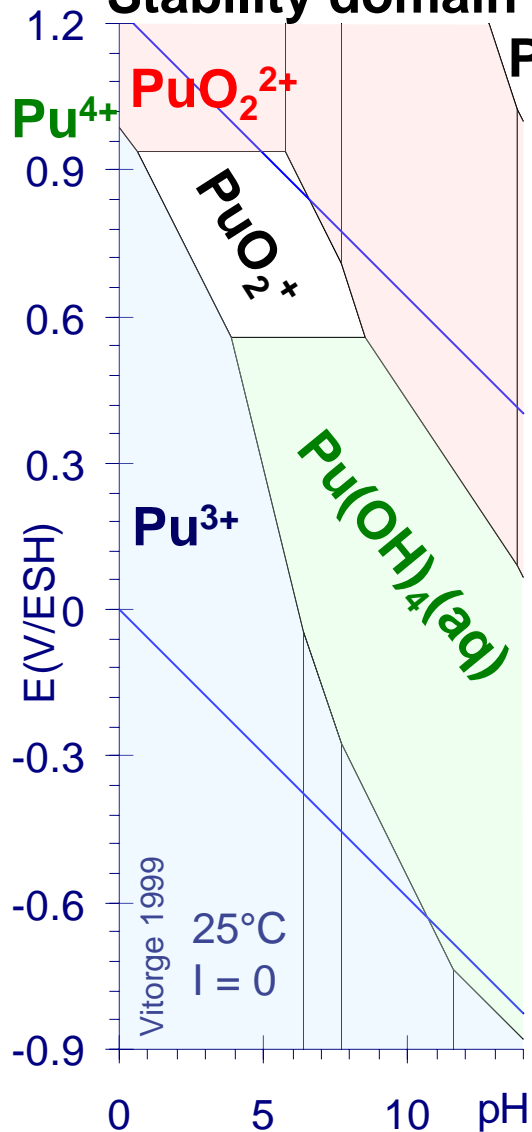
➔ **Using analogies for checking consistency or estimating missing data**



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# Pourbaix diagram of Pu

## Stability domain of Pu(VII) from an Np(VII)/Pu(VII) analogy



Pu(VII)

$E(\text{Pu}_{\text{VII/VI}})$  in 1 M NaOH<sup>1,2</sup>

$$\Delta_r E = E(\text{Pu}_{\text{VII/VI}}, 1 \text{ M NaOH}) - E(\text{Pu}_{\text{VII/VI}}, 1 \text{ M HClO}_4)$$

$$\sim \lg(\beta_{\text{VII,hydrolysis}}/\beta_{\text{VI,hydrolysis}})$$

$$\Delta_r E(\text{Pu}) = \Delta_r E(\text{Pu})$$

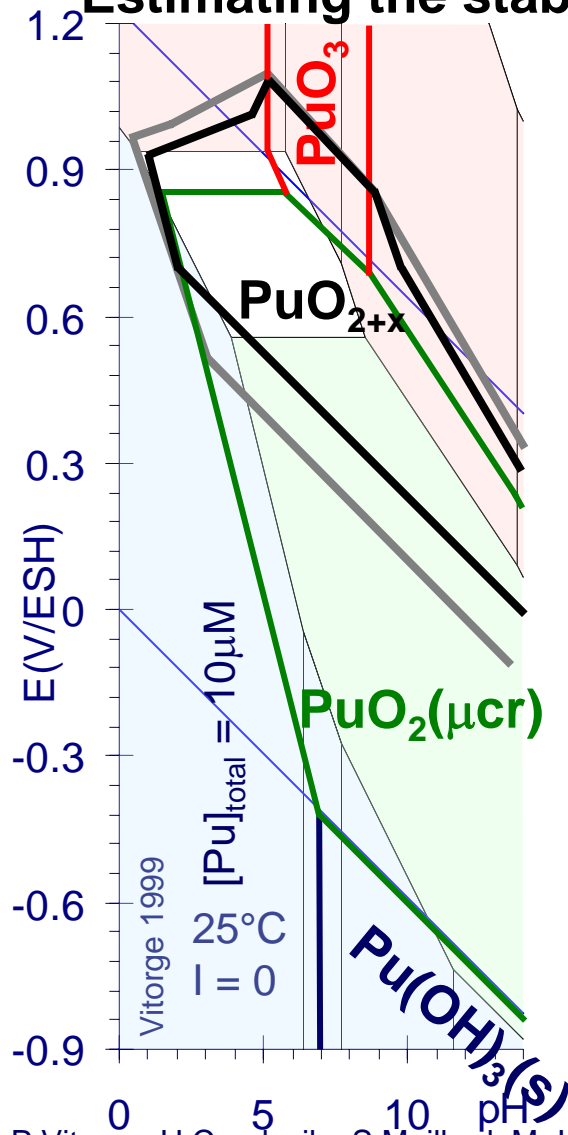
Ionic strength correction (SIT Formula)

1	2	3	4	5	6	7	8	9	10	...
H										
Li	Be	B	C	...						
Na	Mg	Al	Si	P	...					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	...
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	...
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Pt	...
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	...
1										
	2									
		3			3	3	3	3	3	
			4	4	4	4	4			
				5	5	5	5	5		
					6	6	6			
						7	7			

<sup>1</sup>Peretrushkin, V., Shilov, V., Pikaev, A., WHC-EP-0817 (1995) - <sup>2</sup>Peretrushkin, V., Krot, N., Gelman, A., Radiokhimiya 14 (1972) 72-77

# Pourbaix diagram of Pu

## Estimating the stabilities of $\text{PuO}_{2+x}$ by using U/Pu analogies



**Actinides ions are hard cations:** in most cases the stabilities of their complexes and hydrolysis behaviour are correlated to Ratio Charge/(ionic Radius)

➔ **analogy at the same oxidation state**

➔ **specific redox stabilities**

Assuming



or



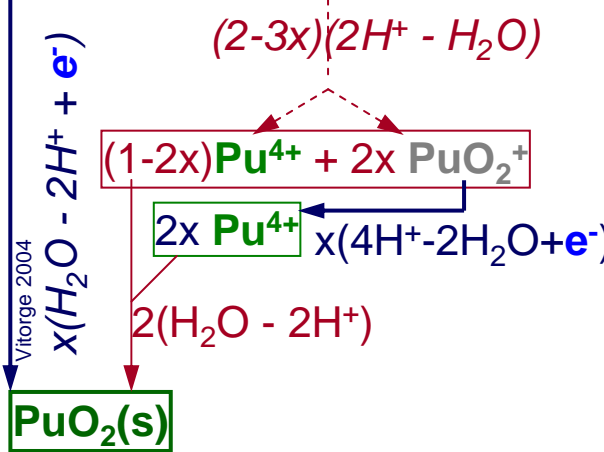
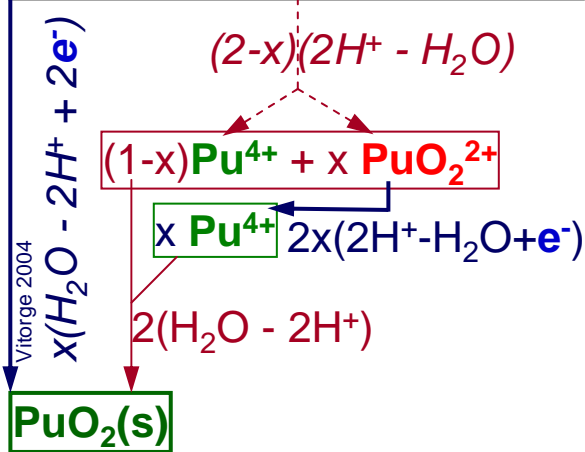
P.Vitorge, H.Capdevila. Radiochim. Acta 91, 623–631 (2003)

P.Vitorge, H.Capdevila, S.Maillard, M.-H. Fauré, T.Vercouter. J. Nuclear Sc. Techno. Supplement 3. p713-716(2002)



# Pourbaix diagram of Pu

## Thermodynamic cycles for estimating the stabilities of $\text{PuO}_{2+x}$



**Actinides ions are hard cations:** in most cases the stabilities of their complexes and hydrolysis behaviour are correlated to Ratio Charge/(ionic Radius)

➔ **analogy at the same oxidation state**

➔ **specific redox stabilities**

Assuming



or



Attributing atomic or molecular charges in solids is not straightforward.

However, recent EXAFS studies can be interpreted with the characteristic Pu-O(yl) bond length of  $\text{PuO}_2^{2+}$ .

(S.Conradson *et al.* Inorg. Chem.; 2004; 43(1) pp 116 – 131.

S.Conradson *et al.* J.A.C.S. in press.

S.Conradson *et al.* J. Solid State Chem. in press.)

P.Vitorge, H.Capdevila. Radiochim. Acta 91, 623–631 (2003)

P.Vitorge, H.Capdevila, S.Maillard, M.-H. Fauré, T.Vercouter. J. Nuclear Sc. Techno. Supplement 3. p713-716(2002)



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# Actinide chemistry in aqueous solutions for waste disposal and environmental studies



Introduction. For the management of radioactive wastes, Equilibrium speciation is studied in aqueous solutions: Chemistry of Actinides and other Radionuclides (critical reviewing and measuring thermodynamic data), also thermodynamics, methodologies...

Mass Action Law

in Nature

in Laboratory (measuring equilibrium constants and stoichiometries)

...for solid solutions ...and ionic exchange equilibria

Activity coefficients

SIT (and Pitzer) formula = extended Debye and Hückel formula

= Boltzmann – Poisson calculus ...as for surface complexation formula

**Consistency**

of thermochemical data

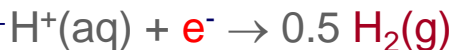
**between different scientific fields, *i.e.* Reference states ...e<sup>-</sup> notation**

Ab initio calculations

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# Consistency of thermochemical data

## Notation $e^-$



**$\Delta_r G_{ox/red} = -R T \ln K_{ox/red} = -n F E_{ox/red}$**

**$\Delta_f G_e = R T \ln a_e = -F E$**

### Notation for Electrochemistry

Standard Hydrogen Electrode (SHE)

### Notation for Thermodynamics

Corresponding equilibrium constant

Corresponding  $e^-$  activity

$0 = \Delta_r G_{SHE} = 0.5 \Delta_f G_{H_2(g)} - \Delta_f G_{H^+(aq)} - \Delta_f G_{e^-}$ , also  $0 = \Delta_f G_{H_2(g)}$  (Reference State)

when  $0 = \Delta_f G_{H^+(aq)}$

**$\Delta_f G_{e^-} = 0$**

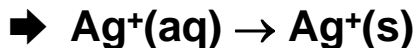
similarly

**$\Delta_f H_{e^-} = 0$**

and

**$S_{e^-} = 0.5 S_{H_2(g)} - S_{H^+(aq)}$**

➔  $e^-$  is not  $e^-(aq)$ , neither  $e^-(s)$ , it is rather  $e^-_{SHE}$



**Actual mechanism<sup>1</sup> ?**

however this notation does not include charge balance in each phase

<sup>1</sup>Eliezer Gileadi. Chem.Phys.Letters 393 (2004) 421–424



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Activity coefficients

SIT (and Pitzer) formula = extended Debye and Hückel formula

= Boltzmann – Poisson calculus ...as for surface complexation formula

Consistency

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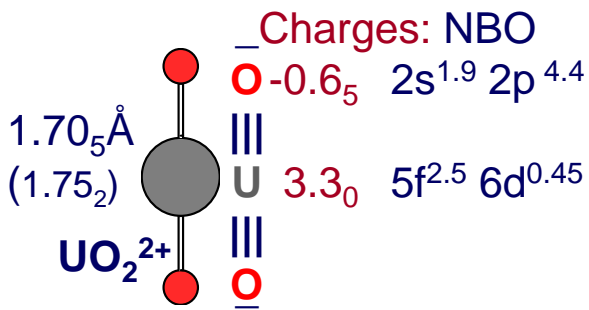
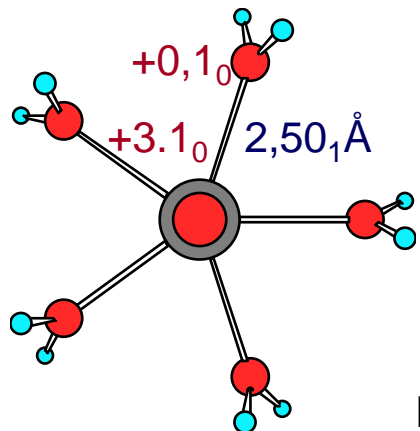
between different scientific fields, *i.e.* Reference states ... $e^-$  notation

**Ab initio calculations**

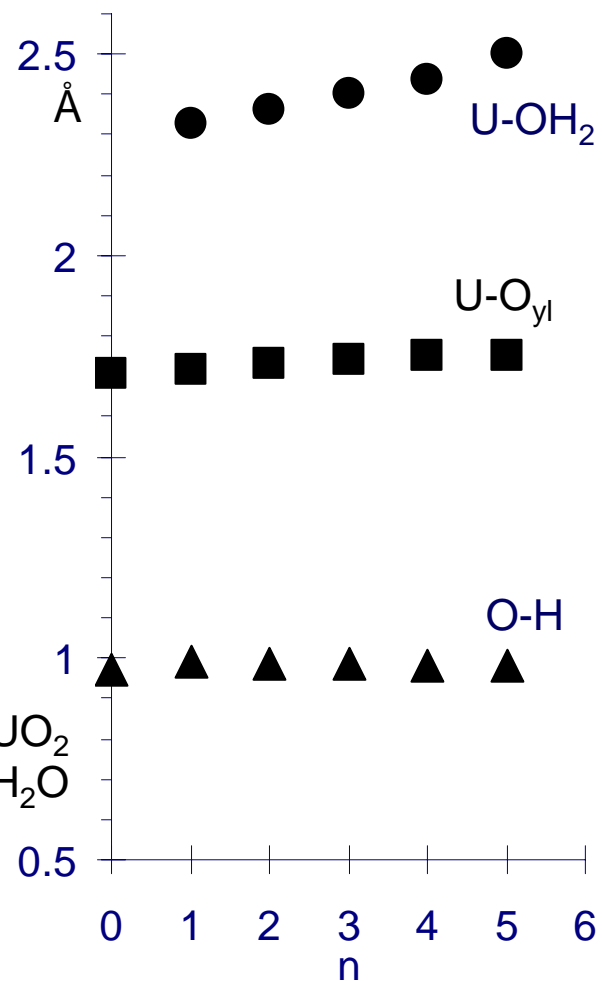
# UO<sub>2</sub><sup>2+</sup> hydrolysis, an ab initio study



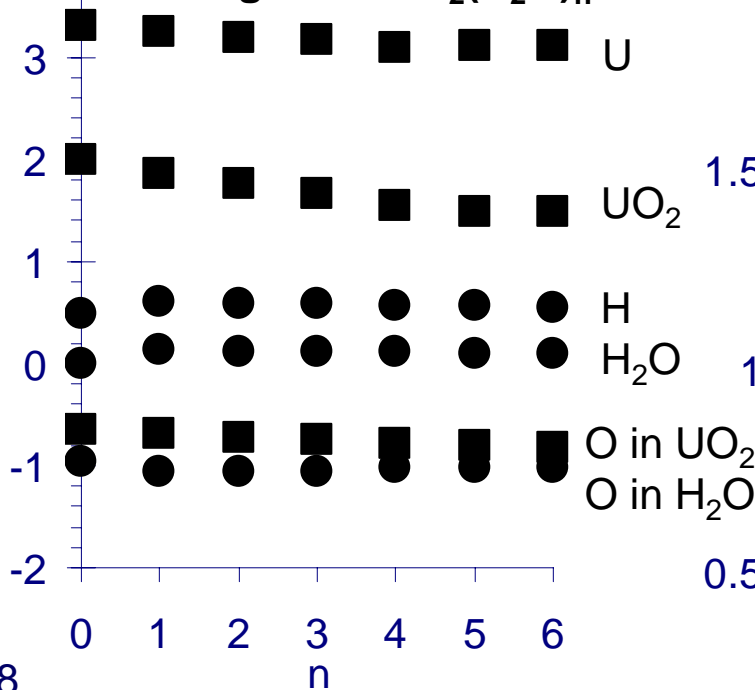
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Distances in UO<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub><sup>2+</sup>



NBO charges in UO<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub><sup>2+</sup>



Expected trends are obtained from ab initio calculations for bonding distances, electronic configurations and (NBO) charges.

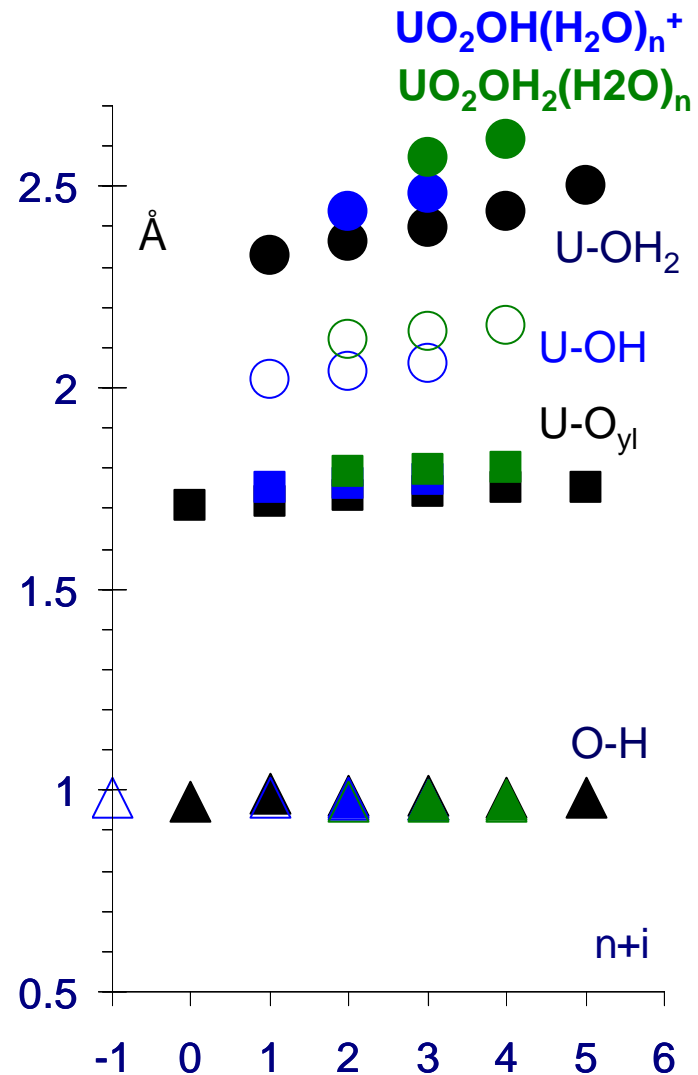
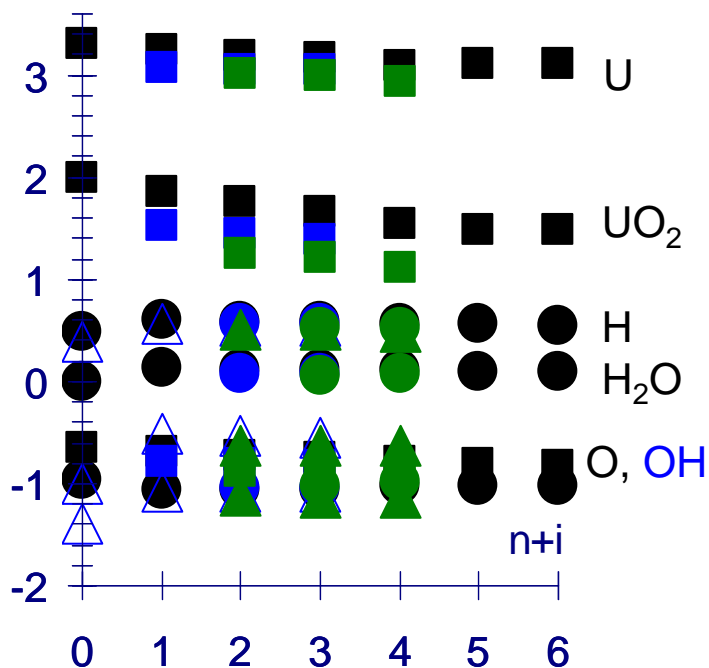
B3LYP, Gaussian 98

# UO<sub>2</sub><sup>2+</sup> hydrolysis, an ab initio study



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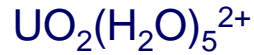
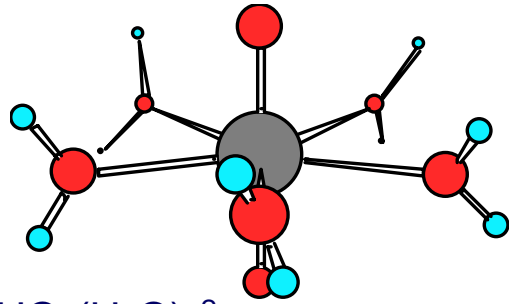
B3LYP, Gaussian 98



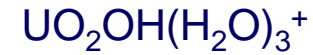
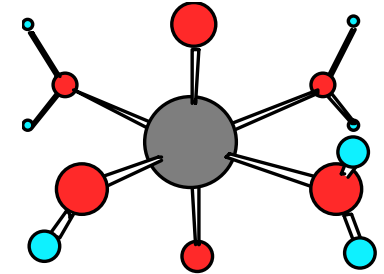
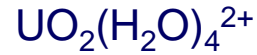
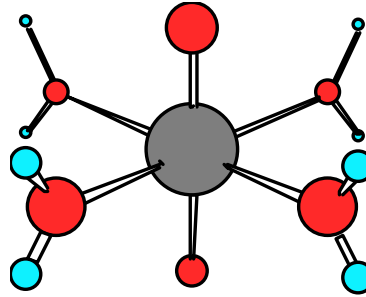
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# UO<sub>2</sub><sup>2+</sup> hydrolysis, an ab initio study

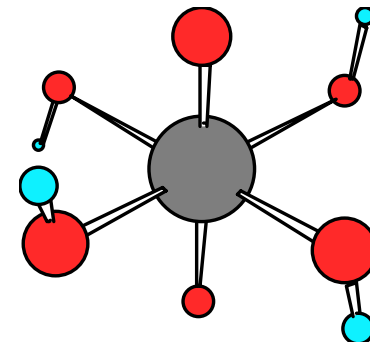
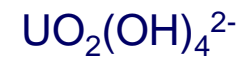
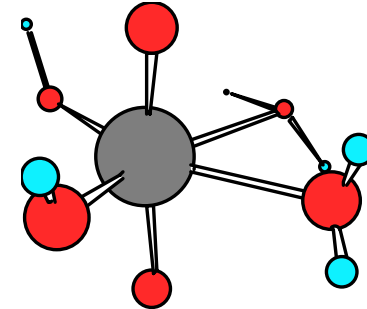
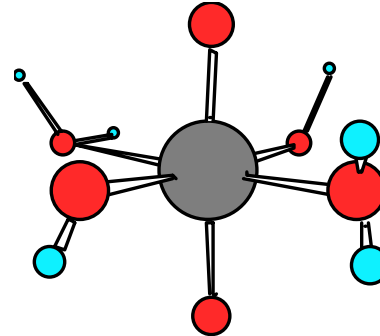
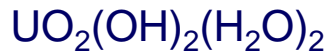
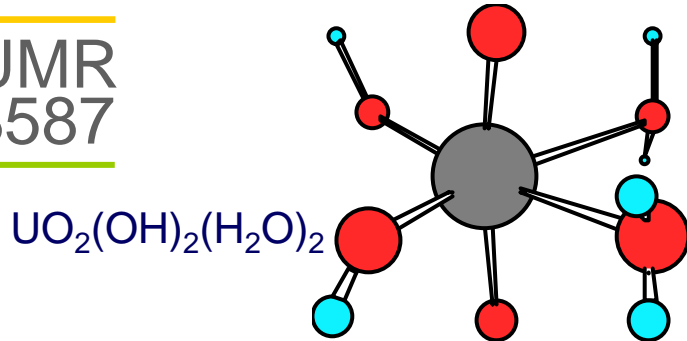
cea



## geometries

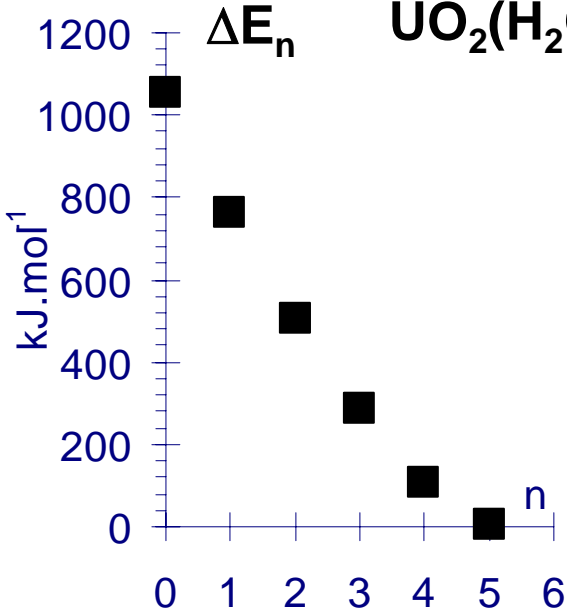


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# UO<sub>2</sub><sup>2+</sup> hydrolysis, an ab initio study



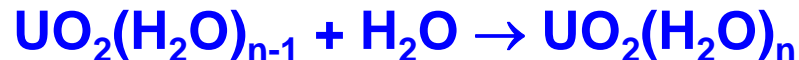
➔ **Temperature (and other) corrections:**

$$G_{n,\text{geom}}^\# = E_{n,\text{geom}} + \delta_{\text{vib},n,\text{geom}} (+ \delta_{\text{PCM}} + \dots)$$

➔ **Several geometries (mixing term):**

$$G_n^\# = \sum_{\text{geom}} \chi_{n,\text{geom}} (G_{n,\text{geom}}^\# + R T \ln \chi_{n,\text{geom}})$$

➔ **Several stoichiometries, typically:**



$$\Delta_r G = R T \ln |\text{H}_2\text{O}|_{1/2}$$

$$= G_{\text{UO}_2(\text{H}_2\text{O})_i^{2+}} - G_{\text{H}_2\text{O}} - G_{\text{UO}_2(\text{H}_2\text{O})_{i-1}^{2+}} = -R T \ln K$$

$$K = \frac{|\text{UO}_2(\text{H}_2\text{O})_i^{2+}|}{|\text{UO}_2(\text{H}_2\text{O})_{i-1}^{2+}| |\text{H}_2\text{O}|} = \frac{1}{|\text{H}_2\text{O}|_{1/2}}$$

where  $|\text{H}_2\text{O}| = a_{\text{H}_2\text{O}}, [\text{H}_2\text{O}(\text{l})]$  or  $P_{\text{H}_2\text{O}(\text{g})}$

$$\text{Similarly } K = \frac{[\text{UO}_2\text{OH}^+(\text{aq})][\text{H}^+(\text{aq})]}{[\text{UO}_2^{2+}(\text{aq})]} = [\text{H}^+(\text{aq})]_{1/2}$$

B3LYP, Gaussian 98



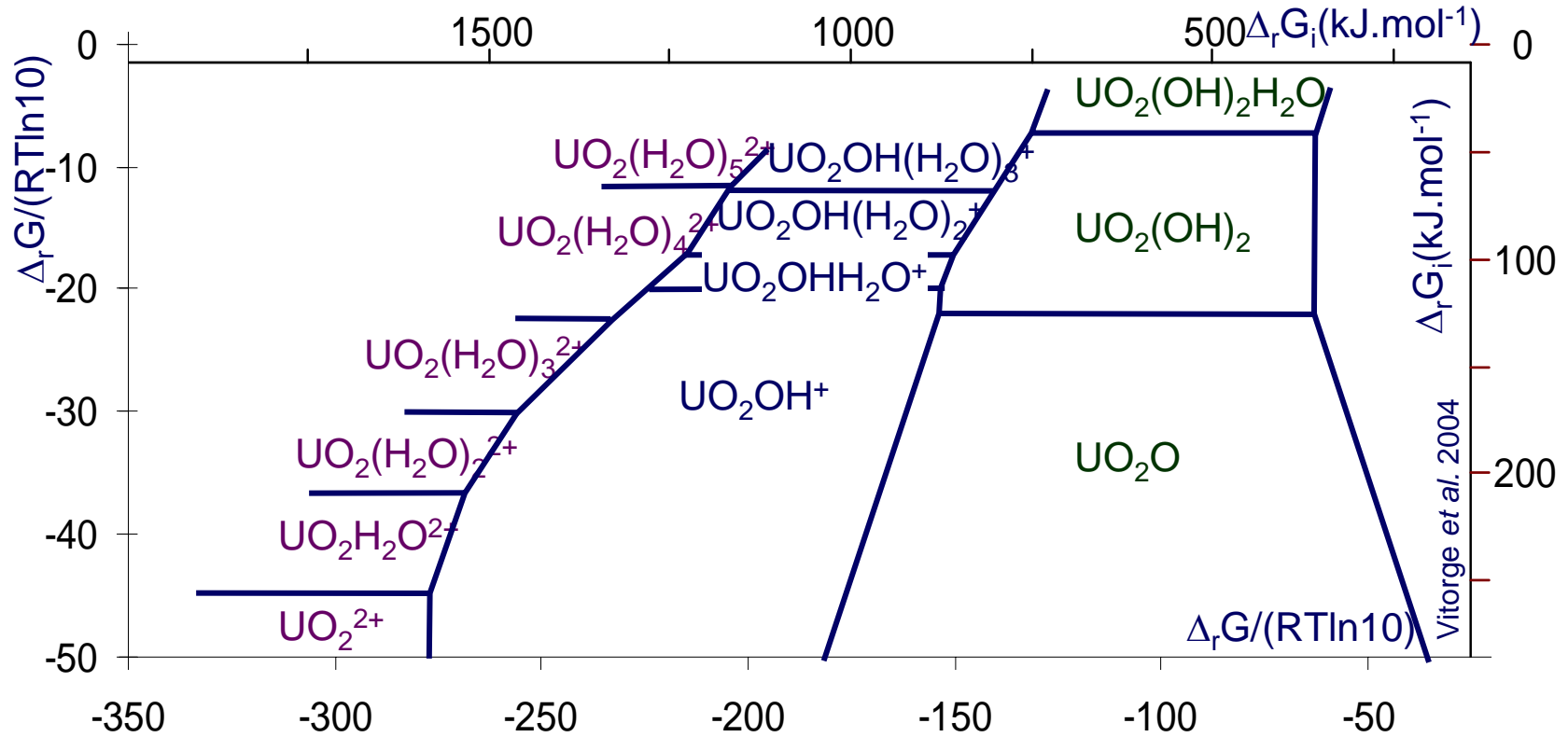
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# UO<sub>2</sub><sup>2+</sup> hydrolysis, an ab initio study stability domains



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B3LYP, Gaussian 98, 25°C