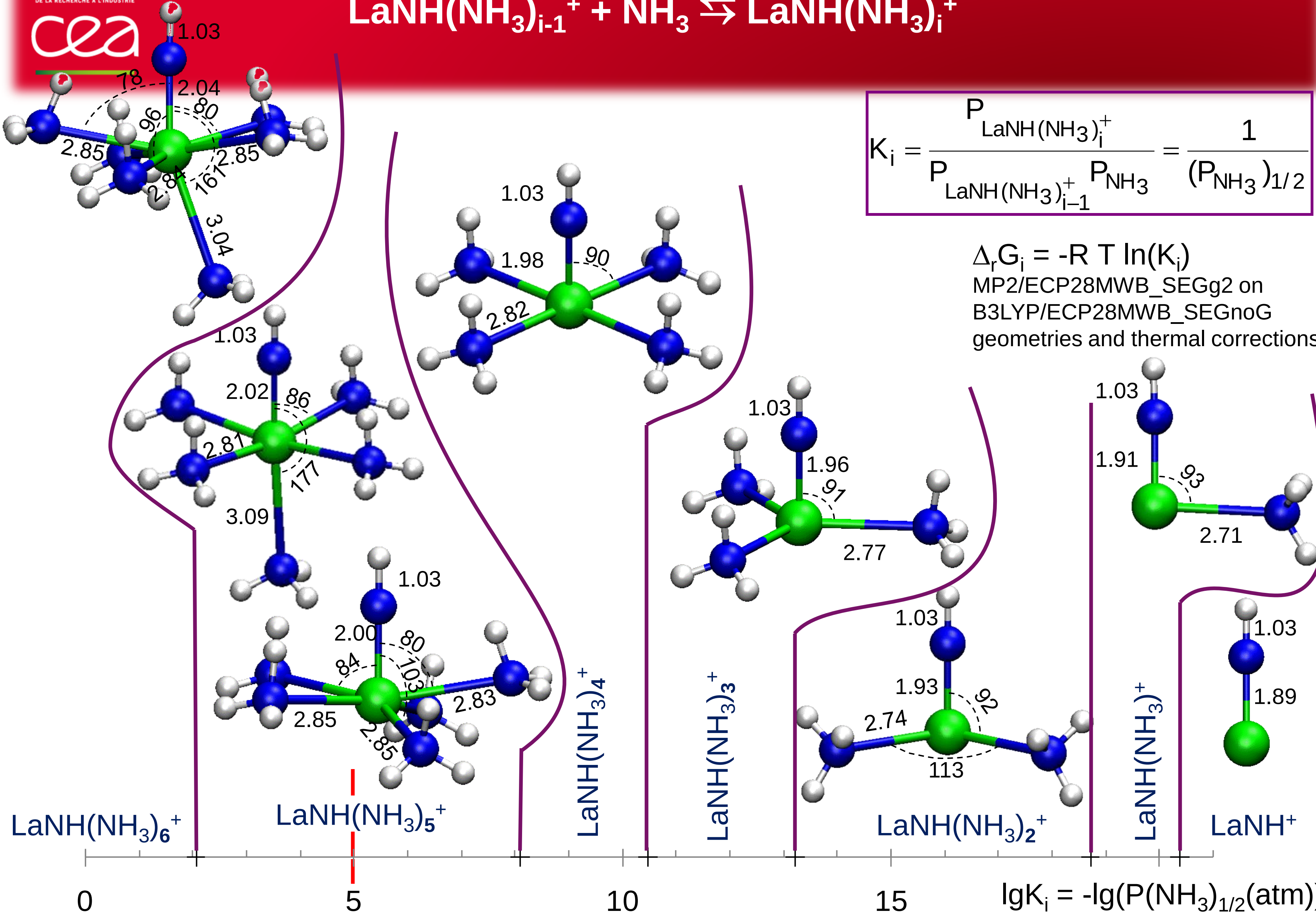
$LaNH(NH_3)_{i-1}^+ + NH_3 \leftrightarrows LaNH(NH_3)_i^+$

$$K_i = \frac{P_{LaNH(NH_3)_i^+}}{P_{LaNH(NH_3)_{i-1}^+} P_{NH_3}} = \frac{1}{(P_{NH_3})_{1/2}}$$

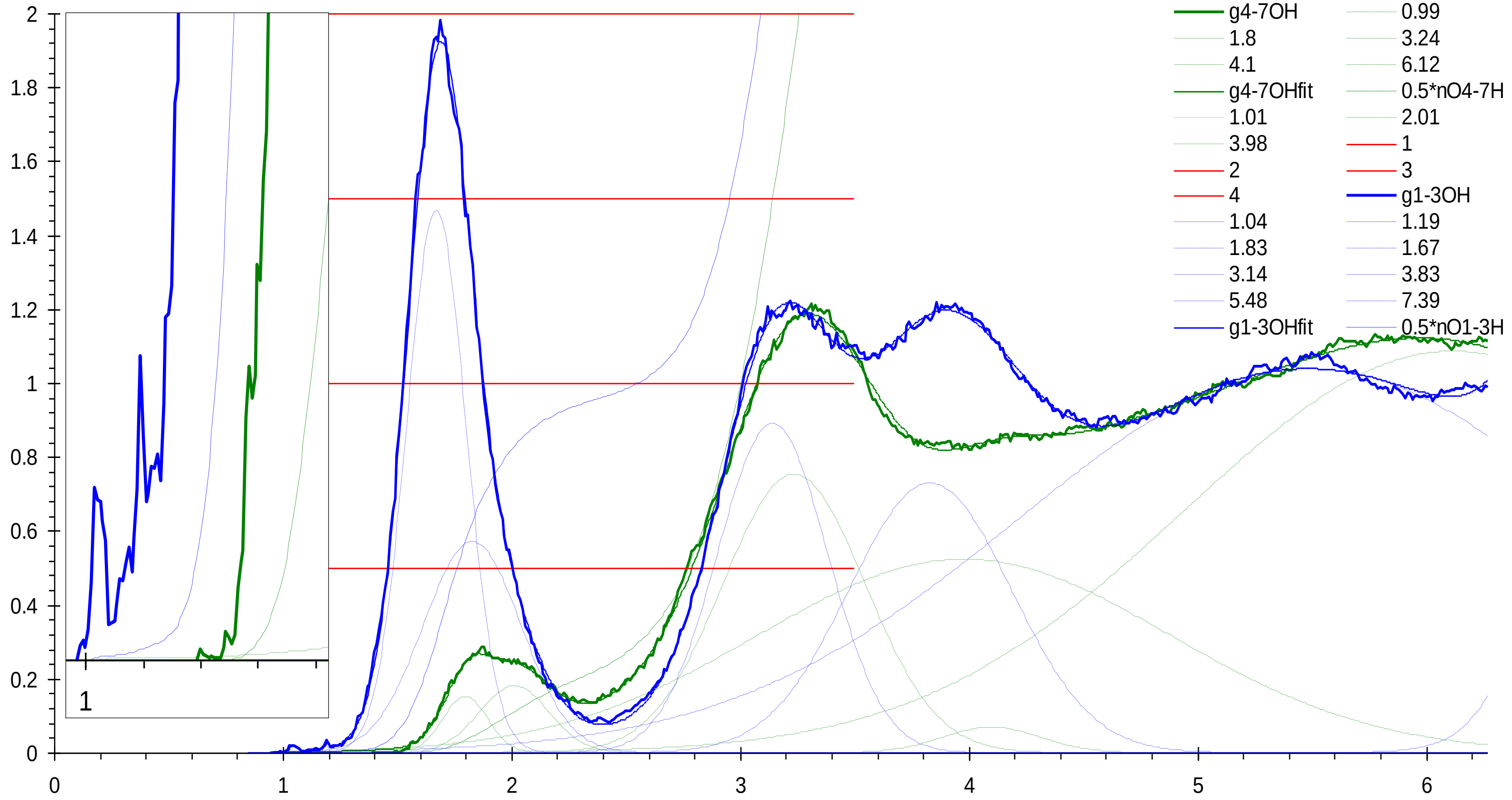
$\Delta_r G_i = -R\ T\ \ln(K_i)$

MP2/ECP28MWB_SEGg2 on B3LYP/ECP28MWB_SEGnoG geometries and thermal corrections



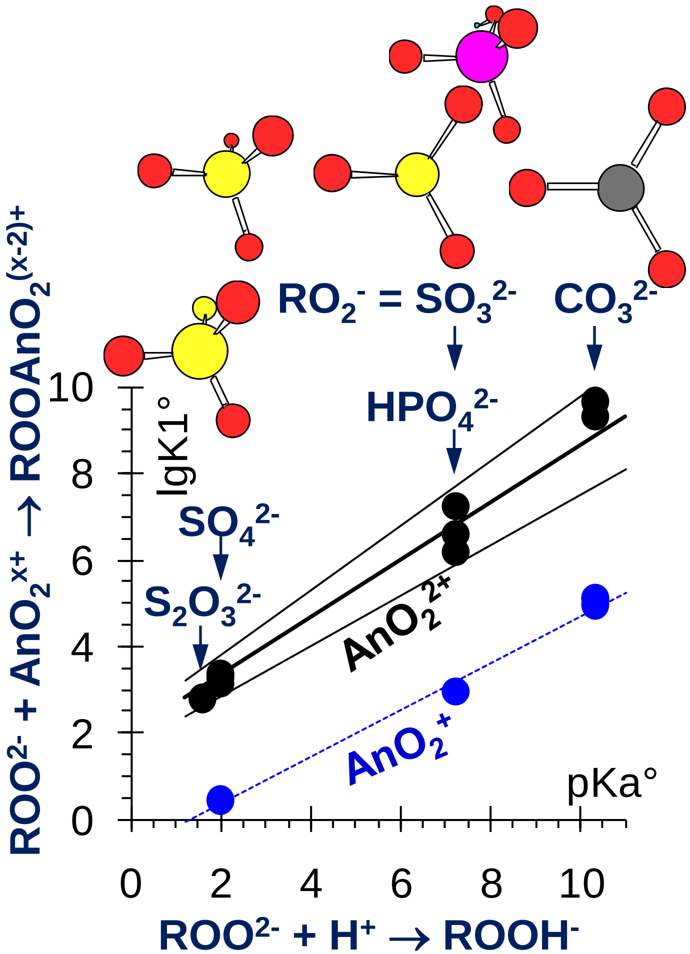
Exchanges of protons: O-H RDF for OH⁻ and OH$_2$ in the first coordination sphere of La(OH)$_3$(OH$_2$)$_4$

Solution



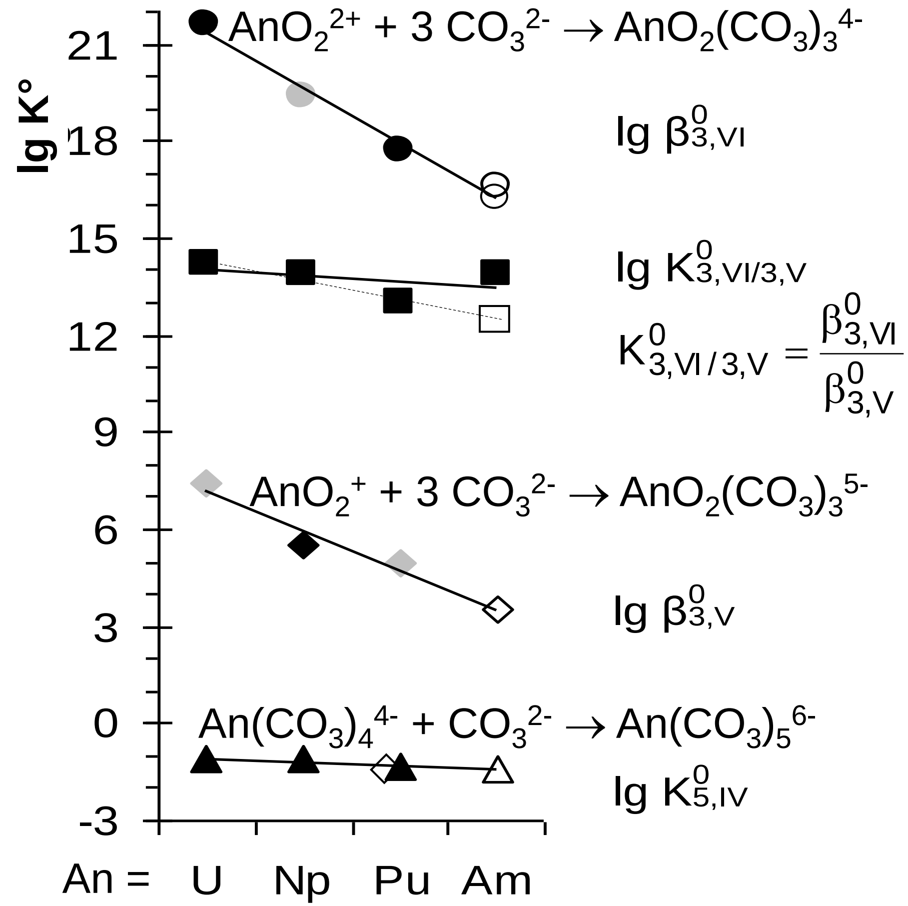
Linear correlations for complexing constants of actinoids

ROO^{2-} basic and complexing strenghts



Phrommavanh, *et al.* Migration'05, Vitorge *et al.* C.R.Acad.Sci. Chim. (2007) 978. See also Carbonaro *et al.* Geochim. Cosmochim. (2011) 2499 and Ref.s therin for similar correlations

CO_3^{2-} limiting complexes of analogous ions



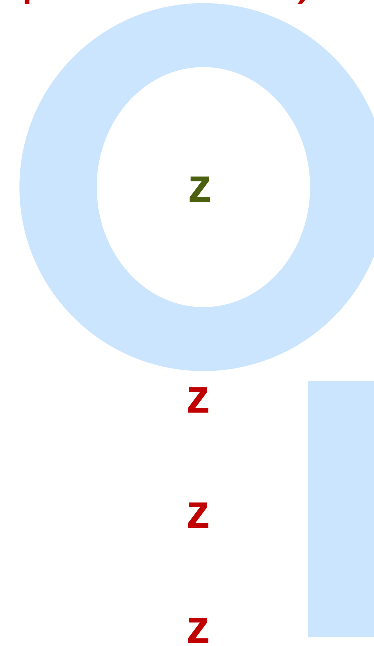
Capdevila, *et al.* J. Radioanal. Nucl. Chem. (1990) 403
Capdevila, *et al.* Radiochim. Acta. (1996) 93
Capdevila, *et al.* Czech. J. Phys. (1999) 603

Non-ideality:

Activity coefficients (γ) in aqueous solution (Debye Hückel)

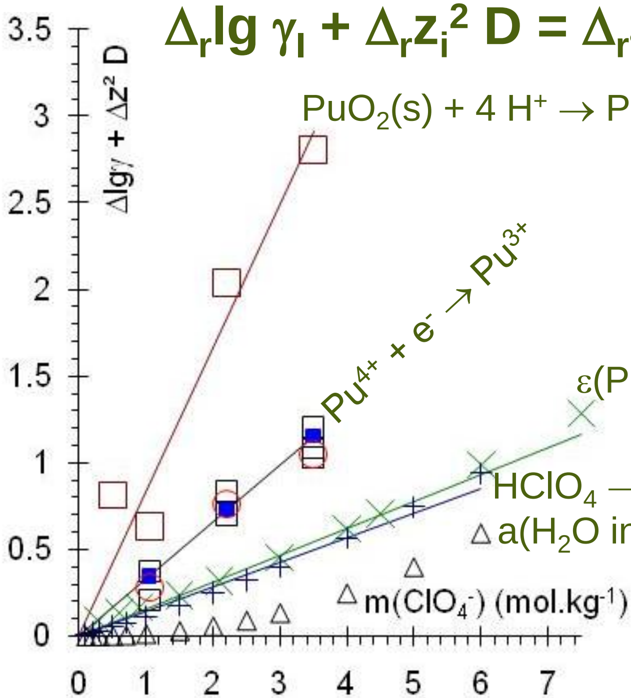
Surface complexation formula (Helmholtz Gouy Chapman Stern)

both based on Boltzmann Poisson equation

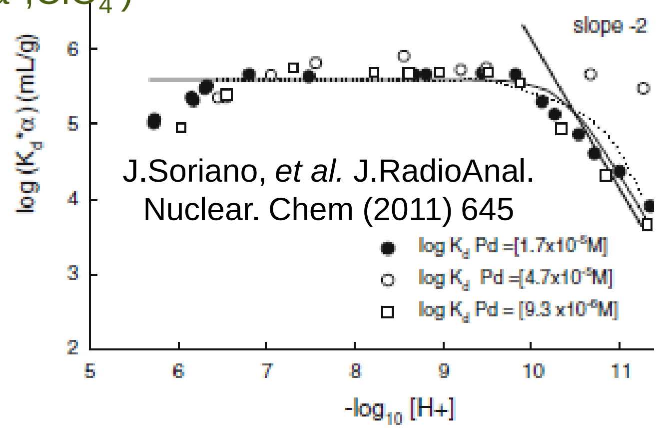


SIT formula

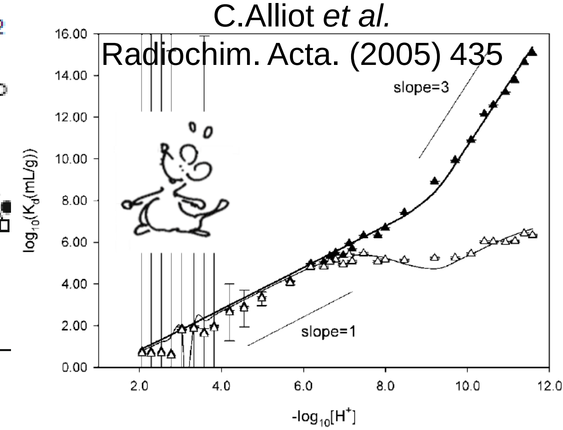
$$\Delta_r \lg \gamma_l + \Delta_r z_i^2 D = \Delta_r \varepsilon_{l,j}\, m_j$$



C.Riglet *et al.* Radiochim. Acta (1989) 85
H.Capdevila *et al.* Radiochim. Acta (1992) 45
H.Capdevila *et al.* Radiochim. Acta (1995) 51
H.Capdevila *et al.* Radiochim. Acta (1998) 11
P.Vitorge *et al.* XXXIX Congreso Mexicano de Quimica (2004) Mérida, Yucatán (Mexico)
P.Vitorge *et al.* Actualité Chim. (2005), 285-6, 52



J.Soriano, *et al.* J.RadioAnal. Nuclear. Chem (2011) 645



C.Alliot *et al.* Radiochim. Acta. (2005) 435

Solid solutions or mixtures, 2 equivalent thermodynamic approaches.

The **(set of 2)** equations are known for the simplest **$AB_{b(1-x)}C_{cx}$** solid solution

$$\begin{cases} K_{s,B} = \dfrac{[A^{z_A}][B^{z_B}]^b}{(1-x)^b} \text{ for : } \overline{AB_b} \Leftrightarrow A^{z_A} + b\,B^{z_B} \\ K_{s,C} = \dfrac{[A^{z_A}][C^{z_C}]^c}{x^c} \text{ for : } \overline{AC_c} \Leftrightarrow A^{z_A} + c\,C^{z_C} \end{cases}$$

$b = -z_B/z_A$ and
$c = -z_c/z_A$ for electro-neutrality.
Upperlined species are in the mixture.

No extra thermodynamic formula is needed, they can equivalently be written:

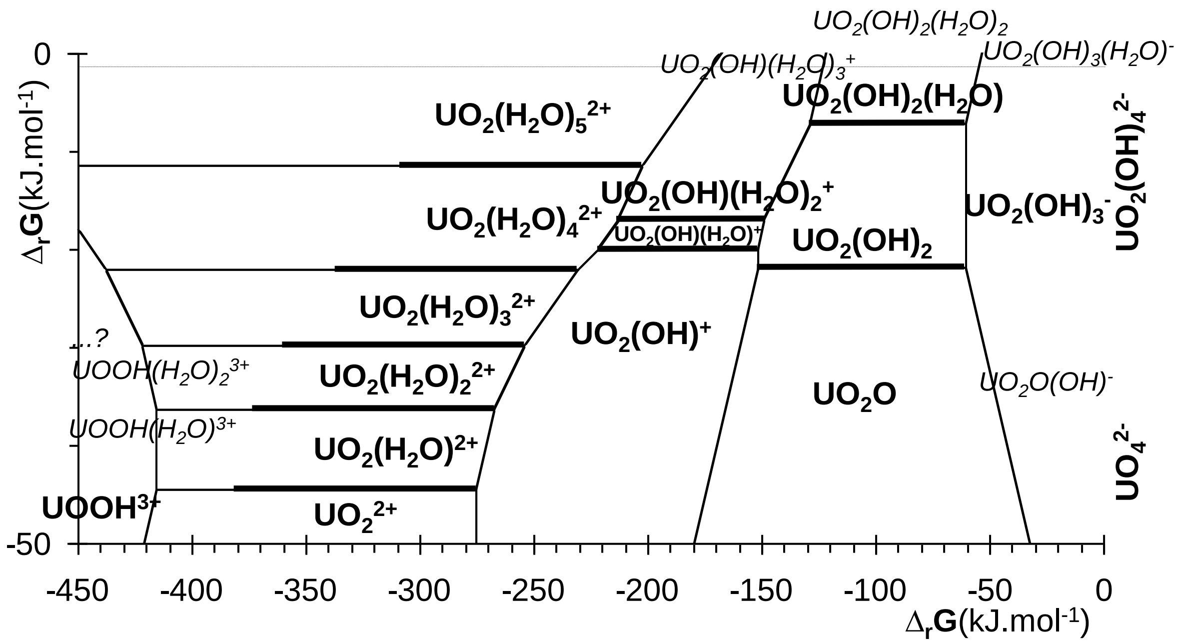
P.Vitorge (2008)
CEA-R-6193

$$\begin{cases} K_{s,B}^{1-x} K_{s,C}^{x} = \dfrac{[A^{z_A}][B^{z_B}]^{b(1-x)}[C^{z_C}]^{c\,x}}{(1-x)^{b(1-x)}\,x^{c\,x}} \text{ for : } AB_{b(1-x)}C_{cx} \Leftrightarrow A^{z_A} + b(1-x)B^{z_B} + c\,x\,C^{z_C} \\ \dfrac{K_{s,C}}{K_{s,B}} = \dfrac{(1-x)^b\,[C^{z_C}]^c}{x^c\,[B^{z_B}]^b} \quad \text{ for : } b\,B^{z_B} + c\,\overline{C^{z_C}} \Leftrightarrow b\,\overline{B^{z_B}} + c\,C^{z_C} \end{cases}$$

Is the product more stable when $\Delta_r G$ < 0?

	log$_{10}$K	$\Delta_r G$ (kJ.mol^{-1})
$UO_2^{2+}(aq) + H_2O(l) \rightarrow UO_2OH^{+}(aq) + H^{+}(aq)$	-5.2_5	$+30._0$
$UO_2^{2+}(aq) + HO^{-}(aq) \rightarrow UO_2OH^{+}(aq)$	$+8.7_5$	$-50._0$

UO_2^{2+} H_2O HO^-



0
-50
ΔrG(kJ.mol-1)
UO2(OH)2(H2O)2
UO2(OH)(H2O)3+
UO2(OH)3(H2O)-
UO2(OH)2(H2O)
UO2(H2O)52+
UO2(OH)(H2O)2+
UO2(H2O)42+
UO2(OH)(H2O)+
UO2(OH)2
UO2(OH)3-
UO2(OH)42-
UO2(H2O)32+
UO2(OH)+
...?
UOOH(H2O)23+
UO2(H2O)22+
UO2O
UO2O(OH)-
UOOH(H2O)3+
UO2(H2O)2+
UO42-
UOOH3+
UO22+
-450
-400
-350
-300
-250
-200
-150
-100
-50
0
ΔrG(kJ.mol-1)

IUPAC Periodic Table of the Elements

Key:

atomic number Symbol name standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen [1.007; 1.009]																	2 He helium 4.003
3 Li lithium [6.938; 6.997]	4 Be beryllium 9.012											5 B boron [10.80; 10.83]	6 C carbon [12.00; 12.02]	7 N nitrogen [14.00; 14.01]	8 O oxygen [15.99; 16.00]	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium 24.31											13 Al aluminium 26.98	14 Si silicon [28.08; 28.09]	15 P phosphorus 30.97	16 S sulfur [32.05; 32.08]	17 Cl chlorine [35.44; 35.46]	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38(2)	31 Ga gallium 69.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.96(3)	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.96(2)	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57-71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium [204.3; 204.4]	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium		114 Fl flerovium		116 Lv livermorium		

57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
89 Ac actinium	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

$UO_2OH(H_2O)_2^+ + H_2O \leftrightarrow UO_2OH(H_2O)_3^+$
Comparing DFT calculations with mass spectrometry results

Pierre Vitorge, Colin Marsden

In the mass spectometer [03GRE/GIA] :

RT ln10 lg $P(H_2O/atm)$ = -5.71 x **8.74** = -50 kJ.mol^{-1}

Interpreting mass spectra : $k_{\rightarrow} / k_{\leftarrow} = \mathbf{K}$

RT ln10 lg **K** = -5.71 x **9.75** = -56 kJ.mol^{-1}

DFT calculations

RT ln10 lg $P(H_2O/atm)$ = -5.71 x **11.40** = -65 kJ.mol^{-1}

$$P_{(H_2O)_{1/2}} = \frac{1}{K} = \frac{[UO_2OH(H_2O)_2^+]}{[UO_2OH(H_2O)_3^+]} P_{H_2O}$$

$\Delta_r G(\text{kJ.mol}^{-1}) = -R\,T \ln \mathbf{K}$

assuming thermal equilibrium was achieved...

25°C, 1atm. B3LYP