Actinide chemistry in aqueous solutions for waste disposal and environmental studies

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CEA – Université d’Evry -CNRS
**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 ...$e^-$ notation

**Ab initio calculations**
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Ab initio calculations
Equilibration of Stripa groundwaters with minerals

Modelled by using mass action law

Chemical analysis on Stripa groundwaters

Calculated from an evolution model essentially based on charge balance.

Solubility products $K_s$'s, have been re-fitted on the experimental observations; however, these $K_s$ changes are within usual uncertainties for solid compounds formed at low temperature: less than 0.6 log$_{10}$ unit (i.e. 0.3 kJ.mol$^{-1}$ on $\Delta_r G$) as compared to Ref (Michard G. (1983) EUR 8590).

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

Solubility product

Modelled by using mass action law

$$\text{NaNpO}_2\text{CO}_3(s) \rightarrow \text{Na}^+ + \text{NpO}_2^{+} + \text{CO}_3^{2-}$$

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

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

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.

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

**Complexing constants**

Modelled by using **mass action law**

---

$$\text{NpO}_2\text{CO}_3^{3-} + \text{Na}^+ \rightarrow \text{NaNpO}_2\text{CO}_3(s)$$

$$\text{NpO}_2\text{CO}_3^{3-} + \text{Na}^+ \rightarrow \text{NaNpO}_2\text{CO}_3(s)$$

**Complexing constants**

Modelled by using the mass action law

$$\text{NaNpO}_2\text{CO}_3(s) \rightarrow \text{Na}^+ + \text{NpO}_2\text{CO}_3^{1-2i} + (1-i)\text{CO}_3^{2-}$$

$$K_{si} = [\text{Na}^+] [\text{NpO}_2\text{CO}_3^{1-2i}] [\text{CO}_3^{2-}]^{1-i}$$

$$\beta_i = \frac{[\text{NpO}_2\text{CO}_3^{1-2i}]}{[\text{Na}^+] [\text{CO}_3^{2-}]^{1-i}}$$

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

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**Sensitivity analysis**

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**DEN Saclay DPC/LSRM**

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**UFR 8587**
Np(V) solubility in CO$_3^{2-}$ / HCO$_3^-$ / CO$_2$ aqueous solutions
Precipitation of a new solid phase

Other stoichiometries of compounds have been proposed in literature$^1$ for Na/NpO$_2$

Vitorge P., Capdevila H., CEA-R-5793 (1998)
**Np(V) solubility in CO$_3^{2-}$/HCO$_3^{-}$/CO$_2$ aqueous solutions**

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

- slope (= \(x\))

\[
\text{lg}[\text{Np(V)}_{\text{total}}] = a \times \text{lg}[\text{CO}_3^{2-}] + b
\]

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

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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.

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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Ab initio calculations
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

Dissolution Reaction
\[
\text{Na}_{2(1-y)}(\text{NpO}_2)_{2y}\text{CO}_3 \rightarrow 2(1-y)\text{Na}^+ + 2y \text{NpO}_2^+ + \text{CO}_3^{2-} \quad (1)
\]

Ionic Exchange Reaction
\[
\text{Na}^+(s) + \text{NpO}_2^+(aq) \rightarrow \text{Na}^+(aq) + \text{NpO}_2^+(s) \quad (2)
\]

Mass Action Law for Reaction(2):
\[
D = \frac{[\text{Na}^+(s)] [\text{NpO}_2^+(aq)]}{[\text{Na}^+(aq)] [\text{NpO}_2^+(s)]} = \frac{2(1-y)[\text{NpO}_2^+(aq)]}{2y [\text{Na}^+(aq)]}
\]

\( D = K_{s1} / K_{s0} \) is obtained by linear combinations of chemical potentials
where \( K_{sy} = [\text{Na}^+(aq)]^{2(1-y)} [\text{NpO}_2^+(aq)]^{2y} [\text{CO}_3^{2-}(aq)] \)
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 \((n_X = \text{number of mole for Species } X)\):

\[
(dn_X)_y = v_X (dn_{A}^{z_A})_y \quad v_A = 1, \quad v_B = b(1-y), \quad v_C = c y, \quad v_X(s) = -v_X
\]

\[b = -z_A/z_B, \quad c = -z_A/z_C, \quad AB_{b(1-y)}C_{c y}(s) = A^{Z_A}(s) + b(1-y)B^{Z_B}(s) + c y C^{Z_C}(s)\]

Dissolution Reaction

\[A^{Z_A}(s) + b(1-y)B^{Z_B}(s) + c y C^{Z_C}(s) \rightarrow A^{Z_A} + b(1-y)B^{Z_B} + c y C^{Z_C} \quad (1)\]

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

\[v'_A = 0, \quad v'_B = b, \quad v'_C = c, \quad v_X(s) = -v_X\]

Ionic Exchange Reaction

\[b B^{Z_B} + c C^{Z_C}(s) \rightarrow b B^{Z_B}(s) + c C^{Z_C} \quad (2)\]

\[
dn_X = d(n_X n_{A}^{Z_A}) = v_X (dn_{A}^{Z_A})_y + n_{A}^{Z_A} v'_X dy + n_{A}^{Z_A} \left(\sum (\mu_X v_X) (dn_{A}^{Z_A})_y\right) dy
\]

\[
\frac{[A^{Z_A}][B^{Z_B}]^{b(1-y)}[C^{Z_C}]^{cy}}{(1-y)^{(1-y)} y^{cy}} = K_{s0}^{-1-y} K_{s1}^{-y} \quad \text{and} \quad \frac{(1-y)^{b} [C^{Z_C}]^{c}}{[B^{Z_B}]^{b} y^{c}} = \frac{K_{s1}}{K_{s0}}
\]

0 < y < 1

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Thermodynamics of solid solutions

Dissolution Reaction ↔ Ionic Exchange Reaction

Dissolution Reaction

\[ \text{A}^{zA}(s) + b(1-y)\text{B}^{zB}(s) + c y \text{C}^{zC}(s) \rightarrow \text{A}^{zA} + b(1-y)\text{B}^{zB} + c y \text{C}^{zC} \]  

(1)

Differentiating:

\[ \frac{d\nu_x}{dy} = \nu'_x \]

Integral calculus:

\[ \nu_x = \int \nu'_x \, dy \]

Ionic Exchange Reaction

\[ b \text{B}^{zB} + c \text{C}^{zC}(s) \rightarrow b \text{B}^{zB}(s) + c \text{C}^{zC} \]

(2)

\[ K_{\text{ex}} = \frac{K_{s1}}{K_{s0}}, \text{ where } K_{\text{ex}} \text{ is the equilibrium constant for a ionic exchange equilibrium.} \]
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Ab initio calculations
H⁺ / NpO₂⁺ 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° is NpO₂⁺ partition coefficient.

α = [NpO₂]_t / [NpO₂⁺]

is calculated from complexing constants

Slope 1 evidences Ionic Exchange Equilibrium

NpO₂⁺(aq) + H⁺(s) → NpO₂⁺(s) + H⁺(aq)

K_ex = \frac{[NpO₂⁺(s)] [H⁺(aq)]}{[NpO₂⁺(aq)] [H⁺(s)]} = K_d \frac{[H⁺(aq)]}{[H⁺(s)]} \approx K_d \frac{[H⁺(aq)]}{CEC}

K_ex = \frac{K_{s1}}{K_{s0}}

\text{Slope 1: } \log K_d° = \log K_d - \log α

y = 1.0067x - 3.8642

R^2 = 0.988

25°C

1 M NaClO₄

0.2M [CO₃]₀

\text{CEC}
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Ab initio calculations
Activity coefficients using SIT formula at 25°C for Reaction Pu$^{4+} + e^- \rightarrow$ Pu$^{3+}$

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

\[ D = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \text{ at } 25°C \]

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

Reference state \( K^{\circ} = K(I \rightarrow O) \)

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

\[ \Delta_r G = -RT \ln K_{Pu^{4+/Pu^{3+}}} = -F E_{Pu^{4+/Pu^{3+}}} \]

\( R \) is the molar gas constant, \( F \) the Faraday constant

\[ \Delta_r G = -RT \ln K_{Pu^{4+/Pu^{3+}}} = -F E_{Pu^{4+/Pu^{3+}}} \]

measured at 25°C

interpolated at 25°C from data at 5 to 65°C

Activity coefficients
SIT formula at 25°C for the highly charged species Pu$^{4+}$

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

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

PuO$_2$(s),nH$_2$O + (4+n)H$^+$ → Pu$^{4+}$ + 4 H$_2$O

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

Pu$^{4+}$ + e$^- \rightarrow$ Pu$^{3+}$

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

Checking by using Thermodynamic Cycle

$$\Delta_r \varepsilon_{\text{Pu}^{4+}/\text{Pu}^{3+}} = \varepsilon_{\text{Pu}^{3+}} - \Delta \varepsilon_{\text{PuO}_2} - 4 \varepsilon_{\text{H}^+,\text{ClO}_4^-}$$

Auxiliary data from isopiestic measurements

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

Activity coefficients

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

$\varepsilon_{M^+,X^-}$ (mol.kg$^{-1}$)

$\varepsilon_{Na^+,X^-}$ (mol.kg$^{-1}$)

$\varepsilon(M^{+3},X^-)$ (kg.mol$^{-1}$)

$\varepsilon$ (kg.mol$^{-1}$)

$z_{eff}/r$(Å)

La$^{3+}$, Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Yb$^{3+}$, Tl$^{3+}$, Ag$^{+}$, K$^{+}$, Rb$^{+}$, Cs$^{+}$, Li$^{+}$, H$^{+}$, NpO$_2^+$, NH$_4^+$, ClO$_4^-$, M$^{4+}$, M$^{3+}$, M$^{2+}$, M$^+$

UMR 8587

Pierre Vitorge et al. (France)

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3 al 7 de octubre del 2004 en Mérida, Yucatán
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Ab initio calculations
Activity coefficients at 25°C: conclusion

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

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).
It appears that

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

Despite this corresponds to the model used to obtained 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**
\[ \psi_{\text{total}} - \psi_{\text{Coulomb}} = \psi_{\text{excess}} \]
\[ \psi = \text{electrostatic potential} \]

**Debye-Hückel Formula**
+ steric exclusion
+ ion pair interactions

**Charge**
\( z \)

**Counter-ions atmosphere**

**Debye distance**
\[ \text{constant} / (\text{ionic strength})^{1/2} \]

**Charges**
\( z \)
\( z \)
\( z \)
\( z \)
\( z \)

**Surface Complexation Formula**
\[ \psi_{\text{total}} \]
**Gouy and Chapman Formula**
+ supplementary layer(s)

The model are different, however, are the physical phenomena actually different?
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**Ab initio calculations**
The surfaces of compounds are ionised, when in contact with water for typically oxides, hydroxides, silicate, apatite compounds:

- \( \text{Solid-O,}_n(\text{H}_2\text{O})_n + \text{H}^+(\text{aq}) \rightarrow \text{Solid-OH}^+ + n \text{H}_2\text{O} \)
- \( \text{Solid-OH}^++ \text{H}^+(\text{aq}) \rightarrow \text{Solid-OH}_2^{2+} \)
- \( \text{Solid-OH} + n \text{H}_2\text{O} \rightarrow \text{Solid-O}_n(\text{H}_2\text{O})_n^+,\text{H}^+ \)
- \( \text{Solid-OH} + \text{H}^+(\text{aq}) \rightarrow \text{Solid-OH}_2^+ \)

This is at the origin of the surface charges (and double layer) and ionic exchanges typically:

- \( \text{Solid-OH} + \text{Na}^+(\text{aq}) \rightarrow \text{Solid-ONa} + \text{H}^+(\text{aq}) \)
- \( \text{Solid-OH} + \text{Am(OH)}_3(\text{aq}) \rightarrow \text{Solid-OAm(OH)}_2 + \text{H}_2\text{O}(l) \)

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?
Surface chemistry:
Pyrite (FeS$_2$) oxidative dissolution... and disproportionation

FeS$_2$(s) $^{2(\text{n}+1)}$e$^-$ $\rightarrow$ 2 S$^{(\text{n})}$ -Fe$^{2+}$
2(1-n/n')S$^{(0)}$ $\rightarrow$ 2n/n' S$^{(n')}$$\rightarrow$ 2n/n' S$^{(\text{VI})}$

\[
\begin{array}{c|c|c|c|c|c|c|c|c}
\text{oxidation number, n} & -2 & -1 & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\
\end{array}
\]

FeS$_2$ $\rightarrow$ 2 S$^{(\text{n})}$ + Fe$^{2+}$ + 2(n+1)e$^-$
2{S$^{(\text{n})}$ $\rightarrow$ (1-n/n')S$^{(0)}$ + n/n' S$^{(n')}$}
2n/n' {S$^{(n')}$ $\rightarrow$ S$^{(\text{VI})}$ + (6-n')e$^-$}

- S$_4$O$_6$$^{2-}$ species are formed in the course of Oxidative Pyrite Dissolution,
- they are not stable in aqueous solutions
- are they stable at the surface?

Are the sorption properties of Pyrite analogous to those of O containing compounds?

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Ab initio calculations
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
Pourbaix diagram of Pu

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

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

\[ \sim \log\left(\frac{\beta_{\text{VI/VI,hydrolysis}}}{\beta_{\text{VI,hydrolysis}}}\right) \]

\[ \Delta_r E(\text{Pu}) = \Delta_r E(\text{Pu}) \]

Ionic strength correction (SIT Formula)

\[ \Delta_r E = \Delta_r E \]

\[ E(\text{Pu}_{\text{VI/VI}}) \text{ in 1 M NaOH}^{1,2} \]

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

\[ \sim \log\left(\frac{\beta_{\text{VI/VI,hydrolysis}}}{\beta_{\text{VI,hydrolysis}}}\right) \]

\[ \Delta_r E(\text{Pu}) = \Delta_r E(\text{Pu}) \]

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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

 PuO^{2+x} = Pu(IV) + Pu(VI)

or

 PuO^{2+x} = Pu(IV) + Pu(V)


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Assuming

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or

\[ \text{PuO}_{2+x} = \text{Pu(IV)} + \text{Pu(V)} \]

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 PuO$_2^+$.

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

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Notation $e^-$

$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$

$\text{H}^+(aq) + e^- \rightarrow 0.5 \text{H}_2(g)$

Notation for Electrochemistry
Standard Hydrogen Electrode (SHE)

$\text{Ag}^+(aq) + 0.5 \text{H}_2(g) \rightarrow \text{Ag}(s) + \text{H}^+(aq)$

Notation for Thermodynamics
Corresponding equilibrium constant

$K = \frac{[\text{red}]}{[\text{ox}]} a_{e^-}$

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

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

Corresponding $e^-$ activity

$0 = \Delta_r G_{\text{SHE}} = 0.5 \Delta_f G_{\text{H}_2(g)} - \Delta_f G_{\text{H}^+(aq)} - \Delta_f G_{e^-}$, also $0 = \Delta_f G_{\text{H}_2(g)}$ (Reference State)

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

similarly

and

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

$\implies$ $\text{Ag}^+(aq) \rightarrow \text{Ag}^+(s)$

Actual mechanism$^1$?

however this notation does not include charge balance in each phase

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⁻ notation

Ab initio calculations
UO$_2^{2+}$ hydrolysis, an ab initio study

**UO$_2$(H$_2$O)$_n^{2+}$**

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

**B3LYP, Gaussian 98**

**Charges: NBO**
- U: 3.30
- 5f: 2.5
- 6d: 0.45
- O: -0.65
- 2s: 1.9
- 2p: 4.4

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

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**Distances in UO$_2$(H$_2$O)$_n^{2+}$**

**U-O$_y$**

**O-H**

**U-OH$_2$**

**B3LYP, Gaussian 98**

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**Expected trends are obtained from ab initio calculations for bonding distances, electronic configurations and (NBO) charges.**
**UO₂²⁺ hydrolysis, an ab initio study**

**UO₂(OH)ₙH₂O)ₙ²⁻**

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**NBO charges in UO₂(H₂O)ₙ²⁺**

- **UO₂OH(H₂O)ₙ⁺**
- **UO₂OH₂(H₂O)ₙ**

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**Distances in UO₂(H₂O)ₙ²⁺**

- **UO₂OH(H₂O)ₙ⁺**
- **UO₂OH₂(H₂O)ₙ**

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**B3LYP, Gaussian 98**

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Pierre Vitorge et al.,

DEN Saclay DPC/LSRM

Actinide chemistry in aqueous solutions for waste disposal and environmental studies

XXXIX CONGRESO MEXICANO DE QUÍMICA

3 al 7 de octubre del 2004 en Mérida, Yucatán
Actinide chemistry in aqueous solutions for waste disposal and environmental studies

UO$_2^{2+}$ hydrolysis, an ab initio study

Umilities

B3LYP, Gaussian 98

UO$_2$(H$_2$O)$_5^{2+}$

UO$_2$(H$_2$O)$_4^{2+}$

UO$_2$(H$_2$O)$_3$OH$(H_2$O)$_2^+$

UO$_2$(OH)$_2(H_2$O)$_2$

UO$_2$(OH)$_3H_2$O$^-$

UO$_2$(OH)$_4^{2-}$

Pierre Vitorge et al. (France)

DEN Saclay DPC/LSRM

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**Temperature (and other) corrections:**
\[ G_{n,\text{geom}}^\# = E_{n,\text{geom}} + \delta_{\text{vib},n,\text{geom}} + \delta_{\text{PCM}} + \ldots \]

**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:**

\[
\begin{align*}
\Delta r G &= R T \ln |H_2O|^{1/2} \\
&= G_{UO_2(H_2O)^{2+}} - G_{H_2O} - G_{UO_2(H_2O)_{i-1}^{2+}} = -R T \ln K \\
K &= \frac{|UO_2(H_2O)_{i}^{2+}|}{|UO_2(H_2O)_{i-1}^{2+}| |H_2O|^{1/2}} \\
&= \frac{1}{|H_2O|^{1/2'}}
\end{align*}
\]

where \(|H_2O| = a_{H_2O}, [H_2O(l)] or P_{H_2O(g)}

Similarly \( K = \frac{[UO_2OH^+(aq)][H^+(aq)]}{[UO_2^{2+}(aq)]} = [H^+(aq)]^{1/2} \)
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Vitorge et al. 2004

B3LYP, Gaussian 98, 25°C

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