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

by Pierre Vitorge¹,²
Catherine Beaucaire², Colin Marsden³, Michael Descostes², Dominique You², Patrick Lovera², Hélène Capdevila⁴
(¹) UMR 8587 Université d’Evry-CNRS-CEA, pierre.vitorge(at)cea.fr.
(²) CEA DEN Saclay DPC/SECR, F91191 Gif sur Yvette cedex, France
(³) LPQ IRSAMC Université Paul Sabatier, 118 route de Narbonne, F31062 Toulouse cedex⁴, France
(⁴) CEA DEN Cadarache DTCD/SPDE, 13108 Saint-Paul-lez-Durance cedex, France

1. Introduction
The solubilities of radionuclides in groundwaters can be increased by the formation of soluble complexes, which also lowers their retention on surfaces of natural minerals and engineered barriers. This has been studied for managing radioactive wastes, typically for possible deep disposals, an option for long live radionuclides such as minor Actinides. Besides basic knowledge on redox, hydrolysis and complexing chemical equilibria of Actinides and analogue hard cations, these studies provided few methodological developments useful for many other elements, and for the chemical scientific community. In this paper, we outline some of these methodologies through examples for solution chemistry of Actinide chemistry.

Equilibrium Aqueous Speciation, the ratios of the soluble species is currently predicted by Thermodynamics, namely Mass Action Law as reflected by equilibrium constants K, at given temperature T, and pressure P. This is well established for ideal systems –typically at constant high ionic strength I– providing numerical values of K’s are known. In a first part we show examples in nature and in laboratory, where mass action law was used for interpreting experimental data, or for producing Gibbs energies of reactions ΔrG (=-RTlnK). We then indicate further Thermodynamics developments:

• activity coefficients for extrapolating to zero ionic strength, the standard state,
• solid solutions for predicting retention of trace elements; dissolution of solid solutions can be interpreted as reactions of two advancement variables, one of them typically for the corresponding ionic exchange equilibrium; conversely any ionic exchange equilibrium can be implicitly associated with the dissolution/precipitation reactions of the matrix supporting the ionic exchange sites,
• comparing semi-empirical formula used for activity coefficients and surface complexation, since they both derive from similar physical models.

When K values are not known, chemical analogies can be used for estimating them, as typically for the stabilities of PuO₂⁺ ions. Finally we discuss the using of molecular modelling and ab initio calculations for understanding solution coordination chemistry.

2. THERMODYNAMICS

2.1 Speciation
In this Section we illustrate Mass Action Law is experimentally validated in natural systems and in laboratory experiments. Aqueous speciation in deep groundwaters is usually controlled by the geological media, i.e. by solid compounds usually formed by precipitation after and during the lixiviation of original minerals. This is used by geochemists for understanding and even modelling aqueous speciation: Figure 1 typically illustrates such control for Stripa groundwaters [96TRO, 00BEA, 02COU and 03BEA].
Figure 1 Equilibration of groundwaters.

From chemical analysis on Stripsa groundwaters their equilibration with minerals and their slow evolution were modelled by using Mass Action Law [90GRI]. In the upper part of the phase diagram (bolded black points and solid straight lines), the experimental dots appeared to be on the frontiers between the stability domains of Albite and Laumontite or Prehnite, while in the kaolinite domain the dotted line was calculated from an evolution model based on Charge Balance Equation. Values of solubility products $K_s$'s, have been re-fitted on the experimental observations; however, these changes in $K_s$ values are within usual uncertainties for solid compounds formed at low temperatures: less than 0.6 log$_{10}$ unit (i.e. 0.3 kJ.mol$^{-1}$ on $\Delta G$) as compared to Ref.[83MIC].

Similar approaches are used in laboratory for modelling Radionuclide Speciation and deducing equilibrium constants (Figure 2); providing equilibrium conditions are achieved, and the chemical system is ideal (within experimental accuracy): Mass Action Law quantitatively models Aqueous Speciation and Solubility in deep groundwaters (Figure 1) and in laboratory experiments (Figure 2). For making aqueous solutions ideal high and constant concentration of an inert electrolyte is classically used: high Na$^+$ concentration was typically used for the data reported in Figure 2, which allowed sensitivity analysis, i.e. testing all possible stoichiometries for soluble complexes $(\text{NpO}_2)_p(\text{CO}_3)_q(\text{OH})_{2-q-r}$. This type of approach is classical; however, it has always been debated, whether adding new minor species is meaningful, i.e. are the fitted values of their formation constants meaningful, or do they only "fit the uncertainty". Alternatively, we proposed to only estimate maximal possible values for such formation constants (see typically Ref.[01LEM and 03VIT]), this also allows finding chemical conditions, in which such minor species should eventually be better evidenced.

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

$\text{Np}(\text{V})$ solubilities were measured in our laboratory in various pH conditions -grey and black points- [84VIT, 85COM, 85KIM, 86GRE, 89RIG, 98VIT and 03VIT] and in other laboratories. All the published experimental data on this system were reviewed and eventually quantitatively reinterpreted with a single chemical model [98VIT] in the course of the NEA TDB project [01LEM]. When $\lg([\text{CO}_3^{2-}]) < -5$, experimental solubilities are on a straight line of slope -1: this, and the other slope analysis written on the figure illustrates Mass Action Law accounts for the experimental solubilities, even in oversaturated solutions (dashed lines) i.e. before the transformation of Na$_3\text{NpO}_2\text{CO}_3$(s) into Na$_3\text{NpO}_2(\text{CO}_3)_2$(s).
### 2.2 Activity coefficients

Activity coefficients $\gamma$'s, are classically introduced for comparing the values of an equilibrium constant measured in different aqueous ionic media, and for extrapolating to zero ionic strength; however there is no international conventions on the way to obtain the numerical values of the activity coefficients, despite they actually define Standard State -zero ionic strength or equivalently infinite dilution- for aqueous solutions. We tested several formula for calculating $\gamma$'s [87RIG, 87ROB and 89RIG], typically Debye-Hückel and Davies formula can only be used for $I < 0.01$ and $0.1 \text{ mol.L}^{-1}$ respectively in aqueous solutions, while in more concentrated ionic media empirical fitted parameters are needed. We used **SIT Formula** for calculating $\gamma_i$, the activity coefficient of ion $i$, with charge $z_i$

$$\lg \gamma_i = -z_i^2 D + \epsilon_{ij} m_i$$

where $D = A I_m^{0.5} / (1+B I_m^{0.5})$ is Debye-Hückel Term, $A = 0.509 \text{ kg}^{0.5} \text{mol}^{-0.5}$ and $B = 1.5 \text{ kg}^{0.5} \text{mol}^{-0.5}$ at $25^\circ C$ [01LEM]. $I_m$ is molal (mol.kg$^{-1}$) $I$, $m_i$ is the molal concentration (mol.kg$^{-1}$) of ion $j$, $\epsilon_{ij}$ is an empirical fitted parameter for ions $i$ and $j$, $z_i z_j <0$, $j$ is the major ion (if needed summation on $j$ is performed), this usual notation is confusing, since $\epsilon_{ij}$ is not a dielectric constant. Reporting SIT Formula into the definition of equilibrium constant $K$,

$$\lg K^0 = \lg K_m - \Delta z^2 D + \Delta \epsilon m$$

where $K^0$ is the $K$ value at zero ionic strength, $m$ is the molality of the salt used to maintain constant high ionic strength, $K_m$ is $K$ value using molal units, $\Delta z^2 = \Sigma \nu_i z_i^2$, $\Delta \epsilon = \Sigma \nu_i \epsilon_{ij}$, $\nu_i$'s are the stoichiometric coefficients for the reaction of Equilibrium constant $K$, and Term $\nu_{H_2O} \Delta \epsilon_{H_2O}$ is eventually included in Term $\Delta \epsilon m$. These formulas

- can be used at up to 4 mol.kg$^{-1}$ concentrations even for aqueous ions highly charged -typically Pu$^{4+}$ (Figure 3 and Figure 4) or NpO$_2$(CO$_3$)$_3^{5-}$, 
- only one parameter -namely $\epsilon_{ij}$- is used for each ion pair, it is symmetric ($\epsilon_{ij} = \epsilon_{ji}$) which allows simplifications as typically using the same ion pair fitted parameters for trace and macro concentrations, conversely this simplification is not consistent when higher order terms -typically proportional to $m_i^2$- are added, 
- it was adopted by the NEA TDB reviews.

We tested the SIT formula on several systems: Actinides in non complexing [87RIG, 89RIG2, 90CAP, 92CAP, 95CAP and 98CAP] and carbonate media [86GRE, 90CAP, 92CAP, 96CAP, 98RIG and 99CAP]. Extrapolating to zero ionic strength by using the SIT formula was illustrated for $E_{Pu^{4+}/Pu^{3+}}$, the potential of the Pu$^{4+}$/Pu$^{3+}$ redox couple measured at $25^\circ C$ (Figure 3): despite Pu$^{4+}$ and Pu$^{3+}$ are quite highly charged species $\Delta \epsilon_{Pu^{4+}/Pu^{3+}}$ appears to be constant to surprisingly high ionic strength. This is actually only plotted for $\Delta \epsilon_{Pu^{4+}/Pu^{3+}} = \epsilon_{Pu^{3+}} - \epsilon_{Pu^{4+}}$ on Figure 3; however, this was as well observed for $\epsilon_{Pu^{4+}}$ and $\epsilon_{Pu^{3+}}$ each alone (Figure 4). For applications, beside **ionic strength corrections**, **temperature corrections** are needed. Among others, SIT Formula can be used at any constant temperature $T$, for extrapolating $K$ -including normal potentials $E_{ox/red}$ (Figure 3)- giving $K^0(T)$ and $\Delta \epsilon(T)$ at $T = 298.15 \text{ K} \ (i.e. 25^\circ C)$. At other temperatures quite few $K$ values are published, and even fewer $\Delta \epsilon(T)$ values: we measured some of them in narrow temperature ranges (Figure 5).
We also proposed SIT based equations for modelling temperature influence on $\Delta$'s, or equivalently for ionic strength corrections on $\Delta_{H}$, $\Delta_{S}$ and $\Delta_{C}$ [93GIF]. In the SIT formula $\Delta_{m}$ m term is introduced as a virial expansion, or equivalently from van der Waals Equation for gas: in both cases this term is predicted to be proportional to $m/T$ - not only $m$; to our knowledge, this was not really systematically tested in literature. However, we plotted experimental values of $\Delta_{m}/T$, or equivalently $\Delta_{m}T/T$ (Figure 5). There are no data on enough experimental systems to draw general conclusions. However $\Delta_{m}$ values are constant within uncertainty, and no trend with T can be inferred. This is less clear for $\Delta_{m}T/T$ values at available higher temperatures (at equilibrium $H_{2}O$ partial pressure), while $m$ $\Delta_{m}NP_{O2}(CO_{3})_{3}^{5-}/NP_{O2}(CO_{3})_{3}^{3-}$ appears to vary with $T$, which might reflect ion pairing at low $T$, as we already suggested for $U_{O2}(CO_{3})_{3}^{5-}$, a species analogous to $NP_{O2}(CO_{3})_{3}^{5-}$ [89RIG]. Nevertheless, assuming $\gamma T = e^{\gamma T} T/T$ seems a reasonable approximation for extrapolating activity coefficients in the range 0 to 150°C from data at 25°C without any new fitted parameter, and this did not increase uncertainties dramatically for most of the above systems.
horizontal straight lines in Figure 5 are mean values ±1.96σ (dashed lines) measured at 25°C. This was not specially expected since fitted parameters - i.e. ε's and Δε's- have not necessarily the physical meaning used to introduce them in semi-empirical formulas: ε - numerical values might very well fit approximations used for obtaining SIT Formula. At higher temperatures our estimations of Δε values are certainly not much accurate. They were obtained by subtracting ΔεD (a Debye-Hückel term) from measured Δlg γ's (see Eq.2 and the caption of Figure 3), where for calculating D values at different temperatures, A and B parameters were taken from Ref.[01LEM]. However it is not clear whether ρ, the molar to molal conversion factor is actually taken into account in literature, while it should be since A = be²/(8πrdkT), b = e(2000Na/(pdkT))0.5, where B = b r, d is the dielectric constant (we are avoiding the more usual notation ρ, since it is already used for SIT ion pair coefficients), k is Boltzman Constant, e is the elementary charge, Na is Avogadro Number and r is the ionic radius assumed to be the same for any ion, and here assumed to be independent from T.

Finally, ε coefficients, the ion pair parameters seem to reproduce reasonably well temperature influence on experimental Δlg γ values, despite they were fitted at constant temperature (25°C) for reproducing ionic strength -not T- influence: this was not specially expected, since fitted ε coefficients certainly fit several physical phenomena not taken into account in the physical demonstration of SIT Formula, these phenomena were known to vary as εl / T. It is certainly not understood, why SIT Formula is valid in these I and T domains. Nevertheless, it can easily be used for applications providing ε values are available: we tabulated several of them (Table 3 and Table 4) see also Ref.[01LEM]. ε values can be estimated by analogy with similar ions of similar effective charge z, and size (Figure 6, Figure 7 and Figure 8) for -4 < z < +4.

2.3 Formation data for e-
Identifying consistent Reference State is needed, when using data from different scientific communities; typically ε', the notation of electrochemists actually corresponds to E = -(RT/F)ln a_e, where E is the redox potential of the solution, and a_e the activity of e': when E is measured vs. SHE, for consistency with the usual reference state
\[ ΔX_e = 0.5 \, ΔX_{H^+} - ΔX_{H^0}. \]
where X is a thermodynamic function, typically G, H [94GIF], and subscript f, means formation. $\Delta G$ is another notation for $\mu^g$, the standard chemical potential of species i. e. Notation is useful for ionic strength corrections [01LEM], and for charge balance, nevertheless this notation is not always accepted, moreover $\Delta G_{H^+}^{\text{aq}} = 0$, a usual convention might be quite misleading. For clarity, we now recall usual conventions.

Thermochemical data bases often tabulate $\Delta G$, $\Delta H$, S, C_p at 25°C and eventually coefficient for computing $T$ dependency of $C_p$ by using these coefficients in empirical formula. As for any element in the reference state, $\Delta G_{H^+}^{\text{aq}} = 0$ and $\Delta H_{H^+}^{\text{aq}} = 0$, i.e. $H_2(g)$ is the reference state for Element H. $\Delta X_i$ is $\Delta_X_i$ (subscript r, means reaction) for the reaction, where a product is Species i, and all the other reactants and products are species in their reference state. Since $\Delta S = (\Delta H - \Delta G)/T$, $\Delta S_{H_2}^{\text{aq}} = 0$; however, $\Delta S$ is not usually tabulated, while one usually tabulates S, the entropy values at 25°C consistent with the third principle of thermodynamics (Entropy is 0 at 0 K). Typically $S_{H_2}^{\text{aq}}$ is not zero.

Only neutral species have been chosen in the reference state, which cannot generate charged species, however SHE Convention is a way to generate ions. $\Delta G_{H^+}^{\text{aq}} = 0$ and $\Delta H_{H^+}^{\text{aq}} = 0$ are often written, which might be misleading: the reference state for Element H, is $H_2(g)$, not $H^+(aq)$. Notation (aq) is usually omitted, however $H^+(aq)$ –not $H^+$ data are usually tabulated in thermochemical databases, which can be checked by calculated the standard ionic product of water at 25°C ($10^{-14.00}$) from $\Delta G_{H^+}^{\text{aq}}$ and $\Delta G_{H_2O}^{\text{aq}}$. However $S_{H^+} = 0$ is often tabulated, which actually means $S_{H^+}^{\text{aq}} = 0$ at 25°C –not at 0 K. This is perfectly correct, but quite misleading, specially when 0 is ab initio calculated for $H^+$, since $H^+$ has no electron.

**Figure 7 SIT on pair parameters $\varepsilon$ vs. $r$.**

Linear regressions written on the figures are for $M^{z+} = M^{2+}$, $(M^{z+}$ and $M^{3+})$, and $(M^{2+}$, $M^{3+}$ and $M^{4+})$ hard cations (Figure 7a, b and c respectively) in $\text{ClO}_4^-$ aqueous solutions at 25°C (see also Table 1 and Figure 6).

Smaller symbols are used for non hard cations. Figure 7a is reproduced in Figure 7b where $M^{z+}$ ions are added, similarly $M^{z+}$ ions are added in Figure 7c. Linear regression were performed only for hard cations in $\text{ClO}_4^-$ media, since the other systems might not correspond to strong electrolytes. $r$ is ionic radius of M in solid compounds [88WEA], $z_{\text{eff}}$ is the charge z, of cation $M^{z+}$, while $z_{\text{eff}} = z - 1$ for $MO_2^{z+}$ cations (actinides). The $z_{\text{eff}}$ values were calculated for 4 molal aqueous solutions when available, or taken from the NEA-TDB [01LEM]. These figures can be used for estimating unknown $\varepsilon$ values and corresponding uncertainties for similar ions, even for complexes [01LEM].
Finally for consistency with usual conventions of classical thermodynamics:

- $e^-$, the notation of electrochemists is defined by its charge, and by $\tilde{a}_{e^-}$, its activity. Thermodynamic molal Activity is another definition of Chemical Potential; the chemical potential of $e^-$ is actually $\mu_{e^-} = -F E = RT \ln \tilde{a}_{e^-}$, where $E$ is the redox potential of the solution measured vs. SHE, and $\mu_{e^-}^0 = \Delta G_{e^-} = 0$ (see below).

This recalls $e^-$ is a characteristic of the solution. In opposition to all other species, $a_{e^-}$ is not simply related to [$e^-$], the concentration of $e^-(aq)$, the solvated electron, despite $e^-(aq)$ can be involved in kinetic studies, as typically a consequence of the radiolysis of water. Depending on the electrodes, the domain of electroactivity of water spans over about 1 or 2 V; this corresponds to 16.90 or 33.81 log unit of $a_{e^-}$ respectively, since at 25°C $(RT/F)\ln10 = 0.05916$ V.

- $\Delta G_{H^+}^0 = 0$ and $\Delta H_{H^+}^0 = 0$ are conventions, they actually account for the convention $0 = \Delta X_{ESH} = 0.5 \Delta X_{H_2(g)} - \Delta X_{H^+(aq)} - \Delta X_{e^-}$, where $\Delta X_{H_2(g)} = 0$, since $H_2(g)$ is the reference state for Element H. $\Delta X_{H_2(g)}$ and $\Delta X_{H^+(aq)}$, the two first terms in $\Delta X_{ESH}$ definition could in theory be calculated by dynamic ab initio calculations, since they correspond to actual species, namely $H_2(g)$ and $H^+(aq)$; however this might not be the same for $\Delta X_{e^-}$: for this reason a convention -as typically SHE- can be chosen. SHE Convention is not specially based on physical properties of $H^+(aq)$, neither of $e^-(aq)$ nor $e^-$. Actually when $\Delta X_{e^-}$ is omitted, it is in fact set to zero, and $\Delta X_{H^+(aq)} = 0$. This does not mean $H^+(aq)$ is the reference state for H. Similarly $S_{e^-} = 0.5 S_{H_2(g)} - S_{H^+(aq)}$, choosing $S_{H_2(g)} = 0$, induces $S_{e^-} = 0.5 S_{H_2(g)}$ which is not zero at 25°C; but $S_{H_2(g)} = 0$ at 0 Kelvin.

### 2.4 Solid Solutions

Solid solutions are solid phases of variable stoichiometries, also called non-stoichiometric compounds, typically in $AB_{1-x}C_x(s)$, a solid solution formed with ions $A^{z_A}$, $B^{z_B}$ and $C^{z_C}$, where $b = -z_A/z_B$ and $c = -z_A/z_C$, the stoichiometric coefficients are $v_A = 1$, $v_B = b(1-x)$ and $v_C = c x$. When $z_A z_C > 0$, for electroneutrality $z_A z_B < 0$ and $z_A z_C < 0$; exchanging ions $B^{z_B}$ and $C^{z_C}$ is a way for varying the stoichiometry within the solid solution, hence at constant $v_A$, this is how the notations were chosen; and for this reason $b > 0$ and $c > 0$. Several approaches are used in geochemical literature for modelling solid solutions, they eventually include empirical parameters to account for experimental observations, despite more sophisticated modelling was developed for metallurgy at higher temperature.

Solid-solution dissolutions are reactions of at least two advancement variables, which, a priori, does not allow the using of the classical form for mass action law, because its classical thermodynamic demonstration involves $d[X] = d(v_i \xi) = v_i d\xi$ terms for minimizing $\Delta G$, the Gibbs energy of the reaction, where $[X]$ and $v_i$ are the concentration and the constant stoichiometric coefficient for species $X_i = A, B$ and $C$, and $\xi$ is the advancement variable of the reaction. Nevertheless, equations similar to Mass Action Law are often used, and they are correct. They are usually introduced by avoiding mathematical derivations ($v_i d\xi$ terms for minimizing $\Delta G$); which might look like a non convincing mathematical paradox. For clarity, thermodynamic description of solid solutions can be obtained by minimizing $\Delta G$ in the a similar way as for the thermodynamic demonstration of Mass Action Law; which we are essentially doing in this section.
In solid solutions stoichiometric coefficients $\nu_i$ vary: new $\nu_i$ terms appear when developing $d(\nu_i \xi)$, which will introduce $\nu_i'$, the stoichiometric coefficients of the ionic exchange reaction corresponding to the variation of the stoichiometry of the solid solution. Conversely $\nu_i$ can be obtained from $\nu_i'$: any ionic exchange equilibrium can be considered as deriving from a solid solution, which is the matrix supporting the ionic exchange sites [99VIT/BEA, 03VIT]. To our knowledge, this approach was not systematically used: we outline it for Dissolution Reaction 3

$$A_{zA} + b(1-x)B_{zB} + c x C_{zC} \rightarrow A^{zA} + b(1-x)B^{zB} + c x C^{zC}$$

where \((A_{zA} + b(1-x)B_{zB} + c x C_{zC})\) is another notation for Solid Solution \(AB_{(1-x)}C_x\), and \(X_s\) is species \(X\), in the solid solution. The advancement variable at constant \(x\) value is typically $\xi = [A]$; \((dX_i)_x = \nu_i \xi_i\), while when \(x\) varies $dX_i = \nu_i \xi_i' + \xi_i d\nu_i$, and since $d\nu_i = \nu_i' dx$, where $\nu_i' = d\nu_i/dx$

$$dX_i = \nu_i dx + \xi_i d\nu_i$$

Since $\nu_i' = 0$, $\nu_i' = -b$ and $\nu_i' = c$, $\nu_i'$'s appear to be the stoichiometric coefficients in

$$b B_{zB} + c C_{zC} \rightarrow b B_{zB} + c C_{zC}$$

a classical ionic exchange equilibrium - i.e. with constant stoichiometric coefficients. For stoichiometric solids (at constant value for \(x = \alpha\))

$$\Delta_r G_{\alpha} = -RT \ln K_{\alpha}$$

$$K_{\alpha} = |A_{zA}| |B_{zB}|^{b(1-x)} |C_{zC}|^c$$

where $|X|$ is the activity of \(X\). Solubility Product Law (i.e. Mass Action Law for stoichiometric solids, Eq.7) is coming from terms $\nu_i \xi_i$ in Eq.4; while for solid solutions the two terms of Eq.4 give two equations (see ¡Error! No se encuentra el origen de la referencia.

5.1 Solid solutions)

$$[A^{zA}][B^{zB}]^{b(1-x)}[C^{zC}]^c = K_{\alpha}^{1-x} K_{\alpha} x (1-x)^{b(1-x)} x^c$$

$$[C^{zC}]/[B^{zB}]^b = (K_{\alpha}^{1-x} K_{\alpha} x)$$

which are also, by definition, the set of equations for ideal solid solutions, since in this cases activities are concentrations, i.e. in this case $K_{\alpha} = K_i$.

Eq.8 can as well be written $([A^{zA}][B^{zB}]^{b(1-x)}) ([A^{zA}][C^{zC}]^c)^x = (K_{\alpha}^{1-x} K_i x^c)$, which was proposed by several authors.

Eq.9 appears to be classical Mass Action Law for Equilibrium 5

Rearranging Eq.8 and 9 typically gives

$$[A^{zA}][B^{zB}]^{b(1-x)} = K_{\alpha}^{1-x} (1-x)^{b(1-x)} x^c$$

$$[A^{zA}][C^{zC}]^c = K_{\alpha} x^c$$

an equivalent set of equations, which are clearly Mass Action Law for $A^{zA}/B^{zB}$ and $A^{zA}/C^{zC}$ Ionic Exchange Equilibria. Since $0 < x < 1$ Eq.10 and 11 mean the end-members are not formed, when the ideal solid solution is stable: ideal solid solutions are always stable - however real solid solutions are not always observed, when this is not for kinetics reasons, they are not ideal- actually a consequence of how the stoichiometric coefficients were chosen - i.e. the way of splitting the solid solutions into two more solid compounds of varying ratios-, intuitively this should respect actual ionic exchanges, and this is not predicted by Thermodynamics. Ideal solid solutions are always stable, is a consequence of a more general Thermodynamics properties of ideal systems

$$\Delta_{mix} G = G_x - G_2$$

the mixing Gibbs energy is always negative, where

$$G_x = \mu_{x \cdot s} + b(1-x)\mu_{b \cdot s} + c x \mu_{c \cdot s}$$

is the Gibbs Energy of the solid solution, and

$$G_x = (1-x)G_0 + x G_1$$

is the Gibbs Energy, when the solid solution is not formed. Reporting $\mu_{x \cdot s} = \mu_{x \cdot s}^s + R T \ln a_{x \cdot s}$ in Eq.13 and 14, and since for consistency with Standard State, in endmembers activities are concentrations, Eq.12 writes

$$\Delta_{mix} G = R T \ln ([A^{zA}]^b/[B^{zB}]^b (b(1-x))/[C^{zC}]^c )$$

for ideal solid solutions $|A^{zA}| = 1$, $|B^{zB}| = b(1-x)$ and $|C^{zC}| = c x$

$$\Delta_{mix} G_{id} = R T \ln ((1-x)^{b(1-x)} x^c)$$
which is indeed negative, when the ideal solid solution is formed \((0 < x < 1)\). This can equivalently be written as

\[
\Delta_{mix_{Gid}} = R\ T\ \ln([A^{z_A}][B^{z_B}]^{b(1-x)}[C^{z_C}]^{a_x}/(K_{s1}^{1-x}K_{s0}^x))\tag{17}
\]

or

\[
\Delta_{mix_{Gid}} = R\ T\ \ln([B^{z_B}]^{b(1-x)}((C^{z_C})/(C^{z_C})^{1-x}))\tag{18}
\]

by comparing Eq.8 and 16, or by writing Eq.10 and 11 as \([A^{z_A}][B^{z_B}]^{b} = [A^{z_A}]_{B} [B^{z_B}]_{B} (1-x)^{b}\) and \([A^{z_A}][C^{z_C}] = [A^{z_A}]_{C} [C^{z_C}]_{C}\ K_{s1} x^{c}\), where \([X^{z_X}]\) is \(X\) solubility as controlled by endmember \(AY_{y(s)}\): \(\Delta_{mix_{Gid}}\) is linked to the decreases of \([B^{z_B}]\) and \([C^{z_C}]\) resulting from the formation of the solid solution.

Actually the thermodynamic calculation is the same for liquid or surface ionic exchangers, which is a theoretical way to identify their reference state with the usual standard state. Typically for ionic exchange sorption reactions (as typically Eq.5), equilibrium constant \(K\) is often measured, it can be interpreted as \(K = K_{s1}/K_{s0}\) (Eq.9), specially when \(K_{s0}\), the solubility product of the pure matrix is known: \(K_{s1}\) is deduced as \(K_{s1} = K K_{s0}\), however \(K_{s1}\) can very well be for a surface precipitate.

### 2.5 Surface complexation formulas

We outlined above formula for calculating activity coefficients. Surface complexation formula are very popular in literature for modelling sorption. In this section we essentially point out both formula are based on similar physical models.

For calculating \(D\), the Debye-Hückel term in \(\gamma_i\), the activity coefficient for ion \(i\), of charge \(z_i\), Boltzmann and Poisson equations are solved in spherical geometry. One obtains \(\psi\), the total electrostatic potential generated by \(z_i\) and its counter-ion atmosphere. \(\psi\) is subtracted from \(\psi_i\), where \(\psi_i\) is the electrostatic potential generated only by Charge \(z_i\), in vacuum. Surface complexation formula are based on Gouy and Chapman formula also obtained by solving Boltzmann and Poisson equations, but in planar semi-infinite geometry. However it seems \(\psi\) -not \(\psi_i\)- was used for obtaining surface complexation formulas, which also use a simpler form for \(D\), and do not include fitted ion pair terms, despite it was recently suggested they are certainly important for modelling other surface properties [04PEL]. Surface complexation formulas often include many fitted parameters, that cannot easily be measured independently, this because chemical bonding (complex formation) -not only weak interactions- are often included in the fit, while this is not the case for Solution Chemistry, where equilibrium constants are measured at constant ionic strength \(I\), and \(\Delta_{Gid}\) are measured in a second independent step.

![Figure 9 Pyrite oxidative dissolution](image)

Pyrite (FeS\(_2\)) is first oxidised into \(S^{(n)}\), a metastable species, where the oxidation number of \(S\) is \(n\), \(S^{(n)}\) further disproportionates into \(S^{(0)}\) and \(S^{(n')}\), which is finally oxidised into \(SO_2^{2-}\), the only stable \(S\) species in oxidising aqueous solutions. Based on batch dissolution experiments \(2n/n' = 1.6\) was determined, consistent with \(S^{(n)} = S_2O_3^{2-}\) and \(S^{(n')} = S_4O_6^{2-}\) [04DES].

It might be worthwhile to compare Boltzmann - Poisson calculations in both situations. To our knowledge this has not systematically be done, while it might be interesting introducing ion pair parameters in the surface complexation formulas, providing these formulas are changed for being consistent with the usual standard state of aqueous solutions, this needs treating independently chemical bonding (i.e. surface complexing) and non ideality (i.e. aqueous counter ion effects on surface complexes) as reflected by \(\psi\) -not \(\psi_i\)-. Anyhow surface complexation formulas might not be specially needed, since Ion Exchange Theory reasonably well accounts for many experimental results. It is an Ion Exchange Model based on a thermodynamic approach for ideal systems, in most cases it requires fewer fitted parameters. As outlined above for solid solutions, it is also easier to link this type of models to the standard state, a problem also debated in literature for Surface Complexation Formulas.
3. GEOCHEMISTRY

Actinide solubilities are very low in reducing conditions, as typically in deep groundwaters. In groundwaters, reducing conditions are maintained by several natural minerals: typically oxidative dissolution of Pyrite, a mineral containing S(-I) and Fe(II), two elements in reduced forms (Figure 9).

When waste disposal studies started -in the early eighties- few and contradictory equilibrium constants and standard potentials of redox couples were published. We reinterpreted most of the publications on redox hydrolysis and oxidation states predicted by their position in Mendeleyev Table: in the first columns the most stable oxidation number-: Np(III) (as NpO_2^0), Pu(III) (as PuO_2^0), Pu(IV) (as PuO_2^+) and Pu(VI) (as PuO_2^2+). The oxidation states of actinides are based on classical qualitative chemical rules. Many species dissolved in water are ions of oxidation states predicted by their position in Mendeleev Table: in the first columns the most stable oxidation number -: Np(III) (as NpO_2^0), Pu(III) (as PuO_2^0), Pu(IV) (as PuO_2^+) and Pu(VI) (as PuO_2^2+). The stability of PuO_{2+x}(s) was estimated by analogy assuming MO_{2+x}(s) compounds include M^{2+} and MO_{2+x}^{2+} ions for M = U or Pu; however, for x ≤ 0.5 they could as well be formed with MO_{2+x}^{3+} instead of MO_{2+x}^{2+}, which would increase the stability domains of PuO_{2+x}(s) decreasing the domain of PuO_2(s).

Pu(III) > Pu(IV) > Pu(V) (as PuO_2^+). PuO_2(s) ? PuO_{2+x}(s)? . The stability of PuO_{2+x}(s) was estimated by analogy assuming MO_{2+x}(s) compounds include MO_{2+x}^{2+} ions for M = U or Pu; however, for x ≤ 0.5 they could as well be formed with MO_{2+x}^{3+} instead of MO_{2+x}^{2+}, which would increase the stability domains of PuO_{2+x}(s) decreasing the domain of PuO_2(s). Since Pu(V) is more stable than U(V) (Figure 11a, [02VIT]). The red straight lines represent a part of a Pourbaix diagram near an U ore. The red bolded curve models oxidising waters arriving on the U ore. The dashed domains represent the influence of carbonate complexes (at P_{CO_2} = 0.01 atm) on the aqueous speciation of Pu: this would typically reduce the domain of Pu(IV), however this might merely reflect missing complexing data for Pu(IV).

Figure 11: Estimating the stability of PuO_{2+x}(s) by using analogies (dashed lines) for non-redox reactions [03VIT], assuming MO_{2+x}^{2+} (Figure 10 and Figure 11a) or MO_{2+x}^{3+} (Figure 11b) in MO_{2+x}.
are hard cations [63PEA, 73 PEA and 93PEA], i.e. they have strong interactions with hard anions or electronenegative donor atoms of neutral molecules, typically in ground waters H₂O, CO₃²⁻, OH... This hard/soft concept is a qualitative guideline; however, treating hard ions as hard charged spheres is a too rough approximation for quantitative molecular modelling [02DER, 03CLA]. Moreover, covalent bounding typically explains the differences in geometries between the iso-electronic UO₂²⁺ and ThO₂ molecules [81WAD]. This is certainly at the origin of the Pa(V) exception, the actinide element between Th and U in Mendeleev Table: in contrast with linear UO₂⁺, NpO₂⁺, PuO₂⁺ and AmO₂⁺ ions, PaO₂⁺ is not stable in acidic media. Beside this exception, Actinide ions at the same oxidation state are chemical analogues, and are chemical analogues of hard cations of similar Ratio z/r, where z is the charge of the cation and r its ionic radius. For this reason it is usually enough to study one analogue, making only verifications for the other ones. The chemical reactivities of Actinide ions An²⁺, usually vary in the order:

An⁴⁺ >> AnO₂²⁻ >> An³⁺ >> An²⁺

There ionic radii and mobilities vary in the reverse order: we indeed calculated the (NBO) charge of U in UO₂²⁺ is 3 or a little more (Figure 14). Conversely, charge transfers vary a lot within the actinide series as expected from their position in Mendeleev Table: typically the most stable oxidation numbers are

Ac(III), Th(IV), Pa(V), U(VI), Np(V), Pu(IV), Am(III), Cm(III)...

however charge transfers are involved (by definition) in redox reactions; but intra-molecular charge transfers are not much involved in most bonding for complexes of hard ions (by definition of hard ions), again this is only a thumb rule, since it seems very strong electrostatic interactions can also result in charge transfers as typically in NpO₂⁺, UO₂²⁺, UF₆(g) quite covalent species i.e. electrostatic interactions can be enough (vs. temperature random energy) to form ionic complexes in aqueous solutions, while stronger interactions would enough decrease chemical bounds lengths for allowing stabilizing charge transfer, which also contributes to shortening chemical bounds. However, electrostatic reasoning is often enough for understanding chemical reactivity of hard ions, and when using analogies for estimating their missing data.

Typically for Actinides at oxidation state +4 An(IV), the solubility is very low in a wide domain of pH values, and solubility measurements are practically the only direct experimental technique for determining aqueous speciation; unfortunately An(IV) oxides or hydroxides are ill defined, when obtained by precipitation in aqueous solution, i.e. at relatively low temperature. Nevertheless we could extract thermodynamic data from such experimental studies for Pu [98CAP, 99RAI and 03 VIT], despite Pu(IV) disproportionates in the chemical conditions, where many published experimental studies were performed for measuring *Ks, the solubility product of PuO₂(s). However, we took advantage of these disproportionation reactions for measuring *Ks (Figure 12).

4. MOLECULAR MODELING
Gibbs energies of reactions (ΔG = -RT ln K) are needed for predicting equilibrium aqueous speciation at constant temperature and pressure. Despite considerable efforts are currently devoted for developing methodologies and
computer programs based on Quantum Mechanics or Statistical Physics, it is still not clear, whether atomistic modelling can provide reliable numerical values for ∆rG's in aqueous solutions, since ∆rG is quite a small fraction of the total energy ab initio calculated. Ab initio calculations provide energies and optimised geometry in gas phase; atomic charges in molecules and some of the temperature contributions to the energy can also be estimated. This is at least a quantitative support for checking usual intuitive descriptions of chemical bonding and reactivity, as outlined here for hydrolysis of hard cations.

Ab initio and DFT calculations are typically used in literature for studying hydrated cations [M(H2O)n]z, usually limited to the first hydration shell, which is, indeed, the "simplest" M system in aqueous chemistry. However, we are interested in MLnz(aq), complexes with ligands Lz: in the first hydration shell H2O's are substituted by L's. The simplest ligand is L1 = OH−, which, anyhow, needs to be studied, since most actinide cations are hydrolysed in neutral conditions of environmental waters. Be2+ is a hard cation, quite analogue to UO22+, first hydrolysis, and even for polynuclear hydrolysed species (Figure 13). Be is a light element which simplify ab initio calculations. Its first hydration shell is limited to n ≤ 4, which limit the number of species to be calculated. We reproduced published ab initio calculations for the system Be2+/H2O, and it was even easier to calculate clusters, where n H+’s were suppressed corresponding to System Be2+/H2O/OH−. However this was not enough to obtain realistic estimations of numerical values for ∆rG in liquid water at 298.15 K [00VIT]. The solvent can be modelled as a dielectric continuum; however this would not take into account water polymers modified – i.e. destroyed or stabilised- by an hydrated cation, which might very well be needed for such modelling.

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Nevertheless, we started a similar study on System UO22+/H2O/OH−. We calculated several geometries for typically UO2(OH)2(H2O)2, while only one geometry was obtained for UO2OH(H2O)3+ (Figure 14). Many ab initio studies focus on the geometry of minimum energy, while we are rather interested in the Gibbs energy for the Systems including all possible geometries, intuitively the most stable species and those of energies higher by about k T (or R T for 1 mole). The total energy can be deduced from the partition function with usual approximations. The total energy is the mean energy on each geometry weighted by a Boltzmann factor, however, it is also stabilised by configurational entropy (see Error! No se encuentra el origen de la referencia).

5.2 Gibbs energy for several conformations, assuming Species A, actually correspond to several Ai, species of same stoichiometry:

\[ G = G^\circ + G_c \]

where

\[ G^\circ = \Sigma (n_i G^\circ_i) \]

is the mean of Gi values weighted by

\[ n_i = (e^{-G^\circ_i - G_c^i}/RT)/(\Sigma (e^{-G^\circ_i - G_c^i}/RT)) \]
the fraction of moles of Species $A_i$; $G_i^\#$ is the Gibbs energy for 1 mole of species $A_i$ alone. When $A_0$ is the most stable geometry, $n_i$ appears to be Boltzmann factor.

$$G_c = \Sigma (n_i \cdot RT \cdot \ln n_i)$$  \hspace{1cm} (22)

is the mixing term. For close $G_i^\#$ values, \textit{i.e.} $G = G_i^\#$ for any $i$, $n_i = 1/n$,

$$G_c = -RT \ln n$$  \hspace{1cm} (23)

where $n$ is the number of conformers of similar energies, which gives the order of magnitude of $G_c$: at 25°C $RT \ln 10 = 5.7$ kJ.mol$^{-1}$ corresponding to 1 order of magnitude on Equilibrium Constant $K$, or equivalently 1 log$_{10}$ unit on pK$_a$. This is not negligible as compared to the length of stability domains of aqueous species, typically the stability domain of $UO_2OH^+$ or $AmOH^{2+}$ is quite smaller than the stability domain of $UO_2(OH)_2(aq)$ or $Am(OH)_2^{+}$ respectively: for the later ones several conformers can be imagined (Figure 14).

However successive hydrolysis might very well be associated with changing coordination number, typically for U(VI) the most hydrated species in gas phase is certainly $UO_2(H_2O)_5^{2+}$ taking into account only the first hydration shell, while its first hydrolysis species might very well be a mixture of $UO_2OH(H_2O)_3^{+}$ and $UO_2OH(H_2O)_4^{+}$ (Figure 14), with this rough models the first hydrolysis reaction is associated with the lost of 0 or 1 $H_2O$ molecule: corresponding $G_{H_2O}$ is certainly more important than $G_c$. A realistic model for liquid water might very well need several $M(H_2O)^{z+}$ species \textit{-i.e.} several $i$ values for any cation $M^{z+}$- which formally gives similar supplementary $G$ terms; however, again $G_{H_2O}$ terms are certainly more important. This stresses it is of interest to determine the relevant number of water molecules for each hydrolysis species.

Various criteria are commonly \textit{-even implicitly-} used in literature, we now will point out mass spectrometry results can give experimental information on this problem; however, this needs correct interpretation since we will see \textbf{hydration numbers determined by mass spectrometry} might be smaller than actual hydration numbers in aqueous solutions, because the activity of water is much smaller in mass spectrometers, than in liquid water. Moreover, mass spectrometry has also been extensively used for checking ab initio calculations of ions in vacuum. Gresham et al. produced $M^+$ ions by bombarding $UO_3$ in an IT-SIMS for $M^+ = UO(OH)^+$, $UO_2^+$ and $UO_2(OH)^+$, where Uranium is at oxidation states 4, 5 and 6 respectively [03GRE]. Each ion was selected for further reactions, which produced the hydrates at controlled water partial pressure of typically 1.2 to 1.4 $10^6$ Torr. They interpreted their observations with Reactions

$$M(H_2O)_n^{z+} + H_2O \rightarrow M(H_2O)_{n+1}^{z+}$$  \hspace{1cm} (24)

where $n = 0, 1, 2, 3$ and 4 for U(IV) and U(V), and $n = 0, 1, 2$ and 3 for U(VI). $M(H_2O)_3^{z+}$ ions were the major products after about 0.9, 0.4 and 1.2 second respectively for U(IV), U(V) and U(VI) respectively. For U(V), after about 1.4 second $UO_2(H_2O)_2^{+}$ had about the same concentration as $UO_2(H_2O)_3^{+}$. The authors modelled the kinetic curves with Reactions 24, and fitted the corresponding forward and reverse kinetic constants. This interpretation seems reasonable; despite there possibly were too many fitted parameters for allowing sensitivity analysis. Nevertheless, we estimated equilibrium constants 

$$K_{n+1} = [M(H_2O)_{n+1}^{+}]/(\{M(H_2O)_n^{+}\}P_{H_2O})$$  \hspace{1cm} (25)
The horizontal lines indicate $\Delta G$, the Gibbs energies (kJ mol$^{-1}$) of Reactions 24 calculated at level B3LYP (in gas phase) with the suite of softwares Gaussian98 [98GAU] at 25°C for the most stable species of each stoichiometry (i.e. non including conformation energy). $\Delta G/(RT \ln 10)$ is $\log_{10}$ of the corresponding equilibrium constant: it is interpreted as $\log_{10}$ of the H$_2$O partial pressure (atm) for the half point reaction, which is the frontier of the predominance domains of UO$_2$(OH)$_i$(H$_2$O)$_{n-1}^{2-i}$ and UO$_2$(OH)$_i$(H$_2$O)$_n^{2-i}$ species. The upper limit of the diagram correspond to Reaction H$_2$O(g) $\rightarrow$ H$_2$O(l). Similarly the vertical lines are for Reactions UO$_2$(OH)$_{i-1}(H_2O)_n^{3-i}$ + OH$^-$ $\rightarrow$ UO$_2$(OH)$_i$(H$_2$O)$_n^{2-i}$. UO$_2$O(H$_2$O) and UO$_2$(OH)$_2$ typically have the same stoichiometry, however the later geometry in the most stable.

as the ratios of the forward / reverse kinetic constants ($\frac{1}{K_{n+1}}$ is $\log_{10}$ of the H$_2$O partial pressure at the half point reaction - i.e. for $[M(H_2O)_{n+1}^+] = [M(H_2O)_n^{+}]$ - a classical interpretation used for solution chemistry. However the unit conversions (they are in atm) depends on temperature, while it is not clear whether thermal equilibrium was achieved: this is certainly the reason why the authors did not write this type of interpretation.

The values we calculated for $P_{(H_2O)_{1/2,n}}$ are all in the range $10^{-6.1}$ - $10^{-7.1}$ atm, this would apparently mean the intermediary species would not be much stable; however, as discussed just below, this is rather originated in kinetics control of first hydration reactions, while only the higher hydrated species were in equilibrium conditions, or close to. $10^{-6.1}$ - $10^{-7.1}$ atm, the values we calculated for $P_{(H_2O)_{1/2,n}}$ are close to $10^{-8.8}$ atm, the experimental $P_{H_2O}$ in the mass spectrometer (Table 2). Our calculations relied on several assumptions; but it seems the most important one, is a
constant value for each $K_n$ during each experiment, as a consequence of constant values for the experimental kinetic constants. This was not specially expected since $K_n$ is a (actually thermodynamic) constant at constant pressure and temperature, while the relevant experimental temperature is difficult to estimate and was even probably not defined at short times. The intermediary species were rather produced at the beginning of the experimental observations, while the major species were rather produced at the end. For this reason, the corresponding relevant temperatures might be different for the different species, *i.e.* for their calculated characteristic $P_{\text{H}_2\text{O}_{1/2,n}}$ values. Gresham et al. did not produced any sensitivity analysis of their model, however the shapes of the experimental curves for the intermediary species, might very well accommodate models with non-constant kinetic "constants". Anyhow, since the calculated $P_{\text{H}_2\text{O}_{1/2,n}}$ values are of the order of magnitude of the experimental $P_{\text{H}_2\text{O}}$ values, this is an indication that they are indeed estimations of the minimal $P_{\text{H}_2\text{O}}$ value required to form the final products: $\text{UO(OH)(H}_2\text{O)}_3^{+}$, $\text{UO}_2(\text{H}_2\text{O})_3^{+}$, $\text{UO}_2(\text{H}_2\text{O})_4^{+}$ and $\text{UO}_2(\text{OH)(H}_2\text{O})_3^{+}$. Higher hydrates would probably form at higher $P_{\text{H}_2\text{O}}$ value. This also means this technique does not necessarily provide the numbers of water molecules in the first hydration shells of hydrated cations in liquid water.

$\Delta G$ *calculated ab initio* also indicate $\text{UO}_2(\text{OH)(H}_2\text{O})_3^{+}$ is the most stable (V) monocation at $10^{-8.8}$ atm (Figure 15). These calculations also indicate the maximum number of water molecules in the first hydration shell might be limited by the activity of water, and not always by steric considerations.

### 5. Appendix

#### 5.1 Solid solutions

In this Appendix we indicate some details of the calculations given in the above text.

\[
\Delta G_{x} = \mu_x - b(1-x)\mu_y + c x \mu_z \tag{26}
\]

where $\mu_x$ is the standard chemical potential of $X^x$, an aqueous ion, and $\{X^x\}$ its activity, here superscript ° means in the standard state, *i.e.* activities are used, not concentrations. When $x$ varies, term $\xi \nu_i dx$ in Eq.4 generate another set of equations. However at constant $x = \alpha$, $\mu_x$'s were constant, included in equilibrium constant $K_{x\alpha}$, where $\mu_x$ is the chemical potential of ion $X^x$ in the solid. Introducing $\delta x = \mu_x - \mu_{x\alpha}$, the two sets of equations for solid solutions are

\[
\begin{align*}
\Delta G_{x} &= -RT\ln K_x \\
\Delta G_{x} &= \delta_x + b(1-x)\delta_y + c x \delta_z \\
K_x &= \left[ \frac{|x|}{|A|} \right] \left[ \frac{|B^{x}|}{|B|} \right]^{(1-x)} \\
\delta_x &= \frac{|C^{x}|}{|C|}
\end{align*}
\]

Now superscript# means in a reference state, which is not the standard state, namely $\mu_A = \mu_A^\circ$, $\mu_B = \mu_B^\circ$, $\mu_C = \mu_C^\circ$, $\mu_{A^x} = \mu_{A^x}^\circ = \mu_{B^x}^\circ = \mu_{C^x} = 0$, but $\mu_{B^x} = -RT\ln \chi_{B}^\circ$ and $\mu_{C^x} = -RT\ln \chi_{C}^\circ$. For convenience, we use the following concentrations in the solid: $\chi_{A} = 1$, $\chi_{B} = b(1-x)$ and $\chi_{C} = c$, and $\chi_{B}^\circ = b$ and $\chi_{C}^\circ = c$. For concentration units, we chose ratios $n_x/n_A$, which is not exactly the usual mole fraction, thermodynamics does not indicate which units and notations should be chosen for concentrations and stoichiometric coefficients, however, concentrations must be intensive variables, and their unity is linked to the definition of the reference state.

Eq.32 is a classical form of mass action law for Eq.5, a classical equilibrium - *i.e.* with constant stoichiometric coefficients. However, neither $\Delta G_{x\alpha}$ nor $K_x$ are constant. Equivalent sets of equations were already established [02MIC], we only clarified that both sets of equations must be solved simultaneously: for ideal solid solutions this is enough to calculate aqueous and solid speciations. These equations had been obtained by identifying standard states, *i.e.* for endmembers, where $x = 0$ or 1 respectively. Solubility is the same, when calculated as for stoichiometric...
(Eq.7) or non-stoichiometric (Eq.29) compounds. For this the following linear combination can also be used
\[ \Delta G_x = (1-x)\Delta G_0 + x \Delta G_1 \]
\[ \Delta G_{BC} = \Delta G_1 - \Delta G_0 \]
By definition the endmembers are ideal, i.e. \(|A_0|^z = 1, |B_0|^z = b(1-x)\) and \(|C_0|^z = c x\) for \(x = 0\) and 1: \(K_{00} = K_0 b^z\) and \(K_{11} = K_1 c^z\). The stoichiometric coefficients are also the concentrations in the solid solution. Finally, including the activity coefficients in the equilibrium constants, the working equations are:
\[ [A_0^z] [B_0^z]^{b(1-x)} [C_0^z]^{cx} = K_{00}^{1-z} K_{01} [1-z]^{b(1-x) z} \]
\[ [C_0^z]^{y}/[B_0^z]^{b} = (K_{10}/K_{00}) (x^y/(1-x)^y) \]

5.2 Gibbs energy for several conformations
Soluble species are often stable with different geometries of similar energies, namely species A actually corresponds to different geometries \(A_0, A_1, \ldots A_{n-1}\). The stability of A is given by its Gibbs energy
\[ G = \sum n_i G_i \]
where \( G_i \) is the Gibbs energy of \( A_i \) as typically ab initio calculated.
\[ K_i = [A_i]/[A_0] \]
is the equilibrium constant for Reaction
\[ A_0 \rightarrow A_i \]
where
\[ \Delta G_i = -RT \ln K_i = G_i^* - G_i^\# \]
\([A_i] = n_i/V\), where \(V\) is the volume of the system is the concentration of \(A_i\), similarly its partial pressure could be used for calculations in gas phase. \(G_i^\#\) is \(G_i\) value in the reference state, for convenience we chose it as 1 mol of hypothetic pure \(A_i\). \(G_i^\#\) is typically given by usual ab initio softwares, when calculating frequencies after a geometry optimisation. For a system of 1 mol of
\[ 1 = \sum n_i \]
\[ G_i = G_i^* + RT \ln n_i \]
where \(R = k N_A\) where \(k\) is Boltzmann constant, \(N_A\) is Avogadro number, \(n_i\) is the number of mol of \(A_i\), rearranging the above equations for ideal systems \(K_i = n_i/n_0 = e^{(G_i^\# - G_0^\#)/RT}\)
\[ 1 = n_0 \sum (e^{(G_i^\# - G_0^\#)/RT}) \]
\[ G = n_0 \sum (e^{(G_i^\# - G_0^\#)/RT} (G_i^\# + RT \ln n_i)) \]
which is rearranged as
\[ G = G^\# + G_c \]
where
\[ G^\# = \sum (n_i G_i^\#) \]
appears to be the mean value of \(G_i^\#\) values weighted by \(n_i\), where \(G_i^\#\) is the \(G_i\) value for hypothetical pure \(A_i\) and
\[ n_i = (e^{(G_i^\# - G_0^\#)/RT})/(\sum (e^{(G_i^\# - G_0^\#)/RT})) \]
is the Boltzmann factor when choosing the most stable geometry as \(A_0\). \(G_c = \Sigma(n_i RT \ln n_i)\) appears to be a mixing term. Typically for 2 species, \(n_0 = x \) and \(n_1 = 1-x\), \(G_c\) is similar to \(\Delta_{m1}G_i\) (Eq.16).

5.3 Treatment of mass spectrometry data from Ref.[03gre]
Gresham et al. provided numerical values for \(k_{\text{forward}}\) (cm³.molecule⁻¹.s⁻¹), the kinetic constants for reaction
\[ M(H_2O)_n^+ + H_2O \rightarrow M(H_2O)_{n+1}^+ \]
\[ k_{\text{forward}} = 10^{-3} N_A k_{\text{forward}} (L.mol⁻¹.s⁻¹) \]
and \(k_{\text{reverse}}(s⁻¹)\)s for the reverse reaction. We assumed their definition were
\[ k_{\text{forward}} \{M(H_2O)_n^+\} \{H_2O\} \ dt = -d\{M(H_2O)_n^+\} \]
\[ k_{\text{reverse}} \{M(H_2O)_{n+1}^+\} \ dt = d\{M(H_2O)_n^+\} \]
where \(\{X\}\) is X concentration (molecule.cm⁻³); however, more usual macroscopic concentration units are (mol.L⁻¹), we calculated
\[ k_i = 10^{-3} N_A k_{\text{forward}} (L.mol⁻¹.s⁻¹) \]
\[ k_r = k_{\text{reverse}}(s^{-1}) \]
\[ k_f/k_r = \frac{[M(H_2O)_{n+1}^+]}{[M(H_2O)_n^+][H_2O]} = K \]
is the constant of Equilibrium 24. At half reaction (i.e. for \([M(H_2O)_{n+1}^+] = [M(H_2O)_n^+]\))
\[ [H_2O]_{1/2} = 1/K. = (1000/N_A)k_{\text{reverse}}/k_{\text{forward}} \]
Since pressures were low \(P_{(H_2O)_{1/2}}\) the corresponding water pressure can be calculated by using \(PV = nRT\), where \(n/V\)
and \(P\) units are \(\text{mol.m}^{-3}\) (i.e. \(10^{-3}\ \text{mol.L}^{-1}\)) and \(\text{Newton.m}^{-2}\) (i.e. \(1/101325\ \text{atm}\)) respectively:
\[ P_{(H_2O)_{1/2}} = \frac{(1000 [H_2O]_{1/2}/101325)RT}{10^6 \ R \ T \ k_{\text{reverse}}/(101325 \ N_A \ k_{\text{forward}})} \]
Using the values of the following table

| \(N_A\) | \(6.0221367 \times 10^{23}\) mol\(^{-1}\) |
| \(R\) | \(8.31453 \times 10^{\text{ J.K}^{-1}.\text{mol}^{-1}}\) |
| \(T\) | \(298.15\) K |
| \(R \ T\) | \(2.47897\) kJ.mol\(^{-1}\) |
| \(R \ T \ ln10\) | \(5.70804\) kJ.mol\(^{-1}\) |

\(Pa^0 = 1\ \text{atm} = 101325\) Pa (= Newton.m\(^{-2}\))
\(10^6 \ R \ T \ /(/Pa^0) = 4.0626 \times 10^{20}\)
\(N_A\) \(= 10^{-19.3912}\)

\[ \lg P_{(H_2O)_{1/2}} = -19.39 + \lg(k_{\text{reverse}}/k_{\text{forward}}) \]
Experimental water partial pressures \(P\), were given in Torr, for comparison, we calculated
\[ \lg P_{H_2O(\text{atm})} = \lg P - \lg(760) = \lg P - 2.8808. \]
Table 2 Fitted kinetic constants to model 1T-SIMS experimental observations for hydrates of U(IV), U(V) and U(VI) monocations [03GRE]. 

$k_{\text{forward}}$ and $k_{\text{reverse}}$ are the kinetic constants fitted in Ref.[03GRE] for Reactions 24, the $P_{H2O}$ values are also given in Ref.[03GRE]. $P_{H2O1/2}$ is calculated from the kinetic constants (see text)°.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$K_{\text{forward}}$ ($s^{-1}$)</th>
<th>$K_{\text{reverse}}$ ($s^{-1}$)</th>
<th>$P_{H2O}$ (Torr)</th>
<th>$lg P_{H2O1/2}$ (lg(atm))</th>
<th>$lg(P_{H2O})$ (lg(atm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 $[\text{UOOH}^+] + \text{H}_2\text{O} \leftrightarrow [\text{UO}^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$8 \times 10^{-11}$</td>
<td>9</td>
<td>$1.4 \times 10^6$</td>
<td>-8.3°</td>
<td>-8.7°</td>
</tr>
<tr>
<td>3 $[\text{UOOH}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UOO}^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$2 \times 10^{-10}$</td>
<td>2</td>
<td></td>
<td>-9.3°</td>
<td></td>
</tr>
<tr>
<td>4 $[\text{UOOH}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UOO}^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$3 \times 10^{-11}$</td>
<td>0.14</td>
<td></td>
<td>-9.7°</td>
<td></td>
</tr>
<tr>
<td>5 $[\text{UOOH}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UOO}^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$3 \times 10^{-11}$</td>
<td>11</td>
<td></td>
<td>-7.8°</td>
<td></td>
</tr>
<tr>
<td>6 $[\text{UO}^+\text{O}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UO}^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$6 \times 10^{-11}$</td>
<td>8</td>
<td>$1.2 \times 10^6$</td>
<td>-8.2°</td>
<td>-8.8°</td>
</tr>
<tr>
<td>7 $[\text{UO}_2^+\text{O}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UO}_2^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$3 \times 10^{-10}$</td>
<td>15</td>
<td></td>
<td>-8.6°</td>
<td></td>
</tr>
<tr>
<td>8 $[\text{UO}_2^+\text{O}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UO}_2^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$4 \times 10^{-10}$</td>
<td>2.2</td>
<td></td>
<td>-9.6°</td>
<td></td>
</tr>
<tr>
<td>9 $[\text{UO}_2^+\text{O}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UO}_2^+\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$6 \times 10^{-11}$</td>
<td>1.7</td>
<td></td>
<td>-8.9°</td>
<td></td>
</tr>
<tr>
<td>10 $[\text{UO}_2\text{OH}^+] + \text{H}_2\text{O} \leftrightarrow [\text{UO}_2\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$4 \times 10^{-11}$</td>
<td>1</td>
<td>$1.4 \times 10^6$</td>
<td>-8.9°</td>
<td>-8.7°</td>
</tr>
<tr>
<td>11 $[\text{UO}_2\text{O}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UO}_2\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$1 \times 10^{-10}$</td>
<td>0.8</td>
<td></td>
<td>-9.4°</td>
<td></td>
</tr>
<tr>
<td>12 $[\text{UO}_2\text{O}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \leftrightarrow [\text{UO}_2\text{O}(\text{H}_2\text{O})]^+$</td>
<td>$5 \times 10^{-11}$</td>
<td>0.22</td>
<td></td>
<td>-9.7°</td>
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</tbody>
</table>

°Equilibrium constant $K$, is calculated as $k_{\text{forward}}/k_{\text{reverse}}$, with unit conversions its thermodynamics interpretation is $K = 1/P_{H2O1/2}$ assuming equilibrium was achieved, which was certainly not for most species, excepted maybe for the most hydrated ones, namely Equilibria 5, 9 and 12.

Table 3 $\varepsilon_{\text{Ln}^3+,\text{ClO}_4^-}$ estimated from $\varepsilon_{\text{Ln}^{4+,\text{CO}_4^-}}$ values

<table>
<thead>
<tr>
<th>Ln</th>
<th>3/r</th>
<th>$\varepsilon_{\text{Ln}^{3+,\text{ClO}_4^-}}$</th>
<th>An</th>
<th>3/r</th>
<th>$\varepsilon_{\text{An}^{3+,\text{CO}_4^-}}$</th>
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<tbody>
<tr>
<td>La</td>
<td>2,308</td>
<td>0.462</td>
<td>Ac</td>
<td>2,381</td>
<td>0.454</td>
</tr>
<tr>
<td>Ce</td>
<td>2,338</td>
<td>0.458</td>
<td>Th</td>
<td>2,459</td>
<td>0.46</td>
</tr>
<tr>
<td>Pr</td>
<td>2,370</td>
<td>0.454</td>
<td>Pa</td>
<td>2,542</td>
<td>0.487</td>
</tr>
<tr>
<td>Nd</td>
<td>2,402</td>
<td>0.454</td>
<td>U</td>
<td>2,575</td>
<td>0.492</td>
</tr>
<tr>
<td>Pm</td>
<td>2,433</td>
<td>0.458</td>
<td>Np</td>
<td>2,609</td>
<td>0.494</td>
</tr>
<tr>
<td>Sm</td>
<td>2,461</td>
<td>0.461</td>
<td>Pu</td>
<td>2,632</td>
<td>0.491</td>
</tr>
<tr>
<td>Eu</td>
<td>2,488</td>
<td>0.469</td>
<td>Am</td>
<td>2,691</td>
<td>0.499</td>
</tr>
<tr>
<td>Gd</td>
<td>2,515</td>
<td>0.476</td>
<td>Cm</td>
<td>2,703</td>
<td>0.5</td>
</tr>
<tr>
<td>Tb</td>
<td>2,542</td>
<td>0.487</td>
<td>Bk</td>
<td>2,727</td>
<td>0.503</td>
</tr>
<tr>
<td>Dy</td>
<td>2,571</td>
<td>0.493</td>
<td>Cf</td>
<td>2,752</td>
<td>0.506</td>
</tr>
<tr>
<td>Ho</td>
<td>2,597</td>
<td>0.490</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>2,622</td>
<td>0.493</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>2,646</td>
<td>0.492</td>
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</tr>
<tr>
<td>Yb</td>
<td>2,667</td>
<td>0.495</td>
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<tr>
<td>Lu</td>
<td>2,686</td>
<td>0.490</td>
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</table>
Table 4 $\varepsilon_{Mz+,Xz-}$ values

$\varepsilon_{Mz+,Xz-}$ is calculated from $\lg \gamma_\pm$, the decimal log of the mean activity coefficient calculated from Pitzer coefficients (as explained for Figure 4), in $m = 4 \text{ mol.kg}^{-1}$ aqueous solutions, or for the maximum $m$ values, where $\gamma_\pm$ values are available. Uncertainty is the maximum value of $|\varepsilon(m) - \varepsilon(4)|$ for $0.5 < m < 4 \text{ mol.kg}^{-1}$, this only reflects the theoretical error of the SIT formula; however, it is virtually the total uncertainty on $\lg \gamma$ when calculated with this formula. Three digits are tabulated despite this is not meaningful, when compared with the uncertainty: however, this avoids propagating rounding errors in calculations, since SIT Formula can be used up to $4 \text{ mol.kg}^{-1}$ for estimating $\lg \gamma = \varepsilon_{Mz+,Xz-} D_{\pm \rightarrow m}$. The numerical values here tabulated reproduce isopiestic measurements with enough accuracy for speciation calculations; however, $\varepsilon$ values can include possible weak complexing in the activity coefficient, for this reason, it would not be consistent to use these $\varepsilon$ values with the corresponding complexing constant.

<table>
<thead>
<tr>
<th>Ion</th>
<th>NO$_3^-$</th>
<th>Cl$^-$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$^{2+}$</td>
<td>0.086±0.019</td>
<td></td>
<td>Li$^+$ 0.027±0.049</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>-0.260±0.093</td>
<td>0.178±0.021</td>
<td>Na$^+$ 0.053±0.034</td>
</tr>
<tr>
<td>UO$_2^{2+}$</td>
<td>0.239±0.008</td>
<td>0.511±0.052</td>
<td>0.207±0.012</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td></td>
<td>0.376±0.002</td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td></td>
<td>0.317±0.002</td>
<td></td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>0.186±0.014</td>
<td>0.339±0.058</td>
<td></td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>0.079±0.016</td>
<td>0.462±0.025</td>
<td>0.270±0.030</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td></td>
<td>0.2490.006</td>
<td></td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>0.082±0.010</td>
<td>0.454±0.022</td>
<td>0.282±0.039</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>0.083±0.003</td>
<td>0.454±0.021</td>
<td>0.289±0.046</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>0.087±0.001</td>
<td>0.461±0.023</td>
<td>0.294±0.041</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>0.097±0.000</td>
<td></td>
<td>0.299±0.039</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>0.114±0.009</td>
<td>0.476±0.023</td>
<td>0.309±0.046</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>0.136±0.016</td>
<td>0.487±0.023</td>
<td>0.319±0.049</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>0.151±0.012</td>
<td>0.493±0.022</td>
<td>0.325±0.051</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>0.165±0.013</td>
<td>0.490±0.023</td>
<td>0.331±0.052</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>0.183±0.021</td>
<td>0.493±0.022</td>
<td>0.336±0.061</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>0.193±0.021</td>
<td>0.492±0.020</td>
<td>0.339±0.065</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>0.197±0.017</td>
<td>0.495±0.023</td>
<td>0.343±0.069</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>0.199±0.010</td>
<td>0.490±0.019</td>
<td>0.343±0.070</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.285±0.008</td>
<td>-0.255±0.113</td>
<td>0.331±0.002</td>
</tr>
<tr>
<td>Ga$^{3+}$</td>
<td></td>
<td>0.547±0.006</td>
<td></td>
</tr>
<tr>
<td>Th$^{4+}$</td>
<td>0.160±0.020</td>
<td></td>
<td>0.350±0.013</td>
</tr>
</tbody>
</table>
Table 4 $\varepsilon_{Mz+,Xz-}$ values (continued)

<table>
<thead>
<tr>
<th></th>
<th>NO$_3^-$</th>
<th>ClO$_4^-$</th>
<th>Cl$^-$</th>
<th>I$^-$</th>
<th>Br$^-$</th>
<th>F$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>0.060±0.012</td>
<td>0.142±0.033</td>
<td>0.125±0.016</td>
<td>0.185±0.019</td>
<td>0.157±0.007</td>
<td></td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.077±0.005</td>
<td>0.148±0.008</td>
<td>0.109±0.019</td>
<td>0.155±0.004</td>
<td>0.106±0.009</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-0.034±0.039</td>
<td>0.013±0.016</td>
<td>0.037±0.024</td>
<td>0.080±0.008</td>
<td>0.055±0.020</td>
<td>-0.039±0.012</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-0.101±0.083</td>
<td>0.004±0.031</td>
<td>0.020±0.015</td>
<td>0.009±0.027</td>
<td>0.011±0.013</td>
<td></td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>-0.104±0.097</td>
<td>0.005±0.044</td>
<td>-0.009±0.049</td>
<td>-0.009±0.043</td>
<td>0.042±0.006</td>
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</tr>
<tr>
<td>Cs$^+$</td>
<td>-0.176±0.039</td>
<td>-0.017±0.071</td>
<td>-0.041±0.061</td>
<td>-0.023±0.078</td>
<td>0.068±0.012</td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>-0.055±0.056</td>
<td>-0.110±0.034</td>
<td>0.000±0.031</td>
<td>0.011±0.002</td>
<td>-0.010±0.012</td>
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</tr>
<tr>
<td>Ti$^+$</td>
<td>0.165±0.001</td>
<td>0.337±0.014</td>
<td>0.248±0.074</td>
<td>0.377±0.062</td>
<td>0.309±0.052</td>
<td>0.245±0.067</td>
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<tr>
<td>Mg$^{2+}$</td>
<td>0.017±0.010</td>
<td>0.266±0.005</td>
<td>0.194±0.053</td>
<td>0.262±0.006</td>
<td>0.197±0.006</td>
<td>0.142±0.007</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>-0.051±0.012</td>
<td>0.223±0.004</td>
<td>0.160±0.052</td>
<td>0.237±0.008</td>
<td>0.164±0.001</td>
<td>0.163±0.047</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>0.150±0.005</td>
<td>0.224±0.006</td>
<td>0.123±0.002</td>
<td>0.069±0.005</td>
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<tr>
<td>Mn$^{2+}$</td>
<td>0.015±0.007</td>
<td>0.145±0.008</td>
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<tr>
<td>Fe$^{2+}$</td>
<td>0.163±0.026</td>
<td>0.348±0.028</td>
<td>0.277±0.039</td>
<td>0.177±0.026</td>
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<tr>
<td>Co$^{2+}$</td>
<td>0.071±0.007</td>
<td>0.196±0.045</td>
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<tr>
<td>Ni$^{2+}$</td>
<td>0.134±0.021</td>
<td>0.075±0.004</td>
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<tr>
<td>Cu$^{2+}$</td>
<td>0.162±0.005</td>
<td>0.299±0.021</td>
<td>0.175±0.044</td>
<td>0.015±0.031</td>
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</table>

Table 4 $\varepsilon_{Mz+,Xz-}$ values (continued)

<table>
<thead>
<tr>
<th></th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
<th>NH$_4^+$</th>
</tr>
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<tbody>
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<td>ClO$_4^-$</td>
<td>0.0990.017</td>
<td>-0.0020.035</td>
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<td>BrO$_3^-$</td>
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<tr>
<td>SCN$^-$</td>
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<td>-0.0050.023</td>
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<tr>
<td>NO$_3^-$</td>
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<td>0.0010.047</td>
<td>-0.0320.079</td>
<td>-0.0430.108</td>
<td>-0.0210.056</td>
<td>-0.1250.182</td>
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<tr>
<td>HPO$_4^{2-}$</td>
<td>-0.0720.090</td>
<td>-0.1760.042</td>
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<td>HASO$_4^{2-}$</td>
<td>-0.0810.004</td>
<td>-0.1360.026</td>
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<td>SO$_4^{2-}$</td>
<td>0.0600.076</td>
<td>-0.0540.138</td>
<td>-0.1200.039</td>
<td>-0.0990.036</td>
<td>-0.0670.170</td>
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<td>-0.1210.036</td>
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<tr>
<td>HASO$_4^{2-}$</td>
<td>-0.1030.007</td>
<td>-0.0330.004</td>
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</table>

Table 4 $\varepsilon_{Mz+,Xz-}$ values (continued)

<table>
<thead>
<tr>
<th></th>
<th>Na$^+$</th>
<th>K$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSe$^-$</td>
<td>0.015±0.007</td>
<td>0.292±0.059</td>
</tr>
<tr>
<td>B(OH)$_4^-$</td>
<td>0.047±0.091</td>
<td>0.005±0.035</td>
</tr>
<tr>
<td>BF$_4^-$</td>
<td>0.054±0.045</td>
<td>0.002±0.008</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>0.071±0.021</td>
<td>0.036±0.017</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>0.055±0.041</td>
<td></td>
</tr>
<tr>
<td>Pt(CN)$_4^{2-}$</td>
<td>0.139±0.016</td>
<td></td>
</tr>
<tr>
<td>P$_3$O$_9^{4-}$</td>
<td>0.114±0.024</td>
<td></td>
</tr>
</tbody>
</table>
6. REFERENCE


[88WEA] Handbook


Jensen S. (1982) EUR 7676


