

# From uranothorites to coffinite: a solid solution route to the thermodynamic properties of $\text{USiO}_4$

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**Table S1.** Equilibrium constants and variations of the standard enthalpy associated with the main reactions considered in the speciation calculations. Thermodynamic data are extracted from the LLNL database<sup>1</sup> included in the Phreeqc.2 geochemical code<sup>2</sup>.

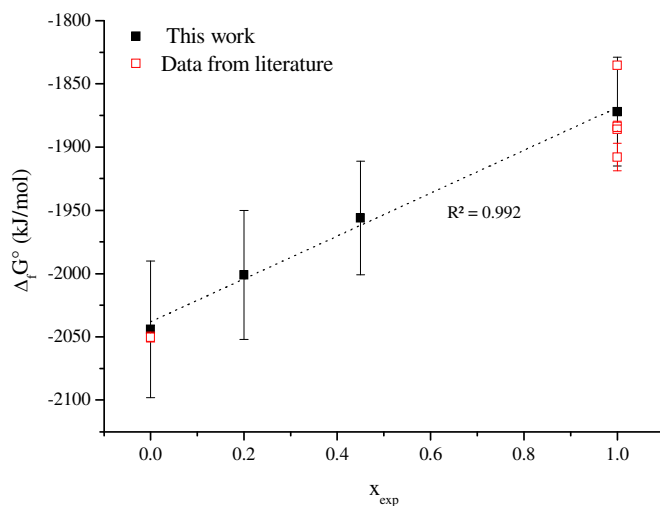
Reaction stoichiometry	log (K)	$\Delta_R H^\circ$ (kJ·mol <sup>-1</sup> )
$2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	-85.9951	559.543
$\text{SiO}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{HSiO}_3)^- + \text{H}^+$	-9.9525	25.991
$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{SiO}_4)^{2-} + 2\text{H}^+$	-22.96	-
$4\text{SiO}_2 + 8\text{H}_2\text{O} \rightleftharpoons [\text{H}_4(\text{H}_2\text{SiO}_4)_4]^{4-} + 4\text{H}^+$	-35.94	-
$4\text{SiO}_2 + 8\text{H}_2\text{O} \rightleftharpoons [\text{H}_6(\text{H}_2\text{SiO}_4)_4]^{2-} + 2\text{H}^+$	-13.64	-
$\text{U}^{4+} + \text{H}_2\text{O} \rightleftharpoons [\text{U}(\text{OH})]^{3+} + \text{H}^+$	-0.5472	46.9183
$\text{U}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{U}(\text{OH})_4 + 4\text{H}^+$	-4.54	78.755
$\text{U}^{4+} + \text{Cl}^- \rightleftharpoons (\text{UCl})^{3+}$	+1.7073	-18.9993
$\text{UCl}_4 + \rightleftharpoons \text{U}^{4+} + 4\text{Cl}^-$	21.9769	-240.719
$(\text{UO}_2)^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-10.3146	-
$(\text{UO}_2)^{2+} + 3\text{H}_2\text{O} \rightleftharpoons [\text{UO}_2(\text{OH})_3]^- + 3\text{H}^+$	-19.2218	-
$(\text{UO}_2)^{2+} + 4\text{H}_2\text{O} \rightleftharpoons [\text{UO}_2(\text{OH})_4]^{2-} + 4\text{H}^+$	-33.0291	-
$(\text{UO}_2)^{2+} + \text{Cl}^- \rightleftharpoons (\text{UO}_2\text{Cl})^+$	+0.1572	8.00167
$(\text{UO}_2)^{2+} + 2\text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}_2$	-1.1253	15.0013
$(\text{UO}_2)^{2+} + 2\text{H}_2\text{O} + \text{SiO}_2 \rightleftharpoons (\text{UO}_2\text{H}_3\text{SiO}_4)^+ + \text{H}^+$	-1.9111	-
$\text{Th}^{4+} + \text{Cl}^- \rightleftharpoons (\text{ThCl})^{3+}$	+0.9536	-
$\text{Th}^{4+} + 2\text{Cl}^- \rightleftharpoons (\text{ThCl}_2)^{2+}$	+0.6758	-
$\text{Th}^{4+} + 3\text{Cl}^- \rightleftharpoons (\text{ThCl}_3)^+$	+1.4975	-
$\text{Th}^{4+} + 4\text{Cl}^- \rightleftharpoons \text{ThCl}_4$	+1.0731	-
$2\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons [\text{Th}_2(\text{OH})_2]^{6+} + 2\text{H}^+$	-6.4618	63.718
$4\text{Th}^{4+} + 8\text{H}_2\text{O} \rightleftharpoons [\text{Th}_4(\text{OH})_8]^{8+} + 8\text{H}^+$	-21.7568	245.245
$6\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons [\text{Th}_6(\text{OH})_{15}]^{9+} + 15\text{H}^+$	-37.7027	458.248

**Table S2.** Thermodynamic data at 298 K selected in the NEA-TDB II<sup>3</sup> used for the determination of  $\Delta_R G^\circ$ ,  $\Delta_R H^\circ$ ,  $\Delta_R S^\circ$ .

Species	$\Delta_f G^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta_f H^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta_f S^\circ$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )*	Ref.
H <sup>+</sup>	0	0	0	3
OH <sup>-</sup>	-157.22 ± 0.07	-230.02 ± 0.04	-244.3 ± 0.2	3
H <sub>2</sub> O	-237.14 ± 0.04	-285.83 ± 0.04	-163.4 ± 0.1	3
U <sup>4+</sup>	-529.86 ± 1.76	-591.2 ± 3.3	-205.8 ± 1.8	3
Th <sup>4+</sup>	-704.78 ± 5.3	-768.7 ± 2.3	-214.5 ± 2.2	4
H <sub>4</sub> SiO <sub>4</sub> (aq)	-1307.7 ± 1.2	-1456.96 ± 3.16	-500.9 ± 1.6	3
UO <sub>2</sub> (cr)	-1031.83 ± 1.00	-1085 ± 1	-178.4 ± 0.3	3
ThO <sub>2</sub> (cr)	-1168.99 ± 3.50	-1226.4 ± 3.5	-192.7 ± 1.1	4
SiO <sub>2</sub> (cr)	-856.287 ± 1.16	-910.7 ± 1.0	-182.6 ± 0.4	3

\*standard entropy of formation of compounds calculated from the compounds in their

standard state with:  $\Delta_f S^\circ = \sum_i \nu_i S^\circ_{m,i}$



**Figure S1.** Variation of  $\Delta_f G^\circ$  of uranothorite solid solutions versus the uranium mole fraction. Data from literature are listed in Table 5.

## REFERENCES

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