

## Equilibrium constants for hydrolysis and associated equilibria in critical compilations

# Thorium

Equilibrium reactions	lgK at infinite dilution and $T = 298\text{ K}$			
	Baes and Mesmer, 1976	Rand et al., 2008	Thoenen et al, 2014	Brown and Ekberg, 2016
$\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ThOH}^{3+} + \text{H}^+$	-3.20	$-2.5 \pm 0.5$	$-2.5 \pm 0.5$	$-2.5 \pm 0.5$
$\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_2^{2+} + 2\text{H}^+$	-6.93	$-6.2 \pm 0.5$	$-6.2 \pm 0.5$	$-6.2 \pm 0.5$
$\text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_3^+ + 3\text{H}^+$	$< -11.7$			
$\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_4 + 4\text{H}^+$	-15.9	$-17.4 \pm 0.7$	$-17.4 \pm 0.7$	$-17.4 \pm 0.7$
$2\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}_2(\text{OH})_2^{6+} + 2\text{H}^+$	-6.14	$-5.9 \pm 0.5$	$-5.9 \pm 0.5$	$-5.9 \pm 0.5$
$2\text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}_2(\text{OH})_3^{5+} + 3\text{H}^+$		$-6.8 \pm 0.2$	$-6.8 \pm 0.2$	$-6.8 \pm 0.2$
$4\text{Th}^{4+} + 8\text{H}_2\text{O} \rightleftharpoons \text{Th}_4(\text{OH})_8^{8+} + 8\text{H}^+$	-21.1	$-20.4 \pm 0.4$	$-20.4 \pm 0.4$	$-20.4 \pm 0.4$
$4\text{Th}^{4+} + 12\text{H}_2\text{O} \rightleftharpoons \text{Th}_4(\text{OH})_{12}^{4+} + 12\text{H}^+$		$-26.6 \pm 0.2$	$-26.6 \pm 0.2$	$-26.6 \pm 0.2$
$6\text{Th}^{4+} + 15\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Th}_6(\text{OH})_{15}^{9+} + 15\text{H}^+$	-36.76	$-36.8 \pm 1.5$	$-36.8 \pm 1.5$	$-36.8 \pm 1.5$
$6\text{Th}^{4+} + 14\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Th}_6(\text{OH})_{14}^{10+} + 14\text{H}^+$		$-36.8 \pm 1.2$	$-36.8 \pm 1.2$	$-36.8 \pm 1.2$
$\text{ThO}_2(\text{c}) + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2\text{H}_2\text{O}$	6.3			
$\text{ThO}_2(\text{am}) + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2\text{H}_2\text{O}$				$8.8 \pm 1.0$
$\text{ThO}_2(\text{am,hyd,fresh}) + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2\text{H}_2\text{O}$			$9.3 \pm 0.9$	

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$\text{ThO}_2(\text{am,hyd,aged}) + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2\text{H}_2\text{O}$			$8.5 \pm 0.9$	
$\text{Th}^{4+} + 4\text{OH}^- \rightleftharpoons \text{ThO}_2(\text{am,hyd,fresh}) + 2\text{H}_2\text{O}$		$46.7 \pm 0.9$		
$\text{Th}^{4+} + 4\text{OH}^- \rightleftharpoons \text{ThO}_2(\text{am,hyd,aged}) + 2\text{H}_2\text{O}$		$47.5 \pm 0.9$		

C.F. Baes and R.E. Mesmer, The Hydrolysis of Cations. Wiley, New York, 1976, p. 168.

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M. Rand, J. Fuger, I. Grenthe, V. Neck and D. Rai, Chemical Thermodynamics of Thorium, OECD Pub., 2008.

T. Thoenen, W. Hummel, U. Berner and E. Curti, The PSI/Nagra Chemical Thermodynamic Database 12/07, Villigen: Paul Scherrer Institute PSI, 2014 pp. 259–263.

# Distribution diagrams

These diagrams have been computed at two Th(IV) concentrations (1 mM =  $1 \times 10^{-3}$  mol L<sup>-1</sup> and 1  $\mu$ M =  $1 \times 10^{-6}$  mol L<sup>-1</sup>) with the 'best' equilibrium constants above (in green). Calculations assume  $T = 298$  K for the limiting case of zero ionic strength (*i.e.*, even neglecting plotted ions).

