

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

# Thorium

Equilibrium reactions	lgK at infinite dilution and $T = 298$ 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			
$\text{ThO}_2(\text{am}) + 4 \text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2 \text{H}_2\text{O}$				$8.8 \pm 1.0$
$\text{ThO}_2(\text{am,hyd,fresh}) + 4 \text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2 \text{H}_2\text{O}$			$9.3 \pm 0.9$	

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

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

P.L. Brown and C. Ekberg, *Hydrolysis of Metal Ions*. Wiley, 2016, pp. 462–498.

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).

