

## 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			
$\text{ThO}_2(\text{am}) + 4 \text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2 \text{H}_2\text{O}$				$8.8 \pm 1.0$
$\text{ThO}_2(\text{am,hyd,fresh}) + 4 \text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2 \text{H}_2\text{O}$			$9.3 \pm 0.9$	

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

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).

