

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

# Zirconium

Equilibrium reactions	lgK at infinite dilution and T = 298 K		
	Baes and Mesmer, 1976	Thoenen et al., 2014	Brown and Ekberg, 2016
$\text{Zr}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ZrOH}^{3+} + \text{H}^+$	0.3	$0.32 \pm 0.22$	$0.12 \pm 0.12$
$\text{Zr}^{4+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_2^{2+} + 2 \text{H}^+$	(-1.7)*	$0.98 \pm 1.06^*$	$-0.18 \pm 0.17^*$
$\text{Zr}^{4+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_3^+ + 3 \text{H}^+$	(-5.1)		
$\text{Zr}^{4+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_4 + 4 \text{H}^+$	-9.7*	$-2.19 \pm 0.70^*$	$-4.53 \pm 0.37^*$
$\text{Zr}^{4+} + 5 \text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_5^- + 5 \text{H}^+$	-16.0		
$\text{Zr}^{4+} + 6 \text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_6^{2-} + 6 \text{H}^+$		$-29 \pm 0.70$	$-30.5 \pm 0.3$
$3 \text{Zr}^{4+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Zr}_3(\text{OH})_4^{8+} + 4 \text{H}^+$	-0.6	$0.4 \pm 0.3$	$0.90 \pm 0.18$
$3 \text{Zr}^{4+} + 5 \text{H}_2\text{O} \rightleftharpoons \text{Zr}_3(\text{OH})_5^{7+} + 5 \text{H}^+$	3.70		
$3 \text{Zr}^{4+} + 9 \text{H}_2\text{O} \rightleftharpoons \text{Zr}_3(\text{OH})_9^{3+} + 9 \text{H}^+$		$12.19 \pm 0.20$	$12.19 \pm 0.20$
$4 \text{Zr}^{4+} + 8 \text{H}_2\text{O} \rightleftharpoons \text{Zr}_4(\text{OH})_8^{8+} + 8 \text{H}^+$	6.0	$6.52 \pm 0.05$	$6.52 \pm 0.05$
$4 \text{Zr}^{4+} + 15 \text{H}_2\text{O} \rightleftharpoons \text{Zr}_4(\text{OH})_{15}^+ + 15 \text{H}^+$		$12.58 \pm 0.24$	
$4 \text{Zr}^{4+} + 16 \text{H}_2\text{O} \rightleftharpoons \text{Zr}_4(\text{OH})_{16} + 16 \text{H}^+$		$8.39 \pm 0.80$	
$\text{ZrO}_2(\text{s}) + 4 \text{H}^+ \rightleftharpoons \text{Zr}^{4+} + 2 \text{H}_2\text{O}$	-1.9*		$-5.37 \pm 0.42^*$

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ZrO <sub>2</sub> (s, baddeleyite) + 4 H <sup>+</sup> ⇌ Zr <sup>4+</sup> + 2 H <sub>2</sub> O		-7 ± 1.6	
Zr(OH) <sub>4</sub> (am) + 4 H <sup>+</sup> ⇌ Zr <sup>4+</sup> + 4 H <sub>2</sub> O		-3.24 ± 0.10	-2.97 ± 0.18

\*Errors in compilations concerning equilibrium and/or data elaboration. Data not recommended. It is strongly suggested to refer to the original papers.

C.F. Baes and R.E. Mesmer, *The Hydrolysis of Cations*. Wiley, New York, 1976, pp. 158.

P.L. Brown and C. Ekberg, *Hydrolysis of Metal Ions*. Wiley, 2016, pp. 442–460.

T. Thoenen, W. Hummel, U. Berner and E. Curti, *The PSI/Nagra Chemical Thermodynamic Database 12/07*, 2014.

# Distribution diagrams

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

