



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

## Chromium(II)

The divalent state is unstable in water, producing hydrogen whilst being oxidised to a higher valency state (Baes and Mesmer, 1976). The reliability of the data is in doubt.

Equilibrium reactions	$\lg K$ at infinite dilution and $T = 298 \text{ K}$	
	NIST46	Ball and Nordstrom, 1988
$Cr^{2+} + H_2O \rightleftharpoons CrOH^+ + H^+$	-5.5	
$Cr(OH)_2(s) \rightleftharpoons Cr^{2+} + 2 OH^-$		-17 ± 0.02

J.W. Ball and D.K. Nordstrom, Critical evaluation and selection of standard state thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides and hydroxides. J. Chem. Eng. Data, 43, 895–918 (1998).

NIST46, NIST Critically Selected Stability Constants of Metal Complexes: Version 8.0. Available at: <a href="https://www.nist.gov/srd/nist46">www.nist.gov/srd/nist46</a>





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

## Chromium(III)

Equilibrium reactions	$\lg K$ at infinite dilution and $T = 298 \text{ K}$			
	Baes and Mesmer, 1976	Rai et al., 1987	Ball and Nordstrom, 1988	Brown and Ekberg, 2016
$Cr^{3+} + H_2O \rightleftharpoons CrOH^{2+} + H^+$	-4.0	-3.57 ± 0.08		-3.60 ± 0.07
$Cr^{3+} + 2 H_2O \rightleftharpoons Cr(OH)_2^+ + 2 H^+$	-9.7	-9.84		-9.65 ± 0.20
$Cr^{3+} + 3 H_2O \rightleftharpoons Cr(OH)_3 + 3 H^+$	-18	-16.19		-16.25 ± 0.19
$Cr^{3+} + 4 H_2O \rightleftharpoons Cr(OH)_4^- + 4 H^+$	-27.4	-27.65 ± 0.12		-27.56 ± 0.21
$2 \text{ Cr}^{3+} + 2 \text{ H}_2\text{O} \rightleftharpoons \text{Cr}_2(\text{OH})_2^{4+} + 2 \text{ H}^+$	-5.06	-5.0		-5.29 ± 0.16
$3 \text{ Cr}^{3+} + 4 \text{ H}_2\text{O} \rightleftharpoons \text{Cr}_3(\text{OH})_4^{5+} + 4 \text{ H}^+$	-8.15	-10.75 ± 0.15		-9.10 ± 0.14
$Cr(OH)_3(s) + 3 H^+ \rightleftharpoons Cr^{3+} + 3 H_2O$	12		9.35	9.41 ± 0.17
$Cr_2O_3(s) + 6 H^+ \rightleftharpoons 2 Cr^{3+} + 3 H_2O$			8.52	
$CrO_{1.5}(s) + 3 H^+ \rightleftharpoons Cr^{3+} + 1.5 H_2O$				7.83 ± 0.10

C.F. Baes and R.E. Mesmer, The Hydrolysis of Cations. Wiley, New York, 1976, p. 220.

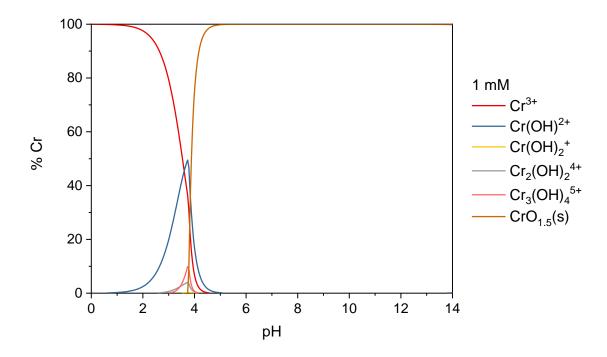
J.W. Ball and D.K. Nordstrom, Critical evaluation and selection of standard state thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides and hydroxides. J. Chem. Eng. Data, 43, 895–918 (1998).

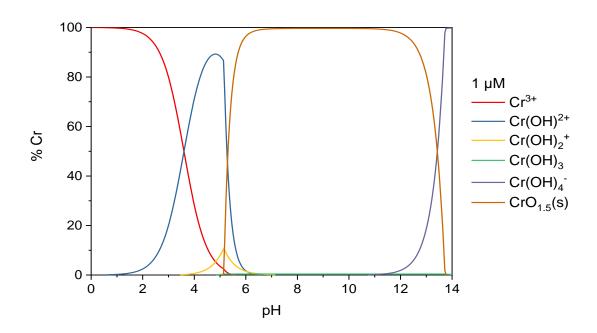
P.L. Brown and C. Ekberg, Hydrolysis of Metal Ions. Wiley, 2016, pp. 541–555.



### Distribution diagrams

These diagrams have been computed at two Cr(III) concentrations (1 mM =  $1x10^{-3}$  mol L<sup>-1</sup> and 1  $\mu$ M =  $1x10^{-6}$  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).









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

# Chromium(VI)

Equilibrium reactions	lgK at infinite dilution and $T = 298  K$		
	Baes and Mesmer, 1976	Ball and Nordstrom, 1998	
$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-$	6.51	6.55 ± 0.04	
$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4$	-0.20		
$CrO_4^{2-} + 2 H^+ \rightleftharpoons H_2CrO_4$		6.31	
$2 \text{ HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	1.523		
$2 \text{ CrO}_4^{2-} + 2 \text{ H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$		14.7 ± 0.1	

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

J.W. Ball and D.K. Nordstrom, Critical evaluation and selection of standard state thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides and hydroxides. J. Chem. Eng. Data, 43, 895–918 (1998).

### Distribution diagrams

These diagrams have been computed at two Cr(VI) 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).

