

# AquaEnv - Constants and Formulae

A.F. Hofmann

November 26, 2008

## 1 Chemical constants used in AquaEnv

### 1.1 Elements of list Constants

absZero	-273.15	°C	[Dickson et al., 2007]	absolute zero
R	83.14472	(bar*cm3)/(mol*K)	[Dickson et al., 2007]	ideal gas constant
F	96485.3399	C/mol	[Dickson et al., 2007]	Faraday constant
e	79	-	[Zeebe and Wolf-Gladrow, 2001]	relative dielectric constant of seawater
K_HNO2	1.584893e-3	mol/l	[Riordan et al., 2005]	approximative dissociation constant of HNO <sub>2</sub> , NBS pH scale, hybrid constant
K_HNO3	23.44	mol/kg-soln	(Soetaert pers. comm.)	approximative dissociation constant of HNO <sub>3</sub> , assumed on mol/kg-soln and free pH scale, stoichiometric constant
K_H2SO4	100	mol/kg-soln	[Atkins, 1996]	approximative dissociation constant of H <sub>2</sub> SO <sub>4</sub> , assumed on mol/kg-soln and free pH scale, stoichiometric constant
K_HS	1.1e-12	mol/kg-soln	[Atkins, 1996]	approximative dissociation constant of HS, assumed on mol/kg-soln and free pH scale, stoichiometric constant

### 1.2 Elements of list Fugacity

Note that here we do not distinguish between fugacity and the partial pressure.

CO2	0.000383	atm	[Borges et al., 2004]	fugacity of CO <sub>2</sub>
O2	0.20946	atm	[Williams, 2004]	fugacity of O <sub>2</sub>

### 1.3 Elements of list MeanMolecularWeight

The list `MeanMolecularWeight` contains mean molecular masses ("mean molecular weights") in g/mol. The list is taken from DOE [1994, chap. 5, p. 3] and Dickson et al. [2007, chap. 5, p. 4].

Cl	35.453
S04	(32.065+4 (15.999))
Br	79.904
F	18.998
Na	22.990
Mg	24.3050
Ca	40.078
K	39.098
Sr	87.62
B	10.811

<sup>3</sup>corresponding author (a.hofmann@nioo.knaw.nl)

## 1.4 Elements of list ConcRelCl

The list `ConcRelCl` contains relative concentrations of key chemical species in seawater with respect to chlorinity [DOE, 1994, chap. 5, p. 11] and [Dickson et al., 2007, chap. 5, p. 10]

Cl	0.99889
SO4	0.1400
Br	0.003473
F	0.000067
Na	0.55661
Mg	0.06626
Ca	0.02127
K	0.0206
Sr	0.00041
B	0.000232

## 2 Chlorinity Cl as a function of salinity S

Chlorinity `Cl` (in ‰) is calculated from salinity `S` using a relation given in DOE [1994, chap. 5, p. 11] and Zeebe and Wolf-Gladrow [2001, p. 100]

$$Cl = \frac{S}{1.80655} \quad (1)$$

## 3 Total concentrations of key chemical species in seawater as a function of chlorinity Cl

As described in DOE [1994, chap. 5, p. 11] and Dickson et al. [2007, chap. 5, p. 10], values in lists `MeanMolecularWeight` and `ConcRelCl` are used to calculate the total concentration `[X]` (in mol/kg-soln) of chemical species `X` in seawater<sup>1</sup> according to the relation

$$[X] = \frac{\text{ConcRelCl}\$X}{\text{MeanMolecularWeight}\$X} Cl \quad (2)$$

## 4 Ionic strength I as function of salinity S

According to DOE [1994, chapter 5, p. 13, 15], Zeebe and Wolf-Gladrow [2001, p.12], and Roy et al. [1993c, p.257], `I` (in mol/kg-H<sub>2</sub>O) is calculated by

$$I = \frac{19.924 S}{1000 - 1.005 S} \quad (3)$$

Note that the approximation  $I/(\text{mol/kg-solution}) \approx 0.0199201 S$  is given in Millero [1982, p. 428.]. This relationship converted into mol/kg-H<sub>2</sub>O and the last digits adjusted (from 0.0199201 to 0.019924) results in the formula used here.

---

<sup>1</sup>Note that the solution must have seawater composition, otherwise the relation given here is void.

## 5 Hydrostatic pressure hypdroP as function of water depth d

The hydrostatic pressure increases per m of water depth  $d$  by  $\frac{1}{10}$  of 1 atm (= 1.01325 bar [Dickson et al. \[2007, chap. 5, p. 3\]](#)), thus

$$\text{hydroP} = 0.1 \, d \, 1.01325 \quad (4)$$

## 6 Seawater density as function of temperature Tc and salinity S

According to [Millero and Poisson \[1981, 1981\]](#) as reprinted in [DOE \[1994, chap. 5, p. 6f\]](#) the density of seawater  $\rho_{SeaWater}$  (in  $\frac{kg}{m^3}$ ; **density** in an object of class *aquaenv*) can be calculated as

$$\rho_{SeaWater} = \rho_{Water} + A \, S + B \, S^{1.5} + C \, S^2 \quad (5)$$

$$A = 0.824493 - 4.0899 \, 10^{-3} \, T_c + 7.6438 \, 10^{-5} \, T_c^2 - 8.2467 \, 10^{-7} \, T_c^3 \quad (6)$$

$$+ 5.3875 \, 10^{-9} \, T_c^4 \quad (7)$$

$$B = -5.72466 \, 10^{-3} + 1.0227 \, 10^{-4} \, T_c - 1.6546 \, 10^{-6} \, T_c^2 \quad (8)$$

$$C = 4.8314 \, 10^{-4} \quad (9)$$

$$\rho_{Water} = 999.842594 + 6.793952 \, 10^{-2} \, T_c - 9.095290 \, 10^{-3} \, T_c^2 \quad (10)$$

$$+ 1.001685 \, 10^{-4} \, T_c^3 - 1.120083 \, 10^{-6} \, T_c^4 + 6.536332 \, 10^{-9} \, T_c^6 \quad (11)$$

with  $T_c$  representing the temperature in °C and  $\rho_{Water}$  the density of fresh water in in kg/m<sup>3</sup>.

## 7 Gas-exchange constants, dissociation constant, and solubility products as functions of temperature Tk, salinity S and depth d

Empirical formulations for the temperature and salinity dependency of all gas exchange constants, equilibrium constants and solubility products calculated in *AquaEnv* can be brought into the generic forms

$$\ln \frac{K_X}{k_0^\circ} = A + \frac{B}{T_k} + C \ln(T_k) + D \, T_k + E \, T_k^2 \quad (12)$$

or

$$\log_{10} \frac{K_X}{k_0^\circ} = A' + \frac{B'}{T_k} + C' \log_{10}(T_k) + D' \, T_k + E' \, T_k^2 \quad (13)$$

with  $T_k$  being the temperature in Kelvin,  $S$  the salinity,  $k_0^\circ$  the concentration unit of the constant, and  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ , and the respective variables with a prime (') being functions of salinity  $S$ . In the following we will give  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  or  $A'$ ,  $B'$ ,  $C'$ ,  $D'$ , and  $E'$  for each calculated constant.

### 7.1 Gas exchange constants (Henry's constants)

The following table shows the coefficients for gas exchange constants in *AquaEnv*, with  $fCO_2$  being the fugacity (assumed to be equal to the partial pressure) of  $CO_2$ .

K0_C02 : solubility of CO <sub>2</sub> in seawater	
A = 0.023517S - 167.81077 B = 9345.17 C = 23.3585 D = -2.3656 10 <sup>-4</sup> S E = 4.7036 10 <sup>-7</sup> S	$\text{C02\_sat} = f\text{CO}_2 \text{ K0\_C02}$  $k_0^\circ = \left[ \frac{\text{mol}}{\text{kg-solution atm}} \right]$
References: Weiss [1974] (original), DOE [1994, chap. 5, p. 13], Millero [1995, p. 663], Zeebe and Wolf-Gladrow [2001, p. 257], and Dickson et al. [2007, chap. 5, p. 12]	
K0_O2 : solubility of O <sub>2</sub> in seawater (micromol per kg-soln and atm)	
A = -846.9975 - 0.037362 S B = 25559.07 C = 146.4813 D = -0.22204 + 0.00016504 S E = -2.0564 10 <sup>-7</sup> S	$\text{O2\_sat} = f\text{O}_2 \text{ K0\_O2}$  $k_0^\circ = \left[ \frac{\mu\text{mol}}{\text{kg-solution atm}} \right]$
References: derived from Weiss [1970], agrees with data in Murray and Riley [1969]	

Note that the formulation for K0\_O2 has been derived using the formulation for a gravimetric [O<sub>2</sub>]<sub>sat</sub> given in Weiss [1970, Weiss, 1970]. It has been converted from ml-O<sub>2</sub>/kg-soln to μmol-O<sub>2</sub>/kg-soln using the molar volume of O<sub>2</sub> calculated with the virial equation using a first virial coefficient for oxygen at 273.0 Kelvin of -22 cm<sup>3</sup>/mol Atkins [1996], a value of 8.314 Nm/(Kelvin mol) for the gas constant R and an ambient pressure of 101300 N/m<sup>2</sup>. The expression for the Henry's constant has then been created by dividing the expression for the saturation concentration by fO<sub>2</sub> = 0.20946 atm [Williams, 2004].

## 7.2 Stoichiometric acid base dissociation constants

The following table gives the coefficients of for stoichiometric acid base dissociation constants in AquaEnv. Note that not mentioned coefficients A to E are zero and note also that given references sometimes contain the formulae in different units or on different pH scales. The formulae provided in this table yield the dissociation constants on different pH scales and concentration units. In AquaEnv, constants that are not already on the free pH scale and in mol/kg-soln are converted to the free pH scale and mol/kg-soln.

K_HS04 : HSO <sub>4</sub> <sup>-</sup> ⇌ H <sup>+</sup> + SO <sub>4</sub> <sup>2-</sup>		free pH scale
A = 324.57 $\sqrt{\left(\frac{\text{I}}{m^\circ}\right)} - 771.54 \frac{\text{I}}{m^\circ} + 141.328$ B = 35474 $\frac{\text{I}}{m^\circ} + 1776 \left(\frac{\text{I}}{m^\circ}\right)^2 - 13856 \sqrt{\left(\frac{\text{I}}{m^\circ}\right)} - 2698 \left(\frac{\text{I}}{m^\circ}\right)^{\frac{3}{2}} - 4276.1$ C = 114.723 $\frac{\text{I}}{m^\circ} - 47.986 \sqrt{\left(\frac{\text{I}}{m^\circ}\right)} - 23.093$	$\text{K\_HS04} = \frac{[\text{H}^+]_F [\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$  $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$  $m^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: DOE [1994, c. 5, p. 13], Zeebe and Wolf-Gladrow [2001, p. 260], Dickson [1990b] (original)		
K_HF: HF ⇌ H <sup>+</sup> + F <sup>-</sup> ("dickson")		free pH scale
A = 1.525 $\sqrt{\frac{\text{I}}{m^\circ}} - 12.641$ B = 1590.2	$\text{K\_HF} = \frac{[\text{H}^+]_F [\text{F}^-]}{[\text{HF}]}$  $k^\circ = m^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: Dickson and Riley [1979a, p. 91] (original), Dickson and Millero [1987, p. 1783], Roy et al. [1993b, p. 257], DOE [1994, c. 5, p. 15], Millero [1995, p. 664], Zeebe and Wolf-Gladrow [2001, p. 260]		

K_HF: $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$ ("perez")		total pH scale	
$A = -9.68 + 0.111 \sqrt{S}$ $B = 874$		$\text{K\_HF} = \frac{[\text{H}^+]_F [\text{F}^-]}{[\text{HF}]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
References: <a href="#">Perez and Fraga [1987, p. 91]</a> (original), <a href="#">Dickson et al. [2007, chap. 5, p. 14]</a>			
K_CO2: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} (\rightleftharpoons \text{H}_2\text{CO}_3) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ("roy"; high salinities: $S > 5$ )		total pH scale	
$A = 2.83655 - 0.20760841 \sqrt{S} + 0.08468345 S - 0.00654208 S^{\frac{3}{2}}$ $B = -2307.1266 - 4.0484 \sqrt{S}$ $C = -1.5529413$		$\text{K\_CO2} = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: <a href="#">Roy et al. [1993b, p. 254]</a> (original), <a href="#">DOE [1994, c. 5, p.14]</a> , <a href="#">Millero [1995, p. 664]</a> , <a href="#">Zeebe and Wolf-Gladrow [2001, p. 255]</a>			
K_CO2: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} (\rightleftharpoons \text{H}_2\text{CO}_3) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ("roy"; low salinities: $S \leq 5$ )		total pH scale	
$A = 290.9097 - 228.39774 \sqrt{S} + 54.20871 S - 3.969101 S^{\frac{3}{2}} - 0.00258768 S^2$ $B = -14554.21 + 9714.36839 \sqrt{S} - 2310.48919 S + 170.22169 S^{\frac{3}{2}}$ $C = -45.0575 + 34.485796 \sqrt{S} - 8.19515 S + 0.60367 S^{\frac{3}{2}}$		$\text{K\_CO2} = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: <a href="#">Roy et al. [1993b, p. 256]</a> (original, based on a temperature dependency restated in <a href="#">Millero [1979]</a> , originally given in <a href="#">Harned and Davis [1943]</a> . Note that there is a typesetting error in <a href="#">Roy et al. [1993b]</a> : The third value for $B$ is 2310.48919, not 310.48919) <a href="#">Millero [1995, p. 664]</a> (the typesetting error is corrected here. also, here it is mentioned that this formula should be used for $S \leq 5$ . Note that both functions do not always intersect at $S=5$ . The true intersection is a function of $T_c$ , is calculated in AquaEnv, and is used to decide which formula to use.)			
K_CO2: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} (\rightleftharpoons \text{H}_2\text{CO}_3) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ("lueker")		total pH scale	
$A' = 61.2172 + 0.011555 S - 0.0001152 S^2$ $B' = -3633.86$ $C' = -9.67770$		$\text{K\_CO2} = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
References: <a href="#">Lueker et al. [2000]</a> (original), <a href="#">Dickson et al. [2007, chap. 5, p.13-14]</a>			
K_HCO3: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ ("roy"; high salinities: $S > 5$ )		total pH scale	
$A = -9.226508 - 0.106901773 \sqrt{S} + 0.1130822 S - 0.00846934 S^{\frac{3}{2}}$ $B = -3351.6106 - 23.9722 \sqrt{S}$ $C = -0.2005743$		$\text{K\_HCO3} = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: <a href="#">Roy et al. [1993b, p. 254]</a> (original), <a href="#">DOE [1994, c. 25, p.15]</a> , <a href="#">Millero [1995, p. 664]</a> , <a href="#">Zeebe and Wolf-Gladrow [2001, p. 255]</a>			
K_HCO3: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ ("roy"; low salinities: $S \leq 5$ )		total pH scale	
$A = 207.6548 - 167.69908 \sqrt{S} + 39.75854 S - 2.892532 S^{\frac{3}{2}} - 0.00613142 S^2$ $B = -11843.79 + 6551.35253 \sqrt{S} - 1566.13883 S + 116.270079 S^{\frac{3}{2}}$ $C = -33.6485 + 25.928788 \sqrt{S} - 6.171951 S + 0.45788501 S^{\frac{3}{2}}$		$\text{K\_HCO3} = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: <a href="#">Roy et al. [1993b, p. 256]</a> (original, based on a temperature dependence restated in <a href="#">Millero [1979]</a> , originally given in <a href="#">Harned and Scholes [1941]</a> ), <a href="#">Millero [1995, p. 664]</a> (here it is mentioned that this formula should be used for $S \leq 5$ . Note that both functions do not always intersect at $S=5$ . The true intersection is a function of $T_c$ , is calculated in AquaEnv, and is used to decide which formula to use.)			

<b>K_HC03: <math>\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}</math> ("lueker")</b>		<b>total pH scale</b>
$A' = -25.9290 + 0.01781 \text{ S} - 0.0001122 \text{ S}^2$ $B' = -471.78$ $C' = 3.16967$	$K_{\text{HC03}} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> <a href="#">Lueker et al. [2000]</a> (original), <a href="#">Dickson et al. [2007, chap. 5, p.14]</a>		
<b>K_W: <math>\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-</math></b>		<b>total pH scale</b>
$A = 148.9652 - 5.977 \sqrt{\text{S}} - 0.01615 \text{ S}$ $B = -13847.26 + 118.67 \sqrt{\text{S}}$ $C = -23.6521 + 1.0495 \sqrt{\text{S}}$	$K_W = [\text{H}^+][\text{OH}^-]$ $k^\circ = \left( \frac{\text{mol}}{\text{kg-solution}} \right)^2$	
<i>References:</i> <a href="#">Millero [1995, p.670]</a> (original), <a href="#">DOE [1994, c. 5, p. 18]</a> (update 1997 cites <a href="#">Millero [1995]</a> ), <a href="#">Zeebe and Wolf-Gladrow [2001, p. 258]</a> , <a href="#">Dickson et al. [2007, chap. 5, p.16]</a>		
<b>K_BOH3: <math>\text{B(OH)}_3 \rightleftharpoons \text{H}^+ + \text{B(OH)}_4^-</math></b>		<b>total pH scale</b>
$A = 148.0248 + 137.1942 \sqrt{\text{S}} + 1.62142 \text{ S}$ $B = -8966.90 - 2890.53 \sqrt{\text{S}} - 77.942 \text{ S} + 1.728 \text{ S}^{\frac{3}{2}} - 0.0996 \text{ S}^2$ $C = -24.4344 - 25.085 \sqrt{\text{S}} - 0.2474 \text{ S}$ $D = 0.053105 \sqrt{\text{S}}$	$K_{\text{BOH3}} = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> <a href="#">Dickson [1990a, p. 763]</a> (or.), <a href="#">DOE [1994, c. 5, p. 14]</a> , <a href="#">Millero [1995, p. 669]</a> , <a href="#">Zeebe and Wolf-Gladrow [2001, p. 262]</a> , agrees with data in <a href="#">Roy et al. [1993a]</a>		
<b>K_NH4: <math>\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3</math></b>		<b>SWS pH scale</b>
$A = -0.25444 + 0.46532 \sqrt{\text{S}} - 0.01992 \text{ S}$ $B = -6285.33 - 123.7184 \sqrt{\text{S}} + 3.17556 \text{ S}$ $D = 0.0001635$	$K_{\text{NH4}} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> <a href="#">Millero [1995, p. 671]</a> , <a href="#">Millero et al. [1995]</a> (original), corrections of <a href="#">Millero [1995]</a> in <a href="#">Lewis and Wallace [1998]</a> give pH scale		
<b>K_H2S: <math>\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-</math></b>		<b>total pH scale</b>
$A = 225.838 + 0.3449 \sqrt{\text{S}} - 0.0274 \text{ S}$ $B = -13275.3$ $C = -34.6435$	$K_{\text{H2S}} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> <a href="#">Millero [1995, p. 671]</a> , <a href="#">Millero et al. [1988]</a> (original), corrections of <a href="#">Millero [1995]</a> in <a href="#">Lewis and Wallace [1998]</a> give pH scale		
<b>K_H3P04: <math>\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-</math></b>		<b>total pH scale</b>
$A = 115.525 + 0.69171 \sqrt{\text{S}} - 0.01844 \text{ S}$ $B = -4576.752 - 106.736 \sqrt{\text{S}} - 0.65643 \text{ S}$ $C = -18.453$	$K_{\text{H3P04}} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> <a href="#">DOE [1994, chap. 5, p 16]</a> , <a href="#">Millero [1995, p.670]</a> , (original) <a href="#">Dickson et al. [2007, chap. 5, p.15]</a> agrees with data in <a href="#">Dickson and Riley [1979b]</a>		
<b>K_H2P04 : <math>\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}</math></b>		<b>total pH scale</b>
$A = 172.0883 + 1.3566 \sqrt{\text{S}} - 0.05778 \text{ S}$ $B = -8814.715 - 160.340 \sqrt{\text{S}} + 0.37335 \text{ S}$ $C = -27.927$	$K_{\text{H2P04}} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> <a href="#">DOE [1994, chap. 5, p 16]</a> , <a href="#">Millero [1995, p.670]</a> (original), <a href="#">Dickson et al. [2007, chap. 5, p.15]</a> , agrees with data in <a href="#">Dickson and Riley [1979b]</a>		

K_HP04 : $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$		total pH scale
$A = -18.141 + 2.81197 \sqrt{S} - 0.09984 S$	K_HP04	$= \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$
$B = -3070.75 + 17.27039 \sqrt{S} - 44.99486 S$	$k^\circ$	$= \frac{\text{mol}}{\text{kg-solution}}$
References: DOE [1994, chap. 5, p 17], Millero [1995, p.670] (original), Dickson et al. [2007, chap. 5, p.15], agrees with data in Dickson and Riley [1979b]		
K_Si0H4: $\text{Si}(\text{OH})_4 \rightleftharpoons \text{H}^+ + \text{SiO}(\text{OH})_3^-$		total pH scale
$A = 117.385 + 3.5913 \sqrt{\frac{I}{m^\circ}} - 1.5998 \frac{I}{m^\circ} + 0.07871 \left(\frac{I}{m^\circ}\right)^2$	K_Si0H4	$= \frac{[\text{H}^+][\text{SiO}(\text{OH})_3^-]}{[\text{Si}(\text{OH})_4]}$
$B = -8904.2 - 458.79 \sqrt{\frac{I}{m^\circ}} + 188.74 \frac{I}{m^\circ} - 12.1652 \left(\frac{I}{m^\circ}\right)^2$	$k^\circ$	$= \frac{\text{mol}}{\text{kg-H}_2\text{O}}$
$C = -19.334$	$m^\circ$	$= \frac{\text{mol}}{\text{kg-H}_2\text{O}}$
References: Millero et al. [1988] (original), DOE [1994, chapter 5, p 17], Millero [1995, p.671]		
K_Si00H3: $\text{SiO}(\text{OH})_3^- \rightleftharpoons \text{H}^+ + \text{SiO}_2(\text{OH})_2^{2-}$		total pH scale
$A = 8.96$	K_Si00H3	$= \frac{[\text{H}^+][\text{SiO}_2(\text{OH})_2^{2-}]}{[\text{SiO}(\text{OH})_3^-]}$
$B = -4465.18$	$k^\circ$	$= \frac{\text{mol}}{\text{kg-H}_2\text{O}}$
$D = 0.021952$		
References: Wischmeyer et al. [2003] (original; including corrections by co-author D. Wolf-Gladrow)		

## 8 Stoichiometric solubility products

The following table shows the coefficients for the stoichiometric solubility products for calcite and aragonite in AquaEnv.

Ksp_calcite : solubility product of calcite	
$A' = -171.9065 - 0.77712 \sqrt{S} - 0.07711 S + 0.0041249 S^{1.5}$	Ksp_cal = $[\text{CO}_3^{2-}][\text{Ca}^{2+}]$
$B' = 2839.319 + 178.34 \sqrt{S}$	$k_0^\circ = \left[ \left( \frac{\text{mol}}{\text{kg-solution}} \right)^2 \right]$
$C' = 71.595$	
$D' = -0.077993 + 0.0028426 \sqrt{S}$	
References: Mucci [1983] (original), Boudreau [1996, p. 160], (note that the second value for $A'$ is -0.77712 not -0.7712 as cited in Boudreau [1996])	
Ksp_aragonite : solubility product of aragonite	
$A' = -171.945 - 0.068393 \sqrt{S} - 0.10018 S + 0.0059415 S^{1.5}$	Ksp_ara = $[\text{CO}_3^{2-}][\text{Ca}^{2+}]$
$B' = 2903.293 + 88.135 \sqrt{S}$	$k_0^\circ = \left[ \left( \frac{\text{mol}}{\text{kg-solution}} \right)^2 \right]$
$C' = 71.595$	
$D' = -0.077993 + 0.0017276 \sqrt{S}$	
References: Mucci [1983] (original), Boudreau [1996, p. 160], (note that the second value for $D'$ is 0.0017276 not 0.001727 as cited in Boudreau [1996])	

## 9 Pressure correction of dissociation constants and solubility products

Pressure has an effect on the stoichiometric acid-base dissociation constants and the stoichiometric solubility products given in the previous sections. As described in Millero [1995, p. 675] using corrections and assumptions from Lewis and Wallace [1998, p. A-7] the effect of pressure can be

accounted for by the equation<sup>2</sup>:

$$K_{\text{corr}} = K \left( -\frac{a_0 + a_1 T_c + a_2 T_c^2}{R T_k} \text{hydroP} + \frac{b_0 + b_1 T_c + b_2 T_c^2}{1000 R T_k} 0.5 \text{hydroP}^2 \right) \quad (14)$$

Where  $K_{\text{corr}}$  is the pressure corrected constant and  $K$  is the uncorrected constant, both on matching units, e.g., mol/kg-soln,  $T_k$  is the absolute temperature in Kelvin,  $T_c$  is the temperature in °C,  $R$  is the ideal gas constant in (bar cm<sup>3</sup>)/(mol Kelvin), and **hydroP** is the hydrostatic pressure (total pressure minus one atm) in bar. The  $a$  and  $b$  coefficients (according to [Millero \[1995\]](#) which is partly a restatement of [Millero \[1979\]](#), corrected by [Lewis and Wallace \[1998\]](#)) for constants in **AquaEnv** (stored in the data frame **DeltaPcoeffs**) are given in the following table<sup>3</sup>.

	$a_0$	$a_1$	$a_2$	$b_0$	$b_1$	$b_2$
K_HSO4	-18.03	0.0466	0.3160 10 <sup>-3</sup>	- 4.53	0.0900	0
K_HF	-9.78	-0.0090	-0.9420 10 <sup>-3</sup>	- 3.91	0.0540	0
K_CO2	-25.50	0.1271	0.0000 10 <sup>-3</sup>	- 3.08	0.0877	0
K_HCO3	-15.82	-0.0219	0.0000 10 <sup>-3</sup>	1.13	-0.1475	0
K_W	-25.60	0.2324	-3.6246 10 <sup>-3</sup>	- 5.13	0.0794	0
K_BOH3	-29.48	0.1622	2.6080 10 <sup>-3</sup>	- 2.84	0.0000	0
K_NH4	-26.43	0.0889	-0.9050 10 <sup>-3</sup>	- 5.03	0.0814	0
K_H2S	-14.80	0.0020	-0.4000 10 <sup>-3</sup>	2.89	0.0540	0
K_H3PO4	-14.51	0.1211	-0.3210 10 <sup>-3</sup>	- 2.67	0.0427	0
K_H2PO4	-23.12	0.1758	-2.6470 10 <sup>-3</sup>	- 5.15	0.0900	0
K_HPO4	-26.57	0.2020	-3.0420 10 <sup>-3</sup>	- 4.08	0.0714	0
K_SiOH4	-29.48	0.1622	2.6080 10 <sup>-3</sup>	- 2.84	0.0000	0
K_SiOOH3	-29.48	0.1622	2.6080 10 <sup>-3</sup>	- 2.84	0.0000	0
Ksp.calcite	-48.76	0.5304	0.0000 10 <sup>-3</sup>	-11.76	0.3692	0
Ksp.aragonite	-45.96	0.5304	0.0000 10 <sup>-3</sup>	-11.76	0.3692	0

## 10 Conversion factors

The following list gives a basic list of concentration and pH scale conversion factors used in **AquaEnv**. All other conversion factors, e.g., to be used in the function **convert**, are calculated from the factors given here. Note that the factors given below are multiplicative factors that can be used to convert e.g. dissociation constants or proton concentration values. To convert pH values, one needs to use the negativ decadal logarithm of the factors below as an additive term. **molal2molin** signifies conversion from mol/kg-H<sub>2</sub>O to mol/kg-soln, **free2tot** signifies conversion from the free to the total pH scale, **free2sws** signifies conversion from the free to the seawater pH scale (for a general treatment of the free, total and seawater pH scale see [Dickson \[1984\]](#) and [Zeebe and Wolf-Gladrow \[2001\]](#)), and **free2nbs** signifies conversion from the free to the NBS pH scale [\[Durst, 1975\]](#).

<b>molal2molin</b>	(1 - 0.001005 S)	<a href="#">Roy et al. [1993b, p. 257]</a> , <a href="#">DOE [1994, chap. 5, p. 15]</a>
<b>free2tot</b>	$(1 + \frac{S_T}{K_{\text{HSO4}}})$	<a href="#">Dickson [1984, p. 2302]</a> , <a href="#">DOE [1994, chap. 5, p. 16]</a> , <a href="#">Zeebe and Wolf-Gladrow [2001, p. 57, p. 261]</a>
<b>free2sws</b>	$(1 + \frac{S_T}{K_{\text{HSO4}}} + \frac{F_T}{K_{\text{HF}}})$	<a href="#">Dickson [1984, p. 2303]</a> , <a href="#">Zeebe and Wolf-Gladrow [2001]</a>
<b>free2nbs</b>	$\gamma_{\text{H}^+}$	<a href="#">Dickson [1984]</a> , <a href="#">Zeebe and Wolf-Gladrow [2001]</a>

<sup>2</sup>It is not stated in [Millero \[1995\]](#) but since this pressure correction is a multiplicative factor, it can be inferred that the unit and pH scale of the corrected constant only depends on the unit and pH scale of the uncorrected constant. This formula thus can be applied to any constant with no respect to its unit and pH scale.

<sup>3</sup>Note that in [Lewis and Wallace \[1998\]](#) it is stated that the  $a$  values for H<sub>2</sub>O and H<sub>2</sub>S are *freshwater* values! And that the coefficients for the silicate species are assumed to be the same as the ones for the borate species.



In the above table  $S$  is salinity,  $S_T = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] \approx [\text{SO}_4^{2-}]$ ,  $F_T = [\text{HF}] + [\text{F}^-] \approx [\text{F}^-]$ , both in mol/kg-soln, and  $\gamma_{\text{H}^+}$  is the activity coefficient for the proton. The dissociation constants  $K_{\text{HSO4}}$  and  $K_{\text{HF}}$  are on the free pH scale and in mol/kg-soln as well. Note that, as given in [Dickson \[1984, p. 2303\]](#) and [Dickson and Riley \[1979a, p. 91f\]](#) all concentrations appearing in the definition for the total and the seawater pH scale are molal, i.e. mol/kg-H<sub>2</sub>O, concentrations. But in [Roy et al. \[1993b, p. 257\]](#) and in [DOE \[1994, chap.. 4, SOP 6, p. 1\]](#) it is stated, that concentrations for the seawater and total pH scale are molin, i.e. mol/kg-soln. To be consistent with [DOE \[1994\]](#) mol/kg-soln is chosen here.

## 11 Activity coefficient for the proton

In AquaEnv a complex ion-interaction model like, e.g., [Millero and Pierrot \[1998\]](#) is NOT implemented. According to [Zeebe and Wolf-Gladrow \[2001\]](#) the activity coefficient for the proton  $\gamma_{\text{H}^+}$  can be approximated by the Davies equation as long as the ionic strength of the solution in question remains below 0.5 mol/kg-H<sub>2</sub>O. This means for solutions with a salinity of less than 24.48. Since NBS scale pH values are mostly not used for open ocean applications but mainly in brackish and fresh waters, the Davies equation has been assumed to be a sufficient approximation for  $\gamma_{\text{H}^+}$ . Important to note, however, is that **the conversion from and to the NBS pH scale in AquaEnv for salinities above 24.48 is only a rough approximation!**. The Davies equation is used as given in [Zeebe and Wolf-Gladrow \[2001\]](#)

$$\gamma_{\text{H}^+} = 10^{-\left(1.82 \cdot 10^6 \cdot (\epsilon \cdot \text{Tk})^{-\frac{3}{2}}\right) \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 I\right)} \quad (15)$$

where  $\epsilon$  is the relative dielectric constant of seawater (`Constants$e` in AquaEnv),  $\text{Tk}$  is the temperature in Kelvin, and  $I$  is the ionic strength in mol/kg-H<sub>2</sub>O. Note that the squared charge of the ion before the brackets with the ionic strength terms which is present in the generic form of the Davies equation has been omitted here since for the proton, this factor is 1.

## 12 The revelle factor

In [Zeebe and Wolf-Gladrow \[2001, p.73\]](#) the revelle factor is given as

$$\text{revelle} = \frac{d[\text{CO}_2]}{[\text{CO}_2]} \bigg/ \frac{d[\sum \text{CO}_2]}{[\sum \text{CO}_2]} \bigg|_{[\text{TA}]=\text{const.}} \quad (16)$$

in AquaEnv `revelle` is calculated numerically.

## 13 Partial derivatives of total alkalinity

The values for `dTAdKdKdS`, `dTAdKdKdT`, `dTAdKdKdKd`, `dTAdKdKdSumH2SO4`, and `dTAdKdKdSumHF` are calculated numerically as described in [Hofmann et al. \[2008b\]](#).

The values for `dTAdH`, `dTAdSumCO2`, `dTAdSumBOH3`, `dTAdSumH2SO4`, and `dTAdSumHF` are calculated analytically as given in [Hofmann et al. \[2008a\]](#).

## References

Peter W. Atkins. *Physikalische Chemie*. VCH Weinheim, 2nd edition, 1996. [1.1](#), [7.1](#)

- A. V. Borges, B. Delille, L. S. Schiettecatte, F. Gazeau, G. Abril, and M. Frankignoulle. Gas transfer velocities of CO<sub>2</sub> in three European estuaries (Randers Fjord, Scheldt, and Thames). *Limnology and Oceanography*, 49(5):1630–1641, 2004. URL [\(GotoISI\)://000224979900015](#). 1.2
- B. P. Boudreau. A method-of-lines code for carbon and nutrient diagenesis in aquatic sediments. *Computers & Geosciences*, 22(5):479–496, 1996. URL [\(GotoISI\)://A1996UQ20500003](#). 3
- A. G. Dickson. Ph Scales and Proton-Transfer Reactions in Saline Media Such as Sea-Water. *Geochimica Et Cosmochimica Acta*, 48(11):2299–2308, 1984. URL [\(GotoISI\)://A1984TT08000013](#). 10
- A. G. Dickson. Standard Potential of the Reaction - AgCl(S)+1/2h-2(G)=Ag(S)+HCl(Aq) and the Standard Acidity Constant of the Ion HSO<sub>4</sub><sup>-</sup> in Synthetic Sea-Water from 273.15-K to 318.15-K. *Journal of Chemical Thermodynamics*, 22(2):113–127, 1990a. URL [\(GotoISI\)://A1990CY50200001](#). 2
- A. G. Dickson. Thermodynamics of the Dissociation of Boric-Acid in Synthetic Seawater from 273.15-K to 318.15-K. *Deep-Sea Research Part a-Oceanographic Research Papers*, 37(5):755–766, 1990b. URL [\(GotoISI\)://A1990DK56300004](#). 2
- A. G. Dickson and F. J. Millero. A Comparison of the Equilibrium-Constants for the Dissociation of Carbonic-Acid in Seawater Media. *Deep-Sea Research Part a-Oceanographic Research Papers*, 34(10):1733–1743, 1987. URL [\(GotoISI\)://A1987L675400008](#). 2
- A. G. Dickson and J. P. Riley. Estimation of Acid Dissociation-Constants in Seawater Media from Potentiometric Titrations with Strong Base .2. Dissociation of Phosphoric-Acid. *Marine Chemistry*, 7(2):101–109, 1979a. URL [\(GotoISI\)://A1979GJ26800002](#). 2, 10
- A. G. Dickson and J. P. Riley. Estimation of Acid Dissociation-Constants in Seawater Media from Potentiometric Titrations with Strong Base .1. Ionic Product of Water - Kw. *Marine Chemistry*, 7(2):89–99, 1979b. URL [\(GotoISI\)://A1979GJ26800001](#). 2
- A. G. Dickson, C. Sabine, and J. R. Christian. Guide to best practices for ocean CO<sub>2</sub> measurements. *PICES special publications*, (3):1–191, 2007. 1.1, 1.3, 1.4, 3, 5, 1, 2
- DOE. *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water*. ORNL/CDIAC-74, 1994. 1.3, 1.4, 2, 3, 4, 6, 1, 2, 10
- A. Durst. *Standard Reference Materials: Standardization of pH Measurements*, volume 260-53 of *NBS Spec. Publ.* National Bur. Standards, Washington, D.C., 1975. 10
- Herbert S. Harned and Raymond Davis. The Ionization Constant of Carbonic Acid in Water and the Solubility of Carbon Dioxide in Water and Aqueous Salt Solutions from 0 to 50 deg C. *Journal of the American Chemical Society*, 65(10):2030–2037, 1943. URL <http://pubs.acs.org/doi/abs/10.1021/ja01250a059>. 2
- Herbert S. Harned and Samuel R. Scholes. The Ionization Constant of HCO<sub>3</sub><sup>-</sup> from 0 to 50 deg C. *Journal of the American Chemical Society*, 63(6):1706–1709, 1941. URL <http://pubs.acs.org/doi/abs/10.1021/ja01851a058>. 2
- A. F. Hofmann, F. J. R. Meysman, K. Soetaert, and J. J. Middelburg. A step-by-step procedure for pH model construction in aquatic systems. *Biogeosciences J1 - BG*, 5(1):227–251, 2008a. URL <http://www.biogeosciences.net/5/227/2008/L1-http://www.biogeosciences.net/5/227/2008/bg-5-227-2008.pdf>. 13
- A.F. Hofmann, F.J.R. Meysman, K. Soetaert, and J.J. Middelburg. Factors governing the pH in a heterotrophic, turbid, tidal estuary. *Biogeosciences Discussion*, 2008b. 13

- E. L. Lewis and D. W. R. Wallace. Program Developed for CO<sub>2</sub> System Calculations, 1998. [2](#), [9](#), [9](#), [3](#)
- T. J. Lueker, A. G. Dickson, and C. D. Keeling. Ocean pCO<sub>2</sub> calculated from dissolved inorganic carbon, alkalinity, and equations for K-1 and K-2: validation based on laboratory measurements of CO<sub>2</sub> in gas and seawater at equilibrium. *Marine Chemistry*, 70(1-3):105–119, 2000. URL [\(GotoISI\)://000087534100009](#). [2](#)
- F. J. Millero. Thermodynamics of the Carbonate System in Seawater. *Geochimica Et Cosmochimica Acta*, 43(10):1651–1661, 1979. URL [\(GotoISI\)://A1979HP85900006](#). [2](#), [9](#)
- F. J. Millero. The Thermodynamics of Seawater, Part 1. The PVT Properties. *Ocean Science and Engineering*, 7(4):403–460, 1982. [4](#)
- F. J. Millero. Thermodynamics of the Carbon-Dioxide System in the Oceans. *Geochimica Et Cosmochimica Acta*, 59(4):661–677, 1995. URL [\(GotoISI\)://A1995QH99100003](#). [1](#), [2](#), [9](#), [9](#), [2](#)
- F. J. Millero and D. Pierrot. A chemical equilibrium model for natural waters. *Aquatic Geochemistry*, 4(1):153–199, 1998. URL [\(GotoISI\)://000082329000007](#). [11](#)
- F. J. Millero and A. Poisson. International One-Atmosphere Equation of State of Seawater. *Deep-Sea Research Part a-Oceanographic Research Papers*, 28(6):625–629, 1981. URL [\(GotoISI\)://A1981LY51900008](#). [6](#)
- F. J. Millero, T. Plese, and M. Fernandez. The Dissociation of Hydrogen-Sulfide in Seawater. *Limnology and Oceanography*, 33(2):269–274, 1988. URL [\(GotoISI\)://A1988N101700008](#). [2](#)
- F. J. Millero, W. S. Yao, and J. Aicher. The Speciation of Fe(II) and Fe(III) in Natural-Waters. *Marine Chemistry*, 50(1-4):21–39, 1995. URL [\(GotoISI\)://A1995RV93400004](#). [2](#)
- A. Mucci. The Solubility of Calcite and Aragonite in Seawater at Various Salinities, Temperatures, and One Atmosphere Total Pressure. *American Journal of Science*, 283(7):780–799, 1983. URL [\(GotoISI\)://A1983RF42100006](#). [3](#)
- C. N. Murray and J. P. Riley. Solubility of Gases in Distilled Water and Sea Water .2. Oxygen. *Deep-Sea Research*, 16(3):311–&, 1969. URL [\(GotoISI\)://A1969D542000006](#). [1](#)
- F. F. Perez and F. Fraga. Association Constant of Fluoride and Hydrogen-Ions in Seawater. *Marine Chemistry*, 21(2):161–168, 1987. URL [\(GotoISI\)://A1987J311800005](#). [2](#)
- E. Riordan, N. Minogue, D. Healy, P. O’Driscoll, and J. R. Sodeau. Spectroscopic and optimization modeling study of nitrous acid in aqueous solution. *Journal of Physical Chemistry A*, 109(5):779–786, 2005. URL [\(GotoISI\)://000226779800009](#). [1.1](#)
- R. N. Roy, L. N. Roy, M. Lawson, K. M. Vogel, C. P. Moore, W. Davis, and F. J. Millero. Thermodynamics of the Dissociation of Boric-Acid in Seawater at S=35 from 0-Degrees-C to 55-Degrees-C. *Marine Chemistry*, 44(2-4):243–248, 1993a. URL [\(GotoISI\)://A1993MT06600012](#). [2](#)
- R. N. Roy, L. N. Roy, M. Lawson, K. M. Vogel, C. P. Moore, W. Davis, and F. J. Millero. Thermodynamics of the Dissociation of Boric-Acid in Seawater at S=35 from 0-Degrees-C to 55-Degrees-C. *Marine Chemistry*, 44(2-4):243–248, 1993b. URL [\(GotoISI\)://A1993MT06600012](#). [2](#), [10](#)
- R. N. Roy, L. N. Roy, K. M. Vogel, C. PorterMoore, T. Pearson, C. E. Good, F. J. Millero, and D. M. Campbell. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45 degrees C (vol 44, pg 249, 1996). *Marine Chemistry*, 52(2):183–183, 1993c. URL [\(GotoISI\)://A1996UH75200007](#). [4](#)

- R. F. Weiss. Solubility of Nitrogen, Oxygen and Argon in Water and Seawater. *Deep-Sea Research*, 17(4):721–735, 1970. URL [⟨GotoISI⟩://A1970H126100004](#). 1, 7.1
- R. F. Weiss. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry*, 2:203–215, 1974. 1
- D. R. Williams. NASA Earth Fact Sheet, 2004. URL <http://nssdc.gsfc.nasa.gov/planetary/factsheet/earthfact.html>. 1.2, 7.1
- A. G. Wischmeyer, Y. Del Amo, M. Brzezinski, and D. A. Wolf-Gladrow. Theoretical constraints on the uptake of silicic acid species by marine diatoms. *Marine Chemistry*, 82(1-2):13–29, 2003. URL [⟨GotoISI⟩://000183605000002](#). 2
- Richard E. Zeebe and Dieter Wolf-Gladrow. *CO<sub>2</sub> in Seawater: Equilibrium, Kinetics, Isotopes*. Number 65 in Elsevier Oceanography Series. Elsevier, first edition, 2001. 1.1, 2, 4, 1, 2, 10, 11, 12