

AquaEnv - Constants and Formulae

A.F. Hofmann

April 5, 2011

1 Constants and formulae

1.1 Chemical constants used in AquaEnv

1.1.1 Elements of list PhysChemConst

absZero	-273.15	°C	[Dickson et al., 2007]	absolute zero
R	83.14472	(bar*cm ³)/(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 constanf of seawater
K_HNO2	1.584893e-3	mol/l	[Riordan et al., 2005]	approximative dissociation constant of HNO ₂ , NBS pH scale, hybrid constant
K_HNO3	23.44	mol/kg-soln	[Boudreau, 1996, Soetaert et al., 2007]	approximative dissociation constant of HNO ₃ , assumed on mol/kg-soln and free pH scale, stoichiometric constant
K_H2SO4	100	mol/kg-soln	[Atkins, 1996]	approximative dissociation constant of H ₂ SO ₄ , 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

1.1.2 Elements of list MeanMolecularMass

The list `MeanMolecularMass` contains 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

1.1.3 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])

³corresponding author (a.hofmann@nioo.knaw.nl)

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

1.2 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]

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

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 MeanMolecularMass and ConcRelCl\$X are used to calculate the total concentration [X] (in mol/kg-soln) of chemical species X in seawater¹ according to the relation

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

1.4 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-H₂O) is calculated as

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

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-H₂O and the last digits adjusted (from 0.0199201 to 0.019924) results in the formula used here.

1.5 Relation between water depth d and gauge pressure p

Although the relation between gauge pressure p (total pressure minus atmospheric pressure, see Feistel [2008]) and water depth d can be approximated by

$$p = 0.1 d \cdot 1.01325 \quad (4)$$

since p increases per m of water depth d by approximately $\frac{1}{10}$ of 1 atm (= 1.01325 bar Dickson et al. [2007, chap. 5, p. 3]), here, the relation given by Fofonoff and Millard [1983] as implemented in Soetaert et al. [2009] is used

$$d = \frac{(9.72659 + (-2.2512 \cdot 10^{-5} + (2.279 \cdot 10^{-10} - 1.82 \cdot 10^{-15} p) p) p) p}{g + 1.092 \cdot 10^{-6} p} \quad (5)$$

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

where p is the gauge pressure in dbar (deci-bar) and g the earth's gravity in m/s^2 . g is calculated from the latitude lat (in degrees, -90 to 90, if not given $lat=0$ is assumed) as given in [Fofonoff and Millard \[1983\]](#) and implemented in [Soetaert et al. \[2009\]](#)

$$g = 9.780318 \left(1 + (0.0052788 + 2.36 \cdot 10^{-5} \sin(lat \frac{\Pi}{180})) \sin(lat \frac{\Pi}{180}) \right) \quad (6)$$

1.6 Seawater density as function of salinity S and temperature t

According to [\[Millero and Poisson, 1981\]](#), [Millero \[1982, p. 434\]](#), 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

$$\rho_{SeaWater} = \rho_{Water} + A S + B S^{1.5} + C S^2 \quad (7)$$

$$A = 0.824493 - 4.0899 \cdot 10^{-3} t + 7.6438 \cdot 10^{-5} t^2 - 8.2467 \cdot 10^{-7} t^3 \quad (8)$$

$$+ 5.3875 \cdot 10^{-9} t^4 \quad (9)$$

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

$$C = 4.8314 \cdot 10^{-4} \quad (11)$$

$$\rho_{Water} = 999.842594 + 6.793952 \cdot 10^{-2} t - 9.095290 \cdot 10^{-3} t^2 \quad (12)$$

$$+ 1.001685 \cdot 10^{-4} t^3 - 1.120083 \cdot 10^{-6} t^4 + 6.536332 \cdot 10^{-9} t^5 \quad (13)$$

with t representing the temperature in $^{\circ}C$ and ρ_{Water} the density of fresh water in kg/m^3 .

1.7 Gas-exchange constants, dissociation constant, and solubility products as functions of salinity S , (absolute) temperature T , and gauge pressure p

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

$$\ln \frac{K_X}{k_0^{\circ}} = A + \frac{B}{T} + C \ln(T) + D T + E T^2 \quad (14)$$

or

$$\log_{10} \frac{K_X}{k_0^{\circ}} = A' + \frac{B'}{T} + C' \log_{10}(T) + D' T + E' T^2 \quad (15)$$

or

$$\log_{10} \frac{K_X}{k_0^{\circ}} = A'' + \frac{B''}{T} + C'' \ln(T) + D'' T + E'' T^2 \quad (16)$$

with T being the temperature in Kelvin, S the salinity, k_0° 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' , or A'', B'', C'', D'' , and E'' for each calculated constant.

1.7.1 Gas-exchange constants (Henry's constants) as functions of salinity S and temperature T

The following table shows the coefficients for gas exchange constants in *AquaEnv*, with fCO_2 being the fugacity of CO_2 .

K0_CO2 : solubility of CO ₂ in seawater	
A = 0.023517S - 167.81077 B = 9345.17 C = 23.3585 D = -2.3656 10 ⁻⁴ S E = 4.7036 10 ⁻⁷ S	$\text{CO2_sat} = f\text{CO}_2 \text{ K0_CO2}$ $k_0^\circ = \left[\frac{\text{mol}}{\text{kg-solution atm}} \right]$
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 ₂ in seawater (micromol per kg-soln and atm)	
A = -846.9978 - 0.037362 S B = 25559.07 C = 146.4813 D = -0.22204 + 0.00016504 S E = -2.0564 10 ⁻⁷ 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 $[\text{O}_2]_{\text{sat}}$ given in Weiss [1970, Weiss, 1970]. It has been converted from ml-O₂/kg-soln to $\mu\text{mol-O}_2/\text{kg-soln}$ using the molar volume of O₂ calculated with the virial equation using a first virial coefficient for oxygen at 273.15 Kelvin of -22 cm³/mol Atkins [1996], a value of 8.314472 Nm/(Kelvin mol) for the gas constant R and an ambient pressure of 101325 N/m². The expression for the Henry's constant has then been created by dividing the expression for the saturation concentration by $f\text{O}_2 = 0.20946 \text{ atm}$ [Williams, 2004].

1.7.2 Stoichiometric acid base dissociation constants as functions of salinity S and temperature T

The following table gives the coefficients of stoichiometric acid base dissociation constants in AquaEnv. Note that if some of the coefficients A to E are not listed, they are to be considered zero. 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 : $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$ ("dickson")		free pH scale
A = $324.57 \sqrt{\left(\frac{I}{m^\circ}\right)} - 771.54 \frac{I}{m^\circ} + 141.328$ B = $35474 \frac{I}{m^\circ} + 1776 \left(\frac{I}{m^\circ}\right)^2 - 13856 \sqrt{\left(\frac{I}{m^\circ}\right)} - 2698 \left(\frac{I}{m^\circ}\right)^{\frac{3}{2}} - 4276.1$ C = $114.723 \frac{I}{m^\circ} - 47.986 \sqrt{\left(\frac{I}{m^\circ}\right)} - 23.093$	$\text{K_HS04} = \frac{[\text{H}^+]_F [\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$ $m^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: DOE [1994, c. 5, p. 13], Zeebe and Wolf-Gladrow [2001, p. 260], Dickson [1990b] (original)		
K_HS04 : $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$ ("khoo")		free pH scale
A = $6.3451 + 0.5208 \sqrt{\left(\frac{I}{m^\circ}\right)}$ B = -647.59 D = -0.019085	$\text{K_HS04} = \frac{[\text{H}^+]_F [\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$ $m^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: Khoo et al. [1977] (original), Roy et al. [1993b], Millero [1995], Lewis and Wallace [1998]		

K_HF: $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$ ("dickson")		free pH scale
A = $1.525 \sqrt{\frac{I}{m^\circ}} - 12.641$ B = 1590.2	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	K_HF = $\frac{[\text{H}^+]_F [\text{F}^-]}{[\text{HF}]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
References: Perez and Fraga [1987, p. 91] (original), Dickson et al. [2007, chap. 5, p. 14]		
K_C02: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} (\rightleftharpoons \text{H}_2\text{CO}_3) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ("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	K_C02 = $\frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: Roy et al. [1993b, p. 254] (original), DOE [1994, c. 5, p.14], Millero [1995, p. 664], Zeebe and Wolf-Gladrow [2001, p. 255]		
K_C02: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} (\rightleftharpoons \text{H}_2\text{CO}_3) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ("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 = $-45.0575 + 34.485796 \sqrt{S} - 8.19515 S + 0.60367 S^{\frac{3}{2}}$	K_C02 = $\frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: Roy et al. [1993b, p. 256] (original, based on a temperature dependency restated in Millero [1979], originally given in Harned and Davis [1943]. Note that there is a typesetting error in Roy et al. [1993b]: The third value for B is 2310.48919, not 310.48919) Millero [1995, p. 664] (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 , is calculated in AquaEnv, and is used to decide which formula to use.)		
K_C02: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} (\rightleftharpoons \text{H}_2\text{CO}_3) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ("lueker")		total pH scale
A" = $61.2172 + 0.011555 S - 0.0001152 S^2$ B" = -3633.86 C" = -9.67770	K_C02 = $\frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
References: Lueker et al. [2000] (original), Dickson et al. [2007, chap. 5, p.13-14]		
K_C02: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} (\rightleftharpoons \text{H}_2\text{CO}_3) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ("millero")		SW pH scale
A" = $126.34048 - 0.0331 S + 0.0000533 S^2 - 13.4191 \sqrt{S}$ B" = $-6320.813 + 6.103 S + 530.123 \sqrt{S}$ C" = $-19.568224 + 2.06950 \sqrt{S}$	K_C02 = $\frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
References: Millero et al. [2006] (original)		
K_HC03: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ ("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	K_HC03 = $\frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
References: Roy et al. [1993b, p. 254] (original), DOE [1994, c. 25, p.15], Millero [1995, p. 664], Zeebe and Wolf-Gladrow [2001, p. 255]		

K_HC03: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ ("roy"; low salinities: $S \leq 5$)		total pH scale
$A = 207.6548 - 167.69908 \sqrt{S} + 39.75854 S - 2.892532 S^{\frac{3}{2}} - 0.00613142 S^2$ $B = -11843.79 + 6551.35253 \sqrt{S} - 1566.13883 S + 116.270079 S^{\frac{3}{2}}$ $C = -33.6485 + 25.928788 \sqrt{S} - 6.171951 S + 0.45788501 S^{\frac{3}{2}}$		$K_{\text{HC03}} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$
<i>References:</i> Roy et al. [1993b, p. 256] (original, based on a temperature dependence restated in Millero [1979], originally given in Harned and Scholes [1941]), Millero [1995, p. 664] (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 , is calculated in AquaEnv, and is used to decide which formula to use.)		
K_HC03: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ ("lueker")		total pH scale
$A'' = -25.9290 + 0.01781 S - 0.0001122 S^2$ $B'' = -471.78$ $C'' = 3.16967$		$K_{\text{HC03}} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$
<i>References:</i> Lueker et al. [2000] (original), Dickson et al. [2007, chap. 5, p.14]		
K_HC03: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ ("millero")		SW pH scale
$A'' = 90.18333 - 0.1248 S + 0.0003687 S^2 - 21.0894 \sqrt{S}$ $B'' = -5143.692 + 20.051 S + 772.483 \sqrt{S}$ $C'' = -14.613358 + 3.3336 \sqrt{S}$		$K_{\text{HC03}} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$
<i>References:</i> Millero et al. [2006] (original)		
K_W: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$		total pH scale
$A = 148.9652 - 5.977 \sqrt{S} - 0.01615 S$ $B = -13847.26 + 118.67 \sqrt{S}$ $C = -23.6521 + 1.0495 \sqrt{S}$		$K_W = \frac{[\text{H}^+][\text{OH}^-]}{1}$ $k^\circ = \left(\frac{\text{mol}}{\text{kg-solution}} \right)^2$
<i>References:</i> Millero [1995, p.670] (original), DOE [1994, c. 5, p. 18] (update 1997 cites Millero [1995]), Zeebe and Wolf-Gladrow [2001, p. 258], Dickson et al. [2007, chap. 5, p.16]		
K_BOH3: $\text{B(OH)}_3 \rightleftharpoons \text{H}^+ + \text{B(OH)}_4^-$		total pH scale
$A = 148.0248 + 137.1942 \sqrt{S} + 1.62142S$ $B = -8966.90 - 2890.53 \sqrt{S} - 77.942S + 1.728 S^{\frac{3}{2}} - 0.0996 S^2$ $C = -24.4344 - 25.085 \sqrt{S} - 0.2474 S$ $D = 0.053105 \sqrt{S}$		$K_{\text{BOH3}} = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$
<i>References:</i> Dickson [1990a, p. 763] (or.), DOE [1994, c. 5, p. 14], Millero [1995, p. 669], Zeebe and Wolf-Gladrow [2001, p. 262], agrees with data in Roy et al. [1993a]		
K_NH4: $\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$		SW pH scale
$A = -0.25444 + 0.46532 \sqrt{S} - 0.01992 S$ $B = -6285.33 - 123.7184 \sqrt{S} + 3.17556 S$ $D = 0.0001635$		$K_{\text{NH4}} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$
<i>References:</i> Millero [1995, p. 671], Millero et al. [1995] (original), corrections of Millero [1995] in Lewis and Wallace [1998] give pH scale		
K_H2S: $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$		total pH scale
$A = 225.838 + 0.3449 \sqrt{S} - 0.0274 S$ $B = -13275.3$ $C = -34.6435$		$K_{\text{H2S}} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$
<i>References:</i> Millero [1995, p. 671], Millero et al. [1988] (original), corrections of Millero [1995] in Lewis and Wallace [1998] give pH scale		

K_H3P04: $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$		total pH scale
$A = 115.525 + 0.69171 \sqrt{S} - 0.01844 S$ $B = -4576.752 - 106.736 \sqrt{S} - 0.65643 S$ $C = -18.453$	$K_{\text{H3P04}} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> DOE [1994, chap. 5, p 16], Millero [1995, p.670], (original) Dickson et al. [2007, chap. 5, p.15] agrees with data in Dickson and Riley [1979b]		
K_H2P04 : $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$		total pH scale
$A = 172.0883 + 1.3566 \sqrt{S} - 0.05778 S$ $B = -8814.715 - 160.340 \sqrt{S} + 0.37335 S$ $C = -27.927$	$K_{\text{H2P04}} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> DOE [1994, chap. 5, p 16], Millero [1995, p.670] (original), Dickson et al. [2007, chap. 5, p.15], agrees with data in Dickson and Riley [1979b]		
K_HP04 : $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$		total pH scale
$A = -18.141 + 2.81197 \sqrt{S} - 0.09984 S$ $B = -3070.75 + 17.27039 \sqrt{S} - 44.99486 S$	$K_{\text{HP04}} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> 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
$A = 117.385 + 3.5913 \sqrt{\frac{I}{m^\circ}} - 1.5998 \frac{I}{m^\circ} + 0.07871 \left(\frac{I}{m^\circ}\right)^2$ $B = -8904.2 - 458.79 \sqrt{\frac{I}{m^\circ}} + 188.74 \frac{I}{m^\circ} - 12.1652 \left(\frac{I}{m^\circ}\right)^2$ $C = -19.334$	$K_{\text{Si0H4}} = \frac{[\text{H}^+][\text{SiO}(\text{OH})_3^-]}{[\text{Si}(\text{OH})_4]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$ $m^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
<i>References:</i> 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
$A = 8.96$ $B = -4465.18$ $D = 0.021952$	$K_{\text{Si00H3}} = \frac{[\text{H}^+][\text{SiO}_2(\text{OH})_2^{2-}]}{[\text{SiO}(\text{OH})_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-H}_2\text{O}}$	
<i>References:</i> Wischmeyer et al. [2003] (original; including corrections by co-author D. Wolf-Gladrow)		

1.8 Stoichiometric solubility products as functions of salinity S and temperature T

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

Ksp_calcite : solubility product of calcite	
$A' = -171.9065 - 0.77712 \sqrt{S} - 0.07711 S + 0.0041249 S^{1.5}$ $B' = 2839.319 + 178.34 \sqrt{S}$ $C' = 71.595$ $D' = -0.077993 + 0.0028426 \sqrt{S}$	$K_{\text{sp-cal}} = [\text{CO}_3^{2-}][\text{Ca}^{2+}]$ $k_0^\circ = \left[\left(\frac{\text{mol}}{\text{kg-solution}} \right)^2 \right]$
<i>References:</i> 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	
$A' = -171.945 - 0.068393 \sqrt{S} - 0.10018 S + 0.0059415 S^{1.5}$ $B' = 2903.293 + 88.135 \sqrt{S}$ $C' = 71.595$ $D' = -0.077993 + 0.0017276 \sqrt{S}$	$K_{sp_ara} = [CO_3^{2-}] [Ca^{2+}]$ $k_0^\circ = \left[\left(\frac{mol}{kg-solution} \right)^2 \right]$
<i>References:</i> 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])	

1.9 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

$$K_{corr} = K \left(-\frac{a_0 + a_1 t + a_2 t^2}{R T} p + \frac{b_0 + b_1 t + b_2 t^2}{1000 R T} 0.5 p^2 \right) \quad (17)$$

Where K_{corr} is the pressure corrected constant and K is the uncorrected constant, both on matching units, e.g., mol/kg-soln, T is the absolute temperature in Kelvin, t is the temperature in °C, R is the ideal gas constant in (bar cm³)/(mol Kelvin), and p is the gauge pressure (total pressure minus one atm, see [Feistel \[2008\]](#) for a definition) 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 table².

Note that, while not stated in [Millero \[1995\]](#), it can be inferred from [Lewis and Wallace \[1998\]](#) and the code given by [van Heuven et al. \[2009\]](#), that the pressure correction is valid for `K_HF` and `H_H2SO4` on the free scale and for all other dissociation constants on the seawater pH scale. To be consistent with [Lewis and Wallace \[1998\]](#) and [van Heuven et al. \[2009\]](#), in AquaEnv all dissociation constants obtained from the original formulae are first converted to the free or seawater scale respectively using scale conversion factors with `K_HF` and `H_H2SO4` being not pressure corrected. Then the pressure correction is applied. Subsequently, the dissociation constants are converted to the desired pH scale with scale conversion factors with `K_HF` and `H_H2SO4` being pressure corrected.

	a_0	a_1	a_2	b_0	b_1	b_2
K_HS04	-18.03	0.0466	0.3160 10 ⁻³	- 4.53	0.0900	0
K_HF	-9.78	-0.0090	-0.9420 10 ⁻³	- 3.91	0.0540	0
K_CO2	-25.50	0.1271	0.0000 10 ⁻³	- 3.08	0.0877	0
K_HC03	-15.82	-0.0219	0.0000 10 ⁻³	1.13	-0.1475	0
K_W	-25.60	0.2324	-3.6246 10 ⁻³	- 5.13	0.0794	0
K_BOH3	-29.48	0.1622	2.6080 10 ⁻³	- 2.84	0.0000	0
K_NH4	-26.43	0.0889	-0.9050 10 ⁻³	- 5.03	0.0814	0
K_H2S	-14.80	0.0020	-0.4000 10 ⁻³	2.89	0.0540	0
K_H3PO4	-14.51	0.1211	-0.3210 10 ⁻³	- 2.67	0.0427	0
K_H2PO4	-23.12	0.1758	-2.6470 10 ⁻³	- 5.15	0.0900	0
K_HPO4	-26.57	0.2020	-3.0420 10 ⁻³	- 4.08	0.0714	0
K_SiOH4	-29.48	0.1622	2.6080 10 ⁻³	- 2.84	0.0000	0
K_SiOOH3	-29.48	0.1622	2.6080 10 ⁻³	- 2.84	0.0000	0
Ksp_calcite	-48.76	0.5304	0.0000 10 ⁻³	-11.76	0.3692	0
Ksp_aragonite	-45.96	0.5304	0.0000 10 ⁻³	-11.76	0.3692	0

²Note that in [Lewis and Wallace \[1998\]](#) it is stated that the a values for H₂O and H₂S are *freshwater* values! And that the coefficients for the silicate species are assumed to be the same as the ones for the borate species.

1.10 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 negative decadal logarithm of the factors below as an additive term. `molal2molin` signifies conversion from mol/kg-H₂O 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 [\[Durst, 1975\]](#).

<code>molal2molin</code>	$(1 - 0.001005 S)$	Roy et al. [1993b, p. 257] , DOE [1994, chap. 5, p. 15]
<code>free2tot</code>	$(1 + \frac{S_T}{K_{\text{HSO4}}})$	Dickson [1984, p. 2302] , DOE [1994, chap. 5, p. 16] , Zeebe and Wolf-Gladrow [2001, p. 57, p. 261]
<code>free2sws</code>	$(1 + \frac{S_T}{K_{\text{HSO4}}} + \frac{F_T}{K_{\text{HF}}})$	Dickson [1984, p. 2303] , Zeebe and Wolf-Gladrow [2001]
<code>free2nbs</code>	$\frac{\gamma_{\text{H}^+} \text{free2sws}}{\text{molal2molin}}$	Dickson [1984] , Lewis and Wallace [1998] , Zeebe and Wolf-Gladrow [2001]

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 γ_{H^+} is the activity coefficient for the proton. The dissociation constants K_{HSO4} and K_{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-H₂O, 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 \[1994\]](#) and [Dickson et al. \[2007\]](#) mol/kg-soln is chosen here for the free, total and seawater scale. To be consistent with [Lewis and Wallace \[1998\]](#), the NBS scale is based on the proton concentration on mol/kg-H₂O.

1.11 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 γ_{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-H₂O. 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 γ_{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 \[2001\]](#)

$$\gamma_{\text{H}^+} = 10^{-\left(1.82 \cdot 10^6 (\epsilon T)^{-\frac{3}{2}}\right) \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 I\right)} \quad (18)$$

where ϵ is the relative dielectric constant of seawater (`PhysChemConst$e` in AquaEnv), T is the temperature in Kelvin, and I is the ionic strength in mol/kg-H₂O. 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.

1.12 The revelle factor

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

$$\text{revelle} = \frac{d[\text{CO}_2]}{[\text{CO}_2]} \bigg/ \frac{d[\sum \text{CO}_2]}{[\sum \text{CO}_2]} \bigg|_{[\text{TA}]=\text{const.}} \quad (19)$$

in AquaEnv `revelle` is calculated numerically.

1.13 Partial derivatives of total alkalinity

The values for `dTAdKdKdS`, `dTAdKdKdT`, `dTAdKdKdd`, `dTAdKdKdSumH2SO4`, and `dTAdKdKdSumHF` are calculated numerically as described in ?.

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

References

- Peter W. Atkins. *Physikalische Chemie*. VCH Weinheim, 2nd edition, 1996.
- 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](#).
- 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](#).
- A. G. Dickson. Standard Potential of the Reaction - $\text{AgCl}(\text{S}) + 1/2\text{H}_2(\text{G}) = \text{Ag}(\text{S}) + \text{HCl}(\text{Aq})$ and the Standard Acidity Constant of the Ion HSO_4^- in Synthetic Sea-Water from 273.15-K to 318.15-K. *Journal of Chemical Thermodynamics*, 22(2):113–127, 1990a. URL [<GotoISI>://A1990CY50200001](#).
- 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](#).
- 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](#).
- 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](#).
- 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](#).
- A. G. Dickson, C. Sabine, and J. R. Christian. Guide to best practices for ocean CO2 measurements. *PICES special publications*, (3):1–191, 2007.
- DOE. *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water*. ORNL/CDIAC-74, 1994.
- A. Durst. *Standard Reference Materials: Standardization of pH Measurements*, volume 260-53 of *NBS Spec. Publ.* National Bur. Standards, Washington, D.C., 1975.

- R. Feistel. A Gibbs function for seawater thermodynamics for -6 to 80 degrees C and salinity up to 120 g kg⁻¹. *Deep-Sea Research Part I-Oceanographic Research Papers*, 55(12):1639–1671, 2008. URL [<GotoISI>://000261725600003](http://dx.doi.org/10.1016/j.dsrp.2008.06.003).
- N. P. Fofonoff and R. C. Jr. Millard. Algorithms for computation of fundamental properties of seawater. *Unesco technical papers in marine science*, 44:55 pp, 1983.
- 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>.
- Herbert S. Harned and Samuel R. Scholes. The Ionization Constant of HCO₃⁻ 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>.
- 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, 2008. URL <http://www.biogeosciences.net/5/227/2008/L1-http://www.biogeosciences.net/5/227/2008/bg-5-227-2008.pdf>.
- K. H. Khoo, R. W. Ramette, C. H. Culberson, and R. G. Bates. Determination of hydrogen ion concentrations in seawater from 5 to 40 °C: standard potentials at salinities from 20 to 45 ‰. *Analytical Chemistry*, 49:29–34, 1977.
- E. L. Lewis and D. W. R. Wallace. Program Developed for CO₂ System Calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 1998.
- T. J. Lueker, A. G. Dickson, and C. D. Keeling. Ocean pCO₂ calculated from dissolved inorganic carbon, alkalinity, and equations for K₁ and K₂: validation based on laboratory measurements of CO₂ in gas and seawater at equilibrium. *Marine Chemistry*, 70(1-3):105–119, 2000. URL [<GotoISI>://000087534100009](http://dx.doi.org/10.1016/S0304-4203(00)00009-9).
- F. J. Millero. Thermodynamics of the Carbonate System in Seawater. *Geochimica Et Cosmochimica Acta*, 43(10):1651–1661, 1979. URL [<GotoISI>://A1979HP85900006](http://dx.doi.org/10.1016/0016-7037(79)90006-6).
- F. J. Millero. The Thermodynamics of Seawater, Part 1. The PVT Properties. *Ocean Science and Engineering*, 7(4):403–460, 1982.
- F. J. Millero. Thermodynamics of the Carbon-Dioxide System in the Oceans. *Geochimica Et Cosmochimica Acta*, 59(4):661–677, 1995. URL [<GotoISI>://A1995QH99100003](http://dx.doi.org/10.1016/0016-7037(95)00003-6).
- F. J. Millero and D. Pierrot. A chemical equilibrium model for natural waters. *Aquatic Geochemistry*, 4(1):153–199, 1998. URL [<GotoISI>://000082329000007](http://dx.doi.org/10.1016/S0967-6369(98)00007-7).
- 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](http://dx.doi.org/10.1016/0197-9181(81)90008-8).
- 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](http://dx.doi.org/10.4319/limnol.1988.33.2.0269).
- 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](http://dx.doi.org/10.1016/0304-4203(95)00004-4).
- F. J. Millero, T. B. Graham, F. Huang, H. Bustos-Serrano, and D. Pierrot. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry*, 100(1-2):80–94, 2006.

- 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](#).
- 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](#).
- 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](#).
- 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](#).
- 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](#).
- 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](#).
- 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](#).
- Karline Soetaert, Andreas F. Hofmann, Jack J. Middelburg, Filip J.R. Meysman, and Jim Greenwood. The effect of biogeochemical processes on pH. *Marine Chemistry*, 105(1-2): 30–51, 2007. URL <http://www.sciencedirect.com/science/article/B6VC2-4MM7TG0-3/2/339315cfb5d4942bb35620925fab25d>.
- Karline Soetaert, Thomas Petzoldt, and Filip Meysman. *marelac: Constants, conversion factors, utilities for the Marine, Riverine, Estuarine, LAustrine and Coastal sciences*, 2009. URL <http://r-forge.r-project.org/projects/marelac/>. R package version 1.4.
- S. van Heuven, D. Pierrot, E. Lewis, and D. W. R. Wallace. MATLAB Program Developed for CO₂ System Calculations. ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 2009.
- R. F. Weiss. Solubility of Nitrogen, Oxygen and Argon in Water and Seawater. *Deep-Sea Research*, 17(4):721–735, 1970. URL [<GotoISI>://A1970H126100004](#).
- R. F. Weiss. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry*, 2:203–215, 1974.
- D. R. Williams. NASA Earth Fact Sheet, 2004. URL <http://nssdc.gsfc.nasa.gov/planetary/factsheet/earthfact.html>.
- 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](#).
- Richard E. Zeebe and Dieter Wolf-Gladrow. *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*. Number 65 in Elsevier Oceanography Series. Elsevier, first edition, 2001.