

AquaEnv - Constants and Formulae

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1 Chemical constants used in AquaEnv

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_HN02	1.584893e-3	mol/l	[Riordan et al., 2005]	approximative dissociation constant of HNO ₂ , NBS pH scale, hybrid constant
K_HN03	23.44	mol/kg-soln	(Soetaert pers. comm.)	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

1.2 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 ₂
O2	0.20946	atm	[Williams, 2004]	fugacity of O ₂

1.3 Elements of list MeanMolecularMass

The list `MeanMolecularMass` contains mean molecular masses 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

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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 seawater¹ 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-H₂O) 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-H₂O and the last digits adjusted (from 0.0199201 to 0.019924) results in the formula used here.

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

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

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

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

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

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 give $lat=0$ is assumed) as given in [Fofonoff and Millard \[1983\]](#) and implemented in [Soetaert et al. \[2009\]](#)

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

6 Seawater density as function of temperature T_c 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

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

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

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

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

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

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

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

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

7 Gas-exchange constants, dissociation constant, and solubility products as functions of temperature T_k , 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

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

or

$$\log_{10} \frac{K_X}{k_0} = A' + \frac{B'}{T_k} + C' \log_{10}(T_k) + D' T_k + E' T_k^2 \quad (15)$$

with T_k 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' 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 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	$\text{C02_sat} = f\text{CO}_2 \text{ K0_C02}$ $k_0^\circ = \left[\frac{\text{mol}}{\text{kg-solution atm}} \right]$
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 ₂ 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 ^{–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 [O₂]_{sat} given in Weiss [1970, Weiss, 1970]. It has been converted from ml-O₂/kg-soln to μmol-O₂/kg-soln using the molar volume of O₂ calculated with the virial equation using a first virial coefficient for oxygen at 273.0 Kelvin of –22 cm³/mol Atkins [1996], a value of 8.314 Nm/(Kelvin mol) for the gas constant R and an ambient pressure of 101300 N/m². The expression for the Henry's constant has then been created by dividing the expression for the saturation concentration by fO₂ = 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 : $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$		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: $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$ ("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: Perez and Fraga [1987, p. 91] (original), Dickson et al. [2007, chap. 5, p. 14]			
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: 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_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: 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_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: Lueker et al. [2000] (original), Dickson et al. [2007, chap. 5, p.13-14]			
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: 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_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: 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_c , 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
$A' = -25.9290 + 0.01781 \text{ S} - 0.0001122 \text{ S}^2$ $B' = -471.78$ $C' = 3.16967$	$K_{\text{HC03}} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> Lueker et al. [2000] (original), Dickson et al. [2007, chap. 5, p.14]		
K_W: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$		total pH scale
$A = 148.9652 - 5.977 \sqrt{\text{S}} - 0.01615 \text{ S}$ $B = -13847.26 + 118.67 \sqrt{\text{S}}$ $C = -23.6521 + 1.0495 \sqrt{\text{S}}$	$K_W = [\text{H}^+][\text{OH}^-]$ $k^\circ = \left(\frac{\text{mol}}{\text{kg-solution}} \right)^2$	
<i>References:</i> 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
$A = 148.0248 + 137.1942 \sqrt{\text{S}} + 1.62142 \text{ S}$ $B = -8966.90 - 2890.53 \sqrt{\text{S}} - 77.942 \text{ S} + 1.728 \text{ S}^{\frac{3}{2}} - 0.0996 \text{ S}^2$ $C = -24.4344 - 25.085 \sqrt{\text{S}} - 0.2474 \text{ S}$ $D = 0.053105 \sqrt{\text{S}}$	$K_{\text{BOH3}} = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> 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: $\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$		SWS pH scale
$A = -0.25444 + 0.46532 \sqrt{\text{S}} - 0.01992 \text{ S}$ $B = -6285.33 - 123.7184 \sqrt{\text{S}} + 3.17556 \text{ S}$ $D = 0.0001635$	$K_{\text{NH4}} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> 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
$A = 225.838 + 0.3449 \sqrt{\text{S}} - 0.0274 \text{ S}$ $B = -13275.3$ $C = -34.6435$	$K_{\text{H2S}} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> 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
$A = 115.525 + 0.69171 \sqrt{\text{S}} - 0.01844 \text{ S}$ $B = -4576.752 - 106.736 \sqrt{\text{S}} - 0.65643 \text{ S}$ $C = -18.453$	$K_{\text{H3P04}} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> 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
$A = 172.0883 + 1.3566 \sqrt{\text{S}} - 0.05778 \text{ S}$ $B = -8814.715 - 160.340 \sqrt{\text{S}} + 0.37335 \text{ S}$ $C = -27.927$	$K_{\text{H2P04}} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$ $k^\circ = \frac{\text{mol}}{\text{kg-solution}}$	
<i>References:</i> 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
$A = -18.141 + 2.81197 \sqrt{S} - 0.09984 S$	K_HP04	$= \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$
$B = -3070.75 + 17.27039 \sqrt{S} - 44.99486 S$	k°	$= \frac{\text{mol}}{\text{kg-solution}}$
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°	$= \frac{\text{mol}}{\text{kg-H}_2\text{O}}$
$C = -19.334$	m°	$= \frac{\text{mol}}{\text{kg-H}_2\text{O}}$
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°	$= \frac{\text{mol}}{\text{kg-H}_2\text{O}}$
$D = 0.021952$		
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 equation²:

$$K_{\text{corr}} = K \left(-\frac{a_0 + a_1 T_c + a_2 T_c^2}{R T_k} p + \frac{b_0 + b_1 T_c + b_2 T_c^2}{1000 R T_k} 0.5 p^2 \right) \quad (16)$$

Where K_{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 cm³)/(mol Kelvin), and p is the gauge pressure (total pressure minus one atmosphere, 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 table³.

	a_0	a_1	a_2	b_0	b_1	b_2
K_HSO4	-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_HCO3	-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

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-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 [\[Durst, 1975\]](#).

²It 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.

³Note that in [Lewis and Wallace \[1998\]](#) it is stated that the a values for H_2O and H_2S are *freshwater* values! And that the coefficients for the silicate species are assumed to be the same as the ones for the borate species.

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

In the above table S is salinity, $S_T = [SO_4^{2-}] + [HSO_4^-] \approx [SO_4^{2-}]$, $F_T = [HF] + [F^-] \approx [F^-]$, 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] 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 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]

$$\gamma_{H+} = 10^{-\left(1.82 \cdot 10^6 (\epsilon T_k)^{-\frac{3}{2}}\right) \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 I\right)} \quad (17)$$

where ϵ is the relative dielectric constant of seawater (Constants\$ ϵ in AquaEnv), T_k 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.

12 The revelle factor

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

$$\text{revelle} = \frac{d[CO_2]}{[CO_2]} \bigg/ \frac{d[\sum CO_2]}{[\sum CO_2]} \bigg|_{[TA]=\text{const.}} \quad (18)$$

in AquaEnv `revelle` is calculated numerically.

13 Partial derivatives of total alkalinity

The values for `dTAdKdKdS`, `dTAdKdKdT`, `dTAdKdKdd`, `dTAdKdKdSumH2SO4`, and `dTAdKdKdSumHF` are calculated numerically as described in Hofmann et al. [2009].

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

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