AquaEnv - Constants and Formulae

A.F. Hofmann

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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*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 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_2SO_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
SO4	(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])

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

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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]

$$\texttt{Cl} = \frac{\texttt{S}}{1.80655} \tag{1}$$

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` are used to calculate the total concentration [X] (in mol/kg-soln) of chemical species X in seawater[1] according to the relation

$$[\text{X}] = \frac{\texttt{ConcRelCl\$X}}{\texttt{MeanMolecularMass\$X}}\,\texttt{Cl} \tag{2}$$

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-H_2O) is calculated as

$$\texttt{I} = \frac{19.924\,\texttt{S}}{1000 - 1.005\,\texttt{S}} \tag{3}$$

Note that the approximation I/(mol/kg-solution) $\approx$ 0.0199201 `S` is given in Millero [1982, p. 428.]. This relationship converted into mol/kg-H_2O 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

$$\texttt{p} = 0.1\,\texttt{d}\,1.01325 \tag{4}$$

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

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

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[1]Note 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]

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

1.6 Seawater `density` as function of salinity `S` and temperature `t`

According to [Millero and Poisson, 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

$$
\begin{align}
\rho_{\text{SeaWater}} &= \rho_{\text{Water}} + \text{A S} + \text{B S}^{1.5} + \text{C S}^2 \tag{7}\\
\text{A} &= 0.824493 - 4.0899 \, 10^{-3} \, \text{t} + 7.6438 \, 10^{-5} \, \text{t}^2 - 8.2467 \, 10^{-7} \, \text{t}^3 \tag{8}\\
&\quad + 5.3875 \, 10^{-9} \, \text{t}^4 \tag{9}\\
\text{B} &= -5.72466 \, 10^{-3} + 1.0227 \, 10^{-4} \, \text{t} - 1.6546 \, 10^{-6} \, \text{t}^2 \tag{10}\\
\text{C} &= 4.8314 \, 10^{-4} \tag{11}\\
\rho_{Water} &= 999.842594 + 6.793952 \, 10^{-2} \, \text{t} - 9.095290 \, 10^{-3} \, \text{t}^2 \tag{12}\\
&\quad + 1.001685 \, 10^{-4} \, \text{t}^3 - 1.120083 \, 10^{-6} \, \text{t}^4 + 6.536332 \, 10^{-9} \, \text{t}^6 \tag{13}
\end{align}
$$

with `t` representing the temperature in °C and ρ_{Water} the density of fresh water in 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 calcuated in AquaEnv can be brought into the generic forms

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

or

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

or

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

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 $f\text{CO}_2$ being the fugacity of CO_2.

KO_CO2 : solubility of CO_2 in seawater	
$A = 0.023517 S - 167.81077$ $B = 9345.17$ $C = 23.3585$ $D = -2.3656 \ 10^{-4} S$ $E = 4.7036 \ 10^{-7} S$	$\text{CO2\_sat} = f CO_2 \ \text{KO\_CO2}$ $k_0^\circ = \left[\frac{mol}{kg-solution \ atm} \right]$
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]	
KO_O2 : solubility of O_2 in seawater (**micro**mol per kg-soln and atm)	
$A = -846.9978 - 0.037362 \ S$ $B = 25559.07$ $C = 146.4813$ $D = -0.22204 + 0.00016504 \ S$ $E = -2.0564 \ 10^{-7} \ S$	$\text{O2\_sat} = f O_2 \ \text{KO\_O2}$ $k_0^\circ = \left[\frac{\mu mol}{kg-solution \ atm} \right]$
References: derived from Weiss [1970], agrees with data in Murray and Riley [1969]	

Note that the formulation for KO_O2 has been derived using the formulation for a gravimetric $[O_2]_{sat}$ given in Weiss [1970, Weiss, 1970]. It has been converted from ml-O_2/kg-soln to μmol-O_2/kg-soln using the molar volume of O_2 calculated with the virial equation using a first virial coefficient for oxygen at 273.15 Kelvin of -22 cm^3/mol Atkins [1996], a value of 8.314472 Nm/(Kelvin mol) for the gas constant R and an ambient pressure of 101325 N/m^2. The expression for the Henry's constant has then been created by dividing the expression for the saturation concentration by $f O_2 = 0.20946$ 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 not mentioned coefficients A to E are zero and note also that given references somtimes 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_HSO4 : $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	**free** pH scale
$A = 324.57 \sqrt{\left(\frac{I}{m^\circ} \right)} - 771.54 \frac{I}{m^\circ} + 141.328$	$\text{K\_HSO4} = \frac{[H^+]_F \ [SO_4^{2-}]}{[HSO_4^-]}$
$B = 35474 \frac{I}{m^\circ} + 1776 \left(\frac{I}{m^\circ} \right)^2 - 13856 \sqrt{\left(\frac{I}{m^\circ} \right)} - 2698 \left(\frac{I}{m^\circ} \right)^{\frac{3}{2}} - 4276.1$	$k^\circ = \frac{mol}{kg-H_2O}$
$C = 114.723 \frac{I}{m^\circ} - 47.986 \sqrt{\left(\frac{I}{m^\circ} \right)} - 23.093$	$m^\circ = \frac{mol}{kg-H_2O}$
References: DOE [1994, c. 5, p. 13], Zeebe and Wolf-Gladrow [2001, p. 260], Dickson [1990b] (original)	
K_HF: $HF \rightleftharpoons H^+ + F^-$ ("dickson")	**free** pH scale
$A = 1.525 \sqrt{\frac{I}{m^\circ}} - 12.641$ $B = 1590.2$	$\text{K\_HF} = \frac{[H^+]_F \ [F^-]}{[HF]}$ $k^\circ = m^\circ = \frac{mol}{kg-H_2O}$
References: Dickson and Riley [1979a, p. 91] (origninal), 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: $HF \rightleftharpoons H^+ + F^-$ ("perez")		**total** pH scale
$A = -9.68 + 0.111\sqrt{S}$ $B = 874$	K_HF $=$ k° $=$	$\frac{[H^+]_F\,[F^-]}{[HF]}$ $\frac{mol}{kg-solution}$
References: Perez and Fraga [1987, p. 91] (orignial), Dickson et al. [2007, chap. 5, p. 14]		
K_CO2: $CO_2(aq) + H_2O\ (\rightleftharpoons H_2CO_3)\ \rightleftharpoons H^+ + HCO_3^-$ ("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_CO2 $=$ k° $=$	$\frac{[H^+]\,[HCO_3^-]}{[CO_2(aq)]}$ $\frac{mol}{kg-H_2O}$
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: $CO_2(aq) + H_2O\ (\rightleftharpoons H_2CO_3)\ \rightleftharpoons H^+ + HCO_3^-$ ("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_CO2 $=$ k° $=$	$\frac{[H^+]\,[HCO_3^-]}{[CO_2(aq)]}$ $\frac{mol}{kg-H_2O}$
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_CO2: $CO_2(aq) + H_2O\ (\rightleftharpoons H_2CO_3)\ \rightleftharpoons H^+ + HCO_3^-$ ("lueker")		**total** pH scale
$A" = 61.2172 + 0.011555\,S - 0.0001152\,S^2$ $B" = -3633.86$ $C" = -9.67770$	K_CO2 $=$ k° $=$	$\frac{[H^+]\,[HCO_3^-]}{[CO_2(aq)]}$ $\frac{mol}{kg-solution}$
References: Lueker et al. [2000] (original), Dickson et al. [2007, chap. 5, p.13-14]		
K_CO2: $CO_2(aq) + H_2O\ (\rightleftharpoons H_2CO_3)\ \rightleftharpoons H^+ + HCO_3^-$ ("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_CO2 $=$ k° $=$	$\frac{[H^+]\,[HCO_3^-]}{[CO_2(aq)]}$ $\frac{mol}{kg-solution}$
References: Millero et al. [2006] (original)		
K_HCO3: $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ ("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_HCO3 $=$ k° $=$	$\frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$ $\frac{mol}{kg-H_2O}$
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: $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ ("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 $= -11843.79 + 6551.35253\,\sqrt{S} - 1566.13883\,S + 116.270079\,S^{\frac{3}{2}}$	K_HCO3 $= \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$	
C $= -33.6485 + 25.928788\,\sqrt{S} - 6.171951\,S + 0.45788501\,S^{\frac{3}{2}}$	$k^\circ = \frac{mol}{kg-H_2O}$	
References: Roy et al. [1993b, p. 256] (original, based on a temperature depence 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_HCO3: $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ ("lueker")		**total** pH scale
A" $= -25.9290 + 0.01781\,S - 0.0001122\,S^2$	K_HCO3 $= \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$	
B" $= -471.78$	$k^\circ = \frac{mol}{kg-solution}$	
C" $= 3.16967$		
References: Lueker et al. [2000] (original), Dickson et al. [2007, chap. 5, p.14]		

K_HCO3: $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ ("millero")		**SW** pH scale
A" $= 90.18333 - 0.1248\,S + 0.0003687\,S^2 - 21.0894\,\sqrt{S}$	K_HCO3 $= \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$	
B" $= -5143.692 + 20.051\,S + 772.483\,\sqrt{S}$	$k^\circ = \frac{mol}{kg-solution}$	
C" $= -14.613358 + 3.3336\,\sqrt{S}$		
References: Millero et al. [2006] (original)		

K_W: $H_2O \rightleftharpoons H^+ + OH^-$		**total** pH scale
A $= 148.9652 - 5.977\,\sqrt{S} - 0.01615\,S$	K_W $= [H^+]\,[OH^-]$	
B $= -13847.26 + 118.67\,\sqrt{S}$	$k^\circ = \left(\frac{mol}{kg-solution}\right)^2$	
C $= -23.6521 + 1.0495\,\sqrt{S}$		
References: 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: $B(OH)_3 \rightleftharpoons H^+ + B(OH)_4^-$		**total** pH scale
A $= 148.0248 + 137.1942\,\sqrt{S} + 1.62142 S$	K_BOH3 $= \frac{[H^+]\,[B(OH)_4^-]}{[B(OH)_3]}$	
B $= -8966.90 - 2890.53\,\sqrt{S} - 77.942 S + 1.728\,S^{\frac{3}{2}} - 0.0996\,S^2$	$k^\circ = \frac{mol}{kg-solution}$	
C $= -24.4344 - 25.085\,\sqrt{S} - 0.2474\,S$		
D $= 0.053105\,\sqrt{S}$		
References: 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: $NH_4^+ \rightleftharpoons H^+ + NH_3$		**SW** pH scale
A $= -0.25444 + 0.46532\,\sqrt{S} - 0.01992\,S$	K_NH4 $= \frac{[H^+]\,[NH_3]}{[NH_4^+]}$	
B $= -6285.33 - 123.7184\,\sqrt{S} + 3.17556\,S$	$k^\circ = \frac{mol}{kg-solution}$	
D $= 0.0001635$		
References: Millero [1995, p. 671], Millero et al. [1995] (original), corrections of Millero [1995] in Lewis and Wallace [1998] give pH scale		

K_H2S: $H_2S \rightleftharpoons H^+ + HS^-$		**total** pH scale
A $= 225.838 + 0.3449\,\sqrt{S} - 0.0274\,S$	K_H2S $= \frac{[H^+]\,[HS^-]}{[H_2S]}$	
B $= -13275.3$	$k^\circ = \frac{mol}{kg-solution}$	
C $= -34.6435$		
References: Millero [1995, p. 671], Millero et al. [1988] (original), corrections of Millero [1995] in Lewis and Wallace [1998] give pH scale		

K_H3PO4: $\mathrm{H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-}$		**total** pH scale
$A = 115.525 + 0.69171\ \sqrt{\texttt{S}} - 0.01844\ \texttt{S}$ $B = -4576.752 - 106.736\ \sqrt{\texttt{S}} - 0.65643\ \texttt{S}$ $C = -18.453$	K_H3PO4 $=$ $k^\circ\quad =$	$\frac{\mathrm{[H^+]\,[H_2PO_4^-]}}{\mathrm{[H_3PO_4]}}$ $\frac{mol}{kg-solution}$
References: 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_H2PO4 : $\mathrm{H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}}$		**total** pH scale
$A = 172.0883 + 1.3566\ \sqrt{\texttt{S}} - 0.05778\ \texttt{S}$ $B = -8814.715 - 160.340\ \sqrt{\texttt{S}} + 0.37335\ \texttt{S}$ $C = -27.927$	K_H2PO4 $=$ $k^\circ\quad =$	$\frac{\mathrm{[H^+]\,[HPO_4^{2-}]}}{\mathrm{[H_2PO_4^-]}}$ $\frac{mol}{kg-solution}$
References: 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_HPO4 : $\mathrm{HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}}$		**total** pH scale
$A = -18.141 + 2.81197\ \sqrt{\texttt{S}} - 0.09984\ \texttt{S}$ $B = -3070.75 + 17.27039\ \sqrt{\texttt{S}} - 44.99486\ \texttt{S}$	K_HPO4 $=$ $k^\circ\quad =$	$\frac{\mathrm{[H^+]\,[PO_4^{3-}]}}{\mathrm{[HPO_4^{2-}]}}$ $\frac{mol}{kg-solution}$
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_SiOH4: $\mathrm{Si(OH)_4 \rightleftharpoons H^+ + SiO(OH)_3^-}$		**total** pH scale
$A = 117.385 + 3.5913\ \sqrt{\frac{\texttt{I}}{m^\circ}} - 1.5998\ \frac{\texttt{I}}{m^\circ} + 0.07871\ \left(\frac{\texttt{I}}{m^\circ}\right)^2$ $B = -8904.2 - 458.79\ \sqrt{\frac{\texttt{I}}{m^\circ}} + 188.74\ \frac{\texttt{I}}{m^\circ} - 12.1652\left(\frac{\texttt{I}}{m^\circ}\right)^2$ $C = -19.334$	K_SiOH4 $=$ $k^\circ\quad =$ $m^\circ\quad =$	$\frac{\mathrm{[H^+]\,[SiO(OH)_3^-]}}{\mathrm{[Si(OH)_4]}}$ $\frac{mol}{kg-\mathrm{H_2O}}$ $\frac{mol}{kg-\mathrm{H_2O}}$
References: Millero et al. [1988] (original), DOE [1994, chapter 5, p 17], Millero [1995, p.671]		

K_SiOOH3: $\mathrm{SiO(OH)_3^- \rightleftharpoons H^+ + SiO_2(OH)_2^{2-}}$		**total** pH scale
$A = 8.96$ $B = -4465.18$ $D = 0.021952$	K_SiOOH3 $=$ $k^\circ\quad =$	$\frac{\mathrm{[H^+]\,[SiO_2(OH)_2^{2-}]}}{\mathrm{[SiO(OH)_3^-]}}$ $\frac{mol}{kg-\mathrm{H_2O}}$
References: 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**		
$A' = -171.9065 - 0.77712\ \sqrt{\texttt{S}} - 0.07711\ S + 0.0041249\ S^{1.5}$ $B' = 2839.319 + 178.34\ \sqrt{\texttt{S}}$ $C' = 71.595$ $D' = -0.077993 + 0.0028426\ \sqrt{\texttt{S}}$	Ksp_cal $=$ $k_0^\circ\quad =$	$\mathrm{[CO_3^{2-}]\,[Ca^{2+}]}$ $\left[\left(\frac{mol}{kg-solution}\right)^2\right]$
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**		
$A' = -171.945 - 0.068393\ \sqrt{\texttt{S}} - 0.10018\ S + 0.0059415\ S^{1.5}$ $B' = 2903.293 + 88.135\ \sqrt{\texttt{S}}$	Ksp_ara $=$	$\mathrm{[CO_3^{2-}]\,[Ca^{2+}]}$

$C' = 71.595$		k_0°	$=$	$\left[\left(\frac{mol}{kg-solution} \right)^2 \right]$
$D' = -0.077993 + 0.0017276\ \sqrt{\text{S}}$				

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])

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[2]:

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

Where K_{corr} is the pressure corrected constant and K is the uncorrected constant, both on matching units, e.g., mol/kg-soln, $\texttt{T}$ is the absolute temperature in Kelvin, $\texttt{t}$ is the temperature in °C, $\texttt{R}$ is the ideal gas constant in (bar cm^3)/(mol Kelvin), and $\texttt{p}$ 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 table[3].

	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

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-H_2O 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

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[2]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.

[3]Note 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.

Zeebe and Wolf-Gladrow [2001]), and `free2nbs` signifies conversion from the free to the NBS pH scale [Durst, 1975].

`molal2molin`	$(1 - 0.001005\ S)$	Roy et al. [1993b, p. 257], DOE [1994, chap. 5, p. 15]
`free2tot`	$\left(1 + \frac{S_T}{K\_HSO4}\right)$	Dickson [1984, p. 2302], DOE [1994, chap. 5, p. 16], Zeebe and Wolf-Gladrow [2001, p. 57, p. 261]
`free2sws`	$\left(1 + \frac{S_T}{K\_HSO4} + \frac{F_T}{K\_HF}\right)$	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-H$_2$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.

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-H$_2$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 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]

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

where ϵ is the relative dielectric constant of seawater (`PhysChemConst$e` in `AquaEnv`), `T` is the temperature in Kelvin, and `I` is the ionic strength in mol/kg-H$_2$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.

1.12   The revelle factor

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

$$\texttt{revelle} = \frac{d[CO_2]}{[CO_2]} \bigg/ \frac{d[\sum CO_2]}{[\sum CO_2]}\bigg|_{[TA]=\text{const.}} \tag{19}$$

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].

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