

# Package **AquaEnv**: an Aquatic modelling Environment in R

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## Abstract

**AquaEnv** is an integrated development toolbox for aquatic chemical model generation focused on (ocean) acidification and CO<sub>2</sub> air-water exchange.

- It contains all elements necessary to model the pH, the related CO<sub>2</sub> air-water exchange, as well as aquatic acid-base chemistry in general for an arbitrary marine, estuarine or freshwater system. Also chemical batches can be modelled.
- Next to the routines necessary to calculate desired information, **AquaEnv** also contains a suite of tools to visualize this information.
- Furthermore, **AquaEnv** can not only be used to build dynamic models of aquatic systems, but it can also serve as a simple desktop tool for the experimental aquatic chemist to generate and visualize all possible derived information from a set of measurements with one single easy to use R function.
- Additionally, the sensitivity of the system to variations in the input variables can be visualized.
- **AquaEnv** also contains a number of example “applications” that make use of the aquatic modelling toolbox that **AquaEnv** provides:
  - a theoretical titration simulator
  - and a routine to determine total alkalinity ([TA]), the total dissolved inorganic carbon concentration ( $[\sum \text{CO}_2]$ ), as well as additionally the electrode standard potential ( $E_0$ ) and the first dissociation constant of the carbonate system ( $K_{\text{CO}_2}^*$ )

*Keywords:* aquatic modelling, pH, pH scales, dissolved inorganic carbon, total alkalinity, total alkalinity curve fitting, theoretical titration, revelle factor, omega, solubility products, CO<sub>2</sub>, ocean acidification, estuaries, carbonate system, seawater, R.

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# 1 Introduction

**AquaEnv** is a toolbox for aquatic modelling that serves several purposes

- It provides functions to calculate the stoichiometric equilibrium constants ( $K^*$ ) for key acid base systems in natural seawater, the Henry's constants ( $K_0$ ), as well as the solubility products ( $K_{sp}$ ) for calcite and aragonite. This functionality is provided via the functions `K_CO2`, `K_HCO3`, `K_BOH3`, `K_W`, `K_HSO4`, `K_HF`, `K_NH4`, `K_H2S`, `K_H3PO4`, `K_H2PO4`, `K_HPO4`, `K_SiOH4`, `K_SiOOH3`, `KO_CO2`, `KO_O2`, `Ksp_aragonite`, and `Ksp_calcite`.
- It is designed to make its use as easy as possible: all the information that can be calculated from the set of parameters known of a system or sample can be obtained by one single function: `aquaenv`. This function returns a list of class `aquaenv` that contains next to the input parameters
  - the chlorinity, the ionic strength,  $[\sum B(OH)_3]$ ,  $[\sum H_2SO_4]$ ,  $[\sum HF]$ ,  $[Cl^-]$ ,  $[Cl^-]$ ,  $[\sum Br]$ ,  $[Na^+]$ ,  $[Mg^{2+}]$ ,  $[Ca^{2+}]$ ,  $[K^+]$ ,  $[Sr^{2+}]$  calculated from salinity as given in [DOE \(1994\)](#) (Please note that if values for  $[\sum B(OH)_3]$ ,  $[\sum H_2SO_4]$ ,  $[\sum HF]$  are given as input parameters, these parameters are used and not the ones calculated from salinity.)
  - the hydrostatic pressure calculated from the given depth and the seawater density calculated from temperature and salinity as given by [Millero and Poisson \(1981\)](#)
  - a set of conversion factors to convert between different pH scales ([Dickson 1984](#); [Zeebe and Wolf-Gladrow 2001](#)) and between mol/kg-H<sub>2</sub>O and mol/kg-solution (inferred from [Roy, Roy, Vogel, PorterMoore, Pearson, Good, Millero, and Campbell \(1993\)](#) and [DOE \(1994\)](#))
  - the Henry's constants for CO<sub>2</sub> ([Weiss 1974](#)) and for O<sub>2</sub> (inferred from [Weiss 1970](#)) calculated from temperature and salinity as well as the associated saturation concentrations of CO<sub>2</sub> and O<sub>2</sub>.
  - the ion product of water ([Millero 1995](#)), the stoichiometric equilibrium constants of HSO<sub>4</sub><sup>-</sup> ([Dickson 1990a](#)), HF ([Dickson and Riley 1979](#)), CO<sub>2</sub> ([Roy et al. 1993](#)), HCO<sub>3</sub><sup>-</sup> ([Roy et al. 1993](#)), B(OH)<sub>3</sub> ([Dickson 1990a](#)), NH<sub>4</sub><sup>+</sup> ([Millero, Yao, and Aicher 1995](#)), H<sub>2</sub>S ([Millero 1995](#)), H<sub>3</sub>PO<sub>4</sub> ([Millero 1995](#)), H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ([Millero 1995](#)), HPO<sub>4</sub><sup>2-</sup> ([Millero 1995](#)), SiOH<sub>4</sub> ([Millero, Plese, and Fernandez 1988](#)), SiOOH<sub>3</sub><sup>-</sup> ([Wischmeyer, Del Amo, Brzezinski, and Wolf-Gladrow 2003](#)), HNO<sub>2</sub> ([Riordan, Minogue, Healy, O'Driscoll, and Sodeau 2005](#)), HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> ([Atkins 1996](#)), HS ([Atkins 1996](#)) mostly calculated as functions of temperature and salinity and pressure corrected according to [Millero \(1995\)](#).
  - the solubility products of calcite and aragonite ([Mucci 1983](#)) as well as the associated  $\Omega$ 's if a full speciation is calculated (see below)
  - the partial pressure of CO<sub>2</sub> - if a full speciation is calculated (see below)
  - if  $[\sum CO_2]$  and pH are given [TA] is calculated, if  $[\sum CO_2]$  and [TA] are given pH is calculated, if  $[\sum CO_2]$  and [CO<sub>2</sub>] or pCO<sub>2</sub> are given, pH and [TA] are calculated.
  - if either one of the pairs pH and [CO<sub>2</sub>] or pCO<sub>2</sub>, pH and [TA], or [TA] and [CO<sub>2</sub>] or pCO<sub>2</sub> is given,  $[\sum CO_2]$  is calculated

- if sufficient information is given and the flag `speciation=TRUE` is set, a full speciation of  $[\sum \text{CO}_2]$ ,  $[\sum \text{NH}_4]$ ,  $[\sum \text{H}_2\text{S}]$ ,  $[\sum \text{HNO}_3]$ ,  $[\sum \text{HNO}_2]$ ,  $[\sum \text{H}_3\text{PO}_4]$ ,  $[\sum \text{Si}(\text{OH})_4]$ ,  $[\sum \text{B}(\text{OH})_3]$ ,  $[\sum \text{H}_2\text{SO}_4]$ ,  $[\sum \text{HF}]$ , as well as water itself is calculated
  - if the flag `revelle=TRUE` is set, the revelle factor (Zeebe and Wolf-Gladrow 2001) is calculated. item if the flag `revelle=TRUE` is set, all necessary quantities for the explicit “direct substitution approach” (DSA) to pH modelling as given in Hofmann, Meysman, Soetaert, and Middelburg (2008b) are calculated. These are the buffer factor (the partial derivative of  $[\text{TA}]$  with respect to  $[\text{H}^+]$ ) and the partial derivatives of  $[\text{TA}]$  with respect to the other total quantities. Furthermore, the partial derivatives of  $[\text{TA}]$  with respect to changes in the equilibrium constants ( $K^*$ ), multiplied with the partial derivatives of the equilibrium constants with respect to their variables needed for the DSA with time variable equilibrium constants as described in Hofmann, Meysman, Soetaert, and Middelburg (2008a) are calculated. Finally, the ionization fractions as defined by Stumm and Morgan (1996) and used in Hofmann, Middelburg, Soetaert, Wolf-Gladrow, and Meysman (2008c) are calculated for the full speciation.
- Input for `aquaenv` has to be supplied in standard SI units, the free proton pH scale and in molinity<sup>1</sup> (mol/kg-solution). Conversion of input parameters to this necessary units and pH scale can be done with the generic function `convert`.
  - The information created with `aquaenv` is also supplied in standard SI units and in molinity. All elements of an object of class `aquaenv` of a certain unit or pH scale can be converted into other units or pH scales with the function `convert` as well.
  - One can use input vectors of temperature T, salinity S or depth d for `aquaenv` to obtain vectors of all calculated information as function of the input vector. This can be visualized in a large variety of ways using the `plot` function specially defined for objects of type `aquaenv`.
  - Objects of class `aquaenv` can be used in dynamic models to define the state of the system in each timestep of the numerical integration (done e.g. with `deSolve`). with the function `aquaenv` and the flag `from.data.frame=TRUE` it is possible to convert output of those dynamic models into objects of type `aquaenv` which allows the user to use the whole suite of visualisation tools that is provided by the function `plot` in **AquaEnv**.
  - As mentioned above Hofmann *et al.* (2008b), Hofmann *et al.* (2008a), and Hofmann *et al.* (2008c) describe methods for an “explicit” pH modelling which allows for the quantification of the influences of kinetically modelled processes on the pH. Objects of type `aquaenv` provide all needed quantities (partial derivatives of  $[\text{TA}]$ , ionization fractions, etc.) to employ both of those methods in dynamic models. Furthermore, **AquaEnv** provides the functionality to cumulatively plot the obtained influences on the pH.
  - As an example of how to use the toolbox that is **AquaEnv**, two applications are provided

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<sup>1</sup>Note that it is not sufficient to give a gravimetric concentration in mol/kg since there is a substantial difference between mol/kg-H<sub>2</sub>O (molality) and mol/kg-solution (molinity).

- The function **titration**: creates theoretical titrations which can be used e.g. to create bjerrum plots, something that can also be done with the function **plot** in **AquaEnv**.
- The function **TAfit**: a routine based on a method in [DOE \(1994\)](#) that makes use of that theoretical titration function and allows for determining total alkalinity ([TA]), the total dissolved inorganic carbon concentration ( $[\sum \text{CO}_2]$ ), as well as additionally the electrode standard potential ( $E_0$ ) and the first dissociation constant of the carbonate system ( $K_{\text{CO}_2}^*$ ) using the Levenberg-Marquart algorithm (least squares optimization procedure) as provided in **minpack.lm**.

## 2 The elements of an object of class *aquaenv*

The function **aquaenv**, the central function of **AquaEnv**, returns an object of class *aquaenv*. This object is a list of different elements which can be accessed with the **\$** character or with the **[[ ]]** operator

```
> test <- aquaenv(10, 35)
> test$Tc
```

```
[1] 10
attr(,"unit")
[1] "deg C"
```

```
> test[["Tc"]]
```

```
[1] 10
attr(,"unit")
[1] "deg C"
```

Maximally, i.e., if the enough input data is supplied to define the pH of the system and the flags **speciation**, **dsa**, and **revelle** are **TRUE** while the flag **skeleton** is **FALSE**, an object of class *aquaenv* contains the following elements

element	unit	explanation
Tc	°C	temperature
Tk	K	absolute temperature
S	“psu” (no unit)	salinity
Cl	‰	chlorinity
I	mol/kg-H <sub>2</sub> O	ionic strength
d	m	depth
hydroP	bar	hydrostatic pressure
density	kg/m <sup>3</sup>	(seawater) density
SumCO2	mol/kg-soln	$[\sum \text{CO}_2]$ , total dissolved inorganic carbon concentration
SumNH4	mol/kg-soln	$[\sum \text{NH}_4^+]$ , total ammonium concentration
SumH2S	mol/kg-soln	$[\sum \text{H}_2\text{S}]$ , total sulfide concentration

SumHNO3	mol/kg-soln	$[\sum \text{HNO}_3]$ , total nitrate concentration
SumHNO2	mol/kg-soln	$[\sum \text{HNO}_2]$ , total nitrite concentration
SumH3PO4	mol/kg-soln	$[\sum \text{H}_3\text{PO}_4]$ , total phosphate concentration
SumSiOH4	mol/kg-soln	$[\sum \text{Si}(\text{OH})_4]$ , total silicate concentration
SumBOH3	mol/kg-soln	$[\sum \text{B}(\text{OH})_3]$ , total borates concentration
SumH2SO4	mol/kg-soln	$[\sum \text{H}_2\text{SO}_4]$ , total sulfate concentration
SumHF	mol/kg-soln	$[\sum \text{HF}]$ , total fluoride concentration
SumBr	mol/kg-soln	$[\sum \text{HBr}]$ , total bromide concentration
ClConc	mol/kg-soln	$[\text{Cl}^-]$ , chloride concentration
Na	mol/kg-soln	$[\text{Na}^+]$ , sodium concentration
Mg	mol/kg-soln	$[\text{Mg}^{2+}]$ , magnesium concentration
Ca	mol/kg-soln	$[\text{Ca}^{2+}]$ , calcium concentration
K	mol/kg-soln	$[\text{K}^+]$ , potassium concentration
Sr	mol/kg-soln	$[\text{Sr}^{2+}]$ , strontium concentration
molal2molin	(mol/kg-soln)/(mol/kg-H2O)	concentration conversion factor: from molality to molinity
free2tot	-	pH conversion factor: free scale to total scale
free2sws	-	pH conversion factor: free scale to seawater scale
tot2free	-	pH conversion factor: total scale to free scale
tot2sws	-	pH conversion factor: total scale to seawater scale
sws2free	-	pH conversion factor: seawater scale to free scale
sws2tot	-	pH conversion factor: seawater scale to total scale
K0_CO2	mol/(kg-soln*atm)	Henry's constant for CO <sub>2</sub>
K0_O2	mol/(kg-soln*atm)	Henry's constant for O <sub>2</sub>
CO2_sat	mol/kg-soln	CO <sub>2</sub> saturation concentration at an atmospheric partial pressure/fugacity of Fugacity\$CO2
O2_sat	mol/kg-soln	O <sub>2</sub> saturation concentration at an atmospheric partial pressure/fugacity of Fugacity\$O2
K_W	(mol/kg-soln) <sup>2</sup> , free pH scale	stoichiometric equilibrium ion product of H <sub>2</sub> O: $K_W^* = [\text{H}^+][\text{OH}^-]$
K_HSO4	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{HSO}_4}^* = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$
K_HF	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{HF}}^* = [\text{H}^+][\text{F}^-]/[\text{HF}]$
K_CO2	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{CO}_2}^* = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$
K_HCO3	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{HCO}_3}^* = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$
K_BOH3	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{B}(\text{OH})_3}^* = [\text{H}^+][\text{B}(\text{OH})_4^-]/[\text{B}(\text{OH})_3]$
K_NH4	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{NH}_4}^* = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+]$
K_H2S	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{H}_2\text{S}}^* = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}]$
K_H3PO4	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{H}_3\text{PO}_4}^* = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4]$

K_H2PO4	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{H}_2\text{PO}_4^-}^* = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$
K_HPO4	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{HPO}_4^{2-}}^* = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}]$
K_SiOH4	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{Si(OH)}_4}^* = [\text{H}^+][\text{SiO(OH)}_3^-]/[\text{Si(OH)}_4]$
K_SiOOH3	mol/kg-soln, free pH scale	stoichiometric equilibrium constant $K_{\text{SiO(OH)}_3^-}^* = [\text{H}^+][\text{SiO}_2(\text{OH})_2^{2-}]/[\text{SiO(OH)}_3^-]$
K_HNO2	mol/kg-soln; mol/kg-H2O; mol/l	approximate value for equilibrium constant $K_{\text{HNO}_2}^* = [\text{H}^+][\text{NO}_2^-]/[\text{HNO}_2]$
K_HNO3	mol/kg-soln; mol/kg-H2O; mol/l	approximate value for equilibrium constant $K_{\text{HNO}_3}^* = [\text{H}^+][\text{NO}_3^-]/[\text{HNO}_3]$
K_H2SO4	mol/kg-soln; mol/kg-H2O; mol/l	approximate value for equilibrium constant $K_{\text{H}_2\text{SO}_4}^* = [\text{H}^+][\text{HSO}_4^-]/[\text{H}_2\text{SO}_4]$
K_HS	mol/kg-soln; mol/kg-H2O; mol/l	approximate value for equilibrium constant $K_{\text{HS}^-}^* = [\text{H}^+][\text{S}^{2-}]/[\text{HS}^-]$
Ksp_calcite	(mol/kg-soln) <sup>2</sup>	stoichiometric equilibrium solubility product of calcite $K_{\text{sp,cal}}^* = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$
Ksp_aragonite	(mol/kg-soln) <sup>2</sup>	stoichiometric equilibrium solubility product of aragonite $K_{\text{sp,ara}}^* = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$
TA	mol/kg-soln	[TA], total alkalinity
pH	-, free scale	pH
pCO2	atm,	partial pressure ( fugacity) of CO <sub>2</sub> in the water
CO2	mol/kg-soln	[CO <sub>2</sub> ]
HCO3	mol/kg-soln	[HCO <sub>3</sub> <sup>-</sup> ]
CO3	mol/kg-soln	[CO <sub>3</sub> <sup>2-</sup> ]
BOH3	mol/kg-soln	[B(OH) <sub>3</sub> ]
BOH4	mol/kg-soln	[B(OH) <sub>4</sub> <sup>-</sup> ]
OH	mol/kg-soln	[OH <sup>-</sup> ]
H3PO4	mol/kg-soln	[H <sub>3</sub> PO <sub>4</sub> ]
H2PO4	mol/kg-soln	[H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ]
HPO4	mol/kg-soln	[HPO <sub>4</sub> <sup>2-</sup> ]
PO4	mol/kg-soln	[PO <sub>4</sub> <sup>3-</sup> ]
SiOH4	mol/kg-soln	[Si(OH) <sub>4</sub> ]
SiOOH3	mol/kg-soln	[SiO(OH) <sub>3</sub> <sup>-</sup> ]
SiO2OH2	mol/kg-soln	[SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> ]
H2S	mol/kg-soln	[H <sub>2</sub> S]
HS	mol/kg-soln	[HS <sup>-</sup> ]
S2min	mol/kg-soln	[S <sup>2-</sup> ]
NH4	mol/kg-soln	[NH <sub>4</sub> <sup>+</sup> ]
NH3	mol/kg-soln	[NH <sub>3</sub> ]
H2SO4	mol/kg-soln	[H <sub>2</sub> SO <sub>4</sub> ]
HSO4	mol/kg-soln	[HSO <sub>4</sub> <sup>-</sup> ]

SO4	mol/kg-soln	$[\text{SO}_4^{2-}]$
HF	mol/kg-soln	$[\text{HF}]$
F	mol/kg-soln	$[\text{F}^-]$
HNO3	mol/kg-soln	$[\text{HNO}_3]$
NO3	mol/kg-soln	$[\text{NO}_3^-]$
HNO2	mol/kg-soln	$[\text{HNO}_2]$
NO2	mol/kg-soln	$[\text{NO}_2^-]$
omega_calcite	-	saturation state $\Omega$ with respect to calcite
omega_aragonite	-	saturation state $\Omega$ with respect to aragonite
revelle	-	Revelle factor
c1	-	ionization fraction $c_1 = [\text{CO}_2]/[\sum \text{CO}_2]$
c2	-	ionization fraction $c_2 = [\text{HCO}_3^-]/[\sum \text{CO}_2]$
c3	-	ionization fraction $c_3 = [\text{CO}_3^{2-}]/[\sum \text{CO}_2]$
dTAdSumCO2	-	$\frac{\partial[\text{TA}]}{\partial \sum \text{CO}_2}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots)$
b1	-	ionization fraction $b_1 = [\text{B}(\text{OH})_3]/[\sum \text{B}(\text{OH})_3]$
b2	-	ionization fraction $b_2 = [\text{B}(\text{OH})_4^-]/[\sum \text{B}(\text{OH})_3]$
dTAdSumBOH3	-	$\frac{\partial[\text{TA}]}{\partial \sum \text{B}(\text{OH})_3}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots)$
so1	-	ionization fraction $so_1 = [\text{H}_2\text{SO}_4]/[\sum \text{H}_2\text{SO}_4]$
so2	-	ionization fraction $so_2 = [\text{HSO}_4^-]/[\sum \text{H}_2\text{SO}_4]$
so3	-	ionization fraction $so_3 = [\text{SO}_4^{2-}]/[\sum \text{H}_2\text{SO}_4]$
dTAdSumH2SO4	-	$\frac{\partial[\text{TA}]}{\partial \sum \text{H}_2\text{SO}_4}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots)$
f1	-	ionization fraction $f_1 = [\text{HF}]/[\sum \text{HF}]$
f2	-	ionization fraction $f_1 = [\text{F}^-]/[\sum \text{HF}]$
dTAdSumHF	-	$\frac{\partial[\text{TA}]}{\partial \sum \text{HF}}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots)$
dTAdH	-	$\frac{\partial[\text{TA}]}{\partial [\text{H}^+]}$ : buffer factor with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots)$
dTAdKdKdS	-	$\sum_i \frac{\partial[\text{TA}]}{\partial K_i^*} \frac{\partial K_i^*}{\partial S}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots, K_i^*)$
dTAdKdKdT	-	$\sum_i \frac{\partial[\text{TA}]}{\partial K_i^*} \frac{\partial K_i^*}{\partial T}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots, K_i^*)$
dTAdKdKdd	-	$\sum_i \frac{\partial[\text{TA}]}{\partial K_i^*} \frac{\partial K_i^*}{\partial d}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots, K_i^*)$
dTAdKdKdSumH2SO4	-	$\sum_i \frac{\partial[\text{TA}]}{\partial K_i^*} \frac{\partial K_i^*}{\partial [\sum \text{H}_2\text{SO}_4]}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots, K_i^*)$
dTAdKdKdSumHF	-	$\sum_i \frac{\partial[\text{TA}]}{\partial K_i^*} \frac{\partial K_i^*}{\partial [\sum \text{HF}]}$ with $[\text{TA}] = f([\text{H}^+], [\sum \text{CO}_2], \dots, K_i^*)$

For elements that are calculated according to certain literature references, those references are given in appendix [A](#).



## 3 Using AquaEnv

### 3.1 Basic features

#### 3.1.1 calling the “K” functions directly

```
> K_CO2(15, 30)
```

```
[1] 9.089117e-07  
attr(,"unit")  
[1] "mol/kg-soln"  
attr(,"pH scale")  
[1] "free"
```

```
> K_HCO3(15, 30)
```

```
[1] 6.014934e-10  
attr(,"unit")  
[1] "mol/kg-soln"  
attr(,"pH scale")  
[1] "free"
```

```
> K0_CO2(15, 30)
```

```
[1] 0.03852158  
attr(,"unit")  
[1] "mol/(kg-soln*atm)"
```

```
> Ksp_calcite(15, 30, 100)
```

```
[1] 3.644549e-07  
attr(,"unit")  
[1] "(mol/kg-soln)^2"
```

#### 3.1.2 Minimal *aquaenv* definition

```
> ae <- aquaenv(Tc = 15, S = 30)  
> ae$K_CO2
```

```
[1] 9.089117e-07  
attr(,"unit")  
[1] "mol/kg-soln"  
attr(,"pH scale")  
[1] "free"
```

```
> ae$Ksp_calcite
```

```

[1] 3.582242e-07
attr("unit")
[1] "(mol/kg-soln)^2"

> ae$Ksp_aragonite

[1] 5.643199e-07
attr("unit")
[1] "(mol/kg-soln)^2"

> ae <- aquaenv(Tc = 15, S = 30, d = 10)
> ae$K_CO2

[1] 9.09921e-07
attr("unit")
[1] "mol/kg-soln"
attr("pH scale")
[1] "free"

> ae$Ksp_calcite

[1] 3.588429e-07
attr("unit")
[1] "(mol/kg-soln)^2"

> ae$Ksp_aragonite

[1] 5.652276e-07
attr("unit")
[1] "(mol/kg-soln)^2"

> names(ae)

[1] "Tc"           "Tk"           "S"            "Cl"
[5] "I"            "d"            "hydroP"       "density"
[9] "SumCO2"       "SumNH4"       "SumH2S"       "SumHNO3"
[13] "SumHNO2"      "SumH3PO4"     "SumSiOH4"     "SumBOH3"
[17] "SumH2SO4"     "SumHF"        "SumBr"        "ClConc"
[21] "Na"           "Mg"           "Ca"           "K"
[25] "Sr"           "molal2molin"  "free2tot"     "free2sws"
[29] "tot2free"     "tot2sws"      "sws2free"     "sws2tot"
[33] "K0_CO2"       "K0_O2"        "CO2_sat"      "O2_sat"
[37] "K_W"          "K_HSO4"       "K_HF"         "K_CO2"
[41] "K_HCO3"       "K_BOH3"       "K_NH4"        "K_H2S"
[45] "K_H3PO4"      "K_H2PO4"      "K_HPO4"       "K_SiOH4"
[49] "K_SiOOH3"     "K_HNO2"       "K_HNO3"       "K_H2SO4"
[53] "K_HS"         "Ksp_calcite"  "Ksp_aragonite"

```

### 3.1.3 Defining the complete aquaenv system in different ways

```

> Tc <- 15
> S <- 30
> d <- 10
> SumCO2 <- 0.002
> pH <- 8
> TA <- 0.002140323
> pCO2 <- 0.000533576
> CO2 <- 2.055419e-05
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH)
> ae$TA

[1] 0.002140800
attr(,"unit")
[1] "mol/kg-soln"

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA)
> ae$pH

[1] 7.998791
attr(,"pH scale")
[1] "free"

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, CO2 = CO2)
> ae$pH

[1] 7.999293
attr(,"pH scale")
[1] "free"

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pCO2 = pCO2,
+             dsa = TRUE, revelle = TRUE)
> ae$pH

[1] 7.999293
attr(,"pH scale")
[1] "free"

> names(ae)

[1] "Tc"          "Tk"          "S"
[4] "Cl"          "I"           "d"
[7] "hydroP"      "density"     "SumCO2"
[10] "SumNH4"      "SumH2S"      "SumHNO3"
[13] "SumHNO2"     "SumH3PO4"    "SumSiOH4"

```

[16]	"SumBOH3"	"SumH2SO4"	"SumHF"
[19]	"SumBr"	"ClConc"	"Na"
[22]	"Mg"	"Ca"	"K"
[25]	"Sr"	"molal2molin"	"free2tot"
[28]	"free2sws"	"tot2free"	"tot2sws"
[31]	"sws2free"	"sws2tot"	"K0_CO2"
[34]	"K0_O2"	"CO2_sat"	"O2_sat"
[37]	"K_W"	"K_HSO4"	"K_HF"
[40]	"K_CO2"	"K_HCO3"	"K_BOH3"
[43]	"K_NH4"	"K_H2S"	"K_H3PO4"
[46]	"K_H2PO4"	"K_HPO4"	"K_SiOH4"
[49]	"K_SiOOH3"	"K_HNO2"	"K_HNO3"
[52]	"K_H2SO4"	"K_HS"	"Ksp_calcite"
[55]	"Ksp_aragonite"	"TA"	"pH"
[58]	"pCO2"	"CO2"	"HCO3"
[61]	"CO3"	"BOH3"	"BOH4"
[64]	"OH"	"H3PO4"	"H2PO4"
[67]	"HPO4"	"PO4"	"SiOH4"
[70]	"SiOOH3"	"SiO2OH2"	"H2S"
[73]	"HS"	"S2min"	"NH4"
[76]	"NH3"	"H2SO4"	"HSO4"
[79]	"SO4"	"HF"	"F"
[82]	"HNO3"	"NO3"	"HNO2"
[85]	"NO2"	"omega_calcite"	"omega_aragonite"
[88]	"revelle"	"c1"	"c2"
[91]	"c3"	"dTAdSumCO2"	"b1"
[94]	"b2"	"dTAdSumBOH3"	"so1"
[97]	"so2"	"so3"	"dTAdSumH2SO4"
[100]	"f1"	"f2"	"dTAdSumHF"
[103]	"dTAdH"	"dTAdKdKdS"	"dTAdKdKdT"
[106]	"dTAdKdKdd"	"dTAdKdKdSumH2SO4"	"dTAdKdKdSumHF"

```
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, CO2 = CO2, pCO2 = pCO2)
```

```
[1] "Error! Overdetermined system: entered pCO2: 0.000533576 , calculated pCO2: 0.000533576"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."
```

```
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, TA = TA)
```

```
[1] "Error! Overdetermined system: entered TA: 0.002140323 , calculated TA: 0.002140799720"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."
```

```
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, CO2 = CO2)
```

```
[1] "Error! Overdetermined system: entered pH: 8 , calculated pH: 7.99929303203143"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."
```

```

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, pCO2 = pCO2)

[1] "Error! Overdetermined system: entered pH: 8 , calculated pH: 7.99929301525035"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, CO2 = CO2)

[1] "Error! Overdetermined system: entered TA: 0.002140323 , calculated TA: 0.002140520813"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, pCO2 = pCO2)

[1] "Error! Overdetermined system: entered TA: 0.002140323 , calculated TA: 0.002140520806"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."

```

### 3.1.4 Cloning the aquaenv system: 1 to 1 and with different pH or TA

```

> Tc <- 15
> S <- 30
> SumCO2 <- 0.002
> TA <- 0.00214
> ae <- aquaenv(Tc, S, SumCO2 = SumCO2, TA = TA)
> aeclone1 <- aquaenv(ae = ae)
> pH <- 9
> aeclone2 <- aquaenv(ae = ae, pH = pH)
> TA <- 0.002
> aeclone3 <- aquaenv(ae = ae, TA = TA)
> ae$pH

[1] 7.99838
attr(,"pH scale")
[1] "free"

> aeclone1$pH

[1] 7.99838
attr(,"pH scale")
[1] "free"

> aeclone2$TA

[1] 0.002982758
attr(,"unit")
[1] "mol/kg-soln"

> aeclone3$pH

[1] 7.548174
attr(,"pH scale")
[1] "free"

```

### 3.1.5 preparing input variables

```
> Tc <- 15
> S <- 10
> pH_NBS <- 8.142777
> SumCO2molar <- 0.002016803
> pH_free <- convert(pH_NBS, "pHscale", "nbs2free", Tc = Tc,
+   S = S)
> SumCO2molin <- convert(SumCO2molar, "conc", "molar2molin",
+   Tc = Tc, S = S)
> ae <- aquaenv(Tc, S, SumCO2 = SumCO2molin, pH = pH_free)
> ae$pH
```

```
[1] 8
attr(,"pH scale")
[1] "free"
```

```
> ae$SumCO2
```

```
[1] 0.002000000
attr(,"unit")
[1] "mol/kg-soln"
```

```
> ae$TA
```

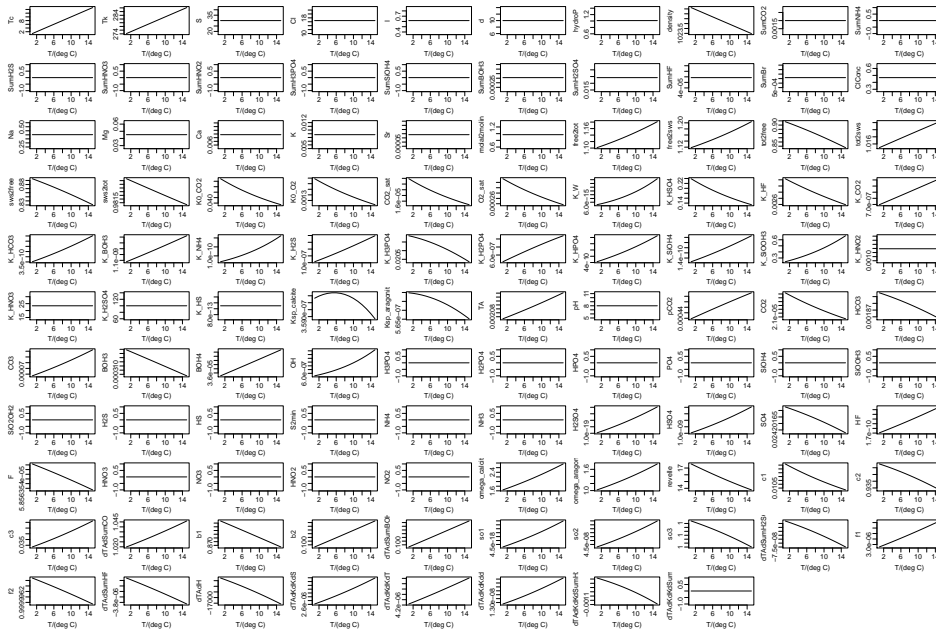
```
[1] 0.002048921
attr(,"unit")
[1] "mol/kg-soln"
```

### 3.1.6 Vectors as input variables

(only ONE input variable may be a vector)

(with full output: including the Revelle factor and the DSA properties)

```
> SumCO2 <- 0.002
> pH <- 8
> Tc <- 1:15
> S <- 30
> d <- 10
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, reveille = TRUE,
+   dsa = TRUE)
> plot(ae, xval = Tc, xlab = "T/(deg C)", newdevice = FALSE)
```



extra examples

```
> options(prompt = " ")
> Tc <- 15
> S <- 1:30
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, revelle = TRUE,
+   dsa = TRUE)
> plot(ae, xval = S, xlab = "S")
> S <- 30
> d <- seq(1, 1000, 100)
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, revelle = TRUE,
+   dsa = TRUE)
> plot(ae, xval = d, xlab = "depth/m")
> TA <- 0.0023
> Tc <- 1:15
> S <- 30
> d <- 10
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, revelle = TRUE,
+   dsa = TRUE)
> plot(ae, xval = Tc, xlab = "T/(deg C)")
> Tc <- 15
> S <- 1:30
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, revelle = TRUE,
+   dsa = TRUE)
> plot(ae, xval = S, xlab = "S")
> S <- 30
> d <- seq(1, 1000, 100)
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, revelle = TRUE,
+   dsa = TRUE)
```

```
> plot(ae, xval = d, xlab = "depth/m")
```

## A Elements of an object of class *aquaenv* are calculated according to

element	references
Cl	DOE (1994) chapter 5, p. 11, and Zeebe and Wolf-Gladrow (2001) p. 100, footnote 3
I	DOE (1994), chapter 5, p. 13, 15, Zeebe and Wolf-Gladrow (2001). p.12, and Roy <i>et al.</i> (1993), p.257. 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.
density	Millero and Poisson (1981) and DOE (1994), chapter 5, p. 6f
SumBr, ClConc, Na, Mg, Ca, K, Sr	DOE (1994), chapter 5, p.11
molal2molin	Roy <i>et al.</i> (1993), p.257. and DOE (1994), chapter 5, p. 15
free2tot, tot2free	Dickson (1984), p.2302, DOE (1994), chapter 4, p.16, Zeebe and Wolf-Gladrow (2001), p.57, 261
free2sws, tot2sws, sws2free, sws2tot	Dickson (1984), p.2303, Zeebe and Wolf-Gladrow (2001), p.57
K0_CO2	Weiss (1974), DOE (1994), chapter 5, p. 13 (here it is stated that the unit is mol/(kg-solution*atm)), Millero (1995), p.663, Zeebe and Wolf-Gladrow (2001), p.257
K0_O2	derived from a formula for the oxygen saturation concentration in ml-O <sub>2</sub> /kg-solution by Weiss (1970) using the first virial coefficient of oxygen (Atkins 1996, p. 41, 1029) and the atmospheric oxygen fugacity (Williams 2004)
K_W	(Millero 1995, p.670) ( <b>original reference</b> , but slightly different formula for SWS pH), (DOE 1994, chapter 5, p. 18) (NOT the original reference! DOE (1994) cites in an update from 1997 Millero (1995)! However the version of the formula used here is the one converted to total pH scale given in DOE (1994)), and (Zeebe and Wolf-Gladrow 2001, p. 258). Constant type (stoichiometric), pH scale (total, converted to free here) , and concentration unit (molinity squared): (DOE 1994, chapter 5, p. 12,18), pH scale also in (Zeebe and Wolf-Gladrow 2001, p. 258).
K_HSO4	(DOE 1994, chapter 5 page 13), (Zeebe and Wolf-Gladrow 2001, p. 260), Dickson (1990b) (original reference). Constant type (stoichiometric), pH scale (free) , and concentration unit (molality converted to molinity here): (DOE 1994, chapter 5, p. 13).
pH	As given in Dickson (1984), p. 2303 (use of "m") and Dickson and Riley (1979), p. 91f all concentrations appearing in the definition of the total and the seawater pH scale are <b>molal</b> (mol/kg-H <sub>2</sub> O) concentrations. But in Roy <i>et al.</i> (1993), p. 257 and in DOE (1994), chapter 4, SOP 6, p. 1 it is stated, that concentrations for the seawater and total pH scale are in mol/kg-solution. To be consistent with DOE (1994) <b>molin</b> concentrations (mol/kg-solution) are chosen for calculating the pH.
dTAdKdKdS, dTAd-KdKdT, dTAd-KdKdd, dTAd-KdKdSumH2SO4, dTAdKdKdSumHF	Hofmann <i>et al.</i> (2008a)

mention that all corrections from Lewis and Wallace (1998) have been applied  
 explain pressure correction: what has been corrected in Millero1995?



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