

Package ‘AquaEnv’

September 6, 2016

Version 1.0-4

Title Integrated Development Toolbox for Aquatic Chemical Model Generation

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Depends R (>= 2.15.0)

Imports minpack.lm, graphics, grDevices, stats

Suggests deSolve

Description Toolbox for the experimental aquatic chemist, focused on acidification and CO₂ air-water exchange. It contains all elements to model the pH, the related CO₂ air-water exchange, and aquatic acid-base chemistry for an arbitrary marine, estuarine or freshwater system. It contains a suite of tools for sensitivity analysis, visualisation, modelling of chemical batches, and can be used to build dynamic models of aquatic systems. As from version 1.0-4, it also contains functions to calculate the buffer factors.

License GPL (>= 2)

LazyData yes

Repository CRAN

Date/Publication 2016-09-06 16:39:52

NeedsCompilation no

Repository/R-Forge/Project aquaenv

Repository/R-Forge/Revision 97

Repository/R-Forge/DateTimeStamp 2016-09-05 13:48:52

R topics documented:

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aquaenv

aquaenv

Description

PUBLIC function: the main function of the package AquaEnv: creates an object of class aquaenv

Usage

```
aquaenv(S, t, p=pmax((P-Pa), gauge_p(d, lat, Pa)),
        P=Pa, Pa=1.01325, d=0, lat=0,
        SumCO2=0, SumNH4=0, SumH2S=0, SumH3PO4=0,
        SumSiOH4=0, SumHNO3=0, SumHNO2=0, SumBOH3=NULL,
        SumH2SO4=NULL, SumHF=NULL, TA=NULL, pH=NULL, fCO2=NULL, CO2=NULL,
        speciation=TRUE, dsa=FALSE, ae=NULL, from.data.frame=FALSE,
        SumH2SO4_Koffset=0, SumHF_Koffset=0, revelle=FALSE, skeleton=FALSE,
        k_w=NULL, k_co2=NULL, k_hco3=NULL, k_boh3=NULL, k_hso4=NULL,
        k_hf=NULL, k1k2="lueker", khf="dickson", khso4="dickson",
        fCO2atm=0.000400, fO2atm=0.20946)
```

Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars, standard is calculated either from the given P, or the given d, lat, and Pa |
| P | total pressure in bars, standard: Pa (at the surface) |
| Pa | atmospheric pressure in bars, standard: 1 atm (at sea-level) |
| d | depth below the surface in meters, standard: 0 (at the surface) |
| lat | latitude in degrees (-90 to +90) to calculate the gravitational constant g for calculating the water depth from the pressure and vice versa, standard: 0 |
| SumCO2 | total carbonate concentration in mol/kg-solution, if NULL is supplied it is calculated |
| SumNH4 | total ammonium concentration in mol/kg-solution, optional |
| SumH2S | total sulfide concentration in mol/kg-solution, optional |
| SumH3PO4 | total phosphate concentration in mol/kg-solution, optional |
| SumSiOH4 | total silicate concentration in mol/kg-solution, optional |
| SumHNO3 | total nitrate concentration in mol/kg-solution, optional |
| SumHNO2 | total nitrite concentration in mol/kg-solution, optional |
| SumBOH3 | total borate concentration in mol/kg-solution, calculated from S if not supplied |
| SumH2SO4 | total sulfate concentration in mol/kg-solution, calculated from S if not supplied |
| SumHF | total fluoride concentration in mol/kg-solution, calculated from S if not supplied |
| TA | total alkalinity in mol/kg-solution, if supplied, pH will be calculated |
| pH | pH on the free proton concentration scale, if supplied, total alkalinity will be calculated |
| fCO2 | fugacity of CO2 in the water in atm (i.e. the fugacity of CO2 in a small volume of air fully equilibrated with a sufficiently large sample of water), can be used with either [TA], pH, or [CO2] to define the system |
| CO2 | concentration of CO2, can be used with either [TA], pH, or fCO2 to define the system |

| | |
|------------------|---|
| speciation | flag: TRUE = full speciation is calculated |
| dsa | flag: TRUE = all information necessary to build a pH model with the direct substitution approach (DSA, Hofmann2008) is calculated |
| ae | either an object of class aquaenv used for the cloning functionality or a dataframe used for the from.data.frame functionality. Note that for cloning the desired k1k2 and khf values need to be specified! (otherwise the default values are used for the cloned object) |
| from.data.frame | flag: TRUE = the object of class aquaenv is built from the data frame supplied in ae |
| SumH2SO4_Koffset | only used internally to calculate dTAdKdKdSumH2SO4 |
| SumHF_Koffset | only used internally to calculate dTAdKdKdSumHF |
| revelle | flag: TRUE = the revelle factor is numerically calculated. We do however strongly encourage to use the analytical calculation from BufferFactors\$RF |
| skeleton | flag: TRUE = a reduced amount of information is calculated yielding a smaller object of type aquaenv |
| k_w | a fixed K_W can be specified |
| k_co2 | a fixed K_{CO2} can be specified; used for TA fitting: give a K_{CO2} and NOT calculate it from T and S: i.e. K_{CO2} can be fitted in the routine as well |
| k_hco3 | a fixed K_{HCO3} can be specified |
| k_boh3 | a fixed K_{BOH3} can be specified |
| k_hso4 | a fixed K_{HSO4} can be specified |
| k_hf | a fixed K_{HF} can be specified |
| k1k2 | either "lueker" (default, Lueker2000), "roy" (Roy1993a), or "millero" (Millero2006) for K_{CO2} and K_{HCO3} . |
| khf | either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) for K_{HF} |
| khso4 | either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) for K_{HSO4} |
| fCO2atm | atmospheric fugacity of CO2 in atm, default = 0.000400 atm |
| fO2atm | atmospheric fugacity of O2 in atm, default = 0.20946 atm |

Value

a list containing: "S" "t" "p" "T" "Cl" "I" "P" "Pa" "d" "density" "SumCO2" "SumNH4" "SumH2S" "SumHNO3" "SumHNO2" "SumH3PO4" "SumSiOH4" "SumBOH3" "SumH2SO4" "SumHF" "Br" "ClConc" "Na" "Mg" "Ca" "K" "Sr" "molal2molin" "free2tot" "free2sws" "tot2free" "tot2sws" "sws2free" "sws2tot" "K0_CO2" "K0_O2" "fCO2atm" "fO2atm" "CO2_sat" "O2_sat" "K_W" "K_HSO4" "K_HF" "K_CO2" "K_HCO3" "K_BOH3" "K_NH4" "K_H2S" "K_H3PO4" "K_H2PO4" "K_HPO4" "K_SiOH4" "K_SiOOH3" "K_HNO2" "K_HNO3" "K_H2SO4" "K_HS" "Ksp_calcite" "Ksp_aragonite" "TA" "pH" "fCO2" "CO2" "HCO3" "CO3" "BOH3" "BOH4" "OH" "H3PO4" "H2PO4" "HPO4" "PO4" "SiOH4" "SiOOH3" "SiO2OH2" "H2S" "HS" "S2min" "NH4" "NH3" "H2SO4" "HSO4" "SO4" "HF" "F" "HNO3" "NO3" "HNO2" "NO2" "omega_calcite" "omega_aragonite" "revelle" "c1" "c2" "c3" "dTAdSumCO2" "b1" "b2" "dTAdSumBOH3" "so1" "so2" "so3" "dTAdSumH2SO4" "f1" "f2" "dTAdSumHF" "dTAdH" "dTAdKdKdS" "dTAdKdKdT" "dTAdKdKdd" "dTAdKdKdSumH2SO4" "dTAdKdKdSumHF" or a subset of this set. Please consult the vignette of AquaEnv for more details

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

Examples

```
## Not run:
#####
# Minimal aquaenv definition
#####
ae <- aquaenv(S=30, t=15)
ae$K_CO2

ae$Ksp_calcite
ae$Ksp_aragonite

ae <- aquaenv(S=30, t=15, p=10)
ae <- aquaenv(S=30, t=15, P=11)
ae <- aquaenv(S=30, t=15, d=100)
ae <- aquaenv(S=30, t=15, d=100, Pa=0.5)
ae$K_CO2

ae$Ksp_calcite
ae$Ksp_aragonite

ae

#####
# Defining the complete aquaenv system in different ways
#####
S <- 30
t <- 15
p <- gauge_p(d=10) # ~ p <- 0.1*10*1.01325
SumCO2 <- 0.0020
pH <- 8
TA <- 0.002140798
fCO2 <- 0.0005326744
CO2 <- 2.051946e-05

ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH)
ae$TA

ae <- aquaenv(S, t, p, SumCO2=SumCO2, TA=TA)
ae$pH

ae <- aquaenv(S, t, p, SumCO2=SumCO2, CO2=CO2)
ae$pH

ae <- aquaenv(S, t, p, SumCO2=SumCO2, fCO2=fCO2)
ae$pH

ae <- aquaenv(S, t, p, SumCO2=SumCO2, CO2=CO2, fCO2=fCO2)
```

```

ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH, TA=TA)
ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH, CO2=CO2)
ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH, fCO2=fCO2)
ae <- aquaenv(S, t, p, SumCO2=SumCO2, TA=TA, CO2=CO2)
ae <- aquaenv(S, t, p, SumCO2=SumCO2, TA=TA, fCO2=fCO2)

#####
# Cloning the aquaenv system: 1 to 1 and with different pH or TA
#####
S      <- 30
t      <- 15
SumCO2 <- 0.0020
TA     <- 0.00214

ae <- aquaenv(S, t, 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$pH
aeclone1$pH
aeclone2$TA
aeclone3$pH

#####
# Vectors as input variables (only ONE input variable may be a vector)
# (with full output: including the Revelle factor and the DSA properties)
#####
SumCO2 <- 0.0020
pH     <- 8

S      <- 30
t      <- 1:15
p      <- gauge_p(10)
ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH, revelle=TRUE, dsa=TRUE)
plot(ae, xval=t, xlab="T/(deg C)", newdevice=FALSE)

S <- 1:30
t <- 15
ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH, revelle=TRUE, dsa=TRUE)
plot(ae, xval=S, xlab="S", newdevice=FALSE)

```

```

S <- 30
p <- gauge_p(seq(1,1000, 100))
ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH, revelle=TRUE, dsa=TRUE)
plot(ae, xval=p, xlab="gauge pressure/bar", newdevice=FALSE)

TA <- 0.0023

S <- 30
t <- 1:15
d <- gauge_p(10)
ae <- aquaenv(S, t, p, SumCO2=SumCO2, TA=TA, revelle=TRUE, dsa=TRUE)
plot(ae, xval=t, xlab="T/(deg C)", newdevice=FALSE)

S <- 1:30
t <- 15
ae <- aquaenv(S, t, p, SumCO2=SumCO2, TA=TA, revelle=TRUE, dsa=TRUE)
plot(ae, xval=S, xlab="S", newdevice=FALSE)

S <- 30
p <- gauge_p(seq(1,1000, 100))
ae <- aquaenv(S, t, p, SumCO2=SumCO2, TA=TA, revelle=TRUE, dsa=TRUE)
plot(ae, xval=p, xlab="gauge pressure/bar", newdevice=FALSE)

#####
# Calculating SumCO2 by giving a constant pH&CO2, pH&fCO2, pH&TA,
# TA&CO2, or TA&fCO2
#####
fCO2 <- 0.0006952296
CO2 <- 2.678137e-05
pH <- 7.888573
TA <- 0.0021

S <- 30
t <- 15
p <- gauge_p(10)

ae <- aquaenv(S, t, p, SumCO2=NULL, pH=pH, CO2=CO2, dsa=TRUE, revelle=TRUE)
ae$SumCO2
ae$revelle
ae$dTAdH

ae <- aquaenv(S, t, p, SumCO2=NULL, pH=pH, fCO2=fCO2)
ae$SumCO2

ae <- aquaenv(S, t, p, SumCO2=NULL, pH=pH, TA=TA)
ae$SumCO2

ae <- aquaenv(S, t, p, SumCO2=NULL, TA=TA, CO2=CO2)
ae$SumCO2

```

```
ae <- aquaenv(S, t, p, SumCO2=NULL, TA=TA, fCO2=fCO2)
ae$SumCO2

t <- 1:15
ae <- aquaenv(S, t, p, SumCO2=NULL, pH=pH, CO2=CO2)
plot(ae, xval=t, xlab="T/(deg C)", mfrow=c(9,10), newdevice=FALSE)

ae <- aquaenv(S, t, p, SumCO2=NULL, pH=pH, CO2=CO2, revelle=TRUE, dsa=TRUE)
plot(ae, xval=t, xlab="T/(deg C)", newdevice=FALSE)

S <- 1:30
t <- 15
ae <- aquaenv(S, t, p, SumCO2=NULL, pH=pH, fCO2=fCO2, revelle=TRUE, dsa=TRUE)
plot(ae, xval=S, xlab="S", newdevice=FALSE)

S <- 30
p <- gauge_p(seq(1,1000, 100))
ae <- aquaenv(S, t, p, SumCO2=NULL, pH=pH, TA=TA, revelle=TRUE, dsa=TRUE)
plot(ae, xval=p, xlab="gauge pressure/bar", newdevice=FALSE)

## End(Not run)
```

AquaEnv_package

AquaEnv - an integrated development toolbox for aquatic chemical model generation

Description

AquaEnv is an integrated development toolbox for aquatic chemical model generation focused on (ocean) acidification and CO₂ air-water exchange.

It contains all elements necessary to model the pH, the related CO₂ 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.

Details

Package: AquaEnv
Type: Package
Version: 1.1

Date: 2016-05-18
License: GNU Public License 2 or above

Author(s)

Karline Soetaert (Maintainer), Andreas F. Hofmann, Mathilde Hagens

References

Hagens M. and J.J. Middelburg, 2016 Generalised expressions for the response of pH to changes in ocean chemistry. *Geochimica et Cosmochimica Acta*, *in press*.

Hofmann A. F., K. Soetaert, J.J. Middelburg, F. J. R. Meysman, 2010 AquaEnv: An Aquatic Acid-Base Modelling Environment in R. *Aquatic Geochemistry* **16**: 507-546.

Examples

```
## Not run:
## show examples (see respective help pages for details)
example(aquaenv)

## open the directory with source code of demos
browseURL(paste(system.file(package="AquaEnv"), "/demo", sep=""))

## run demos
demo(basicfeatures )

## show package vignette with tutorial about how to use aquaenv
vignette("AquaEnv")
edit(vignette("AquaEnv"))
browseURL(paste(system.file(package="AquaEnv"), "/doc", sep=""))

## show index file of package vignettes and documentation files
browseURL(paste(system.file(package="AquaEnv"), "/doc/index.html", sep=""))

## show documentation about private functions in the packet
browseURL(paste(system.file(package="AquaEnv"), "/doc/AquaEnv-PrivateFunctions.pdf", sep=""))

## show documentation about physical-chemical constants and formulae used in the packet
browseURL(paste(system.file(package="AquaEnv"), "/doc/AquaEnv-ConstantsAndFormulae.pdf", sep=""))

## End(Not run)
```

`as.data.frame.aquaenv` *as.data.frame.aquaenv*

Description

PUBLIC function: converts an object of class aquaenv to a standard R data frame

Usage

```
## S3 method for class 'aquaenv'  
as.data.frame(x, ...)
```

Arguments

`x` object of type aquaenv
`...` further arguments are passed on

Value

data frame containing all elements of aquaenv

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

BufferFactors

BufferFactors

Description

PUBLIC function: calculates buffer factors describing the sensitivity of pH and concentrations of acid-base species to a change in ocean chemistry

Usage

```
BufferFactors(ae = NULL, parameters = NA, species = c("SumCO2"),  
              k_w = NULL, k_co2 = NULL, k_hco3 = NULL,  
              k_boh3 = NULL, k_hso4 = NULL,  
              k_hf = NULL, k1k2 = "lueker",  
              khf = "dickson", khso4 = "dickson")
```

Arguments

| | |
|------------|---|
| ae | an object of class 'aquaenv'. An error is produced in case an object is provided that is not of class 'aquaenv', |
| parameters | a vector containing one or more of the following variables: "DIC" (mol/kg-soln), "TotNH3" (mol/kg-soln), "TotP" (mol/kg-soln), "TotNO3" (mol/kg-soln), "TotNO2" (mol/kg-soln), "TotS" (mol/kg-soln), "TotSi" (mol/kg-soln), "TB" (mol/kg-soln), "TotF" (mol/kg-soln), "TotSO4" (mol/kg-soln), "sal" (-), "temp" (deg C), "pres" (bar), "Alk" (mol/kg-soln). If a variable is not supplied and no object of class 'aquaenv' is provided, default values are assigned following Table 4 of Hagens and Middelburg (2016). If both ae and parameters are supplied, given parameters will overwrite the corresponding values of ae |
| species | a vector containing one or more of the following variables: "SumCO2", "SumNH4", "SumH3PO4", "SumHNO3", "SumHNO2", "SumH2S", "SumSiOH4", "SumBOH3", "SumHF", "SumH2SO4", "CO2", "HCO3", "CO3", "BOH3", "BOH4", "OH", "H3PO4", "H2PO4", "HPO4", "PO4", "SiOH4", "SiOOH3", "SiO2OH2", "H2S", "HS", "S2min", "NH4", "NH3", "H2SO4", "HSO4", "SO4", "HF", "F", "HNO3", "NO3", "HNO2", "NO2". Default is c("SumCO2"). This vector defines the species for which the sensitivities are calculated |
| k_w | a fixed K_W can be specified |
| k_co2 | a fixed K_{CO2} can be specified |
| k_hco3 | a fixed K_{HCO3} can be specified |
| k_boh3 | a fixed K_{BOH3} can be specified |
| k_hso4 | a fixed K_{HSO4} can be specified |
| k_hf | a fixed K_{HF} can be specified |
| k1k2 | either "lueker" (default, Lueker2000), "roy" (Roy1993a), or "millero" (Millero2006) for K_{CO2} and K_{HCO3} |
| khf | either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) for K_{HF} |
| khso4 | either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) for K_{HSO4} |

Value

a list containing the objects "ae", "dTA.dH", "dtotX.dH", "dTA.dX", "dtotX.dX", "dTA.dpH", "dtotX.dpH", "dH.dTA", "dH.dtotX", "dX.dTA", "dX.dtotX", "dpH.dTA", "dpH.dtotX", "beta.H" and "RF".

The object 'ae' is of class 'aquaenv' and refers to the output of the aquaenv function that is always run as part of BufferFactors. Consult the vignette of AquaEnv for more information on this object. The other objects are vectors with the length and names of the input species. Exceptions here are dH.dtotX and dpH.dtotX, which also contain the numerically estimated sensitivities with respect to salinity, pressure and temperature, as well as two factors related to pH scale conversion (see the AquaEnv vignette for details on these latter conversion factors).

In case species are defined which corresponding total concentration equals zero, the corresponding output produces 'NaN'. This is with the exception of "dTA.dH" and "dTA.dpH", which are always calculated as they are linked to beta.H. Additionally, the Revelle factor is always calculated, as the function 'aquaenv' requires that the carbonate system be specified.

Author(s)

Mathilde Hagens (<M.Hagens@uu.nl>)

References

Hagens M. and J.J. Middelburg, 2016 Generalised expressions for the response of pH to changes in ocean chemistry. *Geochimica et Cosmochimica Acta*, in press.

Examples

```
## Not run:
# Default run
BufferFactors()

# All carbonate system species
BufferFactors(species = c("CO2", "HCO3", "CO3"))

# Total concentrations of all species
BufferFactors(species = c("SumCO2", "SumNH4", "SumH3PO4", "SumHNO3",
                          "SumHNO2", "SumH2S", "SumSiOH4", "SumBOH3",
                          "SumHF", "SumH2SO4"))

# Different carbonate system equilibrium constants
BufferFactors(k1k2 = "roy")

# Object of class 'aquaenv' as input
ae_input <- aquaenv(S=35, t=25, SumCO2 = 0.0020, pH = 8.1,
                  skeleton = TRUE)
BufferFactors(ae = ae_input)

# Produces some NaNs as certain total concentrations are zero
BufferFactors(ae = ae_input,
              species = c("SumCO2", "SumNH4", "SumH3PO4", "SumHNO3",
                          "SumHNO2", "SumH2S", "SumSiOH4", "SumBOH3",
                          "SumHF", "SumH2SO4"))

# Object of class 'aquaenv' as input, but different total alkalinity
parameters <- c(Alk = 0.0022)
BufferFactors(ae = ae_input, parameters = parameters)

## End(Not run)
```

c.aquaenv

c.aquaenv

Description

PRIVATE function: adds an element to an object of class aquaenv

Usage

```
## S3 method for class 'aquaenv'
c(aquaenv, x, ...)
```

Arguments

| | |
|---------|--|
| aquaenv | object of class aquaenv |
| x | a vector of the form c(value, name) representing the element to be inserted into the object of class aquaenv |
| ... | further arguments will be passed |

Value

object of class aquaenv with the added element

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

ConcRelCl

ConcRelCl

Description

PUBLIC data frame: a collection of concentrations of key chemical species in seawater, relative with respect to chlorinity (DOE1994))

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

convert

convert

Description

PUBLIC function: converts either a single value (the pH scale of a pH value, the pH scale of a dissociation constant (K*), the unit of a concentration value), or all elements of a special unit or pH scale in an object of class aquaenv

Arguments

| | |
|----------|--|
| x | object to be converted: either a single value (pH value, K* value, or concentration value) or an object of class aquaenv |
| vartype | only valid if x is a single value: the type of x, either "pHscale", "KHscale", or "conc" |
| what | only valid if x is a single value: the type of conversion to be done, for pH scales one of "free2tot", "free2sws", "free2nbs", ... (any combination of "free", "tot", "sws", and "nbs"); for concentrations one of "molar2molal", "molar2molin", ... (any combination of "molar" (mol/l), "molal" (mol/kg-H2O), and "molin" (mol/kg-solution)) |
| S | only valid if x is a single value: salinity (in practical salinity units: no unit) |
| t | only valid if x is a single value: temperature in degrees centigrade |
| p | only valid if x is a single value: gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | only valid if x is a single value: total sulfate concentration in mol/kg-solution; if not supplied this is calculated from S |
| SumHF | only valid if x is a single value: total fluoride concentration in mol/kg-solution; if not supplied this is calculated from S |
| khf | only valid if x is a single value: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) for K _{HF} |
| khso4 | only valid if x is a single value: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) for K _{HSO4} |
| from | only valid if x is an object of class aquaenv: the unit which needs to be converted (as a string; must be a perfect match) |
| to | only valid if x is an object of class aquaenv: the unit to which the conversion should go |
| factor | only valid if x is an object of class aquaenv: the conversion factor to be applied: can either be a number (e.g. 1000 to convert from mol to mmol), or any of the conversion factors given in an object of class aquaenv |
| convattr | only valid if x is an object of class aquaenv: which attribute should be converted? can either be "unit" or "pH scale" |

Details

Possible usages are

```
convert(x, vartype, what, S, t, p, SumH2SO4, SumHF, khf)
convert(x, from, to, factor, convattr)
```

Value

converted single value or object of class aquaenv with converted elements

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

Examples

```

## Not run:
### 1
#####

t <- 15
S <- 10

pH_NBS <- 8.142777
SumCO2molar <- 0.002016803

pH_free <- convert(pH_NBS, "pHscale", "nbs2free", S=S, t=t)
SumCO2molin <- convert(SumCO2molar, "conc", "molar2molin", S=S, t=t)

ae <- aquaenv(S, t, SumCO2=SumCO2molin, pH=pH_free)
ae$pH
ae$SumCO2

### 2
#####
ae <- aquaenv(30,10)
ae$SumBOH3
ae <- convert(ae, "mol/kg-soln", "umol/kg-H2O", 1e6/ae$molal2molin, "unit")
ae$SumBOH3

## End(Not run)

```

DeltaPcoeffs

DeltaPcoeffs

Description

PUBLIC data frame: a collection of coefficients for the pressure correction of dissociation constants and solubility products (Millero1995 WITH CORRECTIONS BY Lewis1998 (CO2Sys!))

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

| | |
|----------------------|----------------------|
| <code>gauge_p</code> | <code>gauge\p</code> |
|----------------------|----------------------|

Description

PUBLIC function: calculates the gauge pressure (total pressure minus atmospheric pressure) from the depth (in m) and the latitude (in degrees: -90 to 90) and the atmospheric pressure (in bar)

Usage

```
gauge_p(d, lat=0, Pa=1.01325)
```

Arguments

| | |
|------------------|---|
| <code>d</code> | water depth in meters |
| <code>lat</code> | latitude in degrees: -90 to 90, standard: 0 |
| <code>Pa</code> | atmospheric pressure in bar, standard: 1 atm (at sea level) |

Value

gauge pressure (total pressure minus atmospheric pressure) `p` in bars

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Fofonoff1983

Examples

```
gauge_p(100)
plot(gauge_p(1:100))
```

| | |
|---------------------|---------------------|
| <code>K0_CO2</code> | <code>K0_CO2</code> |
|---------------------|---------------------|

Description

PUBLIC function: calculates the Henry's constant (solubility) for CO2

Usage

```
K0_CO2(S, t)
```


Arguments

S salinity in practical salinity units (i.e. no unit)
 t temperature in degrees centigrade

Value

the Henry's constant for CO2 in mol/(kg-solution*atm)

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Weiss1974, DOE1994, Millero1995, Zeebe2001

Examples

```
K0_CO2(35, 15)
plot(K0_CO2(35, 1:25), xlab="temperature / degC")
```

K0_O2

K0_O2

Description

PUBLIC function: calculates the Henry's constant (solubility) for O2

Usage

```
K0_O2(S, t)
```

Arguments

S salinity in practical salinity units (i.e. no unit)
 t temperature in degrees centigrade

Value

the Henry's constant for CO2 in mol/(kg-solution*atm)

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

derived from a formulation for [O2]sat given in Weiss1970

Examples

```
K0_02(35, 15)
plot(K0_02(35, 1:25), xlab="temperature / degC")
```

Ksp_aragonite

Ksp\aragonite

Description

PUBLIC function: calculates the solubility product for aragonite

Usage

```
Ksp_aragonite(S, t, p=0)
```

Arguments

| | |
|---|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |

Value

the solubility product for aragonite in (mol/kg-solution)²

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Mucci1983, Boudreau1996

Examples

```
Ksp_aragonite(35, 15)
Ksp_aragonite(35, 15, 10)
plot(Ksp_aragonite(35, 1:25), xlab="temperature / degC")
```

| | |
|-------------|--------------------|
| Ksp_calcite | <i>Ksp\calcite</i> |
|-------------|--------------------|

Description

PUBLIC function: calculates the solubility product for aragonite

Usage

```
Ksp_calcite(S, t, p=0)
```

Arguments

| | |
|---|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |

Value

the solubility product for calcite in (mol/kg-solution)²

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Mucci1983, Boudreau1996

Examples

```
Ksp_calcite(35, 15)
Ksp_calcite(35, 15, 10)
plot(Ksp_aragonite(35, 1:25), xlab="temperature / degC")
```

| | |
|--------|---------------|
| K_BOH3 | <i>K\BOH3</i> |
|--------|---------------|

Description

PUBLIC function: calculates the dissociation constant of B(OH)₃

Usage

```
K_BOH3(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of B(OH)₃ in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Dickson1990, DOE1994, Millero1995 (molality version given), Zeebe2001

Examples

```
K_BOH3(35, 15)
K_BOH3(35, 15, 10)
K_BOH3(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_BOH3(35, 1:25), xlab="temperature / degC")
```

K_CO2

K_CO2

Description

PUBLIC function: calculates the dissociation constant of CO₂

Usage

```
K_CO2(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, k1k2="lueker", khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| k1k2 | "lueker", "roy", or "millero": specifies the S, t, dependency to be used. Default is "lueker". (see section below for references) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of CO2 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

k1k2 = "roy": Roy1993b, DOE1994, Millero1995, Zeebe2001; k1k2 = "lueker": Lueker2000; k1k2 = "millero": Millero2006

Examples

```
K_CO2(35, 15)
K_CO2(35, 15, 10)
K_CO2(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_CO2(35, 1:25), xlab="temperature / degC")
```

K_H2PO4

K_H2PO4

Description

PUBLIC function: calculates the dissociation constant of H2PO4

Usage

```
K_H2PO4(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_{HF} needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_{HSO4} needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of H2PO4 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Millero1995 (original, SWS pH version), DOE1994 (in a later revision cites Millero1995)

Examples

```
K_H2PO4(35, 15)
K_H2PO4(35, 15, 10)
K_H2PO4(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_H2PO4(35, 1:25), xlab="temperature / degC")
```

K_H2S

K_H2S

Description

PUBLIC function: calculates the dissociation constant of H2S

Usage

```
K_H2S(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of H2S in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Millero1988, Millero1995

Examples

```
K_H2S(35, 15)
K_H2S(35, 15, 10)
K_H2S(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_H2S(35, 1:25), xlab="temperature / degC")
```

K_H3PO4

K_H3PO4

Description

PUBLIC function: calculates the dissociation constant of H3PO4

Usage

```
K_H3PO4(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of H3PO4 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Millero1995 (original, SWS pH version), DOE1994 (in a later revision cites Millero1995)

Examples

```
K_H3PO4(35, 15)
K_H3PO4(35, 15, 10)
K_H3PO4(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_H3PO4(35, 1:25), xlab="temperature / degC")
```

K_HCO3

K_HCO3

Description

PUBLIC function: calculates the dissociation constant of HCO3

Usage

```
K_HCO3(S, t, p=0, SumH2SO4=NULL, SumHF=NULL,
       k1k2="lueker", khf="dickson", khso4="dickson")
```


Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| k1k2 | "lueker", "roy", or "millero": specifies the S, t, dependency to be used. Default is "lueker". (see section below for references) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of HCO₃ in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

k1k2 = "roy": Roy1993b, DOE1994, Millero1995, Zeebe2001; k1k2 = "lueker": Lueker2000; k1k2 = "millero": Millero2006

Examples

```
K_HCO3(35, 15)
K_HCO3(35, 15, 10)
K_HCO3(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_HCO3(35, 1:25), xlab="temperature / degC")
```

K_HF

K_HF

Description

PUBLIC function: calculates the dissociation constant of HF

Usage

```
K_HF(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | "dickson" or "perez": specifies the S, t, dependency to be used. Default is "dickson". (see section below for references) |
| khso4 | S, t relation for K_ <chem>H2SO4</chem> needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of HF in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

khf = "dickson": Dickson1979a, Dickson1987, Roy1993b, DOE1994, Millero1995, Zeebe2001;
 khf = "perez": Perez1987

Examples

```
K_HF(35, 15)
K_HF(35, 15, 10)
plot(K_HF(35, 1:25), xlab="temperature / degC")
```

K_HPO4

K_HPO4

Description

PUBLIC function: calculates the dissociation constant of HPO4

Usage

```
K_HPO4(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of HPO4 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Millero1995 (original, SWS pH version), DOE1994 (in a later revision cites Millero1995)

Examples

```
K_HPO4(35, 15)
K_HPO4(35, 15, 10)
K_HPO4(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_HPO4(35, 1:25), xlab="temperature / degC")
```

K_HSO4

K_HSO4

Description

PUBLIC function: calculates the dissociation constant of HSO4

Usage

```
K_HSO4(S, t, p=0, khso4="dickson")
```

Arguments

| | |
|-------|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| khso4 | "dickson" or "khoo": specifies the S, t, dependency to be used. Default is "dickson". (see section below for references) |

Value

the dissociation constant of HSO4 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

"dickson": Dickson1990, DOE1994, Zeebe2001; "khoo": Khoo1977, Roy1993, Millero1995

Examples

```
K_HSO4(35, 15)
K_HSO4(35, 15, 10)
plot(K_HSO4(35, 1:25), xlab="temperature / degC")
```

K_NH4

K_NH4

Description

PUBLIC function: calculates the dissociation constant of NH4

Usage

```
K_NH4(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|--|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of NH4 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Millero1995a, Millero1995, corrected by Lewis1998

Examples

```
K_NH4(35, 15)
K_NH4(35, 15, 10)
K_NH4(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_NH4(35, 1:25), xlab="temperature / degC")
```

K_SiOH4

K_SiOH4

Description

PUBLIC function: calculates the dissociation constant of SiOH4

Usage

```
K_SiOH4(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_{HF} needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_{HSO4} needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of SiOH4 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Millero1988, DOE1994, Millero1995

Examples

```
K_SiOH4(35, 15)
K_SiOH4(35, 15, 10)
K_SiOH4(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_SiOH4(35, 1:25), xlab="temperature / degC")
```

K_SiOOH3

K_SiOOH3

Description

PUBLIC function: calculates the dissociation constant of SiOOH3

Usage

```
K_SiOOH3(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khso4="dickson")
```

Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for K_HF needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khso4 | S, t relation for K_HSO4 needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the dissociation constant of SiOOH3 in mol/kg-solution on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Wischmeyer2003 (incl. corrections)

Examples

```
K_Si00H3(35, 15)
K_Si00H3(35, 15, 10)
K_Si00H3(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_Si00H3(35, 1:25), xlab="temperature / degC")
```

K_W

K_W

Description

PUBLIC function: calculates the ion product of H2O

Usage

```
K_W(S, t, p=0, SumH2SO4=NULL, SumHF=NULL, khf="dickson", khs04="dickson")
```

Arguments

| | |
|----------|---|
| S | salinity in practical salinity units (i.e. no unit) |
| t | temperature in degrees centigrade |
| p | gauge pressure (total pressure minus atmospheric pressure) in bars |
| SumH2SO4 | total sulfate concentration in mol/kg-solution (calculated from S if not supplied) |
| SumHF | total fluoride concentration in mol/kg-solution (calculated from S if not supplied) |
| khf | S, t relation for <i>K_HF</i> needed for scale conversion: either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) |
| khs04 | S, t relation for <i>K_HSO4</i> needed for scale conversion: either "dickson" (default, Dickson1990) or "khoo" (Khoo1977) |

Value

the ion product of H2O in (mol/kg-solution)² on the free proton pH scale

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Millero1995 (SWS pH version), DOE1994 (cites Millero1995), Zeebe2001

Examples

```
K_W(35, 15)
K_W(35, 15, 10)
K_W(S=35, t=15, p=10, SumH2SO4=0.03)
plot(K_W(35, 1:25), xlab="temperature / degC")
```

length.aquaenv *length.aquaenv*

Description

PRIVATE function: returns the (maximal) length of the elements in an object of class aquaenv (i.e. > 1 if one of the input variables was a vector)

Usage

```
## S3 method for class 'aquaenv'
length(x, ...)
```

Arguments

x object of class aquaenv
... further arguments will be passed

Value

the maximal length of the elements in the object of class aquaenv

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

MeanMolecularMass *MeanMolecularMass*

Description

PUBLIC data frame: a collection of mean molecular masses of key chemical species in seawater in g/mol (DOE1994))

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

| | |
|---------------|----------------------|
| merge.aquaenv | <i>merge.aquaenv</i> |
|---------------|----------------------|

Description

PRIVATE function: merges the elements of two objects of class aquaenv: element names are taken from the first argument, the elements of which are also first in the merged object

Usage

```
## S3 method for class 'aquaenv'
merge(x, y, ...)
```

Arguments

| | |
|-----|--|
| x | object of class aquaenv: this is where the element names are taken from |
| y | object of class aquaenv: must contain at least all the element (names) as aquaenv1, extra elements are ignored |
| ... | further arguments will be passed |

Value

object of class aquaenv with merged elements

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

| | |
|---------------|----------------------|
| PhysChemConst | <i>PhysChemConst</i> |
|---------------|----------------------|

Description

PUBLIC list: a collection of physical and chemical constants

Value

A list containing:

| | |
|-----------|---|
| R | (bar*cm ³)/(mol*K) the gas constant (corrected after Lewis1998, in Millero1995: R = 83.131); digits extended after Dickson2007) |
| F | C/mol the Faraday constant (charge per mol of electrons) (N _A *e ⁻): Dickson2007 |
| uMolToMol | conversion factor from umol to mol |
| absZero | absolute zero in degrees centigrade |

| | |
|---------|--|
| e | relative dielectric constant of seawater (Zeebe2001) |
| K_HNO2 | dissociation constant of HNO ₂ : mol/l, NBS pH scale, hybrid constant (Riordan2005) |
| K_HNO3 | dissociation constant of HNO ₃ : assumed on mol/kg-soln and free pH scale, stoichiometric constant (Soetaert pers. comm.) |
| K_H2SO4 | dissociation constant of H ₂ SO ₄ : assumed on mol/kg-soln and free pH scale, stoichiometric constant (Atkins1996) |
| K_HS | dissociation constant of H ₂ S: assumed on mol/kg-soln and free pH scale, stoichiometric constant (Atkins1996) |

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

plot.aquaenv

plot.aquaenv

Description

PUBLIC function: high level plot function for objects of class aquaenv

Arguments

| | |
|------------|---|
| x | object of class aquaenv |
| xval | only valid if bjerrum=FALSE: a vector of the (maximal) length of the elements of aquaenv against which they are to be plotted |
| what | a list of names of the elements of aquaenv that are to be plotted, if not supplied and bjerrum=FALSE and cumulative=FALSE: all elements are plotted, if not supplied and bjerrum=TRUE then what is set to be c("CO ₂ ", "HCO ₃ ", "CO ₃ ", "BOH ₃ ", "BOH ₄ ", "OH", "H ₃ PO ₄ ", "H ₂ PO ₄ ", "HPO ₄ ", "PO ₄ ", "SiOH ₄ ", "SiOOH ₃ ", "SiO ₂ OH ₂ ", "H ₂ S", "HS", "S ₂ min", "NH ₄ ", "NH ₃ ", "H ₂ SO ₄ ", "HSO ₄ ", "SO ₄ ", "HF", "F", "HNO ₃ ", "NO ₃ ", "HNO ₂ ", "NO ₂ "), needs to be supplied for cumulative=TRUE |
| bjerrum | flag: TRUE = a bjerrum plot is done (by calling bjerrumplot) |
| cumulative | flag: TRUE = a cumulative plot is done (by calling cumulativeplot) |
| newdevice | flag: if TRUE, new plot device is opened |
| setpar | flag: if TRUE parameters are set with the function par |
| xlab | x axis label |
| log | only valid if bjerrum=TRUE: should the plot be on a logarithmic y axis? |
| total | only valid if cumulative=TRUE: should the sum of all elements specified in what be plotted as well? |
| device | the device to plot on; default: "x11" (can also be "eps" or "pdf") |
| filename | filename to be used if "eps" or "pdf" is selected for device |

| | |
|----------------|--|
| size | the size of the plot device; default: 12 (width) by 10 (height) inches |
| ylim | standard plot parameter; if not supplied it will be calculated by range() of the elements to plot |
| lwd | standard plot parameter; width of the lines in the plot |
| mgp | standard plot parameter; default: axis title on line 1.8, axis labels on line 0.5, axis on line 0 |
| mar | standard plot parameter; default: margin of 3 lines bottom and left and 0.5 lines top and right |
| oma | standard plot parameter; default: no outer margin |
| palette | only valid if bjerrum=TRUE or cumulative=TRUE: a vector of colors to use in the plot (either numbers or names given in colors()) |
| legendposition | only valid if bjerrum=TRUE or cumulative=TRUE: position of the legend |
| legendinset | only valid if bjerrum=TRUE or cumulative=TRUE: standard legend parameter inset |
| legendlwd | only valid if bjerrum=TRUE or cumulative=TRUE: standard legend parameter lwd: line width of lines in legend |
| bg | only valid if bjerrum=TRUE or cumulative=TRUE: standard legend parameter: default background color: white |
| y.intersp | standard legend parameter; if cumulative=TRUE then default: 1.2 lines space between the lines in the legend |
| ... | further arguments are passed on to the plot function |

Details

Top level generic usage is

```
plot.aquaenv(x, xval, what=NULL, bjerrum=FALSE,
             cumulative=FALSE, newdevice=TRUE, setpar=TRUE,
             device="x11", ...)
```

Generic usages for standard plotting are

```
plot.aquaenv(x, xval, ...)
```

```
plot.aquaenv(x, xval, what, mfrow=c(1,1), size=c(7,7), ...)
```

Generic usage for creating a bjerrum plot is

```
plot.aquaenv(x, what, log=FALSE, palette=NULL,
             device="x11", filename="aquaenv",
             size=c(12,10), ylim=NULL, lwd=2, xlab="free scale pH",
             mgp=c(1.8, 0.5, 0), mar=c(3,3,0.5,0.5), oma=c(0,0,0,0),
             legendposition="bottomleft", legendinset=0.05,
             legendlwd=4, bg="white", newdevice=TRUE, setpar=TRUE,
             device="x11",...)
```

Generic usage for creating a cumulative plot is

```
plot.aquaenv(x, xval, what, total=TRUE, palette=NULL,
             device="x11", filename="aquaenv", size=c(12,10), ylim=NULL,
             lwd=2, mgp=c(1.8, 0.5, 0), mar=c(3,3,0.5,0.5), oma=c(0,0,0,0),
             legendposition="bottomleft", legendinset=0.05, legendlwd=4,
             bg="white", y.intersp=1.2, newdevice=TRUE, setpar=TRUE,
             device="x11",...)
```

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

Examples

```
## Not run:
### 0
#####
A <- aquaenv(35, 15, SumCO2=0.003, TA=seq(0.001,0.004, 0.0001))
plot(A, xval=A$TA, xlab="[TA]/(mol/kg-soln)")
plot(A, what=c("CO2", "HCO3", "CO3"), bjerrum=TRUE, log=TRUE)
plot(A, xval=A$TA, xlab="[TA]/(mol/kg-soln)", what=c("CO2", "HCO3", "CO3"),
      cumulative=TRUE, ylab="mol/kg-soln", ylim=c(0,0.0031))

### 1
#####
SumCO2 <- 0.0020
pH <- 8

S <- 30
t <- 1:15
p <- 10
ae <- aquaenv(S, t, p, SumCO2=SumCO2, pH=pH, revelle=TRUE, dsa=TRUE)
plot(ae, xval=t, xlab="T/(deg C)", newdevice=FALSE)

### 2
#####
S <- 35
t <- 15

SumCO2 <- 0.003500
SumNH4 <- 0.000020

mass_sample <- 0.01 # the mass of the sample solution in kg
mass_titrant <- 0.02 # the total mass of the added titrant solution in
# kg
conc_titrant <- 0.01 # the concentration of the titrant solution in
# mol/kg-soln
```

```

S_titrant <- 0.5 # the salinity of the titrant solution (the
                # salinity of a solution with a ionic strength of
                # 0.01 according to: I = (19.924 S) / (1000 - 1.005S)
steps      <- 50 # the amount of steps the mass of titrant is added
                # in
type       <- "HCl"

pHstart <- 11.3

ae <- titration(aquaenv(S=S, t=t, SumCO2=SumCO2, SumNH4=SumNH4,
                    pH=pHstart), mass_sample, mass_titrant, conc_titrant,
                S_titrant, steps, type)

# plotting everything
plot(ae, xval=ae$delta_mass_titrant, xlab="HCl solution added [kg]",
     mfrow=c(10,10))

# plotting selectively
size <- c(12,8) #inches
mfrow <- c(4,4)
what <- c("TA", "pH", "CO2", "HCO3", "CO3", "BOH3", "BOH4", "OH",
          "NH4", "NH3", "H2SO4", "HSO4", "SO4", "HF", "F", "pCO2")

plot(ae, xval=ae$delta_mass_titrant, xlab="HCl solution added [kg]",
     what=what, size=size, mfrow=mfrow)

plot(ae, xval=ae$pH, xlab="free scale pH", what=what, size=size,
     mfrow=mfrow)

# different x values
plot(ae, xval=ae$delta_conc_titrant, xlab="[HCl] offset added
     [mol/kg-soln]", what=what, size=size, mfrow=mfrow)

plot(ae, xval=ae$delta_moles_titrant, xlab="HCl added [mol]", what=what,
     size=size, mfrow=mfrow, newdevice=FALSE)

# bjerrum plots
plot(ae, bjerrum=TRUE)

what <- c("CO2", "HCO3", "CO3")
plot(ae, what=what, bjerrum=TRUE)
plot(ae, what=what, bjerrum=TRUE, lwd=4, palette=c("cyan", "magenta",
          "yellow"), bg="gray", legendinset=0.1, legendposition="topleft")

what <- c("CO2", "HCO3", "CO3", "BOH3", "BOH4", "OH", "NH4", "NH3",

```

```

      "H2SO4", "HSO4", "SO4", "HF", "F")

plot(ae, what=what, bjerrum=TRUE, log=TRUE, newdevice=FALSE)
plot(ae, what=what, bjerrum=TRUE, log=TRUE, ylim=c(-6,-1),
      legendinset=0, lwd=3, palette=c(1,3,4,5,6,colors())[seq(100,250,6)]))

### 3
####
parameters <- list(
  t      = 15      , # degrees C
  S      = 35      , # psu

  SumCO2_t0 = 0.002  , # mol/kg-soln (comparable to Wang2005)
  TA_t0    = 0.0022 , # mol/kg-soln (comparable to Millero1998)

  kc      = 0.5     , # 1/d      proportionality factor
                    #           for air-water exchange
  kp      = 0.000001, # mol/(kg-soln*d) max rate of calcium
                    #           carbonate precipitation
  n       = 2.0     , # -        exponent for kinetic
                    #           rate law of precipitation

  modeltime = 20    , # d        duration of the model
  outputsteps = 100 , #         number of outputsteps
)

boxmodel <- function(timestep, currentstate, parameters)
{
  with (
    as.list(c(currentstate,parameters)),
    {
      ae <- aquaenv(S=S, t=t, SumCO2=SumCO2, pH=-log10(H), SumSiOH4=0,
                    SumBOH3=0, SumH2SO4=0, SumHF=0, dsa=TRUE)

      Rc <- kc * ((ae$CO2_sat) - (ae$CO2))
      Rp <- kp * (1-ae$omega_calcite)^n

      dSumCO2 <- Rc - Rp

      dHRc <- (      -(ae$dTAdSumCO2*Rc      ))/ae$dTAdH
      dHRp <- (-2*Rp -(ae$dTAdSumCO2*(-Rp)))/ae$dTAdH
      dH <- dHRc + dHRp

      ratesofchanges <- c(dSumCO2, dH)

      processrates <- c(Rc=Rc, Rp=Rp)
      outputvars <- c(dHRc=dHRc, dHRp=dHRp)

      return(list(ratesofchanges, list(processrates, outputvars, ae)))
    }
  )
}

```

```

with (as.list(parameters),
      {
        aetmp <- aquaenv(S=S, t=t, SumCO2=SumCO2_t0,
                        TA=TA_t0, SumSiOH4=0, SumBOH3=0,
                        SumH2SO4=0, SumHF=0)
        H_t0 <- 10^(-aetmp$pH)

        initialstate <- c(SumCO2=SumCO2_t0, H=H_t0)
        times <- seq(0,modeltime,(modeltime/outputsteps))
        output <- as.data.frame(vode(initialstate,times,
                                     boxmodel,parameters, hmax=1))
      })

what <- c("SumCO2", "TA", "Rc", "Rp",
          "omega_calcite", "pH", "dHRc", "dHRp")
plot(aquaenv(ae=output, from.data.frame=TRUE), xval=output$time,
      xlab="time/d", mfrow=c(3,3), size=c(15,10), what=what)

what <- c("dHRc", "dHRp")
plot(aquaenv(ae=output, from.data.frame=TRUE), xval=output$time,
      xlab="time/d", what=what, ylab="mol-H/(kg-soln*d)",
      legendposition="topright", cumulative=TRUE)

## End(Not run)

```

sample_dickson1981 sample_dickson1981

Description

PUBLIC dataset: theoretical titration curve for TA determination as given in table 1 of Dickson1981

Meta-data:

x-value mass of titrant added (in g)
y-value pH measured on the free proton scale

| | | |
|----------------------|---------|-------------|
| <i>t</i> | 25 | degC |
| <i>S</i> | 35 | |
| <i>mass_sample</i> | 200 | g |
| <i>conc_titrant</i> | 0.3000 | mol/kg-soln |
| <i>TA</i> | 0.00245 | mol/kg-soln |
| <i>SumCO2</i> | 0.00220 | mol/kg-soln |
| <i>SumBOH3</i> | 0.00042 | mol/kg-soln |
| <i>SumH2SO4</i> | 0.02824 | mol/kg-soln |

| | | |
|----------------|----------|-----------------------------|
| <i>SumHF</i> | 0.00007 | mol/kg-soln |
| <i>K_W</i> | 4.32e-14 | (mol/kg-soln)*(mol/kg-soln) |
| <i>K_CO2</i> | 1.00e-6 | mol/kg-soln |
| <i>K_HCO3</i> | 8.20e-10 | mol/kg-soln |
| <i>K_BOH3</i> | 1.78e-9 | mol/kg-soln |
| <i>K_HSO4</i> | 1/1.23e1 | mol/kg-soln |
| <i>K_HF</i> | 1/4.08e2 | mol/kg-soln |

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

sample_dickson2007 *sample_dickson2007*

Description

PUBLIC dataset: titration curve for TA determination as given on p. 11 of SOP3b in Dickson2007

Metadata:

x-value mass of titrant added (in cubic centimeters)
y-value E in V

| | | |
|------------------------|----------|--------------|
| <i>t</i> | 24.25 | degC |
| <i>S</i> | 33.923 | |
| <i>mass_sample</i> | 140.32 | g |
| <i>conc_titrant</i> | 0.10046 | mol/kg-soln |
| <i>density titrant</i> | 1.02393 | g/cm3 |
| <i>calculated TA</i> | 2260.06 | umol/kg-soln |
| <i>calculated E0</i> | 0.394401 | V |

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

TAfit

TAfit

Description

PUBLIC function: calculates [TA] and [SumCO2] (and optionally K_{CO2} and E0) from a titration curve using an optimization procedure (nls.lm from R package minpack.lm)

Usage

```
TAfit(ae, titcurve, conc_titrant, mass_sample, S_titrant=NULL,
      TASumCO2guess=0.0025, E0guess=0.4, type="HCl", Evals=FALSE,
      electrode_polarity="pos", K_CO2fit=FALSE,
      equalspaced=TRUE, seawater_titrant=FALSE,
      pHscale="free", debug=FALSE, k_w=NULL, k_co2=NULL, k_hco3=NULL,
      k_boh3=NULL, k_hso4=NULL, k_hf=NULL,
      nlscontrol=nls.lm.control(), verbose=FALSE,
      k1k2="roy", khf="dickson", datxbegin=0, SumCO2Zero=FALSE)
```

Arguments

| | |
|--------------------|---|
| ae | an object of type aquaenv: minimal definition, contains all information about the system: T, S, d, total concentrations of nutrients etc (Note that it is possible to give values for SumBOH4, SumHSO4, and SumHF in the sample other than the ones calculated from salinity) |
| titcurve | a table containing the titration curve: basically a series of tuples of added titrant solution mass and pH values (pH on free proton scale) or E values in V |
| conc_titrant | concentration of the titrant solution in mol/kg-soln |
| mass_sample | the mass of the sample solution in kg |
| S_titrant | the salinity of the titrant solution, if not supplied it is assumed that the titrant solution has the same salinity as the sample solution |
| TASumCO2guess | a first guess for [TA] and [SumCO2] to be used as initial values for the optimization procedure |
| E0guess | first guess for E0 in V |
| type | the type of titrant: either "HCl" or "NaOH" |
| Evals | are the supplied datapoints pH or E (V) values? |
| electrode_polarity | either "pos" or "neg": how is the polarity of the Electrode: $E = E0 - (RT/F)\ln(H^+)$ ("pos") or $-E = E0 - (RT/F)\ln(H^+)$ ("neg")? |
| K_CO2fit | should K_{CO2} be fitted as well? |
| equalspaced | are the mass values of titcurve equally spaced? |
| seawater_titrant | is the titrant based on natural seawater? (does it contain SumBOH4, SumHSO4, and SumHF in the same proportions as seawater, i.e., correlated to S?); Note that you can only assume a seawater based titrant (i.e. SumBOH4, SumHSO4, and SumHF ~ S) or a water based titrant (i.e. SumBOH4, SumHSO4, and SumHF = 0). It is not possible to give values for SumBOH4, SumHSO4, and SumHF of the titrant. |

| | |
|------------|--|
| pHscale | either "free", "total", "sws" or "nbs": if the titration curve contains pH data: on which scale is it measured? |
| debug | debug mode: the last simulated titration tit, the converted pH profile calc, and the nls.lm output out are made global variables for investigation and plotting |
| k_w | a fixed K_W can be specified |
| k_co2 | a fixed K_{CO2} can be specified; used for TA fitting: give a K_{CO2} and NOT calculate it from T and S: i.e. K_{CO2} can be fitted in the routine as well |
| k_hco3 | a fixed K_{HCO3} can be specified |
| k_boh3 | a fixed K_{BOH3} can be specified |
| k_hso4 | a fixed K_{HSO4} can be specified |
| k_hf | a fixed K_{HF} can be specified |
| nlscontrol | nls.lm.control() can be specified |
| verbose | verbose mode: show the traject of the fitting in a plot |
| k1k2 | either "roy" (default, Roy1993a) or "lueker" (Lueker2000) for K_{CO2} and K_{HCO3} . |
| khf | either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) for K_{HF} |
| datxbegin | at what x value (amount of titrant added) does the supplied curve start? (i.e. is the complete curve supplied or just a part?) |
| SumCO2Zero | should $SumCO2 == 0$? |

Value

a list of up to five values ([TA] in mol/kg-solution, [SumCO2] in mol/kg-solution, E0 in V, K1 in mol/kg-solution and on free scale, sum of the squared residuals)

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

Examples

```
## Not run:

#####
# Calculating TA from titration data
#####

#### 1.) proof of concept #####
#####
#####

# generate "data":
S <- 35
t <- 15

SumCO2 <- 0.002000
```

```

TA      <- 0.002200
initial_ae <- aquaenv(S=S, t=t, SumCO2=SumCO2, TA=TA)

mass_sample <- 0.01 # the mass of the sample solution in kg
mass_titrant <- 0.003 # the total mass of the added titrant solution
                  # in kg
conc_titrant <- 0.01 # the concentration of the titrant solution in
                  # mol/kg-soln
S_titrant   <- 0.5 # the salinity of the titrant solution (the
                  # salinity of a solution with a ionic strength
                  # of 0.01 according to:
                  # I = (19.924 S) / (1000 - 1.005 S)
steps       <- 20 # the amount of steps the mass of titrant is
                  # added in
type        <- "HCl"

ae <- titration(initial_ae, mass_sample, mass_titrant, conc_titrant,
                S_titrant, steps, type)

plot(ae, ae$delta_mass_titrant, what="pH", newdevice=FALSE)

# the input data for the TA fitting routine: a table with the added
# mass of the titrant and the resulting free scale pH
titcurve <- cbind(ae$delta_mass_titrant, ae$pH)

# for the TA fitting procedure all total quantities except SumCO2
# (SumNH4, SumH2S, SumH3PO4, SumSiOH4, SumHNO3, SumHNO2, SumBOH3,
# SumH2SO4, SumHF) need to be known. However, the latter three
# can be calculated from salinity as it is done in this example.

fit1 <- TAfit(initial_ae, titcurve, conc_titrant, mass_sample,
              S_titrant)
fit1

# E (V) values as input variables: generate E values using
# E0=0.4 V and the nernst equation
tottitcurve <- convert(titcurve[,2], "pHscale", "free2sws", S=S,
                      t=t)

# (Nernst equation relates E to TOTAL [H+] (DOE1994, p.7,
# ch.4, sop.3), BUT, if fluoride is present, its SWS, so
# we use SWS!
Etitcurve <- cbind(titcurve[,1], (0.4 - ((PhysChemConst$R/10)
    *initial_ae$T/PhysChemConst$F)
    *log(10^-tottitcurve))) # Nernst equation

fit2 <- TAfit(initial_ae, Etitcurve, conc_titrant, mass_sample,
              S_titrant, Evals=TRUE, verbose=TRUE)
fit2

# k_co2 fitting: one K_CO2 (k_co2) for the whole titration curve
# is fitted, i.e. there is NO correction for K_CO2 changes due to

```

```

# changing S due to mixing with the titrant
fit3 <- TAfit(initial_ae, titcurve, conc_titrant, mass_sample,
             S_titrant, K_CO2fit=TRUE)
fit3

# assume the titrant has the same salinity as the sample
# (and is made up of natural seawater, i.e. containing SumBOH4,
# SumH2SO4 and SumHF as functions of S), then the "right" K_CO2
# should be fitted i.e we do NOT give the argument S_titrant
# and set the flag seawater_titrant to TRUE
ae      <- titration(initial_ae, mass_sample, mass_titrant,
                    conc_titrant, steps=steps, type=type,
                    seawater_titrant=TRUE)
titcurve <- cbind(ae$delta_mass_titrant, ae$pH)

fit4 <- TAfit(initial_ae, titcurve, conc_titrant, mass_sample,
             K_CO2fit=TRUE, seawater_titrant=TRUE)
fit4

# fitting of TA, SumCO2, K_CO2 and E0
Etitcurve <- cbind(titcurve[,1], (0.4 - ((PhysChemConst$R/10)
                                     *initial_ae$T/PhysChemConst$F)
                                     *log(10^-titcurve[,2])))
fit5 <- TAfit(initial_ae, Etitcurve, conc_titrant, mass_sample,
             K_CO2fit=TRUE, seawater_titrant=TRUE, Evals=TRUE)
fit5

# fitting of non equally spaced data:
neqsptitcurve <- rbind(titcurve[1:9,], titcurve[11:20,])
fit6 <- TAfit(initial_ae, neqsptitcurve, conc_titrant,
             mass_sample, seawater_titrant=TRUE,
             equalspaced=FALSE)
fit6

#add some "noise" on the generated data
noisetitcurve <- titcurve * rnorm(length(titcurve),
                                mean=1, sd=0.01) #one percent error possible
plot(ae, ae$delta_mass_titrant, what="pH", type="l", col="red",
     xlim=c(0,0.003), ylim=c(3,8.1), newdevice=FALSE)
par(new=TRUE)
plot(noisetitcurve[,1],noisetitcurve[,2], type="l",
     xlim=c(0,0.003), ylim=c(3,8.1))

fit7 <- TAfit(initial_ae, noisetitcurve, conc_titrant,
             mass_sample, seawater_titrant=TRUE)
fit7

# 2.) test with generated data from Dickson1981 #
#####
#####

```

```

conc_titrant = 0.3      # mol/kg-soln
mass_sample   = 0.2      # kg
S_titrant     = 14.835  # is aequivalent to the ionic strength
                    # of 0.3 mol/kg-soln

SumBOH3 = 0.00042 # mol/kg-soln
SumH2SO4 = 0.02824 # mol/kg-soln
SumHF    = 0.00007 # mol/kg-soln

# convert mass of titrant from g to kg
sam <- cbind(sample_dickson1981[,1]/1000, sample_dickson1981[,2])

dicksonfit <- TAFit(aquaenv(t=25, S=35, SumBOH3=SumBOH3,
                          SumH2SO4=SumH2SO4, SumHF=SumHF), sam,
                  conc_titrant, mass_sample,
                  S_titrant=S_titrant, debug=TRUE)

dicksonfit
#TA      Dickson1981: 0.00245
#SumCO2 Dickson1981: 0.00220

# => not exactly the same! why?

# a.) does salinity correction (S_titrant) matter or not?
#####

# without salinity correction
dickson1 <- titration(aquaenv(t=25, S=35, SumCO2=0.00220,
                             SumBOH3=SumBOH3, SumH2SO4=SumH2SO4,
                             SumHF=SumHF, TA=0.00245),
                    mass_sample=mass_sample,
                    mass_titrant=0.0025,
                    conc_titrant=conc_titrant,
                    steps=50, type="HCl")

# with salinity correction
dickson2 <- titration(aquaenv(t=25, S=35, SumCO2=0.00220,
                             SumBOH3=SumBOH3, SumH2SO4=SumH2SO4,
                             SumHF=SumHF, TA=0.00245),
                    mass_sample=mass_sample,
                    mass_titrant=0.0025,
                    conc_titrant=conc_titrant,
                    S_titrant=S_titrant,
                    steps=50, type="HCl")

plot(dickson1, xval=dickson1$delta_mass_titrant,
     what="pH", xlim=c(0,0.0025), ylim=c(3,8.2), newdevice=FALSE,
     col="red")
par(new=TRUE)
plot(dickson2, xval=dickson2$delta_mass_titrant,
     what="pH", xlim=c(0,0.0025), ylim=c(3,8.2), newdevice=FALSE,

```

```

        col="blue")
par(new=TRUE)
plot(sam[,1], sam[,2], type="l", xlim=c(0,0.0025), ylim=c(3,8.2))

# => salinity correction makes NO difference, because the relation
# between total sample and added titrant is very large:
# salinity only drops from 35 to 34.75105

#BUT: there is an offset between the "Dickson" curve and our curve:
plot(dicksontitration2$pH - sam[,2])

# b.) does it get better if we fit K_CO2 as well?
#####
dicksonfit2 <- TAfit(aquaenv(t=25, S=35, SumBOH3=SumBOH3,
                          SumH2SO4=SumH2SO4, SumHF=SumHF), sam,
                  conc_titrant, mass_sample,
                  S_titrant=S_titrant, debug=TRUE,
                  K_CO2fit=TRUE)
dicksonfit2
#TA      Dickson1981: 0.00245
#SumCO2 Dickson1981: 0.00220

# => yes it does, but it is not perfect yet!

# c.) differing K values
#####
# Dickson uses fixed K values that are slightly different than ours
dicksontitration3 <- titration(aquaenv(t=25, S=35, SumCO2=0.00220,
                                       SumBOH3=SumBOH3, SumH2SO4=SumH2SO4,
                                       SumHF=SumHF, TA=0.00245, k_w=4.32e-14,
                                       k_co2=1e-6, k_hco3=8.20e-10,
                                       k_boh3=1.78e-9, k_hso4=(1/1.23e1),
                                       k_hf=(1/4.08e2)),
                             mass_sample=mass_sample,
                             mass_titrant=0.0025,
                             conc_titrant=conc_titrant,
                             steps=50, type="HCl",
                             S_titrant=S_titrant, k_w=4.32e-14,
                             k_co2=1e-6, k_hco3=8.20e-10,
                             k_boh3=1.78e-9, k_hso4=(1/1.23e1),
                             k_hf=(1/4.08e2))
plot(dicksontitration3, xval=dicksontitration3$delta_mass_titrant,
     what="pH", xlim=c(0,0.0025), ylim=c(3,8.2), newdevice=FALSE,
     col="blue")
par(new=TRUE)
plot(sam[,1], sam[,2], type="l", xlim=c(0,0.0025), ylim=c(3,8.2))

plot(dicksontitration3$pH - sam[,2])
# => no offset between the pH curves

# => exactly the same curves!

```

```
dicksonfit3 <- TAfit(aquaenv(t=25, S=35, SumBOH3=SumBOH3,
                        SumH2SO4=SumH2SO4, SumHF=SumHF, k_w=4.32e-14,
                        k_co2=1e-6, k_hco3=8.20e-10, k_boh3=1.78e-9,
                        k_hso4=(1/1.23e1), k_hf=(1/4.08e2)),
                    sam, conc_titrant, mass_sample,
                    S_titrant=S_titrant, debug=TRUE,
                    k_w=4.32e-14, k_co2=1e-6, k_hco3=8.20e-10,
                    k_boh3=1.78e-9, k_hso4=(1/1.23e1),
                    k_hf=(1/4.08e2))
dicksonfit3

# PERFECT fit!

plot(sam[,1], sam[,2], xlim=c(0,0.0025), ylim=c(3,8.2), type="l")
par(new=TRUE)
plot(tit$delta_mass_titrant, calc, xlim=c(0,0.0025), ylim=c(3,8.2),
     type="l", col="red")

## End(Not run)
```

 Technicals

Technicals

Description

PUBLIC list: a collection programming-technical constants

Value

A list with elements:

| | |
|------------------|--|
| Haccur | accuracy for iterative (Follows2006) pH calculations (max. deviation in [H+]) |
| Hstart | start [H+] for an iterative pH calculation |
| maxiter | maximum number of iterations for iterative (Follows2006) pH calculation method as well as for the application of the standard R function uniroot |
| unirootinterval | the interval (in terms of [H+]) for pH calculation using the standard R function uniroot |
| uniroottol | the interval (in terms of [H+]) for pH calculation using the standard R function uniroot |
| epsilon_fraction | fraction of disturbance for the numerical calculation of derivatives of TA with respect to changes in the dissociation constants |
| revelle_fraction | fraction of disturbance for the numerical calculation of the revelle factor |
| CO2 | fugacity of CO2 in atm |

Author(s)

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titration

titration

Description

PUBLIC function: creates an object of class aquaenv which contains a titration simulation

Usage

```
titration(aquaenv, mass_sample, mass_titrant, conc_titrant,
          S_titrant=NULL, steps, type="HCl", seawater_titrant=FALSE,
          k_w=NULL, k_co2=NULL, k_hco3=NULL, k_boh3=NULL, k_hso4=NULL,
          k_hf=NULL, k1k2="lueker", khf="dickson")
```

Arguments

| | |
|------------------|---|
| aquaenv | an object of type aquaenv: minimal definition, contains all information about the system: T, S, d, total concentrations of nutrients etc (Note that it is possible to give values for SumBOH4, SumHSO4, and SumHF in the sample other than the ones calculated from salinity) |
| mass_sample | the mass of the sample solution in kg |
| mass_titrant | the total mass of the added titrant solution in kg |
| conc_titrant | the concentration of the titrant solution in mol/kg-soln |
| S_titrant | the salinity of the titrant solution, if not supplied it is assumed that the titrant solution has the same salinity as the sample solution |
| steps | the amount of steps the mass of titrant is added in |
| type | the type of titrant: either "HCl" or "NaOH", default: "HCl" |
| seawater_titrant | is the titrant based on natural seawater? (does it contain SumBOH4, SumHSO4, and SumHF in the same proportions as seawater, i.e., correlated to S?); Note that you can only assume a seawater based titrant (i.e. SumBOH4, SumHSO4, and SumHF ~ S) or a water based titrant (i.e. SumBOH4, SumHSO4, and SumHF = 0). It is not possible to give values for SumBOH4, SumHSO4, and SumHF of the titrant. |
| k_w | a fixed K _W can be specified |
| k_co2 | a fixed K _{CO2} can be specified; used for TA fitting: give a K _{CO2} and NOT calculate it from T and S: i.e. K _{CO2} can be fitted in the routine as well |
| k_hco3 | a fixed K _{HCO3} can be specified |
| k_boh3 | a fixed K _{BOH3} can be specified |
| k_hso4 | a fixed K _{HSO4} can be specified |

k_hf a fixed K_HF can be specified
 k1k2 either "lueker" (default, Lueker2000) or "roy" (Roy1993a) for K_CO2 and
 K_HCO3.
 khf either "dickson" (default, Dickson1979a) or "perez" (Perez1987a) for K_HF

Value

object of class aquaenv which contains a titration simulation

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

Examples

```
## Not run:
#####
# Titration with HCl
#####
S <- 35
t <- 15

SumCO2 <- 0.003500
SumNH4 <- 0.000020

mass_sample <- 0.01 # the mass of the sample solution in kg
mass_titrant <- 0.02 # the total mass of the added titrant solution in
# kg
conc_titrant <- 0.01 # the concentration of the titrant solution in
# mol/kg-soln
S_titrant <- 0.5 # the salinity of the titrant solution (the
# salinity of a solution with a ionic strength of
# 0.01 according to: I = (19.924 S) / (1000 - 1.005S)
steps <- 50 # the amount of steps the mass of titrant is added
# in
type <- "HCl"

pHstart <- 11.3

ae <- titration(aquaenv(S=S, t=t, SumCO2=SumCO2, SumNH4=SumNH4,
pH=pHstart), mass_sample, mass_titrant, conc_titrant,
S_titrant, steps, type)

# plotting everything
plot(ae, xval=ae$delta_mass_titrant, xlab="HCl solution added [kg]",
mfrow=c(10,10))

# plotting selectively
size <- c(12,8) #inches
```

```

mfrow <- c(4,4)
what <- c("TA", "pH", "CO2", "HCO3", "CO3", "BOH3", "BOH4", "OH",
         "NH4", "NH3", "H2SO4", "HSO4", "SO4", "HF", "F", "pCO2")

plot(ae, xval=ae$delta_mass_titrant, xlab="HCl solution added [kg]",
      what=what, size=size, mfrow=mfrow)

plot(ae, xval=ae$pH, xlab="free scale pH", what=what, size=size,
      mfrow=mfrow)

# different x values
plot(ae, xval=ae$delta_conc_titrant, xlab="[HCl] offset added
      [mol/kg-soln]", what=what, size=size, mfrow=mfrow)

plot(ae, xval=ae$delta_moles_titrant, xlab="HCl added [mol]", what=what,
      size=size, mfrow=mfrow)

# bjerrum plots
par(mfrow=c(1,1))
plot(ae, bjerrum=TRUE)

what <- c("CO2", "HCO3", "CO3")
plot(ae, what=what, bjerrum=TRUE)
plot(ae, what=what, bjerrum=TRUE, lwd=4, palette=c("cyan", "magenta",
         "yellow"), bg="gray", legendinset=0.1, legendposition="topleft")

what <- c("CO2", "HCO3", "CO3", "BOH3", "BOH4", "OH", "NH4", "NH3",
         "H2SO4", "HSO4", "SO4", "HF", "F")

plot(ae, what=what, bjerrum=TRUE, log=TRUE)
plot(ae, what=what, bjerrum=TRUE, log=TRUE, ylim=c(-6,-1),
      legendinset=0, lwd=3, palette=c(1,3,4,5,6,colors())[seq(100,250,6)]))

## End(Not run)

```

 watdepth

watdepth

Description

PUBLIC function: calculates the depth (in m) from the gauge pressure p (or the total pressure P) and the latitude (in degrees: -90 to 90) and the atmospheric pressure P_a (in bar)

Usage

```
watdepth(P=Pa, p=pmax(0, P-Pa), lat=0, Pa=1.013253)
```

Arguments

| | |
|-----|---|
| P | total pressure in bar, standard: 1 atm (at the sea surface) |
| p | gauge pressure in bar (total pressure minus atmospheric pressure), standard: 0 (at the water surface) |
| lat | latitude in degrees: -90 to 90, standard: 0 |
| Pa | atmospheric pressure in bar, standard: 1 atm (at sea level) |

Value

water depth d in meters

Author(s)

Andreas F. Hofmann. Maintained by Karline Soetaert (Karline.Soetaert@nioz.nl).

References

Fofonoff1983

Examples

```
watdepth(100)
plot(watdepth(1:100))
```

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